Edited by R. J. Gale, G. Blomgren, and H. Kojima EIGHTH INTERNATIONAL SYMPOSIUM

MOLTEN SALTS

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Edited by

Robert J. Gale Department of Chemistry Louisiana State University Baton Rouge, Louisiana George Blomgren Eveready Battery Company, Inc. Westlake, Ohio

H. Kojima Yamanashi University Kofu, Yamanashi 400, Japan



PHYSICAL ELECTROCHEMISTRY AND HIGH TEMPERATURE MATERIALS DIVISIONS

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PREFACE

The Eighth International Molten Salts Symposium at the 181st Meeting of the Electrochemical Society was held in the Adam's Mark Hotel, St. Louis, Missouri, May 17-21, 1992, which is adjacent to the Gateway Arch, America's tallest monument and the focal point of the Jefferson Expansion Memorial. Symbolically, just as the early American pioneers travelled westward to new frontiers, the field of molten salt chemistry continues to discover new areas for study and application. Such molten salt activities and interests are international, of course, and the Eighth International Symposium was well represented with fifty six contributions from as many as eleven different countries.

The goal of the Symposium, to include all aspects of the study and use of molten salts, was achieved. Papers dealing with traditional academic topics in this field such as spectroscopic elucidations of melt structures, thermodynamics, or theoretical modelling, were interdispersed with practically motivated research such as the purification of tin bromide for arc lamps or the conversion of ilmenite ore to a high grade titanium dioxide feedstock. Interest in molten carbonate fuel cells and miscellaneous battery applications continues unabated as well as a full day's program pertaining to low or room temperature melts. Professor Osteryoung's leadership in this latter area particularly and his research career of molten salt studies, of ever decreasing temperature, were recognized by a Plenary lecture, the Max Bredig Award, and an Award Address, "Through the Years and Temperatures: Adventures in Molten Salt Land". New areas for molten salt research included hot "cold fusion" in the cell Al/LiCl-KCl eut., LiH(D)/Pd and the syntheses, from hydroxide melts, of superconducting oxides by manipulation of acid-base chemistry. The molten salt field is very much alive and expanding!

The assistance of Barbara Marquette and Linda Temple of the office staff of the Chemistry Department, Louisiana State University, in preparing this Proceedings Volume, and the help in organizing the Symposium of a work study student at LSU, Ms. Rachel Rockman, are most gratefully acknowledged.

Robert J. Gale Louisiana State University June, 1992

MAX BREDIG AWARDEE



The Max Bredig Award was presented to Robert A. Osteryoung at the Awards and Recognition Session held on Tuesday, May 19, 1992, at 4:30 p.m. in Promenade Ballroom C and D, 2nd level of the Adam's Mark Hotel. "Through the Years and Temperatures: Adventures in Molten Salt Land" was the title of his award address which he delivered after dinner (approximately 8 p.m.) Wednesday, May 20, in the St. Louis Ballroom H, 4th level of the Adam's Mark Hotel.

Robert Osteryoung was born in Cleveland, Ohio in 1927. He served in the U.S. Navy and then obtained the degree of B.S. in Chemistry in 1949 from Ohio University. In 1951 he received his M.S. from the University of Illinois and obtained his Ph.D. in 1954 from the same institution. From 1951 to 1952 he worked for the Harshaw Chemical Company. From 1954 through 1959 he was Assistant, then Associate, Professor of Chemistry at Rensselaer Polytechnic Institute, Troy, New York. In 1959 he joined the staff of Atomics International Division of what is now Rockwell International, Los Angeles. He moved to Rockwell's Science Center Laboratory as Group Leader of Physical Chemistry in 1966 and in 1968 was named Associate Director. He also served, from 1966 to 1968, as Director of the Materials and Process Laboratory of Rockwell's California Institute of Technology from 1962 to 1968.

In 1968 he was named Professor and Chairman, Department of Chemistry, Colorado State University, Ft. Collins, Colorado, where he served as Chairman through June 1978. From July 1977 through June 1978 he was on leave as a Program Manager at the Air Force Office of Scientific Research in Washington, DC. He joined the faculty of the State University of New York at Buffalo in 1979. In July 1992, he moved to North Carolina State University in Raleigh, North Carolina, as Research Professor.

His research interests are in molten salt chemistry and electrochemistry, in electroanalytical chemistry, with emphasis on fast pulse voltammetric methods, and in the on-line use of computers in electrochemistry. He has published over 200 research papers in these areas. A past Chairman of the Gordon Research Conference on Electrochemistry, he has been an invited speaker at Gordon Research Conferences in electrochemistry, analytical chemistry, and molten salt chemistry. He has also been an invited speaker at numerous other scientific meetings in the United States and abroad.

Having joined The Electrochemical Society in 1969, he has served as Secretary-Treasurer, Vice-Chairman, and Chairman of the Physical Electrochemistry Division, and member of the Board of Directors, and currently serves on the Finance Committee. He was twice nominated as Vice-President of the Society. From 1979-1986 he served as a Divisional Editor of the *Journal of the Electrochemical Society*.

He is a past member of the Advisory Board of Analytical Chemistry, a past Chairman of the Division of Analytical Chemistry of the American Chemical Society, and is currently an Alternate Councilor of that Division to the ACS Council. As Chairman of the Division of Analytical Chemistry's Professional Status Committee, he operated the Division's Summer Intern Program for thirteen years. He was Program Chairman of the Division's 1984 Summer Symposium. He currently serves as an Associate Editor of Analytical Chemistry for electroanalytical chemistry.

He was the 1978 recipient of the Distinguished Service Award of the Colorado Section of the American Chemical Society, the 1987 recipient of the Charles N. Reilley Award in Electroanalytical Chemistry of the Society for Electroanalytical Chemistry, was the winner of the 1990 Schoellkopf Medal of the Western New York section of the American Chemical Society, and, in 1991, received the American Chemical Society's Division of Analytical Chemistry Award in Electrochemistry. He was selected as a Fellow of the Electrochemical Society in 1990.

His other professional affiliations include: founding member and past member of the Board of Directors of the Society of Electroanalytical Chemistry, the International Society of Electrochemistry, Phi Beta Kappa, Sigma Xi, and fellow of the American Association for the Advancement of Science.

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FACTS ABOUT THE ELECTROCHEMICAL SOCIETY, INC.

The Electrochemical Society, Inc., is a nonprofit, scientific, educational, international organization founded for the advancement of the theory and practice of electrochemistry, electrothermics, electronics, and allied subjects. The Society was founded in Philadelphia in 1902 and incorporated in 1930. There are currently over 5000 scientists and engineers from more than 40 countries who hold individual membership; the Society is also supported by more than 100 corporations through Patron and Sustaining Memberships.

The technical activities of the Society are carried on by Divisions and Groups. Local Sections of the Society have been organized in a number of cities and regions.

Major international meetings of the Society are held in the Spring and Fall of each year. At these meetings, the Divisions and Groups hold general sessions and sponsor symposia on specialized subjects.

The Society has an active publications program which includes the following.

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ON CHARGING PALLADIUM IN AN AI | LICI-KCI EUTECTIC, EXCESS LiH(D) | Pd CELL

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An anomalous heat effect was found during high–current–density charging of an Al|LiCl–KCl eutectic with excess LiD|Pd cell at elevated temperatures. The electrochemical and calorimetric behavior of this molten salt approach will be discussed. The thermochemical aspects of possible reactions at each charging stage will be interpreted by cell potential to seek a possible explanation for the anomalous heat. We were unable to identify any conclusive chemical nature of the anomalous phenomenon. The phenomenon is quite irreproducible because of several material–related problems and the lack of understanding of the control of predominant electrochemical reactions during the excess power excursion.

INTRODUCTION

An anomalous heat effect was measured on two separate occasions (1,2) when an Al | LiCl–KCl eutectic, excess LiD | Pd cell was charged under high current densities at elevated temperatures. No anomalous heat was found in similar experiments in the hydrogen–based system. The magnitude of the excess power is at least six times larger than the input electrochemical power that drives the reaction.

The electrochemical and calorimetric aspects of the experiments will be discussed. Various possible reactions might correspond to different stages in the charging process. No known thermochemical explanation can account for the anomalous heat.

EXPERIMENTAL ASPECTS

Pd metal electrodes were flame-torched in air before use. Their surfaces were quite rough and porous. The electrode was held by a steel rod, which served as the lead. Eutectic LiCl-KCl was fabricated by Lithco and used as received. The eutectic salt was melted in a controlled argon atmosphere glove box and heated overnight

to drive off excess moisture before adding LiH(D). A section of 6061 Al alloy tubing supported by several other steel rods was used as the cathode. LiD (Aldrich, > 98 *at*.% purity) and LiH (Alfa, Johnson–Matthey) were used without purification.

A glass dewar and Kaowool were used as insulation materials in the calorimeter cell. A glass-fiber-insulated resistance heating tape was wrapped around the cell to provide constant heating to the melt. Power to the heating tape was maintained steadily throughout the experiment using a high-output dc power supply. A chromel-alumel thermocouple junction with a stainless steel ungrounded sheath (Omega Engineering) was employed as a temperature probe.

Calorimetry

By varying the heating tape power, P_{ht} , we measured the corresponding steady–state temperature changes of the cell, ΔT_{ss} , and used the P_{ht} –vs.– ΔT_{ss} relationship as the calibration curve for each experiment. A calorimeter calibration constant, k, was obtained from the slope of the curve, which allows comparison among calorimetry runs to assure the consistency of the calorimeter. During the charging process, the cell temperature variation, ΔT_r , can thus be interpreted as the measured output power. The calibration curves before and after the experiment were usually obtained, and the post–experiment curve was used in the interpretation of the thermal results.

Figure 1 displays a histogram of a typical calibration process. As power to the heating tape changed, the cell temperature variation was recorded. The steady–state temperature versus the input heating–tape power constitutes the calibration curve. Figure 2 displays an integration of the power to illustrate the consistent energy balance of this calorimetric technique.

Electrochemical Aspects

Figure 3 displays a schematic diagram for a typical calorimetric cell. The cell reactions at the initial stage are:

$$LiD = Li^+ + D^-, \qquad [1]$$

anode: $Pd + x D^- = PdD_x + x e^-$, [2]

cathode: $Al + Li^+ + e^- = "LiAl'$ [3]

which give the total cell reaction:

$$Pd + x Al + x LiD = PdD_x + x "LiAl."$$
[4]

This reaction represents the charging behavior of the Pd anode. The corre-

sponding free energies and enthalpies of reaction are listed in Table I. The reversible cell potential and the thermoneutral potential are thus calculated to be 0.273 and 0.342 V, respectively.

RESULTS

The excess power episode, resulting from one of the charging experiments conducted in the deuterium–based system, is displayed in Figure 4. The upper curve represents the measured cell output power, while the lower curve displays the total input. The difference between the two is interpreted as the excess power. Integrating the excess power over time results in the excess heat. The magnitude of the excess power and heat are on the order of tens of watts and 5 MJ, respectively, over a period of about 100 hours. The corresponding calibration curve and another similar experimental result are displayed in Figure 5. The large difference between the cell thermal response and the calibration curve illustrates a distinct off–background signal of excess power.

Table II lists the relevant parameters measured and derived from these two experiments. The excess power and heat were of the order of 600-1500% and 4-7 MJ mol⁻¹ D₂, respectively.

Figure 6 displays a similar experiment on the Pd–H system. The similar magnitude of the input and output power in the figure indicates that "normal" thermochemical behavior occurred in this case. When experiments conducted on other Pd–D cells that behaved "normally," a similar result was often obtained. The power level of this experiment is much lower than that shown in Figure 4 because the insulation of the calorimeter was greatly improved using a stainless steel dewar.

We include in Figure 7 a cyclic voltammogram of an Al+LiCl–KCl eutectic, excess LiD+Mo cell to illustrate typical deuterium gas evolution behavior. From Table II, the cell potential in the second charging experiment that produced excess heat indicates an linear increase in cell potential with current density. The slope of this relationship permits the estimate of overpotential. Figure 8 shows such a relationship, in which an intercept at zero–current gives a reversible potential of 1.995 V, and the slope gives a resistance of 0.661Ω .

DISCUSSION

Thermodynamic and Electrochemical Considerations

It is quite unusual that a charging reaction, often thermodynamically unfavorable, can be so exothermic. As evidenced in Table I, known chemical reactions considered in the table are all endothermic. Our measured anomalous heat effects contradict accepted thermodynamic principles. As shown in Table II, our reported energy of the order of several MJ mol⁻¹ D₂ cannot be chemical in nature. This large magnitude forces us to consider nuclear explanations. However, the lack of intense radiation or energetic particle emissions is difficult to explain from known nuclear processes. Some recent publications emphasized the aneutronic characteristics of the excess heat process. ⁴He production seems to give a plausible explanation (3).

The excess power and heat episodes occurred only "occasionally" during long-time high-current-density and high-potential excursions in the deuteriumbased system. It is crucial to understand the cell reaction during these excursion periods in order to control the reaction for reproducible results. It is especially important to understand the difference in electrochemical process between the intrinsic, "normal," thermal behavior and the anomalous power/heat generation.

The first step to understand the cell behavior is to interpret the cell potential at various stages of the excursion, based on the determination of the free energy of reaction. Most of the thermodynamic data were obtained from the collection of Kubaschewski and his co-workers (4). The values for the Pd–H(D) system were selected from the work by Flanagan and his co-workers (5–6) and the work by Levine and Weale (7). For convenience in discussion, we reported the cell potential opposite to the convention $E = -\Delta G_r/nF$. Thus, we used the potential of anode versus cathode, which happens to be our reference as well, throughout the paper, including tables and figures.

From Table I, we attempt to identify the cell reaction from the reversible potential calculated for each possible reaction. Considering the cell reaction of the initial Pd charging process, we calculated the reversible cell potential for equation [4] to be 0.273 V (versus the Al | "LiAl" reference/cathode) at 700 K from the free energy of reaction. After the initial hydrogen absorption, the Pd becomes more susceptible to dissolving hydrogen, and the reversible cell potential exhibits a decrease to about 0.129 V at H/Pd = 0.5, as equation [5] in Table I shows. Finally, when the Pd electrode was saturated with hydrogen, gas evolution becomes the primary charging process at 0.073 V, as equation [6] indicates. However, the above situation only applies to the near–equilibrium condition. In fact, the deuterium dissolution process competes with the deuterium gas evolution reaction as the charging current–density and the resulting potential varied. In this case, the contribution from the overpotential has to be considered in the cell potential.

The overpotential for each reaction in the system has not yet been unambiguously determined. We, however, estimated the overpotential from the cyclic voltammogram of an Al | LiCl–KCl eutectic, excess LiD | Mo cell. The cyclic voltammogram shown in Figure 7 displays two distinct peaks: one located at –307.7 mV and the other at about 150 mV vs. an Al/"LiAl" reference. The peak at -307.7 mV is assigned to the reversible Li⁺/Li reaction on the Mo electrode. This is consistent with the results of Wen et al. (7), who reported a temperature-dependent emf of the Al/"LiAl" two-phase plateau in the Li-Al system to be $E(mV \text{ vs. Li}^+/Li) = 451$ -0.220 T(K). From this formula, we expect the peak intersects the zero-current axis at -308.4 mV. The peak at about 150 mV is assigned to deuterium gas evolution. As equation [6] in Table I depicts, the gas evolution reaction is expected to occur at 73 mV at 700 K. At 375° C (648 K) in this particular experiment, the cell potential corresponding to gas evolution should be 106.7 mV, which is close to what we observed. The gas evolution on the Mo electrode is completely irreversible; we thus did not measure a reverse peak. This peak also exhibits two distinct curvatures, representing both the activation and transport-limiting regimes. We thus can calculate the resistance of this particular cell geometry from the slope of the linear portion of the curve to be about 0.513 Ω . This value is of particular interest in the estimation of the overpotential due to the transport of the deuteride ions in the melt. This resistance is similar to the value determined in Figure 8 and that measured by ac electrochemical impedance technique from a similar cell configuration, implying the activation overpotential on both Mo and Al electrodes are negligible, while the transport of LiD in the melt is the limiting process. We, therefore, attribute the overpotential during a gas evolution process primarily to the LiD transport in the melt. For a current of 100 mA, an overpotential of 51.3 mV would be expected. This is consistent with our observation during a typical long-duration charging process in a LiD-saturated cell; for instance, a cell potential of 400-500 mV was often measured at 600 mA.

The cell reaction will vary if the LiD concentration in the melt decreases under a constant–current charging condition, which may result in chloride formation. These chlorination reactions are listed in Table I as equations [7–11]. Following the oxidation potential sequence, the LiAlCl₄ formation in equation [10] is the first among them to occur at about 1.1 V. We have detected Al deposition on Pd using SEM/EDX technique. The detailed mechanism of this deposition process has not been identified yet. It seems to result from a further oxidation of AlCl₄⁻ ion to Al at the Pd anode. The possibility of AlCl₃ deposition on the Pd surface was eliminated because AlCl₃ is liquid at this temperature. However, if equation [10] is to occur, it has to start with Al on both cathode and anode. Therefore, an initial shuttling of Al from cathode to anode (possibly through a redox process) must happen before inducing the depicted reaction. This shuttle process involves AlCl₄⁻ formation at the Al cathode and AlCl₄⁻ oxidation to Al and Cl_{2(g)} at the Pd anode. Because this process is thermodynamically unfavorable, it can occur only under non-equilibrium conditions resulting from a sufficiently large external bias.

The $ZnCl_2$ formation is discussed in equation [11] because the presence of Zn on the spent Pd sample surface was detected by SEM/EDX. Zn is a minor

constituent in the 6061 Al alloy used in the experiments. The Zn deposition was considered to occur via a similar route of the Al deposition, in which Zn was depleted from the Al cathode as $ZnCl_2$ or as $ZnCl_4^{2-}$ in the melt and further oxidized to Zn on the Pd anode at potentials higher than 1.73 V. However, similar to the Al case, Zn has to be on the Pd anode first to permit such a redox reaction.

The formation of iron chlorides are listed in equations [8–9], because Fe is another major impurity from the steel current leads detected on the Pd surface by SEM/EDX. The formation of FeCl₂ occurs at about 2.02 V, while the FeCl₃ formation should take place at a higher potential of about 3.10 V. These reactions exemplify the corrosion of steel leads in the melt, which often caused failure of the cell operation. The deposition of either Fe or its chlorides onto the Pd surface seems to suggest a possible route involving complex ion formations.

It should be noted that, for these metals to be deposited onto the Pd anode through complex chloride ion formation, the oxidation of chloride to metal at the anode should be accompanied by chlorine gas evolution. This can be verified by monitoring the effluent gas composition. The shuttle mechanism discussed above will increase the chloride concentration in the melt as the result of the redox reaction, which also needs to be verified further.

Finally, equation [12] depicts another interesting shuttle reaction in the cell. The reaction in [12] reflects the conversion of deuteride into deuteron at a potential higher than 2.148 V. De-deuterided Pd is an end product with deuteron in the melt. The presence of the deuteron under the charging condition could lead to an intriguing reaction at the cathode, where lithium deuteride could be regenerated. This situation implies a redox shuttling of deuteride into deuteron and subsequently converting back to deuteride between the anode and cathode. The perpetual mechanism consumes the supplied electrical energy to drive the deuterium back and forth in the melt, resulting in the heating of the electrolyte as an IR loss.

Thermochemical Aspects

The large solubility of hydrogen in Pd, and its associated nonstoichiometry, complicate the calorimetric measurements under dynamic charging conditions. As Levine and Weale (6) reported in their paper, the isosteric heat of sorption becomes less negative as the H/Pd ratio increases. For instance, Δ H's are -23.012, -14.226 and -5.858 kJ mol⁻¹ H at H/Pd = 0.225, 0.5 and 0.65, respectively. The increase of the Δ H value results in a progressive endothermic behavior of the cell, as the Δ H_r increases with a similar magnitude. Flanagan and Oates (4) reported the heat of hydrogen solution in Pd as a function of H/Pd ratio. They indicated that the Δ H_H decreases from -8 to -23.67 kJ mol⁻¹ H at H/Pd = 0.5 and then increases to -15.61 kJ mol⁻¹ H at H/Pd = 0.7. This latter increase is the consequence of the electronic contribution.

The endothermic behavior accordingly will decrease in magnitude up to H/Pd = 0.5 and increase beyond this composition.

Considering the enthalpies listed in Table I, we conclude that all reactions are endothermic in nature. The positive enthalpy infers that power has to be consumed in these processes. The power consumption rate in the table refers to a current of 100 mA. This power consumption is similar to the consideration of the thermoneutral potential in the power balance equation used by others in the heavy–water electrolysis experiments. The power consumption level in our experiments at 600 mA could range from 108 mW to 1.962 W, depending on the reaction.

The values listed in Table I allows us to estimate the power balance at each stage of the charging process. Let us consider the beginning of the charging process, where equation [4] applies and a current of 100 mA. The overpotential for hydrogen dissolution is negligible. We thus estimate that an input power of 0.027 W is required for the electrochemical work. This process, however, consumes at least 0.034 W from enthalpy change and results in a 0.007 W loss to compensate the entropy change. This calculation was applied to equations [4–12] to estimate the power balance under 100 mA charging condition. The result is tabulated in Table III for comparison. Equations [4–6, 8, and 12] all show net power loss, indicating a positive entropy change in the reaction. Others exhibit opposite effects. A power loss means a negative cell temperature variation, and vice versa. However, whether it is positive or negative, the magnitude of the power variation is actually quite small. This is consistent with what we observed in the hydrogen–based system and most of the deuterium–based experiments when no excess power or heat was measured.

From the results in Figure 8, we obtained two useful parameters to identify a possible reaction that corresponds to the excess power process. The cell resistance was similar to what LiD–saturated cell exhibits, indicating that the transport property did not deviate much from the original condition after a long-duration charging, although the reversible potential derived from the current–potential curve refers to a reaction at about 1.995 V. This potential corresponds to FeCl₂ and DCl formations. If the FeCl₂ formation is solely responsible for the cell reaction during the 100–hour operation, we calculated the total amount of Fe involved to be 0.835 mol or 46.63 g, which is about 40–50 times more than the amount estimated to be exposed in the melt. Therefore, the FeCl₂ formation could only account for maybe a few per cent of the total reaction. The DCl reaction would then be considered the primary contribution to the current passed through the cell. This is an intriguing conclusion, since the DCl formation will maintain a high deuterium flux toward Pd and thus enhance the loading of deuterium into Pd.

If this interpretation is correct, we then can conclude the following:

• DCl formation was responsible for the high-current charging reaction, which can enhance the loading of deuterium in Pd.

• DCl formation can only occur at potentials higher than 2 V. The presence of Fe and the subsequent FeCl₂ formation can help to stabilize the cell potential in this range. To maintain this condition, the LiD concentration must be below a certain value.

• The DCl formation and the D^+/D^- redox reaction provide an intriguing shuttle process that enables a high current sustained at high potentials without exhausting the LiD in the melt.

The excess power/heat episode was difficult to reproduce. This problem can be attributed to many materials-related issues which inhibit a consistent control of the experimental conditions. The last mechanism implies that the control of the LiD, FeCl₂ and DCl concentration in the melt is very important. This scenario demands careful verification in the near future. Once we have sufficient understanding of the cell reactions at high potentials and current densities, the control of the generation of excess power and heat could be expected.

CONCLUSION

A molten salt technique was used to charge a palladium anode with deuteride at elevated temperatures. Under high charging current densities and potentials, we occasionally measured excess power and heat. This phenomenon cannot be explained thermochemically. From thermodynamic considerations of the cell potential, we concluded that DCl formation in the D⁻-containing melt was responsible for the sustainable loading of deuterium into Pd, which may lead to the generation of excess power and heat. The presence of Fe, and its oxidation into FeCl₂, played an important role in stabilizing the cell potential that facilitated the DCl formation. If this scenario is true, the control of the relative concentration of Li⁺, Fe⁺², D⁺, D⁻ and Cl⁻ in the melt should be crucial for the reproducibility of the excess heat phenomenon.

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Reaction	۵G	Cell potential ^h	ΔH	Power consumed ^d
	kJ mol ⁻¹	V	kJ mol ⁻¹	W
$[4] x LiD + Pd + x Al = x "LiAl" + PdD_{x x->0}$	26.363 ^{g,j}	0.273	37.74 ^{b,f,j} 33.02 ^{g,j}	-0.039 -0.034
[5] $x \operatorname{LiD} + \operatorname{PdD}_{0.5} + x \operatorname{Al}$ = $x \text{``LiAl''} + \operatorname{PdD}_{0.5+x x->0}$	12.41 ^{c,f,j}	0.129	17.79 ^{c,f,j}	-0.018
[6] $LiD + Al = "LiAl" + 0.5 D_2$	7.00 ^{e,f,j}	0.073	41.46 ^{f,j}	-0.043
[7] 2 LiCl + PdD _{0.5} + 2 Al = 2 "LiAl" + PdCl ₂ + 0.25 D ₂	606.637	3.143	567.71	-0.294
[8] 2 LiCl + Fe + 2 Al = 2 "LiAl" + FeCl ₂	390.123	2.021	630.23	-0.327
[9] 3 LiCl + Fe + 3 Al = 3 "LiAl" + FeCl ₃	898.839	3.105	638.96	-0.221
[10] 4 LiCl + 4 Al = 3 "LiAl" + LiAlCl ₄ ⁱ	425.181	1.102	305.31	-0.079
[11] 2 LiCl + 2 Al + Zn = 2 "LiAl" + ZnCl ₂	333.856	1.730	303.56	-0.157
$ [12] 0.5 \text{ LiCl} + \text{PdD}_{0.5} + 0.5 \text{ Al} = 0.5 "\text{LiAl"} + 0.5 \text{ DCl} + \text{Pd} $	103.652 ^j	2.148	1 42 .69 ^j	-0.296

Table I. Free Energies and Enthalpies of Reaction in the Pd-D System at 700 K^a

^a The thermodynamic data were taken from ref. (3) unless specified.

^b The relative partial enthalpy at infinite dilution, $\Delta H^{\circ}_{D} = -3.72$ kJ mol⁻¹ D at 700 K, was reported in (4).

^c Flanagan and Oates reported (4) that ΔH_{H_r} the concentration-dependent partial molar enthalpy of hydrogen dissolution in Pd, exhibits a minimum at $\hat{x} \approx 0.5$ with a value of -23.67 kJ mol⁻¹ H at 500 K, and Δ S_H, the partial molar entropy, is -56.97 J K⁻¹ mol⁻¹ H. These values were considered constant in the temperature range 250-650 K and led to a $\Delta G_{\rm H}$ = 16.21 kJ mol⁻¹ H, which was used in our 700 K calculation. ^d Power consumption is based on the current at 100 mA.

- ^e ΔG_f of LiAl = -28.661 kJ mol⁻¹ at 700 K was reported in (7). ^f The value is based on mol⁻¹ D at 700 K. ^g $\Delta H^\circ_D = -8.473$ kJ mol⁻¹ D and $\Delta S^\circ_D = -55.2$ J mol⁻¹ D were reported by Clewley *et al.* (5). $\Delta G^\circ_D = 30.167$ kJ mol⁻¹ D was thus calculated for 700 K.
- ^h The cell potential refers to anode versus cathode/reference.
- ⁱ ΔG_f and ΔH_f of LiAlCl₄ were reported to be -892.5 and -1168.98 kJ mol⁻¹ at 700 K (8).

^j Thermodynamic data of LiH and HCl were used in the calculation.

Cell potential	Current	Power to	Electrochemical
	density	heating tape	power
V	$mA cm^{-2}$	Ŵ	W
3.230	606	71.91	1.94
2.188	290	69.25	0.63
2.270	420	69.30	0.94
2.453	692	69.25	1.68
Total input	Measured	Excess power	Excess heat
power	power	(gain in %)	
-		(guin in 707	
W	W	W	MJ mol ⁻¹ D ₂
W 73.85	W 86.76	<u>W</u> 12.91 (665%)	MJ mol ⁻¹ D ₂ -4.15
W 73.85 69.88	W 86.76 79.24	12.91 (665%) 9.36 (1486%)	MJ mol ⁻¹ D ₂ -4.15 -6.27
W 73.85 69.88 70.24	W 86.76 79.24 82.81	W 12.91 (665%) 9.36 (1486%) 12.57 (1337%)	MJ mol ⁻¹ D ₂ -4.15 -6.27 -5.83

 Table II. Experimental Parameters and Power Balances During the Pd Charging in the Deuterium-Based System

Table III. Power Balance Under Charging Condition at 100 mA

Reaction	Input power required W	Power consumed W	Power variation W
[4] $x \text{LiD} + \text{Pd} + x \text{Al}$			
= x "LiAl" + PdD _{x x->0}	0.027	-0.034	-0.007
[5] x LiD + PdD _{0.5} + x Al			
$= x "LiAl" + PdD_{0.5+x x->0}$	0.013	-0.018	-0.005
[6] $\text{LiD} + \text{Al} = \text{``LiAl''} + 0.5 \text{ D}_2$	0.012	-0.043	-0.031
$[7] 2 \text{LiCl} + PdD_{0.5} + 2 \text{Al}$			
= 2 "LiAl" + PdCl ₂ + 0.25 E	O ₂ 0.319	-0.294	0.025
[8] 2 LiCl + Fe + 2 Al			
= 2 "LiAl" + FeCl ₂	0.202	-0.327	-0.125
[9] 3 LiCl + Fe + 3 Al			
= 3 "LiAl" + FeCl ₃	0.311	-0.221	0.090
[10] 4 LiCl + 4 Al			
= 3 "LiAl" + LiAlCl ₄ ⁱ	0.110	0.079	0.031
[11] 2 LiCl + 2 Al + Zn			
= 2 "LiAl" + ZnCl ₂	0.173	-0.157	0.016
[12] $0.5 \text{ LiCl} + \text{PdD}_{0.5} + 0.5 \text{ Al}$			
= 0.5 "LiAl" + 0.5 DCl + Pd	0.215	-0.296	-0.081





Figure 5. Thermal responses and calibrations in two separate charging experiments. The current densities are a: 606, b: 290, c: 420, and d: 692 mA cm⁻².



Figure 6. A high-current charging experiment on the Pd-H system



Figure 7. A cyclic voltammogram of an Al | LiCl-KCl eutectic, excess LiD | Mo cell at 375° C



Figure 8. Current-potential relationship of the charging experiment that generated excess heat. An intercept at zero-current gives a reversible potential of 1.995 V, and the slope gives a resistance of 0.661Ω .

STRUCTURE OF MOLTEN IRON CHLORIDE

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The structure of molten FeCl₃ at 320°C has been measured with neutron diffraction at the Intense Pulsed Neutron Source. The results indicate that melting in FeCl₃ is accompanied by a change in local structure from the octahedral environment of the Fe³⁺ in the solid to an Fe₂Cl₆ molecular liquid. This behavior is similar to that observed in AlCl₃ and in contrast to that of YCl₃ where an octahedral coordination is preserved on melting.

INTRODUCTION

The halides of trivalent transition metals crystallize into a variety of structures, generally characterized by a rather close packing of the halide ions with the metal ions occupying the appropriate fraction of tetrahedral sites (1). On melting, they can assume radically different types of structure, either mimicking the close packed arrangement of the crystal or transforming into a more open, molecular type of structure. The different behaviors in melting can be inferred from the

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considerable range in changes in entropy ΔS and specific volume $\Delta V/V$, tabulated in Table I. For example, FeCl₃, with $\Delta S = 17.8$ e.u. and $\Delta V/V = 0.63$, contrasts dramatically with YCl₃ with $\Delta S = 7.6$ e.u. and $\Delta V/V = 0.005$. Our recent work on the structure of molten YCl₃ has shown that it does indeed melt into a close-packed structure, similar to the crystal but with some disordering of the Cl⁻ ions.(2). On the other hand, our studies of graphite intercalated with FeCl₃ have shown that the intercalated layers form a two-dimensional liquid of Fe₂Cl₆ molecules at higher temperatures, while at lower temperatures they form a close-packed hexagonal close packed arrangement similar to the bulk crystal. (3). The object of the present study was to make a careful measurement of the structure of the bulk liquid and determine whether the molecular structure is found here also, as suggested by the thermodynamic data of Table I.

NEUTRON DIFFRACTION EXPERIMENT

FeCl₃ material, 99.999% purity, obtained from APL Engineering Materials, Inc., was encapsulated in vitreous silica tubes 4mm I.D., 5mm O.D., 10 mm high with a loading sufficient to fill the beam height of 50mm when molten. Neutron diffraction measurements were carried out at the Special Environment Powder Diffractometer at the Intense Pulsed Neutron Source. The sample was heated to 320°C in a vacuum furnace inside a cylindrical vanadium element. The structure factor S(Q) was obtained after correcting the measured diffraction patterns for multiple scattering, absorption and inelastic effects using standard procedures (4). For the present sample, it was necessary also to subtract the paramagnetic scattering from the Fe³⁺. This was calculated on the basis of the value of the magnetic moment of the free Fe³⁺ ion, 5.92 μ B (5) and the published free-ion form factor (6).

The corrected structure factor S(Q) is shown in Fig. 1. Strictly speaking this represents a weighted average of the three partial structure factors:

$$S(Q) = 1/\langle b \rangle^{2} \Sigma_{ij} (c_{i}c_{j})^{1/2} b_{i} b_{j} S_{ij}(Q) - \langle b^{2} \rangle/\langle b \rangle^{2} + 1$$
(1)

However, the scattering lengths of Fe and Cl are nearly identical, so S(Q) is very close to the Bhatia-Thornton number density structure factor

$$S_{NN}(Q) = \Sigma_{ij} (c_i c_j)^{1/2} S_{ij}(Q)$$
 (2)

It exhibits a three-peak structure with peaks at wave vectors Q = 0.95, 2.05, and 3.67 Å⁻¹, respectively. Scaling with the nearest-neighbor distance $r_1 \approx 2.28$ Å (see below), these values correspond to scaled wave vectors $Qr_1 \approx 2.2$, 4.7, and 8.4, respectively, typical of values found for the first sharp diffraction peak, the Coulomb peak and the hard sphere peak, respectively, in complex liquids (7).

The total pair correlation function in real space T(r), obtained by Fourier transformation of S(Q), is shown in Fig. 2. It has a well-defined first peak which can be fitted by two gaussian functions centered at 2.19 and 2.37 Å. These values are about 4% larger than the Fe-Cl separation observed for terminal and bridging Clions in Fe₂Cl₆ molecules in the vapor.(8). Converting T(r) to the radial distribution function n(r) gives a total area for the first peak of 1.8; this corresponds to an average coordination number of 3.6 about the Fe³⁺ ions, slightly lower than the value of 4.0 for the isolated molecule. The octahedral coordination found in the crystalline phase is clearly ruled out. There is some possibility of dissociation in molten FeCl₃, leading to FeCl₂ and free Cl₂ (9); however, in the present experiment, since S(Q) is normalized to 1.0 at high Q, values of the coordination number about the Fe³⁺ ions would be 33% higher than those observed, so this is also inconsistent with the data. Thus, these data show unambiguously that the bulk melt is a molecular liquid composed of Fe₂Cl₆ molecules.

The second peak in T(r) is a broad peak with an area in n(r) of 5.9, presumably due to Fe-Fe and Cl-Cl correlations. The isolated Fe_2Cl_6 molecule would give a value of 3.0, so that approximately half the second-neighbor correlations are inter-, as opposed to intra-, molecular. The measured value is, again, considerably lower that the value which applies for the closed-packed structure of the crystal, 9.25.

CONCLUSIONS

The results of these measurements indicate that melting in FeCl₃, associated with a large (63%) volume change, is accompanied by a change in local structure from the octahedral environment of the Fe³⁺ in the solid to an Fe₂Cl₆ molecular liquid.

A suggested geometry of the structural transition is shown in Fig.3. Each Fe^{3+} ion undergoes a substantial displacement, from an octahedral site between two triangles of Cl⁻ ions in adjacent planes, shown in the lower part of the figure, to a tetrahedral site between one Cl⁻ triangle and the Cl⁻ opposite it in the adjacent plane, as observed in the molecular crystals AlBr₃ (10) or GaCl₃(11), shown in the upper part of the figure. At the same time there must be a decrease in the packing of the Cl⁻ to account for the volume expansion. The reduced value for the second-neighbor coordination number observed in molten FeCl₃ is consistent with this reduction in Cl⁻ packing. Melting in FeCl₃ is clearly similar to that observed in AlCl₃ and in contrast to that of YCl₃ where an octahedral coordination is preserved on melting.(2).

Results of detailed model calculations on the structure of molten FeCl₃ are in progress and will be reported in a forthcoming publication (12).

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TABLE I.

$\Delta S_m(e.u.)$ $\sigma(\Omega^{-1}cm^{-1})$ Salt $T_m(K)$ $\Delta V/V^{b}$ InCl₃ 859 0.61 0.42 AlCl₃ 466 18.1 0.88 5x10-7 GaCl₃ 7.4 2x10-6 351 0.17 BiCl₃ 505 5.0 0.22 0.38 SbCl₃ 347 8.7 2x10-4 0.17 YCl₃ 994 7.6 0.005 0.39 FeCl₃ 577 17.8 0.63 ---

Physical properties of some trivalent metal chlorides^a

^aAfter M.P.Tosi, G. Pastore, M.-L. Saboungi, and D. L. Price, *Physica Scripta*, 139, 367 (1991)
^bRelative difference of specific volume of liquid at T_m and that of solid at room temperature



Fig. 2. Pair correlation function of molten FeCl3 at 320°C.



Fig. 3. Schematic illustration of melting in FeCl₃. The black spheres represent a plane of Fe³⁺ ionsin the crystal, and the grey and white spheres represent planes of Cl⁻ ions above and below the plane of Fe³⁺ ions, respectively. The lower cluster represents the octahedral coordination of the Fe³⁺ ions in the crystal, and the upper cluster the Fe₂Cl₆ molecule in the melt. The arrows indicate the required displacement of the two Fe³⁺ ions upon melting.

ELECTRONIC CONDUCTION AND ELECTRON MOBILITIES IN MOLTEN KBr-K SOLUTIONS

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Abstract

The electronic conductivity of molten KBr-K solutions was determined as a function of the activity of K at 780, 800 and $850^{0}C$ by using the Wagner polarization technique. A transient technique was used to determine the diffusion coefficient and the mobility of electrons.

INTRODUCTION

The study of mixtures of molten salts and metals has received much attention. Bredig and coworkers /1/ determined the phase diagram for the KBr-K system and measured the electrical conductivity of solutions of potassium in molten potassium bromide. It was found that **dissolution** of K in molten KBr gives rise to electronic conduction. The system undergoes a continuous transition of the electronic structure from nonmetallic to metallic states as the content of K in solution increases. The properties of dilute solutions of akali metals in molten alkali halides can be explained by using a thermodynamic model proposed by Egan and Freyland /2/. The formation of defects such as electrons and F-centers is considered. Results from spectroscopy /3/ and conductivity measurements /4,5/ are in accordance with predictions from the thermodynamic defect model.

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TECHNIQUES FOR THE MEASUREMENT OF ELECTRONIC CONDUCTION AND ELEC-TRON MOBILITIES

Electronic Conductivity

The Wagner polarization technique is usually used to study electrical conduction in solids exhibiting both ionic and electronic transport. The method has been thoroughly treated in the literature especially by Wagner /6/ and Kroger /7/. It has also been employed to study the movement of electrons in molten salts /4,5,8/. A brief description is presented here for the convenience of the reader.

This is a dc method using cells of the following type

$$Fe(s) \mid KBr(l) \mid K - Bi(l)_{x_{K=0.04}}$$
 (1)

where the K-Bi (1) alloy serves as a reference electrode with known activity of potassium and the iron serves as an inert electron conductor or blocking electrode. One applies potentials across the cell which are lower than those necessary to decompose the KBr, the iron electrode being negative. In this way ionic currents are suppressed and only electronic current flows. There is no gradient of electrical potential within the bulk of the KBr otherwise ions would move. Under steady state conditions which take about 30 minutes after each potential change the current density is given by

$$J_e = \frac{\kappa_e}{F} \left(\frac{\partial \eta_e}{\partial x} \right) \tag{1}$$

where κ_e is the electronic conductivity in KBr, F is the Faraday and η_e is the electrochemical potential of electrons (see Wagner /6/ or Kroger /7/). The ionic current density is given by

$$J_{ion} = -\frac{\kappa_{ion}}{F} \left(\frac{\partial \mu_K}{\partial x} - \frac{\partial \eta_e}{\partial x} \right) = 0$$
⁽²⁾

where μ_K is the chemical potential of K in KBr. Since $J_{ion} = 0$

$$\frac{\partial \mu_K}{\partial x} = \frac{\partial \eta_e}{\partial x} \tag{3}$$
Since the cell is designed (see experimental section) so that the compartment between the two electrodes has a constant cross section, integration of eqn. (1) using eqn. (3) gives

$$lJ_e = \frac{1}{F} \int_{\mu_K^{ref}}^{\mu_K^{Fe}} \kappa_e d\mu_K \tag{4}$$

The chemical potential of K at the iron electrode is related to the voltage impressed across the cell, E, by

$$\mu_K^{Fe} - \mu_K^{ref} = -FE \tag{5}$$

Differentiation of (4) and (5) with respect to μ_K^{Fe} and substitution gives

$$\kappa_e = l \frac{d|J_e|}{dE} = G \frac{d|I|}{dE} \tag{6}$$

where G is the cell constant and I is the steady state current of cell (I).

In order to obtain the electronic conductivity in KBr, steady state currentpotential curves were obtained and then differentiated to yield κ_e . Further, the conductivity was obtained as a function of potassium activity using

$$a_K = exp\left[\frac{(E-E^0)F}{RT}\right] \tag{7}$$

where E^0 is the potential of the K-Bi electrode vs. pure potassium taken from the literature on this system /9,10/.

Electron Mobilities

The diffusion coefficient and mobility of electrons in the melt may also be measured by observing the cell's approach to steady state. When a potential is imposed on the iron electrode, a chemical potential of potassium is produced in the KBr at this point and with it a given concentration of electrons. These electrons then diffuse toward the reference electrode according to Fick's second law. The concentration of electrons as a function of time and distance from the iron electrode is given by the following equation (see for example Crank /11/)

$$c = c_1 + (c_0 - c_1)\frac{x}{l} + \frac{2}{\pi}\sum_{n=1}^{\infty} \frac{c_0 cosn\pi - c_1}{n} sin\frac{n\pi x}{l} exp\left(-\frac{Dn^2\pi^2 t}{l^2}\right) + \frac{4c_0}{\pi}\sum_{m=0}^{\infty} \frac{1}{2m+1} sin\frac{(2m+1)\pi x}{l} exp\left(-\frac{D(2m+1)^2\pi^2 t}{l^2}\right)$$
(8)

where c_1 is the electron concentration at the iron electrode, c_0 is the concentration at the reference electrode, x is the distance from the iron electrode, D is the diffusion coefficient of electrons, l the distance between the iron electrode and the reference electrode, and t is the time in seconds. The flow of electrons, j, is then given by

$$j = -D\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{D(c_1 - c_0)}{l} - \frac{2Dc_0}{l} \sum_{n=1}^{\infty} (-1)^n exp\left(-\frac{Dn^2 \pi^2 t}{l^2}\right) + \frac{2Dc_1}{l} \sum_{n=1}^{\infty} exp\left(-\frac{Dn^2 \pi^2 t}{l^2}\right) - \frac{4Dc_0}{l} \sum_{m=0}^{\infty} \left(-\frac{D(2m+1)^2 \pi^2 t}{l^2}\right)$$
(9)

The quantity of electrons flowing in the cell is given by

$$Q_{t} = \int_{0}^{t} j \, dt = \frac{D(c_{1} - c_{0})}{l} t - \frac{2l}{\pi^{2}} \sum_{n=1}^{\infty} \frac{c_{0} cosn\pi - c_{1}}{n^{2}} \left[1 - exp\left(-\frac{Dn^{2}\pi^{2}t}{l^{2}} \right) \right] - \frac{4c_{0}l}{\pi^{2}} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^{2}} \left[1 - exp\left(-\frac{D(2m+1)^{2}\pi^{2}t}{l^{2}} \right) \right] (10)$$

At longer times with $t \to \infty$ equation (10) reduces to

$$Q_t = \frac{D(c_1 - c_0)}{l}t + \frac{l}{3}(c_1 - c_0)$$
(11)

The total number of coulombs passed through the cell as a function of time is given by

$$Q = \frac{D(c_1 - c_0)FA}{l}t + \frac{l}{3}(c_1 - c_0)FA$$
(12)

where F is the Faraday constant and A is the area of the sodium chloride compartment. Thus if one imposes a voltage across the cell at t = 0 and

measures the coulombs until steady state, one obtains the diffusion coefficient of electrons as follows. The slope of a plot of Q vs. t is given by

$$Slope = \frac{D(c_1 - c_0)FA}{l} \cong \frac{Dc_1FA}{l}$$
(13)

when the concentration of electrons at the reference electrode is much smaller than that generated at the iron electrode. The intercept of the plot is given by

$$Intercept = \frac{l}{3}(c_1 - c_0)FA \cong \frac{l}{3}c_1FA$$
(14)

$$D = \frac{Slope}{Intercept} \frac{l^2}{3} \tag{15}$$

Since I = dQ/dt

$$D = \frac{Il^2}{(Q - It)3} \tag{16}$$

Therefore measurements of Q were taken for a time t until steady state was reached and eqn. (16) used to obtain values of D. The mobility of electrons was then calculated from the Nernst-Einstein equation

$$u_e = (DF)/(RT) \tag{17}$$

EXPERIMENTAL DETAILS

The experimental cell is shown in Figure 1. A tantalum crucible contains the salt (KBr single crystals of optical grade) in contact with a K-Bi alloy (= 4mole% K). The Fe electrode is placed inside a sapphire capillary (4.2 cm long, 3 mm inside diameter). A vacuum tight seal is formed between iron and sapphire. This seal prevents the evaporation of K, which is essential for obtaining good results. A constant potential is imposed across the cell making the Ta cup positive and the Fe electrode negative. The current through the cell is measured as a function of time, and the steady state value is recorded. A series of such corresponding data is measured so that the electronic conductivity can be calculated as a function of potential. The cell constant is determined by the geometry of the sapphire capillary. ac resistance measurements are also made periodically between the Ta cup and the Fe electrode as a control.

A transient technique is applied to the same cell in order to measure the diffusion coefficient of electrons. The current response to a potential applied across the electrodes is measured until steady state is attained. The total number of coulombs passed is recorded and the diffusion coefficient calculated from eqn. (16).

A reference electrode consisting of a K-Bi alloy placed inside an alumina tube is also shown. The amount of Bi is accurately known. This reference electrode is used to check the composition of the K-Bi alloy in the tantalum cup which can vary over a period of several days due to evaporation of potassium. All K is coulometrically removed from the reference electrode and then added again until the potential between the reference alloy and the larger K-Bi alloy is zero. The composition of the K-Bi alloy in the tantalum cup is then known, and the activity of K is calculated from thermodynamic data for K-Bi alloys /9,10/.

RESULTS

The currents measured at various applied potentials on cell (I) are shown in Figure 2 for temperatures of 780, 800 and 850° C. These points were fit to an exponential curve as explained in ref./4/ using the least square routine of Marquart/12/ and the derivative of this curve is then used to obtain the conductivity as a function of K activity according to equation (6) and (7). Results are shown in Figure 3. Transient measurements were also taken on cell (I) for various applied potentials to obtain the electron mobilities using equation (16) and (17) and these results are shown in Tables 1, 2 and 3 for 780, 800 and 850°C.

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$T = 780^{\circ}C \ E^{\circ} = 0.985 \ V_m = 56.96$					
E[volts]	$D[cm^2sec^{-1}]$	$I_{steady}[\mu amps]$	$u_e[cm^2volt^{-1}sec^{-1}]$		
0.700	0.016	617	.176		
0.780	0.016	1207	.176		
0.800	0.017	1391	.187		

Table 1: Results of Transient Measurements on cell (I).

Table 2: Results of Transient Measurements on cell (I).

$T = 800^{\circ}C \ E^{\circ} = 0.986 \ V_m = 57.41$						
E[volts]	$D[cm^2sec^{-1}]$	$I_{steady}[\mu amps]$	$u_e[cm^2volt^{-1}sec^{-1}]$			
0.730	0.016	962	.173			
0.750	0.018	1130	.194			
0.770	0.016	1291	.173			

Table 3: Results of Transient Measurements on cell (I).

$T = 850^{\circ}C \ E^{\circ} = 0.987 \ V_m = 58.58$						
E[volts]	$D[cm^2sec^{-1}]$	$I_{steady}[\mu amps]$	$u_e[cm^2volt^{-1}sec^{-1}]$			
0.608	0.0170	543	.176			
0.750	0.0170	1444	.176			
0.770	0.0170	1712	.176			

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Fig. 1 Experimental Arrangement used for Cell(I)



Fig. 2 Current vs. potential at 780, 800, and 850 °C for cell (I). (top curve 850oC)



Fig. 3 Electronic Conductivity vs. potassium activity at 780, 800, and 850 ${\rm C}$ (top curve 850 ${\rm C}$)

Electronic polarizabilities of LiCl-CsCl, LiI-KI and LiI-CsI binary melts.

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ABSTRACT

Refractive indices and densities of LiCl-CsCl, LiI-KI and LiI-CsI binary melts have been measured. The electronic polarizabilities of the melts have been determined from the measured refractive indices and densities by the Clausius-Mossotti equation. The correlation between the electronic polarizability and the structure of the salts has been examined. The electronic polarizability of the melts has positive temperature dependence and that of the binary melts negatively deviates from the additive value. Factors which affect the electronic polarizabilities of the melts have been investigated.

NOMENCLATURE

 Δh_s , Δh_m head difference, m refers to molten salt, and s to standard liquid.

 ρ_m , ρ_s density, m refers to molten salt, and s to standard liquid.

- A apex angle of prism.
- δ_{\min} minimum deviation angle.
- n refractive index.
- n^{∞} refractive index at infinite wave length.
- α electronic polarizability.
- M molar weight.
- ρ density.
- N Avogadro's number.
- rs first neighboring distance of the crystal at m.p..
- \mathbf{r}_{ℓ} first neighboring distance of the melt.
- Vm_s molar volume of the crystal at m.p..
- Vme molar volume of the melt.
- CN_s coordination number of the crystal at m.p..

CN_l coordination number of the melt.

INTRODUCTION

The alkali halide melts are comprised of spherically symmetric halide anions and alkali cations. Therefore, the alkali halide melt has been considered as a simple ionic liquid. But, it should be noted that electronic polarization of the ions exists even in such a typically ionic melt as alkali halide melts, may cause a local interaction ⁽¹⁾ and may influence the transport and thermodynamic properties ⁽²⁻⁴⁾ of the ionic melts. It has been found that the electronic polarizability of the alkali halide single and binary melts has positive temperature dependence ⁽⁵⁻⁷⁾. We considered that the positive temperature dependence ⁽⁵⁻⁷⁾. We considered that the positive temperature dependence ⁽⁵⁻⁷⁾. We considered that the positive temperature dependence of the electronic polarizability is caused by the decrease of the coordination number between the nearest ions with an increase in temperature. Therefore, the variation of the binary melts. So, it is interesting to determine the electronic polarizability of the alkali halide melts and to clarify the effect of the electronic polarization on physicochemical properties.

This paper reports the results of the measurements of the density and the refractive index at the wave length of 470 to 670 nm for the single melts and the LiCl-CsCl, Lil-KI and Lil-Csl binary systems. The electronic polarizabilities of the melts have been derived from the densities and the refractive indices observed, and the relative importance of the factors that control the electronic polarization has been investigated.

EXPERIMENTAL

I. Density measurement

The density was measured at the temperatures ranging from the m.p. up to 1200K. The density has been determined by a manometric method. The principle of the manometric method is schematically shown in Fig.1. Each head of an ionic melt and a standard liquid in the each U type tube is measured by a telescope. The density of the standard liquid is already known. The densities are determined by Eq.1.

$$\Delta h_{m} \cdot \rho_{m} = \Delta h_{s} \cdot \rho_{s} \tag{1}$$

II. Refractive index measurement

The refractive index was determined by the minimum deviation angle method. The principle of the minimum deviation method is schematically shown in Fig.2. The deviation angle takes minimum value when the incident beam and the refracted beam are symmetrical about the axis of the prism cell. The refracted beam was observed by a telescope. The prism cell was turned to minimize the deviation angle. The refractive index is calculated by eq.2 from the minimum deviation angle, δ_{min} observed.

$$n = \frac{\sin\left(\frac{A + \delta_{min}}{2}\right)}{\sin\left(\frac{A}{2}\right)}$$
(2)

The apex angle, A was measured by means of the auto-collimation method. Therefore, this measurement is an absolute method without a calibration process.

RESULT AND DISCUSSION

I. Density

The density for LiCl-CsCl binary melt is plotted against temperature and shown in Fig.3. The density of these melts decreases linearly with increasing temperature. The same negative temperature dependence has been observed for all the melts measured.

IL Refractive index

The refractive index for LiCl-CsCl binary melt are plotted against temperature and shown in Fig.4. The refractive indices decrease linearly with increasing temperature. The same temperature dependence has been observed for all the melts examined.

III. Electronic Polarizability

III.a. Temperature Dependence of Electronic Polarizability

The electronic polarizabilities of the melts have been determined from the density and the refractive index at the infinite wave length by Clausius-Mossotti relation, eq.3.

$$\frac{n_{\alpha-1}^2}{n_{\alpha}^2+2} = \frac{4\pi}{3} \cdot \alpha \cdot \frac{N}{\varepsilon_0 \cdot V}$$
(3)

The refractive indices observed were extrapolated to obtain the infinite wave length by Cauchy's equation, so as to determine the value of n_{∞} .

The temperature dependence of the electronic polarizabilities of LiCl-CsCl binary melts is shown in Fig.5. The electronic polarizability of the melts increases slightly with increasing temperature. The same positive temperature dependence of the electronic polarizability has been observed for the other melts investigated. The electronic polarizability is a parameter representing the extent of the polarization of ions under the applied electric field, and is proportional to the ionic volume if the electronic structure is the same. According to the quantum mechanical calculations and the calculations of the atomic scattering factor for X-ray of crystalline alkali halides (8-11), the electronic polarizability of the anion decreases, on the contrary, that of the cation increases somewhat in passing from the free ionic state into the condensed state (12). The extent of the variation accompanying the change in state is larger for the anion than the cation (8-13). Wilson (13) pointed out the correlation between the electronic polarizability of ions and the inter-ionic distance of crystalline alkali halide. In molten state, the volume expansion induced by the temperature increase is mainly due to the decrease in coordination number, and the first neighboring ionic-distance is kept almost constant upon an increase in temperature. Therefore, the positive temperature dependence of the electronic polarizability observed in the present investigation are considered to be due to the decrease in coordination number upon temperature increase (5-7). The correlation between the coordination number and the electronic polarizability has not yet been examined for the case of crystalline state. So, the relative importances of the inter-ionic distance and coordination number in molten and solid state have been investigated by taking the cesium halide as a sample substance, because cesium halides show a structural transformation from CsCl type, whose coordination number is 8, to NaCl type, whose coordination number is 6. The electronic polarizabilities of cesium halide melts and crystals (14-15) are plotted against coordination number and shown in Fig.6. The coordination number of the melts has been estimated by eq.4 proposed by Furukawa⁽⁴⁾.

$$\frac{Vm_s}{Vm_\ell} = \begin{pmatrix} r_s \\ r_\ell \end{pmatrix} \frac{CN_\ell}{CN_s}$$
(4)

As shown in Fig.6, the electronic polarizability of each salt decreases with increasing coordination number. Two sets of the plots of each salt at the coordination number 8 represent the values measured at different temperatures. The same coordination number dependence of the electronic polarizabilities are observed for the other salts investigated.

The electronic polarizability decreases with increasing coordination number for the other single salts in a similar way as cesium halides.

III.b Composition Dependence of Electronic Polarizability

The deviation of the electronic polarizabilities from the additive values for LiCl-CsCl binary melt are plotted against composition and shown in Fig.7. The electronic polarizabilities of the binary melt deviate negatively from the additive values. The same negative deviation of the electronic polarizability from the additive values has been observed for the other binary melts investigated. We considered that the negative deviation of the electronic polarizability is due to the change in the structure, that is to say, coordination number and/or inter-ionic distance with composition. To discuss the correlation between the electronic polarizability and the structure of the binary melt, the excess molar volume for LiCl-CsCl binary melt are plotted against composition and shown in Fig.8. The molar volume for LiCl-CsCl binary melts deviates positively from the additive value. The positive deviation of molar volume observed indicates the decrease of the mean coordination number on mixing. The decrease of the coordination number would result in the localization of valence electrons, and would cause the positive deviation from the additive value of the electronic polarizability on mixing. But, this is not the case for the binary melts examined. Therefore, we will focus on the other possibility, the effect of the inter-ionic distance. The electronic polarizability for cesium halide solids ⁽¹⁵⁾ are plotted against the inter-ionic distance and shown in Fig.7. As show in this figure, the electronic polarizability increases with the inter-ionic distance. In the case of solid, the temperature dependence of the coordination number is negligible. Therefore, the correlation observed can be considered as not being affected by the coordination number, but may stands for the melts. In fact, the shrinkage of the inter-ionic distance on mixing of salts is reported by Okada (16-17). Based on the analyses of the neutron scattering experiments and molecular dynamics calculation, they reported that the inter-ionic distance decreases on mixing for the case of LiCl-CsCl binary system. These results coincide with the present results. We considered that the negative deviation of the electronic polarizability is caused by the decrease of the inter-ionic distance for the binary melts. However, the precise inter-ionic distances and coordination numbers are not available for the time being. So, the more precise information about the structure of the binary melts is expected for the detailed discussion on the electronic polarization of the mixtures.

CONCLUSION

The density and the refractive index of the single and the LiCl-CsCl, LiI-Kl and LiI-CsI binary melts have been measured. The electronic polarizabilities of the melts have been determined from the measured densities and refractive indices by Clausius-Mossotti's equation. The factors which affect the electronic polarizabilities of the salts have been investigated. The conclusion to be drawn from these results is as follows: The inter-ionic distance as well as the coordination number is important factor to vary the electronic polarizability for the binary melts. The inter-ionic distance, as well as the coordination number, is an important factor controlling the electronic polarizability of the binary melts.

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Fig.1 Principle of Manometric Method.

Fig.2 Principle of Minimum Deviation Angle Method.







Fig.9 Correlation between electronic polarizability and inter ionc distance for CsCl, CsBr and CsI solids. (by Jaswal)

Computer Assisted Data Acquisition and Analyses of Brillouin spectra of ZnCl2 single and ZnCl2-NaCl Binary Melts.

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ABSTRACT

The Brillouin scattering experiment has been carried out with carefully purified samples of ZnCl₂ single and ZnCl₂-NaCl binary melts. The whole profile of Brillouin spectrum was obtained by the use of a computer assisted data acquisition system. The Brillouin spectra have been analyzed by the viscoelastic theory with the assumption of the single relaxation. The relaxation time and the velocities at limiting low frequency, V_{0} , and high frequency V_{∞} were determined.

INTRODUCTION

Zinc chloride melt is well-known for its unusally high viscosity at temperatures near its melting point. This is due to the presence of the network structure in the melt. However the viscosity of ZnCl2 melt decreases remarkably with an increase in temperature, and also decreases with an addition of basic salts, such as alkali metal halides. These facts suggest that modification of the structure of the melt takes place by the addition of the basic salt, and by the variation in temperature. Sonic spectroscopy is one of the most effective method for the detection of the change in structure, especially for a highly viscous liquid. From the sonic spectroscopy, the relaxation phenomenon can be elucidated.

Zinc chloride single melt has been studied by several investigators by the use of ultrasonic spectroscopy $(1\sim3)$. The existence of shear and structural relaxation have been recognized in these studies. The Brillouin scattering method(4,5) has been also applied to molten ZnCl2. Soltwisch et al.(5) analyzed the Brillouin spectrum of ZnCl2 melt. However, the Brillouin spectra have only been obtained at the frequency range apart from the central line for ZnCl2 melt.

In the case of highly viscous liquids, the central peak of the Brillouin component becomes significant, and extends to the Brillouin doublet, due to the relaxation as described by Mountain(6). Therefore, it is important to obtain the central component of the spectrum

as well as the doublet. In the present work, the Brillouin scattering experiment was carried out for ZnCl2 single melt and ZnCl2-20%NaCl binary melt. To obtain the whole spectra precisely, the scattering experiment was done on a carefully purified sample by using a computer assisted data acquisition system. The profile obtained were analyzed by the viscoelastic theory with the assumption of the single relaxation. The relaxation time and the velocities at limiting low and high frequencies, were obtained at the temperatures ranging from 550 to 1000K.

EXPERIMENTAL

Experimental Set Up

The Brillouin scattering experiment was carried out by the use of a He-Ne gas laser. The laser beam was modulated into 225Hz and focused at the center of a scattering cell placed inside a furnace. The scattering cell was made of fused quartz, and was of 30mm diameter. The light scattered into the angle θ was focused on a pin hole with a collecting lens, was collimated with a collimating lens and was analyzed by a pressure scanned Fabry-Perot interferometer with a spacer of 7mm. The profiles were observed by a X-Y recorder, and were also recorded digitally by a personal computer. The measuring time were about 15 minutes per spectrum. The profile was recorded in about 400 points per free spectral range FSR (FSR=21GHz). The experiment was carried out at the scattering angles of 45°, 90° and 140°.

Sample

In the Brillouin scattering experiment, the inclusion may cause the spikes in the spectrum around the central component. For highly viscous liquids, like ZnCl2 the intensity of the elastic lines scattered from the inclusions is usually very intense compared to the Brillouin component. A typical profile obtained for the sample with light reflecting inclusion is shown in Fig.1(a). In this case the real Brillouin spectrum was burried under the noise and could not be observed. Therefore, the sample must be carefully purifed to remove the inclusions. In this work, the sample was purified in the following manner. The reagent grade salts was loaded into a reaction tube made of quartz, and was dehydrated in Ar flow for 6hr, then was melted. The dehydrated HCl was bubbled into the melt for 3hr to remove the residual trace amount of the moisture. Then the melt was filtered through a quartz filter. The filtrate was sealed under vacuum into a quartz container to which the optical cell had been connected by a glass blowing technique. The purified sample in the container was transfered into the optical cell by distillation. Then, the smple was sealed into the cell, and was provided to the Brillouin scattering measurement. By the use of a well purified sample, the whole spectrum shown in Fig.1(b) was obtained.

RESULTS AND DISCUSSION

Profiles obtained at different temperatures are compared in Fig.2. The shape of the spectrum changes remarkably with the variation in temperature. At the higher temperature(e.g., 933K) the spectrum has a typical shape of a normal liquid, which consists of a central Rayleigh line and a Brillouin doublet. At the middle temperature region (e.g., 773K), the Brillouin peaks become very broad, and overlapped with the central peak. At the lower temperature (e.g., 623K), the central peak increase its intensity, furthermore, there observed a continuous component between the central line and Brillouin doublet, although the separation between the central peak and Brillouin doublet apparently becomes clear. At the lower temperature, the central peak and Brillouin doublet apparently becomes clear. At the lower temperature, the central peak consists of the weak Rayleigh component, clearly observed in the profiles at 933K, and a strong component due to the relaxation to adiabatic pressure fluctuation.

The viscoelastic theory (7) gives the spectral distribution function $\sigma(k,\omega)$ as follows.

$$\sigma(\mathbf{k},\omega) = (1 - \frac{1}{\gamma}) \frac{2(\lambda k^2 / \rho_0 C_p)}{(\lambda k^2 / \rho_0 C_p)^2 + \omega^2} + (\frac{2M_0}{\gamma}) \frac{\eta(\omega) + \eta_0}{\{\omega[\eta(\omega) + \eta_0]\}^2 + \{\rho_0 \omega^2 / k^2 - M(\omega)\}^2}$$
(1)

where k is the shift in wave vector, ω is the shift in angular frequency of the scattered light, λ is the thermal conductivity, $\dot{\rho}_0$ is the density, C_p is the heat capacity at constant pressure, $M(\omega)$ is the longitudinal storage modulus, M_0 is the low-frequency storage modulus, $\eta(\omega)$ is the longitudinal viscosity and η_0 is the nonrelaxing part of the viscosity. The first term in eq.(1) represents the Rayleigh line which is caused by the entropy fluctuation at constant pressure. The second term represents the Brillouin component caused by adiabatic pressure fluctuation.

In most case of liquid, in which the modulation due to dispersion in sound wave propagation is not strong, the Brillouin component in Eq.(1), can be separated approximately into three Lorentzians, which are the Brillouin-doublet and the Mountain line(6). Therefore, the Brillouin spectrum can usually be analysed not by using full spectral shape, but rather its decomposition in the Lorentzian lines. This is the way of analysis taken generally at studies on normal liquids. In this case, the details of the profile of the central peak are not necessarily required for the analysis, if the Brillouin doublet are observed precisely. However, approximated analysis becomes rather poor if the modulation is so strong as in the case of present study. We have therefore, tried to analyse the whole spectrum of the Brillouin scattering.

For single relaxation behavior, following relations hold,

$$\eta(\omega) = \rho_0 (V_0^2 - V_0^2) \tau / (1 + \omega^2 \tau^2)$$
(2)
$$M(\omega) = \rho_0 (V_0^2 + V_\infty^2 \omega^2 \tau^2) / (1 + \omega^2 \tau^2)$$
(3)

where τ is relaxation time, V_0 and V_{∞} are velocities at limiting low and high frequencies, respectively.

The Brillouin spectrum has been analyzed by using eqs.1~3. The spectrum obtained corresponds to the dynamical structure factor $\sigma(k,\omega)$, convoluted with the apparatus profile. The apparatus profile was observed in advance, and is shown in Fig.3. The spectrum was analyzed in the following manner. The theoretical spectrum is computed for a set of initial values of the parameters (V_{o} , V_{w} , τ and η_0) and then convoluted numerically with the apparatus profile, and compared with the experimental spectrum by a least squares scheme to calculate an improved set of parameters. The parameter fitting is repeated until the squares of the deviation become minimum. For each spectrum, then, a set of parameters V_{o} , V_{w} , τ , and η_0 is obtained.

Figure 4 shows the Brillouin spectra of ZnCl₂ at scattering angle of 90° in comparison with the value calculated by best fit of the viscoelastic theory. The circles represent the experimental values, and the lines show the best fit of Eq.(1) with the convolution of the apparatus profile. As shown in Fig.4, eq.1 describes the spectra very well at various temperatures investicated. The spectrum analysis was also done for profiles obtained at other scattering angles, and for ZnCl₂-20%NaCl binary melt, in the same way.

The temperature dependences of V_0 and V_{∞} for ZnCl₂ single melt are shown in Fig.5. The circles represent the data obtained at the scattering angle of 90°, and the squares, those of 140°. As shown in this figure, the results obtained at different scattering angles agree very well. The velocities at limiting low frequency V_0 and high frequency V_{∞} decrease linearly with increasing temperature.

The relaxation time of ZnCl₂ is shown in Fig.6. The value of τ decreases rapidly with increasing temperature. At the temperatures near 600K, the relaxation time is in the order of nanosecond(10°s), when the temperture increases to 900K, the relaxation time decreases to the order of 10 picosecond (10⁻¹¹s). The remarkable variation of relaxation time indicate the structure variation of the melt with temperature change. The structural studies of ZnCl₂ have been done by several researchers (8~10). It has been considered that ZnCl₂ melt consists of polymeric (ZnCl₂)_n species of various sizes. These species are made up of ZnCl₄ tetrahedra bridged at the corners to give three dimensional networks. With increasing temperature the degree of polymerization lowers. Due to the presence of the large sized polymeric species at the lower temperatures, the response of the melt is very slow. This is the reason for the relaxation time being long at the lower temperatures. The response rate increases with increasing temperature. Therefore the relaxation time decreases with increasing temperature.

As has been described, the shape of the Brillouin spectrum of ZnCl2 melt changes

remarkably with the variation in temperature. The spectral shape mostly depends on the value of the relaxation time. The shape of the Brillouin spectrum changes drastically, if the value of $\omega \tau$ is nearly equal to unity (2). For the case of molten ZnCl₂, the relaxation time varies more than 1000 times over the temperature range of 1000 to 580K, and the condition, $\omega \tau \approx 1$ stands in the midst of the temperature range. This is the reason for remakable change observed for the Brillouin spectral shape depending on temperature.

The temperature dependence of V_0 and V_{∞} for ZnCl₂-NaCl binary melts is shown in Fig.7. V_0 and V_{∞} decrease linearly with increasing temperture for each composition. There found about 0.6km.s⁻¹ dispersion in the velocity for ZnCl₂-20%NaCl binary melt.

The relaxation time of the binary melts is plotted against temperature in Fig.8. The relaxation time decreases with an addition of NaCl. This effect is remarkable at the lower temperature region. We consider that this is due to the breakage of the network structure in the melt. It seems that sodium chloride acts as a chloride ion donor when it is added to ZnCl2, and therefore, the addition of NaCl prompts breakage of the network structure in ZnCl2 and results in the decrease of relaxation time.

CONCLUSION

The Brillouin spectra in ZnCl2single and ZnCl2-20%NaCl binary melts were obtained by using a computer assisted data acquisition system. The Brillouin spectra were well described by the viscoelastic theory with the assumption of the single relaxation. The velocities at limiting low frequency, V_{0} and high frequency V_{∞} decerease linearly with increasing temperature. The relaxation time decreases remarkably with an addition of NaCl. It is concluded that both the temperature increase and the addition of NaCl result in the modification of the network structure of ZnCl2 melt.

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Fig.1 Profiles of Brillouin spectrum of ZnCl₂ at 730K, θ =90°, (a) Sample with light reflecting inclusion. (b) refined sample.

Fig. 2 Brillouin spectra of ZnCl₂ at various temperatures, $\theta = 90^{\circ}$.



Fig.3 Apparatus Profile



Fig.4 Brillouin spectra of ZnCl₂ for θ =90°, the lines show the best fit of viscoelastic theory.



Fig. 5 Temperature dependence of V_0 and V_{∞} for ZnCl₂ melt.



Fig. 6 Relaxation time of ZnCl₂ melt.



Fig. 7 Temperature dependence of V_0 and V_{∞} for ZnCl₂-NaCl binary melts.



Fig. 8 Relaxation time of ZnCl₂-NaCl binary melts.

PREPARATION, VAPOR PRESSURE AND THERMOCHEMISTRY

OF

TIN(II) BROMIDE

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ABSTRACT

The synthesis of high-purity tin(II) bromide from the elements is outlined. The vapor pressure of liquid SnBr_2 from 576 to 923 K is measured by the quasistatic method. Previous Knudsen effusion mass spectrometric studies are reviewed. A critical evaluation of the literature values for melting temperature and enthalpy of fusion is presented. The molar heat capacities of $\text{SnBr}_2(s)$ and $\text{SnBr}_2(l)$ are evaluated, and an expression for the molar heat capacity of $\text{SnBr}_2(g)$ is derived from spectroscopic constants and structural data. A complete set of thermochemical data useful in the modelling of discharge arcs containing SnBr_2 is derived from the vapor pressure measurements.

Tin(II) bromide is of considerable interest as a source of radiation in metal halide discharge lamps. This is due in part to the continuum (molecular) radiation in the visible spectrum of arcs containing tin halides (1). When an alkali metal halide, such as NaBr, is also introduced to the arc, the total Na concentration in the vapor phase can be enhanced by formation of vapor phase complexes such as NaSnBr₃ (2). These effects can lead to increased luminous efficacy and improved color rendition, particularly where a warm, lower color temperature light is desired. In spite of the widespread use of SnBr₂ in lamps, only a few references to its use in lamps have appeared in the literature in the last 20 years (1,3-10).

Satisfactory lamp life and performance require metal halides with extremely low levels of oxygen-, hydrogen- and carbon-containing impurities. We describe here the preparation of high-purity SnBr₂ from the elements which yields material suitable for discharge lamps. This method is compared with previously applied methods for the synthesis of SnBr₂, and the advantages and disadvantages of each method are discussed.

The accurate modelling of discharge lamps containing $SnBr_2$ requires a detailed knowledge of the vapor phase species present above the condensed phase, and requires accurate thermochemical data for the vaporization process and for vapor phase processes such as dimerization or dissociation. We have thus performed total vapor pressure measurements above SnBr₂ over the temperature range 576 to 923 K by the quasistatic method (11). This is a wider temperature range than that reported in previous total vapor pressure studies (12,13).

Also included is a brief review of previous Knudsen effusion mass spectrometric studies, and a review of previous melting temperature and enthalpy of fusion results for SnBr₂. Recommended values for the melting temperature and the enthalpy of fusion are based on a critical evaluation of the literature data.

Recommended values for the molar heat capacities of solid, liquid and gaseous $SnBr_2$ are also reported. The recommended molar heat capacities for the condensed phases are based on literature values. The calculation of the molar heat capacity for the gaseous phase is based on a critical evaluation of spectroscopic constants and the product of the principal moments of inertia from the literature.

The vapor pressure data from this study are then used to derive a complete set of thermochemical data useful in the modelling of discharge arcs containing SnBr₂. Enthalpies and entropies of vaporization are derived using both second- and third-law treatments, and are compared with previous literature values. Recommended values for the standard enthalpies of formation of solid, liquid and gaseous SnBr₂ are also reported.

A more detailed account of this work will be published elsewhere.

EXPERIMENTAL

Synthesis of Tin(II) Bromide

Tin(II) bromide was prepared from Sn metal shot (99.999%, Cominco Electronic Materials), and reagent ACS grade bromine. Both were used as received, without further purification. The reaction vessel is fabricated from a fused silica tube, 48 mm o.d. by 50 cm long, closed on the left end, with a depression in the center. A 90 degree cross with 2 necks and a bromine bulb is attached to the right end of the vessel, as shown in Figure 1. The vessel is cleaned with 10% HF, rinsed with deionized H₂O, followed by reagent grade ethanol. It is then evacuated and heated to about 500 K to remove solvent residues.

While holding the main reaction vessel vertically, about 150 g of Sn metal is introduced through neck A, and the vessel is sealed off at point 1 (see Figure 1). The vessel is then heated to about 500 K with a broad-flamed torch and evacuated and refilled with inert gas three times through neck B. It is allowed to cool under vacuum (< 1 Pa) and is then filled with inert gas.

An amount of Br_2 equal to 99% of that required to form $SnBr_2$ is poured into the bulb through neck B. A partial vacuum is then applied through neck B until the bromine begins to boil. The vessel is refilled with He and evacuated to this pressure three times. The bromine bulb is then immersed slowly in liquid nitrogen, a hard vacuum (< 1 Pa) is applied, and the vessel is sealed off at point 2.

The vessel is placed into a two-zone tube furnace as shown in Figure 1. The sealed-tube reaction is carried out behind a blast shield in a fume hood. Each temperature controller is equipped with a temperature overshoot protection circuit (operating from a second, independent thermocouple) which will disconnect power from all furnaces in the event of an overshoot. The left hand (L.H.) zone is heated to 395 K, the right hand (R.H.) zone and bromine bulb being held at ambient temperature until all of the bromine has reacted to form SnBr₄. The vessel is then sealed off at point C, leaving only the large vessel section in the furnace, and the L.H. zone is heated to 395 K to drive all of the SnBr₄ to the R.H. side. The L.H. zone is then raised to 775 K for a minimum of 72 hours until all traces of SnBr₄ have reacted to form SnBr₂.

The final step in the preparation of SnBr₂ consists of melting the product, scrubbing with inert gas and filtering through a porous silica frit. The details of this process have been described in the literature for other metal halides (14). The filtered liquid is jetted through a small orifice, and the molten particles are rapidly quenched. This provides spherical particles with a small surface area to mass ratio, thus reducing potential water or oxygen contamination.

Chemical analysis of the product for total tin by iodometric titration gave (42.46 ± 0.21)% Sn (theory 42.62%), and for bromide by argentometric titration with potentiometric endpoint gave (57.15 ± 0.29)% Br (theory 57.38%), thus confirming the stoichiometry to within experimental uncertainty.

Vapor Pressure Measurements

The vapor pressure measurements were made using the quasistatic method of Rodebush and Dixon (11).

The $SnBr_2$ was loaded into the measurement cell in an inert atmosphere dry box. The cell itself was fabricated from Thermal Syndicate grade four electrically fused silica. No interaction was observed between the sample and this material.

The sample was then heated in a platinum-wound vertical furnace, regulated by a Stanton Redcroft LVP controller. The temperature was maintained within ± 0.2 K. The temperature of the sample was monitored independently by a platinum-to-(platinum +13% rhodium) thermocouple. Cold junction compensation was made with a second thermocouple immersed in an ice/water bath. The potential difference was monitored by a Thurlby 1905a voltmeter with a resolution of 1 μ V.

The pressure measurements were made with a Baratron 170 capacitance gauge with a precision of 0.1 Pa in the range up to 1.3 kPa, 1 Pa in the range from 1.3 to 13.3 kPa, and 10 Pa in the range from 13.3 to 133 kPa.

RESULTS AND DISCUSSION

Synthesis 5 1

Previous approaches to the synthesis of anhydrous $SnBr_2$ include: direct reaction of the elements (15-20), reaction of tin metal with anhydrous HBr (13,21-25), reaction of tin metal with aqueous HBr followed by dehydration (26-33), reaction of tin with butyl bromide and butyl alcohol (34), and simple vacuum distillation of commercial samples (35-38).

Preparations in aqueous and organic media are undesirable from the point of view of potential solvent contamination. Dehydration of commercial samples may also suffer from incomplete removal of water, hydroxide and oxide impurities. The possibility of a volatile $SnOBr_2$ species has been suggested (37), although its existence at high temperatures has not been established.

Reaction of the elements and reaction of tin with anhydrous HBr are most attractive for preparation of high-purity $SnBr_2$. The anhydrous HBr route suffers from very low rates of production and limited batch sizes (23). Synthesis from the elements is easily scaled up to moderate batch sizes (300-500 g) and has the advantage that reactants or solvents containing oxygen, hydrogen or carbon are unnecessary. Higher valent halides (SnBr₄) are potential contaminants(37), but can be minimized by sufficient reaction time at high temperature and by the melting and inert gas scrubbing process employed in this work. Mass spectral analysis of material prepared from the elements shows only SnBr₂ as the product (16).

Vapor Pressure Measurements

The vapor pressure above $SnBr_2(1)$ was measured over the range 576 to 923 K, and the values were first fitted by linear regression to the form:

$$\ln(p/Pa) = -A \cdot (K/T) + B \tag{1}$$

Figure 2 shows the experimental points and the linear least squares fit to equation (1). Table 1 contains the coefficients of this regression and the corresponding coefficients reported in previous vapor pressure studies (12,13).

The data were also subjected to a more accurate regression analysis of $\ln(p/Pa) - (\Delta C_p/R) \cdot \ln(T/K)$ against K/T, where $\Delta C_p = C_p(g) - C_p(l)$ accounts for the change in the difference in heat capacities with temperature. This gives an equation of the form:

$$\ln(p/Pa) = -A' \cdot (K/T) + (\Delta C_p/R) \cdot \ln(T/K) + B'$$
(2)

A constant value of $\Delta C_p/R = -7.500$ was chosen to give the best fit to the data. The coefficients and 95 per cent confidence limits of both regression equations are given in Table 2.

There is generally good agreement between the results presented here and the work of the other authors. However, our results include a considerable increase in the measurement range and a general improvement in the precision of the measurements. The results of Karpenko (12) cover the range 723 to 893 K, and there is very close agreement with our results in this range. The results of Fischer and Gewehr (13) cover the range 729 to 884 K, but the measured

pressures are all about five percent lower at each temperature. There is no obvious reason for this discrepancy. We have not included the results of the Knudsen effusion mass spectrometric studies of Hilpert (2) due to the very limited temperature range of the measurements.

It is interesting to note that coefficients of the linear fit of equation (1) from this work are closer to Fischer's values than to Karpenko's (see Table 1). This odd result is due to the wider temperature and pressure range measured in this work, and to the fact that the simple linear regression of equation (1) does not include the change in heat capacity (*i.e.* the $(\Delta C_n/R) \cdot \ln(T/K)$ term of equation (2)).

Knudsen Effusion Mass Spectrometry

Table 3 lists the appearance potentials for ions detected above solid tin(II) bromide from several sources. Although some mass spectrometric studies (16,39) have not reported ions derived from dimers, the presence of $Sn_2Br_4(g)$ has been confirmed by references (2) and (21). In an elegant study Hilpert (2) has determined the partial pressures of $SnBr_2$ and Sn_2Br_4 over the solid (373 to 501 K) and liquid (501 to 573 K). The enthalpy and entropy for the dissociation of the dimer, equation (3), were found to be (106.8 \pm 3.6) kJ·mol⁻¹ and (153.7 \pm 8.8) J·K⁻¹·mol⁻¹ respectively at 298.15 K.

$$\operatorname{Sn_2Br_4}(g) = 2 \operatorname{SnBr_2}(g) \tag{3}$$

Melting Temperature and Enthalpy of Fusion

The reported melting temperature of tin(II) bromide ranges from a low of 489 K to a high of 509 K as shown in Table 4. These melting temperatures have been measured in the course of a wide variety of synthetic and physico-chemical studies, and represent data gathered over a 67 year time period. The value reported most often in the literature and in reviews is 505 K, which is also that reported in the early work of Kendall *et al.* (32) and Fischer *et al.* (13). The fact that many recent investigations (ostensibly using carefully-prepared, pure materials) report values considerably less than this is a bit disturbing and is not easily explained. A critical evaluation of these data leads us to recommend a value of 507 K as shown in Table 4.

Reported values for the enthalpy of fusion of tin(II) bromide also cover a considerable range as shown in Table 4. The recent differential scanning calorimetric data of Gardner and Preston (45) suggests that the previously reported values may be high. Their data, and further calculations, lead us to recommend a value of $\Delta_{fusion} H^0_m (298.15 \text{ K}) = 13.2 \text{ kJ} \cdot \text{mol}^{-1}$. This corresponds to a value of 15.1 kJ·mol⁻¹ at 507 K.

Molar Heat Capacities

Molar heat capacities for the condensed phases of $SnBr_2$ reported in compilations of thermochemical parameters (*e.g.* reference (43)) are estimates based on extrapolation of the low-temperature values reported in reference (19). Recently Gardner and Preston (45) have determined the molar heat capacities of the solid from 350 K to 500 K and of the liquid from 520 K to 800 K using differential scanning calorimetry. We have used their values together with the values from reference (19) to represent the molar heat capacity of the solid, 298.15 K

to 507 K, and the liquid, 507 to 1000 K. The coefficients for the polynomials representing the molar heat capacities are listed in Table 5.

We have assessed critically the spectroscopic constants ν_1 , ν_2 , ν_3 (the vibration frequencies) and I_{ABC} (the product of the principal moments of inertia) required to calculate the molar heat capacity of SnBr₂(g). The molar heat capacity and entropy were calculated using the method described in the JANAF tables (47).

The spectroscopic constants for SnBr₂(g) and many other species listed in the review of thermodynamic properties of gaseous metal dihalides by Brewer *et al.* (48) were estimated primarily because very few experimental values were available at that time. We have selected the vibration frequencies obtained by matrix isolation-Raman spectroscopy together with depolarization measurements (49,50). There is a significant dependence of the vibrational frequencies on the matrix, the values being lower in a nitrogen matrix than in an argon matrix. In this work we have used the frequencies obtained from an argon matrix. Values for ν_1 and ν_3 measured using matrix isolation-infrared spectroscopy in argon (51) are very similar to those in reference (50). Beattie and Perry (52) report a value for ν_2 similar to that used here from an analysis of the resonance fluorescence spectrum.

The first evidence for the non-linear geometry of $\text{SnBr}_2(g)$ came from high-temperature electron diffraction in 1941 (53). The equilibrium bond length and Br-Sn-Br angle used here are those derived from detailed analysis of electron diffraction data from a series of non-linear symmetric triatomic molecules (54).

Calculations using self-consistent field (SCF) and configuration interaction (CI) theory have yielded vibrational frequencies close to experimental values, but gave larger values for the bond length and bond angle (55). Force constants have been derived from electron diffraction and spectroscopic data (56).

We have assumed the multiplicity of the ground state to be 1 and that there are no lowlying electronic levels that make significant contributions to the partition function below 1500 K.

The selected spectroscopic constants for $SnBr_2(g)$ are listed in Table 6. The coefficients for the polynomial describing the molar heat capacity are given in Table 5. $S^{0}_{m}(SnBr_{2},g,298.15 \text{ K})$ is presented in Table 10.

Thermochemical Parameters

We have derived a comprehensive set of thermochemical parameters for tin(II) bromide assuming that the vapor above the liquid contains only monomers. The literature contains two reports of the monomer-dimer equilibrium for tin(II) bromide. Hilpert's study (2) covers the range 373 to 573 K and reports that the mole fraction of dimer above the liquid decreases with increasing temperature from $x(Sn_2Br_4) = 0.016$ at 510 K to 0.014 at 573 K. Conversely, Karpenko's (12) results indicate that $x(Sn_2Br_4)$ increases from 0.056 at 773 K to 0.094 at 893 K. We have shown previously (57) that it is essential to carry out studies of monomer dimer equilibria over the same temperature range as vapor pressure measurements. In view of the low mole fraction of the dimer and the large uncertainties in the values for the monomerdimer equilibrium, we feel the most reliable treatment of our results is to regard the vapor as containing only monomer.

Thermodynamic quantities for the vaporization of tin(II) bromide derived from the second-law treatment are given in Table 7. The enthalpy of evaporation, $\Delta_{evap} H^{0}_{m}(T)$, is calculated from the slope of the linear regression of $\ln(p/Pa)$ against reciprocal temperature, T being the mid-point temperature of the range of measurement. Similarly, the entropy of evaporation, $\Delta_{evap} S^{0}_{m}(T)$, is calculated from the intercept of the linear regression. The corresponding values at 298.15 K are derived using the molar heat capacities for the liquid and gas given in Table 5.

The enthalpy of evaporation can also be calculated by using the third-law method whereby each experimental measurement gives a value for $\Delta H^0_m(298.15 \text{ K})$. The third-law treatment for evaporation can be expressed in the form:

$$\Delta^{g}_{I}H(298.15 \text{ K})/T = -\Delta^{g}_{I}[\{H^{o}_{m}(T) - H^{o}_{m}(298.15 \text{ K})\}/T -\{S^{o}_{m}(T) - S^{o}_{m}(298.15 \text{ K})\} - S^{o}_{m}(298.15 \text{ K})] - R \cdot \ln(p/p^{0})$$
(4)

The molar heat capacities for the liquid and gas were taken from this work (Table 5) as was $S_m^0(SnBr_2,g,298.15 K)$. The entropy of liquid tin(II) bromide, $S_m^0(SnBr_2,I,298.15 K)$ was determined from $\Delta_{evap}S_m^0(298.15 K)$ and $S_m^0(SnBr_2,g,298.15 K)$. The average of the third-law values differs from the second-law value by only 1 kJ·mol⁻¹. The third-law values show no temperature dependence. A strong dependence of the third-law values on temperature can be taken to be indicative of an incorrect value for $S_m^0(298.15 K)$ (58). The enthalpy of sublimation, $\Delta_{sub}H_m^0(298.15 K)$, is calculated from the enthalpies of evaporation and fusion at 298.15 K.

Values for the thermodynamics of evaporation from second-law treatments are compared in Table 8, and are in close agreement. We have not included the enthalpy and entropy values calculated from the Knudsen effusion mass spectrometric studies of Hilpert (2) and Ciach *et al.* (37) due to the very limited temperature range of the measurements.

Reported values for the enthalpy of formation of $\text{SnBr}_2(s)$ at 298.15 K differ considerably and are listed in Table 9. We have selected the value from reference (59), $\Delta_f H^0(\text{SnBr}_2, s, 298.15 \text{ K}) = -252.923 \text{ kJ} \cdot \text{mol}^{-1}$. Values for the enthalpy of formation for SnBr}_2(l) and SnBr}2(g), derived from this work, are listed in Table 10 together with S⁰_m(298.15 K) for solid, liquid and gas.

Vapor pressures above liquid tin(II) bromide calculated using the thermochemical parameters given here are in close agreement with those calculated from equation (2) using the nonlinear coefficients from Table 2.

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Pressure-temperature relationship above SnBr2(1)

Coefficients of ln(p/Pa) = -A/T + B

Reference and Year	Range/K	Α	В
Karpenko (12) 1969	723-893	$1.2182 \cdot 10 \stackrel{4}{4} \\ 1.2324 \cdot 10 \stackrel{4}{4} \\ 1.2566 \cdot 10 \stackrel{4}{4}$	24.991
Fischer (13) 1939	729-884		25.026
This work 1990	576-923		25.500

TABLE 2

Vapor pressure equations for $SnBr_2$ with the limits of the coefficients at the 95% confidence level.

Linear Form:

 $\ln(p/Pa) = -(1.2566 \pm 0.0247) \cdot 10^4 \cdot K/T + (25.500 \pm 0.332)$

Nonlinear Form:

Appearance potentials for ions detected above SnBr₂(s)

Ion	Precursor	Appearance potential/eV	Reference		
Sn +	$SnBr_2(g)$ (a)	12.8 ± 1.0	(39)		
Sn +	$SnBr_2(g)$ (b)	14.5 ± 1.0	(39)		
Sn +	$SnBr_2(g)$ (b)	14.9 <u>+</u> 0.3	(16)		
SnBr +	$SnBr_{2}(g)$ (c)	11.0 ± 0.4	(39)		
SnBr +	$SnBr_2(g)$ (c)	11.2 ± 0.2	(16)		
SnBr +	$SnBr_2(g)$ (c)	11.0 ± 0.5	(21)		
SnBr ₂ +	$SnBr_2(g)$ (d)	10.0 ± 0.4	(39)		
SnBr2 ⁺	$SnBr_2(g)$ (d)	10.6 ± 0.2	(16)		
Sn2Br3 +	$Sn_2Br_4(g)$ (e)	10.6 ± 0.5	(21)		
(a) $\operatorname{SnBr}_2(g) + e^- = \operatorname{Sn}^+(g) + \operatorname{Br}_2(g) + 2e^-$ (b) $\operatorname{SnBr}_2(g) + e^- = \operatorname{Sn}^+(g) + 2\operatorname{Br}(g) + 2e^-$ (c) $\operatorname{SnBr}_2(g) + e^- = \operatorname{SnBr}^+(g) + \operatorname{Br}^-(g) + e^-$ (d) $\operatorname{SnBr}_2(g) + e^- = \operatorname{SnBr}_2^+(g) + 2e^-$ (e) $\operatorname{SnBr}_4(g) + e^- = \operatorname{SnBr}_2^+(g) + 2e^-$					

TABLE 4

Reported values of the melting temperature and enthalpy of fusion for $SnBr_2$. Melting temperature values have been rounded to the nearest K.

Reference(s)	Melting Temperature/K	$\Delta_{\text{fusion}} H^{0}_{m}(T)/kJ \cdot mol^{-1}$
(40)	489	_
(38)	499	-
(22)	501-502	-
(41)	503	-
(42)	504	17.2 (19.3) *
(30)	504	20.6
(43)	504	17.2
(13, 18, 25, 28, 31, 32, 44)	505	-
(45)	507	14.3
(46)	509	-
Recommended value	507	15.1

* Of two values reported, the first, 17.2 kJ·mol⁻¹, was preferred

Coefficients for the temperature variation of the molar heat capacities of SnBr_2 using the equation:

$C^{0}_{p,m}(T)/J \cdot K^{-1} \cdot mol^{-1} = A + B(T/K) + C(T/K)^{2} + D(T/K)^{-2}$							
	Α	В	С	D			
SnBr ₂ (s)	4.10970 · 10 ¹	1.21581 · 10 ⁻¹	-6.36180 · 10 ⁻⁵	6.47550 · 10 ⁵			
SnBr ₂ (l)	$8.83280\cdot10\ ^{1}$	-4.69880 · 10 ⁻³	4.08791 · 10 ⁻⁵	$-5.40900 \cdot 10^4$			
SnBr ₂ (g)	5.81690 · 10 ¹	1.54000 · 10 ⁻⁵	-1.71000 · 10 ⁻⁹	-1.59110 · 10 ⁵			

TABLE 6

Spectroscopic constants for SnBr 2(g)

Vibrational frequencies

ν 1 ν 2 ν 3	244 cm ⁻¹ 82 cm ⁻¹ 231 cm ⁻¹
Sn-Br bond length	2.504 Å
Br-Sn-Br bond angle	98.6 °
IABC	$3.760 \cdot 10^{-112} \text{ g}^3 \text{ cm}^6$

Thermodynamics of vaporization for SnBr₂

$\Delta_{evap} H^{0} m$ (750 K)	$(105 \pm 2) \text{ kJ} \cdot \text{mol}^{-1}$
$\Delta_{evap} H^{0}_{m}(298.15 \text{ K})$ (a)	$(121 \pm 3) \text{ kJ} \cdot \text{mol}^{-1}$
$\Delta_{evap} H^{0}_{m}(298.15 \text{ K})$ (b)	$(122 \pm 3) \text{ kJ} \cdot \text{mol}^{-1}$
$\Delta_{evap} S^{o}_{m}(750 \text{ K})$	$(116 \pm 3) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
$\Delta_{evap} S^{0}_{m}$ (298.15 K)	$(152 \pm 5) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
$\Delta_{sub}H^{0}m^{(298.15 \text{ K})}$	$(135 \pm 5) \text{ kJ} \cdot \text{mol}^{-1}$
(a) Second-law treatment	

(b) Third-law treatment

TABLE 8

Enthalpies and entropies of evaporation for SnBr₂

Reference	T/K	$\Delta_{evap} H^{0}_{m}(T)/kJ \cdot mol^{-1}$	$\Delta_{evap} S^{o}_{m}(T)/J \cdot K^{-1} \cdot mol^{-1}$
Fischer (13)	811	102 ± 2	112 ± 2
Karpenko (12)	808	101 ± 1	112 ± 1
This work	750	105 ± 2	116 ± 3

TABLE 9

Reported values for the enthalpy of formation of $\text{SnBr}_2(s)^{**}$

Reference	∆ _f H ⁰ m(SnBr ₂ ,s,298.15 K)/kJ·mol ⁻¹
Brewer (48)	-266.102
Wagman et al.(60)	-243.509
Glushko (61)	-259.994
Stenin et al. (59)	-252.923

** Values reported to 3 decimal places as in the usual convention. This does not represent the precision.

Phase	$\Delta_{\rm f} {\rm H^0}_{\rm m}$ (298.15 K)/kJ·mol ⁻¹	S ^o m(298.15 K)/J·K ⁻¹ ·mol ⁻			
SnBr ₂ (s)	-252.923	153.000			
$SnBr_2(l)$	-239.723	176.900			
$SnBr_2(g)$	-118.383	328.764			

Enthalpies of formation and entropies at 298.15 K for SnBr2 **

** Values reported to 3 decimal places as in the usual convention. This does not represent the precision.



Figure 1. Vessel and furnace arrangement for synthesis of tin(II) bromide



Figure 2. Vapor pressure (p/kPa) versus temperature (T/K) for tin(II) bromide. Solid curve is the linear least squares fit of equation (1). Boxes are experimental points.

DEVELOPMENT OF RAMAN SPECTROSCOPIC SENSORS FOR MAGNESIUM IN A MOLTEN SALT SYSTEM

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ABSTRACT

A study of the Raman spectra of the soluble magnesium(II) species in melts such as NaCl-KCl-CaCl₂ (41-41-18 mole %) has been carried out. Over the range of 0 to 25 mole % MgCl₂ in NaCl-KCl-CaCl₂ at 700 °C, the intensity of the MgCl₄² Raman band near 250 cm⁻¹ was found to vary linearly with Mg(II) concentration. Such a correlation was made possible by normalizing the data to the Rayleigh scattering line from the melt. The precision of this determination is ± 1.6 mole %. An all-quartz fiberoptic probe has been developed for measuring Raman spectra of the above melt system remotely.

INTRODUCTION

The light metal, magnesium, is produced today largely through the electrolysis of molten salt systems containing MgCl₂ (1,2). This electrolytic process is energy-consuming. Therefore, intensive research efforts have been initiated to reduce the energy consumption by studying the chemistry of related molten salt systems. Notably, Raman spectroscopic results have revealed the existence of $MgCl_4^{2^*}$ species in several melt systems (3,4). No quantitative experiments have been carried out to demonstrate the direct correlation between concentration of MgCl₂ and the intensity of the the corresponding Raman band, and, to our knowledge, no calibration curves have been determined. We want to report here the Raman spectral determination of soluble magnesium(II) in melts with compositions similar to those used in the electrolytic production of magnesium by the Dow Chemical Company (1). The establishment of the calibration curve in melts of direct interest to the industry will be the first step toward the in-situ monitoring of the industrial electrolytic processes. The second part of this work is the development of a fiberoptic Raman probe for the remote measurement of the magnesium complex in these melts in order to apply this determination to industrial electrolytic process controls. The all-quartz fiberoptic probe developed by us previously (5) has been applied to such measurements.

EXPERIMENTAL

REAGENTS: Anhydrous magnesium chloride was synthesized by the decomposition of the corresponding carnallite salt (6), followed by distillation using a double bulb quartz vessel (7). No IR bands of hydroxide or magnesium oxide species were found in the magnesium chloride thus synthesized (8). The procedure for the purification of the other starting materials (NaCl and KCl) has been described previously (9). Anhydrous calcium chloride was supplied by T. Blanchard (University of Tennessee, Knoxville).

INSTRUMENTATION: Raman spectra were recorded with a Ramanor HG-2S spectrophotometer equipped with concaveaberration-corrected holographic gratings. This instrument, manufactured by Jobin Yvon (Instrument SA), employs a double monochromator. Excitation of the spectra was by means of the 514.5 nm-line from an argon-ion laser (Coherent). Spectral data were stored in a 4096 channel Nicolet model 1170 signal averager which permitted the averaging of spectra over repeated scans. The furnace used in the conventional high temperature Raman measurements has been described previously (10).

The fabrication of the all-quartz probe has been described in detail elsewhere (5). Briefly, the probe was constructed by the fusion of four 600 μ m all-silica fibers into a quartz tube under vacuum. Vacuum was applied to make a seal and minimize bubbling of the quartz during the fusion process. This fusion method is very similar to those used in the fabrication of microelectrodes (11). Once fused, the probe tip was carefully cut and polished with successively finer grades of emery paper to a smooth finish.

PROCEDURE: For conventional Raman measurements, the sample was loaded into a quartz tube in a drybox under an argon atmosphere and sealed off by the use of a vacuum line. For fiberoptic Raman measurements, samples were loaded in a drybox into a quartz tube with a threaded glass connector as the probe port. The probe was inserted into the sample through the port. The whole assembly was then transferred

outside the drybox and put into a furnace. The laser light was focused into the excitation fiber through a microscope objective, and an xyz positioner was employed to optimize the laser input to the single fiber. About two-thirds of the laser power was lost during the laser-fiber coupling. Collection fibers were mounted side by side in another xyz positioner to increase collection efficiency and positioned at the focal point of the spectrometer input collecting lens.

RESULTS AND DISCUSSION

CALIBRATION CURVE: Figure 1 shows the Raman spectra of molten NaCl-KCl-CaCl₂(41-41-18 mole%) containing varying mole percent of MgCl₂ at 720 °C. This melt composition is similar to that used in the electrolytic production of magnesium (1,2). The Raman band near 246 cm⁻¹ is assigned to the totally symmetric stretching mode (A_1) of MgCl₂⁻² (3,4). A calibration curve showing the variation in intensity of this Raman band as a function of $MgCl_2$ mole percent in this series of melts (NaCl-KCl-CaCl₂-MgCl₂) is shown in Figure 2. This calibration was obtained by normalizing the spectra to the intensity of the Rayleigh scattering observed in the sample melts at 100 cm^{-1} . This normalization technique requires the assumption that the intensities of the Rayleigh scattering for the above melts are independent of the concentration of magnesium chloride. We have also shown that the Rayleigh internal standard is insensitive to laser power. This novel use of Rayleigh scattering as an internal standard has not been reported before. With this calibration, one can currently determine the soluble $MgCl_4^{2^2}$ with a relative standard deviation of ±1.6 mole percent. This calibration curve will be used in future studies involving the determination of MgCl,²⁻ in industrial melts.

PROBE: Figure 3a shows the Raman spectrum of $MgCl_4^{2^{-}}$ in a 4-component melt made from NaCl-KCl-CaCl_2-MgCl_2 (35-35-15-15 mole %) recorded by the use of the fiberoptic probe, while the corresponding Raman spectrum recorded by the traditional method is given in Figure 3b. As can be seen in Figure 3a, there is a broad shoulder around 500 cm⁻¹ in addition to the totally symmetric band due to MgCl₄²⁻. This shoulder is caused by the quartz Raman scattering in the optical fibers (12). The signal can be easily removed by baseline subtraction. The base-line subtracted Raman spectrum of Figure 3a is shown in Figure 4. As expected, Figure 4 can be superimposed on Figure 3b. This demonstrates that the calibration curve shown in Figure 2 can be used with remote Raman sensors. A similar Raman spectrum was recorded by the probe for the melt made from NaCl, KCl, CaCl₂ and MgCl₂·2H₂O (35-35-15-15 mole %). The fiberoptic probe can be also used to measure Raman spectra of

powder samples. Figure 5 gives the Raman spectrum of MgCl₂ powder measured with the same probe.

CONCLUSIONS

A calibration curve of Raman intensities vs. concentration of MgCl₂ in molten chloride salts has been obtained. An all-quartz fiberoptic probe was successfully applied to measure Raman spectra of these melts which are similar to melts used in the production of Mg metal.

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FIGURE 1 Raman spectra of molten NaCl-KCl-CaCl₂(41-41-18 mole%) containing varying mole% of MgCl₂ at 720°C, a) 19%;(b)14.2%;d)10.2%;e)5.8%;f)4.8%.



FIGURE 2 The calibration curve of $MgCl_2$ concentrations using Rayleigh line as an internal standard.



FIGURE 3 Raman spectra of $MgCl_4^2$ in molten NaCl-KCl-CaCl_3-MgCl_2, 35-35-15-15 mole%, at 720°C (a) recorded by the use of the fiberoptic probe (b) recorded by conventional method. The frequency of the exciting laser was 514.5 nm, argon-ion laser.



FIGURE 4 Baseline corrected Raman spectrum shown in Figure 3a.



FIGURE 5 Raman spectrum of MgCl₂ powder recorded by an all silica fiberoptic probe. The frequency of the exciting laser was 514.5 nm, argon-ion laser, at 800 mW power.

STRUCTURAL PROPERTIES OF ZINC HALIDE MELTS

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ABSTRACT

Vibrational Raman spectroscopy has been used to identify and determine the structure of species formed in the binary mixtures ZnCl₂-ACl (A=Cs, Li) and ZnCl₂-ZnBr₂. The data indicate that the network-like structure of the zinc halide melts breaks up with the addition of alkali metal halide and with increasing temperature. The tetrahedral structure around the Zn is preserved but one, two, three or four "terminal" halogen atoms having A^+ as nearest neighbors are formed. Different bridging bonding states are proposed to exist in the pure ZnCl₂ glass and liquid.

INTRODUCTION

The structural properties of zinc halide melts and glasses, including their mixtures with alkali halides, have been extensively investigated by a variety of spectroscopic techniques (1). Pure ZnCl₂ has been studied by x-ray scattering (2), EXAFS (3) and neutron diffraction (4,5) while Raman, IR and inelastic neutron scattering spectroscopy have been used for studying both pure ZnCl₂ (6-11) and its mixtures with alkali halides (7,12,13) and with ZnBr₂ (13). All these studies have revealed a commonly adapted structural model for glassy-ZnCl₂ and liquid-ZnCl₂, where the small Zn⁺² ions occupy tetrahedrally coordinated "sites" in a closely packed ion structure with strong intermediate range ordering. For melt mixtures rich in alkali halide, tetrahedral ZnX₄⁻² (X=halide) entities ("complexes") have been argued to exist

(7,12,13) as in general is the case for most first row divalent transition metal halide-alkali halide melts (14,15). For melt mixtures rich in ZnX_2 , the structure is described in terms of either polynuclear in Zn aggregates (7,10) or bridging and non bridging states of the halogen atoms (8,10,12,13). The depolarized low frequency Raman spectra of molten and glassy ZnCl₂ have been associated with the vibrational density of states (10,11), having contributions from internal modes of the local symmetry, some of which are splitted as a consequence of long range interactions (LO-TO splitting (9,11)).

Quasielastic light scattering spectroscopy in $ZnCl_2$ at temperatures from below T_g to above T_m have pointed out, that the present structural entities are important in determining the dynamic processes occurring near T_g (16-19). In a recent photon correlation spectroscopic study (20), at least two dynamic processes have been observed, implying peculiar features for the structure and bonding in ZnCl₂.

In the present work we have undertaken a detailed Raman spectroscopic study of $ZnCl_2$ melts and glasses, as well as, of the binary mixtures of liquid $ZnCl_2$ -CsCl, $ZnCl_2$ -LiCl and of glassy $ZnCl_2$ -ZnBr₂. Systematic temperature and composition dependence measurements are reported, and the data are interpreted in terms of different bonding states of the "network" like structure of these melts.

EXPERIMENTAL

The reagent grade chemicals $ZnCl_2$, $ZnBr_2$, LiCl and CsCl were purchased from Merk Chemical Co. or Cerac Pure Inc. The starting materials were further purified by bubbling gaseous HCl or HBr through the corresponding halide melt and then filtering it under nitrogen atmosphere. All operations with the anydrous chemicals were carried out in a nitrogen filled glove box (<1 ppm H₂O) or in sealed fused silica containers.

The Raman cells were made from fused silica tubes of constant diameter (OD=6 mm, ID=4 mm). The clean and anhydrous chemicals were transfered into the cells and sealed under vacuum. The cell was between 2-3 cm long and was attached to a fused silica manipulation rod of ~10 cm length. The mixtures $ZnCl_2$ -CsCl, $ZnCl_2$ -LiCl and $ZnCl_2$ -ZnBr₂ were made by

mixing into the Raman cell preweighed amounts (0.2 to 0.6 gr total) of the component salts. For making the $ZnCl_2$ - $ZnBr_2$ glasses the cells containing the mixtures, were heated at ~550° C for several hours, and then quenched in water at room temperature. All melts and glasses obtained were clear, transparent and did not fluoresce when the Ar⁺ lines were used to excite the spectra.

The Raman spectroscopic system and the techniques for measuring relative Raman intensities from samples in different cells were the same as before (21,22). The spectrometer was interfaced with a P.C. for recording the spectra and for directly calculating the reduced Raman intensity and the depolarization ratios.

RESULTS AND DISCUSSION

The measured Raman intensity $I(\omega)$ at frequency ω is related to the reduced Raman intensity $R(\omega)$ (15) as follows:

$$\mathbf{R}(\omega) = \mathbf{I}(\omega) \,\omega \left(\omega_{0} - \omega\right)^{-4} \left[n(\omega) + 1 \right]^{-1}$$
[1]

where ω_0 is the excitation laser frequency and $[n(\omega)+1]=[exp\frac{h\omega c}{kT} -1]^{-1}+1$ the Boltzmann thermal population factor.

For amorphous materials the $R(\omega)$ is related to the vibrational density of states (23), and an advantage for using it especially at elevated temperatures, is that it suppresses the Rayleigh and Boson peaks and emphasizes the low frequency (ω <100 cm⁻¹) features of the spectra (15). The effect of the thermal population factor is also important for quantitative measurements of the relative intensities of species in equilibrium, with Raman bands in the intermediate frequency region (ω <500 cm⁻¹) (21).

Most of the Raman spectra reported in the present work are at elevated temperatures, and it is necessary for quantitative comparisons of the intensities to use the $R(\omega)$ representation of the spectra. Frequency and intensity distortions of the bands due to the thermal population factor are thus removed, and temperature dependent effects are revealed.

Temperature Dependence of the ZnCl₂ spectra

Figure 1 shows the Raman spectra of glassy and liquid $ZnCl_2$ at different temperatures. Details for the low frequency spectra of the glass at 130° C are given in Fig. 2. Our spectra are very much in agreement with the spectra reported before (9-11). Apart from the Boson peak measured in our I(ω) spectra at ~25 cm⁻¹, a weak polarized band was present in the VV spectra at ~530 cm⁻¹ which has been also reported in ref. 9. Three strongly polarized bands were measured at 230, ~ 280 and ~380 cm⁻¹ and two depolarized bands at ~75 and ~105 cm⁻¹ are seen in the low frequency region. A third low frequency band, which is deconvoluted in the isotropic spectra of fig. 2 at ~125 cm⁻¹, is polarized.

Increasing temperature did not change drastically the overall intensity of the "raw" $I(\omega)$ spectra, and minor variations of the relative intensities were observed. However, in the thermal factor population free $R(\omega)$ spectra, discreet changes in the relative intensities appear to occur (Fig. 1). The overall $R(\omega)$ intensity decreases with rising temperature, but the band intensities at 280 cm⁻¹ and 380 cm⁻¹ increase relatively to the 230 cm⁻¹ band. These observations indicate that, structural changes occurring with increasing temperature, affect the vibrational frequencies of the ZnCl₄ tetrahedra participating in the "network" like structure.

The only crystalline stable form of pure anhydrous $ZnCl_2$ is an orthorhombic h.c.p. structure (24) having $ZnCl_4$ tetrahedral groups, each sharing vertices with four others. A vertex sharing structure of single bridged Cl atoms has been also accepted for the glass and the liquid. Such structure implies that the coordination sphere of Zn would have four Zn atoms as second nearest neighbors. The diffraction studies (5) however, show that in the liquid the Zn-Zn coordination number is 4.7, indicating that on the average there are more than four ZnCl₄ groups around each ZnCl₄ group. Such coordination can be achieved by having more than two tetrahedral groups bound by a common vertex and/or by connecting the tetrahedra by edges. Structures of the MY₂ salts, having either double bridged (edges) Y atoms in infinite chains (e.g BeCl₄ groups) or layers of tetrahedra sharing vertices and edges (e.g. GaS₄ and PS₄ groups), are rather rare but known to exist (24). If the assumption is made, that the distance between the Y atoms of different MY₄ groups is not less than the edge-length of the tetrahedra

(this restricts the M-Y-M angle to 102°), then the maximum number of tetrahedra that can be met at a common vertex is eight, but the number is reduced to four if edge sharing is not permitted.

The space topology of the tetrahedra and the 4.7 Zn-Zn coordination number, imply that it is possible in the $ZnCl_2$ network to have one Cl atom sharing the vertices with more than two $ZnCl_4$ groups and/or two Cl atoms bound in a common edge of two tetrahedra(edge sharing). In Figure 3 we present schematically three such structures, one having single vertex sharing (SV), the other with a double vertex sharing (DV) and the third with edge sharing (E). These structures create non-equivalent chlorine atoms of the ZnCl₄ groups and thus, different Zn-Cl stretching vibrational frequencies are expected.

The temperature dependence of the Raman spectra (Fig. 1) supports the above model (Fig.3). Thus, the 230 cm⁻¹ band could be assigned to a Zn-Cl stretching mode, which is weakened by either double bridged Cl atoms (edge sharing, structure E) or, single bridging of more than two tetrahedra at a common Cl atom (i.e. structure DV). Increasing temperature tends both to break the double bridges and to reduce the number of tetrahedra bound to a common Cl atom, which in turn strengthens the Zn-Cl bond and moves the vibrational frequency to higher values (i.e the 280 cm⁻¹ band). An equilibrium between species of the type DV and E with SV gives an account for the reversible temperature changes of the relative Raman intensities shown in Fig. 1. In this context, the 380 cm⁻¹ band, seen better in the high temperature spectra, is attributed to Zn-Cl vibrations of non bridged Cl atoms (structure TB in Fig. 3). Such a possible structure is supported by the neutron scattering measurements (5), where a decrease of the coordination number of Zn-Cl occurs with increasing temperature, implying the creation of voids or equivalently the formation of ZnCl₂ units (i.e. structure TB).

The low frequency region of the spectra of $ZnCl_2$ (Fig. 2) was also influenced by the temperature. An overall intensity drop and broadening of the bands was observed, but the relative intensities of the three bands involved did not change drastically. The isotropic spectra show the presence of the ~125 cm⁻¹ polarized band at all temperatures with no shifts of its frequency. It seems that this region of the spectra is not affected by the local thermostructural changes occuring in the "network" structure.

The ZnCl₂-CsCl and ZnCl₂-LiCl liquid systems

Raman spectra of these binary systems were measured at different compositions and at various temperatures above the liquidus and up to 670° C. Figures 4 and 5a show the composition dependence of the $R(\omega)$ spectra at 660° C for the ZnCl₂-CsCl system and at 622° C for the ZnCl₂-LiCl system.

For the mixtures rich in CsCl ($X_{Zn} < 0.33$), the predominant feature of the spectra is a polarized band at 275 cm⁻¹ with intensity that increases proportionally to the amount (mole fraction) of the ZnCl, in the melt. With increasing temperature small "red" shifts of the 275 cm⁻¹ band were observed but no drastic changes in the intensities and the spectra profile were detected. In agreement with previous investigations (6,7,12), the polarized bands at 275 cm⁻¹ in the CsCl melts and at 282 cm⁻¹ in the LiCl melts are assigned to the stretching v_1 frequency of $ZnCl_4^{-2}$ tetrahedral "complexes" formed in the alkali chloride rich mixtures. The red shift in the Li to Cs sequence is also in agreement with the general behavior of the vibrational spectra of the MX_n -AX (A = Li...Cs) binary melts (14, 15). The depolarized band at ~120 cm^{- $\overline{1}$} presumably covers the v₂ and v₄ modes of the tetrahedra, while the v_3 mode as in other cases (15) is too weak to be seen in the spectra. The $ZnCl_4^2$ "complex" is visualized as a Zn atom having a tetrahedral coordination of chlorines as first nearest neighbors, and only alkali metal ions as counter cations in the second coordination with no bridging Cl atoms (Fig. 6, S4). The lifetime of such species is much longer than 10^{-12} sec (14,15) and their presence in the melt has been supported by electronic absorption spectroscopy (25) and enthalpy of mixing measurements (26).

For the mixtures rich in $ZnCl_2$, the following composition and temperature dependent changes are noted in the spectra (Fig. 4,5 and 7):

i. Small additions of CsCl diminish the intensity of the 230 cm⁻¹ ZnCl₂ band and give rise to two new polarized bands $v_{S1} \approx 350$ cm⁻¹ and $v_{S2} \approx 290$ cm⁻¹. The intensities of these bands increase relatively to the 230 cm⁻¹ band with increasing CsCl content and at ~66 % ZnCl₂ mixture the predominant band is the v_{S2} (Fig. 4b).

ii. Similar composition effects are observed in the LiCl mixtures but the v_{S1} and v_{S2} bands are broader, weaker and red shifted by ~20 cm⁻¹ relatively to those of the CsCl mixtures (Fig. 5a)

iii. Increasing temperature decreases the 230 cm⁻¹ band intensity relatively to the v_{S1} and v_{S2} . The effect is more pronounced at 66-90% ZnCl₂ (Fig. 7) for the CsCl mixtures, and at ~77% ZnCl₂ (Fig. 5b) for the LiCl mixtures.

A possible account for the appearance of the v_{S1} and v_{S2} bands could be the formation of polynuclear in Zn "complexes" formed by two or more $ZnCl_4$ groups bound by a vertex, an edge or a plane (e.g. $Zn_2C l_7^{-3}$, $Zn_2C l_6^{-2}$, $Zn_2Cl_5^{-1}$). However, it should be noted that, the enthalpy of mixing interaction parameter (26) of the ZnCl2-CsCl binary possesses a minimum at 33% ZnCl, composition, and changes almost linearly with increasing ZnCl, composition from 33 to 100%. These thermodynamic observations have indicated (26) that: (a) the $ZnCl_4^{-2}$ is the only thermodynamically stable "complex" and (b) the addition of alkali metal chloride brings up continuous changes in the ZnCl₂ "network" structure. Such changes can be visualized as a sequential breakage of the bridging chlorine bonds and the formation of partially charged ZnCl₄ groups, which are bound to segments of the network. Thus, breaking off one bridging chlorine bond gives a charged $ZnCl_{A}$ structure, which is bound to the "network" by three bridging Cl atoms and has the alkali metal cation as nearest neighbor (structure S1, Fig. 7). Similarly, breakage of two, three, or four bridges gives structures S2, S3, or S4 respectively. Structure S4 corresponds to the $ZnCl_4^2$ "complex" that predominates the rich in alkali metal chloride mixtures, while structure S1 is formed with the first small additions of alkali metal chloride in ZnCl₂. In intermediate compositions, an equilibrium mixture of these structures is anticipated with relative concentrations that depend on both temperature and composition.

The Raman activity of the S1 to S4 structures will reflect the nonbridging Zn-Cl "stretching" mode and the frequencies are expected to decrease in the sequence $v_{S1} > v_{S2} > v_{S3} > v_{S4}$. Thus, for the ZnCl₂-CsCl system the 350 and 290 cm⁻¹ bands, observed in the ZnCl₂ rich mixtures, are assigned to the S1 and S2 structures, while the most intense band seen in the 50/50 mixture at ~280 cm⁻¹ is presumably the frequency corresponding to the S3 structure. As the temperature is raised, the "network" structure of ZnCl₂ breaks up giving configuration mainly with single bridged (SV) and terminal bridged Cl atoms (TB). Consequently, when the mixture is formed, the S2 structure will be more favorable at higher temperatures than the S1 structure. For example the addition, of chloride ions, transforms the high temperature TB structure (Fig. 3) into the S2 structure (Fig. 6). Such changes favor, for certain compositions, the $ZnCl_4$ charged groups with a maximum number of non-bridging Cl atoms, and give an account for the experimental observations in Figure 7.

The ZnCl₂ - ZnBr₂ glassy system

Liquid mixtures of $ZnCl_2$ - $ZnBr_2$ can be quenched to room temperature to form glasses at different compositions. Figure 8 shows the "raw" I(ω) Raman spectra of these glasses and compares them with the spectra of the pure components.

In the frequency region above 100-150 cm⁻¹, the spectra of the mixtures show new bands that shift with composition, while the main bands of the pure components appear to either shift or loose their intensity in the mixtures. For example, the ~130 cm⁻¹ ZnBr₂ band is completely absent from the 75% ZnCl₂ spectra. A possible assignment (13) of these bands is to the presence of mixed zinc halide tetrahedral groups of the type ZnCl_xBr_{4-x}, which participate as basic units in the "network" structure of the glass.

However, the absence from the spectra of bands due to pure components, indicate that not all tetrahedral groups are present in the mixture, or in other words, that the mixed glass is not formed by a random distribution of five $\text{ZnCl}_{x}\text{Br}_{4-x}$ (x=0-4) tetrahedral groups. This is in contrast with Raman spectroscopic studies of other mixed halide systems both in the gaseous state (27), and in molecular (28) or ionic melts (29), where the exchange and bonding of the halide to the metal structural group is random.

The enthalpy of mixing of the liquid $ZnCl_2-ZnBr_2$ binary is <u>zero</u> (26), which implies that the Cl and Br sizes and polarizabities do not affect the overall "lattice" energies of the mixed system relatively to those of its components (14). Thus, there is no preferential structural arrangement of the halogen atoms in these mixtures and moreover, the system can be described in terms of a random closest packing of chlorine and bromine atoms which offers tetrahedral sites for the formation of the $ZnCl_xBr_{4-x}$ groups. In such an arrangement, it is rather unlikely to find clusters of the same halogen atoms so as to have one Zn atom sharing vertices with four (or more) tetrahedral groups, all having the same halogen atoms. A cluster of, say, 16 Cl atoms are needed to form one $ZnCl_4$ group bound to four other $ZnCl_4$ groups and thus, giving rise to Raman bands in the mixture, which are close to the bands of the pure $ZnCl_2$. The spectra in Figure 8 exclude the formation of such kind of clusters in the mixed glasses.

In the view of the above proposed model for the bonding in the $ZnCl_2$ "network" (i.e. Fig. 3), it is difficult, just from the room temperature spectra, to make assignments for different types of bridging groups in the mixed glass systems. Detailed temperature and composition dependence studies (30) would be useful for both making the assignment and verifying the proposed model.

In the frequency region below 150 cm⁻¹ the spectra presented in Figure 8, show three bands plus the "Boson" peak. In Figure 9 the $R(\omega)$ form of the low frequency spectra is given for the pure components and for the mixed glasses. The spectra show remarkable similarities, all having a polarized band in the isotropic spectra and two depolarized bands in the anisotropic spectra. The low frequency vibrational spectra of glasses and liquids are not well understood yet (31), but the similarities and systematics followed in the spectra (Fig. 9), indicate a collective character of the vibrational modes in this frequency region.

CONCLUSIONS

Raman spectroscopic studies of $ZnCl_2$ glasses and melts and of the binary mixtures of liquid $ZnCl_2$ -ACl (A=Li,Cs) and glassy $ZnCl_2$ -ZnBr₂ have shown that:

(a) The reduced Raman intensity of pure $ZnCl_2$ changes drastically with temperature. This was interpreted to indicate the presence of different bonding states in the network structure where vertex and/or edge sharing of the $ZnCl_4$ tetrahedral groups occur.

(b) In the $ZnCl_2$ -ACl mixtures the breaking of the network structure occurs both with increasing temperature and ACl composition. With the addition of ACl breakage of certain bridging chlorine bonds occur and charged "tetrahedral" $ZnCl_4$ groups are formed which are bound to segments of the network by one, two or three bridging chlorines atoms. In ACl rich mixtures $ZnCl_4^{-2}$ tetrahedral "complexes" are formed.

(c) The glassy $ZnCl_2$ - $ZnBr_2$ mixtures are formed by a random closest packing of chlorine and bromine atoms. The formation of clusters having locally large numbers of the same atoms (i.e. chlorines or bromines) is excluded.

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Figure 1 . Temperature dependence of the reduced Raman spectra of $\mathsf{ZnCl}_2\textbf{.}$



Figure 2 . Low frequency reduced Raman spectra of ZnCl₂ at 130 °C. Polarizations VV, ANISO=HV, ISO=VV-4/3*HV



Figure 3 . Structural models for bonding of the ZnCl₄ groups in liquid/glass ZnCl₂. SV:Single Vertex, two ZnCl₄ groups bound to one bridging Cl atom. DV:Double Vertex, three ZnCl₄ groups bound to one bridging Cl atom. E:Edge, two ZnCl₄ groups bound to two common bridging Cl atom TB:Terminal Bond, indicates the presence of non bridging Cl atom.



Figure 4 . Composition dependence of the reduced Raman spectra of ZnCl2—CsCl at 660 °C.













PRECISE ANALYSIS OF THE PAIR DISTRIBUTION FUNCTION OF MOLTEN LITHIUM BROMIDE BY THE MD SIMULATION METHOD

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Molecular dynamics simulations of molten lithium bromide were performed using the Born-Mayer-Huggins type pair potentials under the NEV ensamble. The side length of the unit cell was taken based on the experimental density data. The partial pair distribution functions g(r) were examined precisely around 850 K, 1000 K, 1200 K and 1500 K. The first peak position of the g(r)function of the Li-Br interaction shifts to the shorter distance, on the other hand, those of the Li-Li and Br-Br interactions shift to the longer distances with increasing the temperature. The second peak positions, the third peak positions, the first minimum positions, the second minimum positions, and the third minimum positions of the three kinds of the interaction all shift to the longer distances with increasing the temperature.

INTRODUCTION

The structural studies of molten lithium bromide were carried out by the x-ray diffraction method (1, 2). The mass effect has been investigated by the molecular dynamics simulation method (3). The static and dynamic properties of molten lithium bromide at 1000 K and 1500 K has been compared at the CAMSE'90 symposium (4). At this present work the molecular dynamics calculation method was applied to this salt at four temperature conditions in order to see how does the structure change on increasing the temperature by examining the g(r) function precisely.

METHOD

216 Li ions and 216 Br ions were placed in the cubic cell. The side length of the cell was taken assuming that the molar volumes of lithium bromide are 34.6 cm³ at 850 K. 36.0 cm³ at 1000 K. 38.0 cm³ at 1200 K. and 41.6 cm³ at 1500 K. based on the experimental density data.

The periodic boundary condition was introduced to avoid the boundary problems and the Ewald method (5) was employed in the calculation of the coulombic force. The Born-Mayer-Huggins type potential functions with the Tosi-Fumi parameters (6) were used in the simulation.

$$V_{ij} = \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 r} + (1 + \frac{Z_i}{n_i} + \frac{Z_j}{n_j}) bexp[\frac{\sigma_i + \sigma_j - r}{r}] - \frac{c_{ij}}{r^6} - \frac{d_{ij}}{r^8}$$

where Z is an ionic charge number. e the elementary charge, ε_0 the permittivity of vacuum. n the number of the electrons in an outer most shell. b a repulsion parameter. r a softness parameter. The time step of the simulation was taken to be 4 fs and the at the first stage of the simulation a NTV ensamble at each temperature was settled for several thousand steps with a method slightly different (7) from that of Woodcock (8). After the NEV ensemble, and the subsequent calculation have reached the equilibrium, the collection of the data was begun. The present data analyses were made from the the last 12,000 steps, it corresponds to 48 ps.

RESULT AND DISCUSSION

Figure 1 represents the partial pair distribution functions of the Li-Br interaction at four temperatures. The solid line shows the g(r) at 850 K. As shown in Fig. 1 the first peak position shifts to the shorter distance with increasing the temperature. On the other hand the second and the third peak position both shift to the longer distances with increasing the temperature. Figures 2 and 3 show the partial pair distribution functions of the Li-Li and Br-Br interactions, respectively. All peak positions shift to the longer distances with increasing the temperature.

In order to compare the peak profile of the pair distribution functions at verious temperatures more precisely, we name the characteristic point of the g(r) function so as that R_i , r_{Mi} and r_{mi} give the distances in pm where for the i-th time the g(r) crosses unity, have a maximum value and a minimum value. as shown in Fig. 4. Numerical values of the characteristic points of the pair distribution function are tabulated in Table 1. It is noticed that the R_1 value of the Li-Br interaction shifts to the shorter distance with increasing the temperature. On the other hand the R_1 value of Li-Li interaction shifts to the longer distance. and furthermore the R_1 value of the Br-Br interaction has no change with increasing the temperature. It is clearly recognized that the first peak position r_{M1} of the Li-Br interaction

shifts to the longer distance with increasing the temperature. While those of the Li-Li pair and Br-Br pair have the tendency toward longer distances. The R_2 values for the Li-Br pair, the Li-Li pair and the Br-Br pair all shift to the longer distances with increasing the temperature. The characteristic values of the g(r)beyond the R_2 point, $r_{m\,1},\ R_3,\ r_{M2}$ values for three kinds of the interactions shift to the longer distances with increasing the temperature. The first peak heights for three kinds of the interaction become lower and lower and the first minimum heights become higher and higher as the temperature increases as shown in Table 1.

The coordination numbers for the three pairs at four temperatures are listed in Table 2. With increasing the temperature, the coordination numbers of three pairs decrease. It is now under examination that the coordination structure changes or not by the angular correlation function. And I would like to mention that the molecular dynamics simulation under the constant volume condition is now going on whether the volume effect or the temperature effect does cause these phenomena.

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Table 1. Characteristic Values of the Pair Correlation Functions g(r). R_i , r_{Mi} and r_{mi} are the Distances in pm Where for the *i*th Time g(r) Crosses unity, Was a Maximum and a Minimum, Respectively.

	R ₁	r_{M1}	R ₂	r _{m1}	R ₃	r _{M2}	R4	r _{m2}	R ₅	$g(r_{M1})$	$g(r_{m1})$
850 K											
Li-Br	210	241	300	368	498	581	661	737	834	3.89	0.44
Li-Li	340	399	490	565	668	742	838	916	1003	1.85	0.67
Br-Br	348	395	484	560	668	744	833	909	1003	2.24	0.61
1000 K											
Li-Br	208	239	302	375	501	582	665	741	841	3.79	0.46
Li-Li	341	402	494	571	674	749	844	920	1012	1.78	0.70
Br-Br	348	401	487	569	673	754	841	913	1010	2.16	0.64
1200 K											
Li-Ŗr	205	237	304	380	507	585	673	754	853	3.57	0.50
Li-Li	342	405	499	576	680	757	853	932	1025	1.70	0.74
Br-Br	348	399	494	572	681	755	849	927	1025	1.99	0.68
1500 K											
Li-Br	201	235	307	385	513	588	683	761	866	3.48	0.54
Li-Li	344	411	506	583	688	770	867	948	1041	1.61	0.78
Br-Br	348	404	500	577	691	763	865	944	1039	1.85	0.73

		R_2	r_{m1}
850 K	Li-Br	3.2	4.2
	Li-Li	9.1	12.6
	Br-Br	9.1	12.4
1000 K	Li-Br	3.1	4.2
	Li-Li	8.8	12.4
	Br-Br	8.8	12.3
1200 K	Li-Br	3.0	4.1
	Li-Li	8.5	12.0
	Br-Br	8.5	11.9
1500 K	Li-Br	2.8	3.9
	Li-Li	7.9	11.4
	Br-Br	7.8	11.1

Table 2. The Coordination numbers n(r). R_i and r_{mi} are the Distances in pm Where for the *i*th Time g(r) Crosses Unity, Has a Minimum Value, Respectively.



USE OF RAMAN SPECTROSCOPY FOR DETERMINING THE CORROSION OF CERAMICS IN MOLTEN FLUORIDES

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ABSTRACT

Laser Raman Spectroscopy was employed in order to probe the changes caused in the crystal structure of partially and fully stabilized zirconia ceramics after their immersion in the abrasive environment of molten LiF, NaF, KF (FLINAK) eutectic for up to 360 hours from 650 to 900 °C. Phase transformation (corrosion) was observed after 5 h in FLINAK. The degree of corrosion depends on the stabilizer, the stabilizer's percentage and the manufacturer. Corrosion is larger for larger immersion periods and higher FLINAK's temperature. The depth of the corrosion depends on the porosity of the ceramics. From the tested ceramics, ZrO_2 -8 mol % Y_2O_3 exhibits the best resistance to the corrosive influences of molten FLINAK.

INTRODUCTION

Certain ceramics are used as containers of molten salts and as sensors in molten salt baths. The endurance of these materials in such environments depends both on the reactivity as well on changes caused by fused salts on the crystal structure, which in turn reflects a change on properties such as mechanical strength and ionic conductivity.

The crystal structure of zirconia, one of the best corrosion resistant and refractory materials, is known to change from monoclinic to tetragonal and then to cubic at 1150 and 2200 °C respectively (1). ZrO_2 in the monoclinic phase is used rarely in high-temperature applications because monoclinic

zirconia ceramics undergo substantial contraction on heating and a corresponding expansion on cooling leading to a crumpling of the ceramic (2,3). Small additions of oxides such as MgO, CaO, Y_2O_3 et c. have been used to lower the two transition temperatures and thus act as stabilizers for the tetragonal (partially stabilized, PSZ) and the cubic phase (fully stabilized, FSZ) (4). Stabilized zirconia systems have improved mechanical properties with respect to fracture strength and resistant to thermal shock (5). In addition FSZ is known to exhibit high ionic conductivity (6).

A number of techniques such as X-Ray diffraction, IR and Raman spectroscopy have been used in order to study the transitions of pure zirconia and of PSZ and FSZ (7-14) during heating and cooling cycle. In the present work the transformations in the crystal structure of the doped zirconia ceramics, caused under the influence of the molten LiF, NaF, KF (FLINAK) eutectic, were examined with Laser Raman Spectroscopy. The relative intensities of the characteristic peaks of the Raman spectrum for each phase were used in order to estimate the degree of phase transformation (corrosion) in the ceramic samples.

EXPERIMENTAL

 ZrO_2 ceramics with 10 mol % CaO, 10 mol % MgO, and 5 mol % Y_2O_3 manufactured by Friedrichfeld and powders of zirconia with 10.4 mol % CaO (UNITEC), 15 mol % CaO (CERECO), 20 mol % CaO (CERECO), 10 mol % MgO (UNITEC), 15 mol % MgO (CERECO), 20 mol % MgO (CERECO), 3 mol % Y_2O_3 (TOSOH), 3.4 mol % Y_2O_3 (UNITEC), 6 mol % Y_2O_3 (RHONE POULENC), 8 mol % Y_2O_3 (ZIRCONIA SALES), 8 mol % Y_2O_3 (TOSOH), sintered by CERECO at 1600 °C for 2 hours in the form of cubes (1 x 1 x 1 cm), were used. FLINAK was prepared by mixing NaF, KF, LiF (Merck, pro-analysi).

A home-made oven with three heating zones and programmable heating controller and two programmable Scandiaonven furnace were used. All furnaces were equipped with a Ni tube core and were modified in order to accommodate the need for vacuum and/or inert atmosphere.

A conventional, small angle, Raman scattering configuration with a SPEX 1403, a -20° C cooled RCA photomultiplier, and EG&G/ORTEC photon-counting electronics was used to obtain the spectra. The spectra were excited with the 488-nm line of a 4 W Spectra Physics argon laser.
Interfering plasma lines were removed with the use of a two Perin-Broka prisms filter. The laser was cylindrically focused to obtain a probed area of approximately 1 mm². The power of the incident laser beam was about 100 mW at sample's surface. Typical spectral width and time constant were 1 $\rm cm^{-1}$ and 0.3 s respectively.

Each of the PSZ or FSZ ceramics was immersed into 50 g of molten FLINAK for a maximum of 360 hours and at temperatures up to 900 °C under argon atmosphere. Vitreous carbon crucibles (Le Carbone - Lorraine) were chosen as containers for the FLINAK. The solidified FLINAK was removed mechanically after submerging the samples into distilled water for 48 hours. Raman spectra were obtained, at room temperature, before and after the treatment. Ceramics were cut with a diamond disk and the corrosion depth was studied by moving the laser beam, with the help of the cylindrical lens micropositioner, across the transversal cut of the samples. The total open porosity for all tested ceramics was measured by CERECO with a Quantachrome 33 porosimeter.

RESULTS AND DISCUSSION

In Figure 1 the Raman spectrum of the pure monoclinic zirconia powder exhibits 16 out of the 18 theoretical predicted bands while the spectrum of the tetragonal phase displays all six Raman modes predicted by group theory (14). Assuming a fluorite structure for ZrO_2 in the cubic phase, one should expect only one Raman active frequency. The broad peak in the area of 625 cm⁻¹ together with the high background indicating the structural disorder are characteristic for the cubic structure.

The doublet at 177 and 188 cm⁻¹ of the monoclinic structure and the tetragonal bands of 144 and 262 cm⁻¹ were used for the identification of their respective phases since all the other bands are either weak and overlap or coincide. The major difficulty is estimating the cubic presence since two bands of monoclinic appear in the area of cubic's broad band. The number of peaks in the area of 625 cm⁻¹, their sharpness, the degree of separation as well the presence of background were used as criteria for the identification of the cubic phase when coexists with the monoclinic structure. An effort is in progress in order to estimate more accurately the percentage of each phase in a spectrum by preparing pellets of known phase composition from mixed cubic, tetragonal, and monoclinic powders (CERECO). Their Raman spectra can be used as standards and from the ratio of the characteristic peak intensities a calibration curve will be obtained.

The Raman spectra from samples' surface after their immersion for 5, 24, 96, 144, 216 and 360 hours into FLINAK at 700 $^{\circ}$ C (Table I), indicate that all ceramics are easily corroded. The presence of the monoclinic phase is observed even after 5 hours into FLINAK.

The manufacturer and therefore the details of sample's preparation and/or its purity are also an important factor. Ceramics from Friedrichsfeld (ZrO₂ with 10 mol % CaO, 10 mol % MgO, and 5 mol % Y_2O_3), differ drastically with respect to phase change from samples with similar dopant's percentage and crystal structure (ZrO₂ with 10.4 mol % CaO, 10 mol % MgO, and 6 mol % Y_2O_3) sintered by CERECO. ZrO₂ -10.4 mol % CaO (UNITEC/CERECO), ZrO₂ -10 mol% MgO (Friedrichsfeld), and ZrO₂ -5 mol % Y_2O_3 (Friedrichsfeld) exhibit better corrosion resistance than ZrO₂ -10 mol% CaO (INITEC/CERECO), and ZrO₂ -6 mol% Y_2O_3 (UNITEC/CERECO) (Figure 2). A plausible explanation is that some ceramics contain some impurities probably as sintering agents.

The percentage of the monoclinic phase increases progressively with the immersion time in molten fluorides (Figure 3) while an increase in the temperature of FLINAK causes an increase of the monoclinic structure (Figure 4). The ceramics with more dopant's percentage than the fully stabilized structure needs (CaO 20 mol % and MgO 20 mol %) exhibit very drastic phase change. For the corrosion depth measurements the ceramics were cut and the exposed face was probed. The phase change of samples with large total open porosity is observed at more distant areas from external surface than for ceramics with smaller one. The more pronounced example is between the ZrO₂ -10 mol % CaO (UNITEC/CERECO) with 1.6 % open porosity. For the first composition corrosion can be observed even at the center of the cube (5 mm depth), while for the latter the monoclinic phase disappears in less than 1 mm distance from the external surface (Figures 5 and 6).

From all tested ceramics ZrO_2 -10 mol % MgO (Friedrichsfeld) and ZrO_2 -8 mol % Y_2O_3 (ZIRCONIA SALES/CERECO) exhibit the best corrosion resistant behavior since after 15 days into molten fluorides the tetragonal and the cubic structures are still detectable.

		Imme	Immersion Time / hours				
ZrO ₂ with	0	5	24	96	144	216	36
10 mol % CaO (Friedrichsfeld)	T	М					
10.4 mol % CaO (UNITEC/CERECO)	Т	T,M	T,M	T,M	T,M	М	
15 mol % CaO (CERECO)	С	М					
20 mol % CaO (CERECO)	С	М					
10 mol % MgO (Friedrichsfeld)	Т	T,M	T,M	T,M	T,M	T,M	T,
10 mol % MgO (UNITEC/CERECO)	Т	T,M	T,M				
15 mol % MgO (CERECO)	С	C,M	C,M	М			
20 mol % MgO (CERECO)	С	М					
3 mol % Y ₂ O ₃ (tosoh/cereco)	Т	T,M	T,M	T,M	М		
3.4 mol % Y ₂ O ₃ (UNITEC/CEREĈO)	Т	T,M	T,M	М			
5 mol % Y ₂ O ₃ (Friedrichsfeld)	Τ	T,M	T,M	T,M	T,M	T,M	М
6 mol % Y ₂ O ₃ (TECMIC/CERECO)	Т	T,M	T,M	М			
8 mol % Y ₂ O ₃ (ZIRCONIA SALES/CER	C ECO)	C,M	C,M	C,M	C,M	C,M	C,
8 mol % Y ₂ O ₃ (TOSOH/CERECO)	С	C,M	C,M				

Table I. Crystal structures at the surface of PSZ and FSZ ceramics immersed into FLINAK at 700 $^\circ\!C.$

T is for Tetragonal, M for Monoclinic and C for Cubic

CONCLUSIONS

We have shown that laser Raman spectroscopy can be used to examine the corrosion on zirconia stabilized ceramics, after their immersion into molten fluorides. Using this technique we have found that:

1. Monoclinic phase (corrosion) appears on the zirconia stabilized ceramics after short time in FLINAK.

2. The degree of corrosion depends on the dopant, the dopant's percentage and the specific characteristics of sample's preparation and/or manufacturing.

3. Corrosion is more pronounced at higher FLINAK's temperature.

4. Corrosion is larger for larger immersion periods into molten fluorides.

5. Corrosion depth depends on sample's porosity.

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Figure 1: Raman spectra of pure ZrO_2 (monoclinic phase), ZrO_2 -3.4 mol % Y_2O_3 (tetragonal phase) and ZrO_2 -8 mol % Y_2O_3 (cubic phase). Temperature of samples 20 °C; λ_0 =488.0 nm; spectral slit width, 1 cm⁻¹.

Figure 2. Raman spectra of ZrO_2 -10 mol % MgO (Friedrichsfeld) and ZrO_2 -10 mol % MgO (UNITEC / CERECO) before and after the immersion in FLINAK for 24 hours at 700 °C. Temperature of samples 20 °C: λ_0 =488.0 nm; spectra slit width, 1 cm⁻¹.





Figure 3: Raman spectra of ZrO_2 -10.4 mol % CaO (UNITEC/CERECO) after immersion in FLINAK for 5, 24 and 144 hours. Temperature of samples 20 °C; λ_0 =488.0 nm; spectral slit width, 1 cm⁻¹.

Figure 4. Raman spectra of ZrO_2 -10 mol % MgO (UNITEC/CERECO). Samples were immersed in FLINAK for 5 hours at 700, 800 and 900 °C. Temperature of samples 20 °C; λ_0 =488.0 nm; spectral slit width, 1 cm⁻¹.





Figure 5: Raman spectra of surface, 1, and 5 mm depth for ZrO₂-10 mol % CaO (Friedrichsfeld). Sample was immersed in FLINAK for 216 hours at 700 °C. Total open porosity 34.2 %; Temperature 20 °C; λ_0 =488.0 nm; spectral slit width, 1 cm⁻¹.

Figure 6: Raman spectra of surface, 0.5, and 1 mm depth for ZrO_2 -10.4 mol % CaO (UNITEC/CERECO). Sample was immersed in FLINAK for 216 hours at 700 °C. Total open porosity 1.6 %; Temperature 20 °C; λ_0 =488.0 nm; spectral slit width, 1 cm⁻¹.



A NEW SERIES OF COMPLEX METAL OXIDES: CRYSTALLIZATION OF AB_3MO_6 (A = Na, Li; B = Ba, Sr; M = Bi, Sb) FROM HYDROXIDE MELTS.

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Molten hydroxides are excellent solvents for the synthesis of new complex metal oxides. Five new materials with the structure type AB_3MO_6 (NaBa₃BiO₆, NaSr₃BiO₆ LiSr₃BiO₆, NaSr₃SbO₆, and LiSr₃SbO₆) have been crystallized from mixtures of alkali and alkaline earth metal hydroxides at 550°C. In this paper we discuss the synthetic method, as well as the crystal structure and properties of these highly oxidized products.

INTRODUCTION

There has been increased interest in the structure and properties of alkali metal and alkaline-earth metal bismuthates since the discovery of superconductivity in BaPb_{0.6}Bi_{0.4}O₃ [1] and Ba_{0.66}K_{0.34}BiO₃ [2]. These barium bismuthate superconductors are prepared typically by solid state reactions at elevated temperatures, high enough for solid state diffusion (~800°C). Unfortunately, since the alkali metals are volatile at these temperatures, it has been difficult to prepare bismuthates containing alkali metals. In order to synthesize such phases, new low temperature synthetic routes must be developed.

One method of resolving this diffusion vs. volatility problem is to develop solutionbased synthetic routes. We have found that mixtures of alkali and alkaline-earth metal hydroxides are ideal as solvents for the synthesis of complex oxides; these salts are relatively low melting, and are readily available. By using various mixtures of LiOH, NaOH, KOH, RbOH, Sr(OH)₂ and Ba(OH)₂, five new materials with the stoichiometry AB₃MO₆ have been synthesized: NaBa₃BiO₆, NaSr₃BiO₆, LiSr₃BiO₆, NaSr₃SbO₆ and LiSr₃SbO₆. These materials have related structures.

EXPERIMENTAL

General

Reagents were used directly without further purification with the exception of $Sr(OH)_2$ • $8H_2O$ which was stored in a drying oven (125°C) prior to use.

Synthesis

The constituents of the individual reaction mixtures are listed in Table I. These reagents were placed (unmixed [3]) into an Al_2O_3 or Ag crucible which was then placed into a furnace that had been preheated to 550°C. The furnace was open to the ambient atmosphere at all times. The reaction was allowed to proceed for approximately 24 hours at which time transparent yellow crystals could be seen growing on the sides and bottom of the crucible. The crucible was pulled from the furnace and the excess solvent was decanted from the crucible. After the crucible had cooled to room temperature, the crucible was soaked in methanol in order to dissolve the remaining hydroxide. The product was filtered and rinsed with methanol. As the crystals are hygroscopic, the material was stored in a desiccator containing CaSO₄.

In a previous publication [4], we described the crystal structure of NaBa₃BiO₆. A view of the rhombohedral unit cell can be seen in Figure I. Also reported were the lattice parameters for the related structures NaSr₃BiO₆ and LiSr₃BiO₆ [4]. The lattice parameters for these three materials as well as for two new materials (NaSr₃SbO₆ and LiSr₃SbO₆) are summarized in Table II.

CONCLUSIONS

Molten hydroxides are excellent solvents for the synthesis of new complex metal oxides. We have not been successful in preparing the new materials reported here by traditional solid state reaction methods. Moreover, although NaBa₃BiO₆ is synthesized at 550°C in a hydroxide melt, once removed from the melt environment it begins to decompose in air at 400°C. By varying melt conditions such as temperature, melt acidity, and partial pressure of oxygen, we expect to favor the crystallization of new oxides with different compositions and structure-types.

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3. In the case of NaBa₃BiO₆, NaOH, KOH and Bi₂O₃ were initially placed in an Al₂O₃ crucible in the preheated furnace and allowed to equilibrate from 3 to 6 hours. At that time, Ba(OH)₂ was gradually added in 0.5 gram increments over a period of 2 to 3 hours. This procedure eliminated an impurity phase (BaBiO₃) from the product.

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TABLE I

Material	Reactant	(g, mmol)	
NaBa3BiO6	NaOH	(10, 250)	
	Ba(OH) ₂	(5, 32)	
	Bi ₂ O ₃	(0.4, 0.8)	
	КОН*	(5, 90)	
NaSr ₃ BiO ₆	NaOH	(10, 250)	
	Sr(OH) ₂	(5, 41)	
	Bi ₂ O ₃	(0.4, 0.8)	
	KOH*	(5, 90)	
LiSr ₃ BiO ₆ **	LiOH	(7, 300)	
	Sr(OH) ₂	(7, 32)	
	Bi ₂ O ₃	(0.5, 1.0)	
NaSr₃SbO ₆	NaOH	(10, 250)	
	Sr(OH) ₂	(4, 33)	
	Sb ₂ O ₃	(0.15, 0.45)	
	KOH*	(10, 180)	
LiSr ₃ SbO ₆	LiOH	(0.7, 29)	
- •	Sr(OH) ₂	(0.7, 6)	
	Sb ₂ O ₃	(0.07, 0.2)	
	RbOH*	(5, 49)	

REACTION MIXTURES

* Addition of KOH/RbOH improved the quality of the crystals.

** A silver crucible was used for this reaction. All other reactions took place in Al₂O₃ crucibles.

TABLE II

LATTICE PARAMETERS FOR NaBa3BiO₆, NaSr3BiO₆, LiSr3BiO₆, NaSr3SbO₆, LiSr3SbO₆

Material	a (Å)	a (°)	
NaBa3BiO6	7.223(3)	91.79(3)	
NaSr3BiO6	6.930(1)	92.26(1)	
LiSr3BiO6*	6.86(2)	92.2(2)	
NaSr ₃ SbO ₆	6.84(2)	91.1(2)	
LiSr ₃ SbO ₆ *	6.77(2)	92.4(2)	

*Note: these are average lattice parameters. Single crystal X-ray analysis shows the unit cell of LiSr₃BiO₆ to be a = 6.872(1) Å, b = 6.864(2) Å, c = 6.872(1) Å, $a = 92.31(2)^\circ$, $\beta = 92.27(2)^\circ$, $\gamma = 92.29(2)^\circ$. LiSr₃SbO₆ most likely has a triclinic unit cell as well.



FIGURE I

UNIT CELL OF NaBa₃BiO₆

Drawing of the rhombohedral unit cell of $NaBa_3BiO_6$ viewed down the 3-fold symmetry axis. The bismuth atoms are located at the origin and center of the unit cell. The sodium atoms are located above and below each bismuth atom and form a $NaBiO_6^{6-}$ chain. The barium atoms are located between the $NaBiO_6^{6-}$ chains.

INVESTIGATION OF A MOLTEN SALT EXTRACTION/ELECTROLYSIS PROCESS FOR CONVERTING ILMENITE TO IRON AND A HIGH GRADE TIO₂ FEEDSTOCK

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The feasibility of beneficiating (upgrading) ilmenite ores using a molten salt extraction/electrolysis process was investigated. In this process, the iron fraction is selectively extracted from ilmenite and reduced to metallic iron at the cathode; the oxygen species is converted to CO and/or CO₂ at a carbon anode. The beneficiated (upgraded) ore is then recovered from the melt, and the molten salt is recirculated back to the reactor. The high TiO₂ content of the ore after extraction of the iron fraction increases its value as a feedstock for the production of TiO₂ pigment by the Chloride Process. Several salt systems were studied, including LiCl-KCl, NaOH-KOH, LiBO₂-KBO₂, and LiCl-KCl-LiBO₂ system containing 5 to 20 weight % LiBO₂.

INTRODUCTION

In 1991, approximately 1.4 million tons of TiO_2 pigment were produced worldwide using the Chloride Process (1). In this process, titanium ores are chlorinated in large fluidized beds to produce TiCl_4 , which is purified and then oxidized to produce pigmentary TiO_2 particles (2). In the chlorination process, the majority of the ore impurities, predominantly iron, are also chlorinated and subsequently separated from the TiCl_4 . To minimize the generation of metal chloride wastes, it is desirable to remove the impurities prior to chlorinating the ore.

Background

A variety of beneficiation routes for titaniferous ores have been reported in the literature (3,4) yet there are only three major commercial beneficiation routes practiced today: slagging (5), reduction-rusting (6,7), and reduction-leaching (8). In the slagging process, the grade of the TiO₂ product is generally below 86 %, and the slags often contain significant quantities of CaO from the coke used as the reductant. High CaO levels can cause operational difficulties in fluidized-bed chlorinators (9). Both the reduction-rust and reduction-leach processes produce a much higher grade TiO₂ product (90 - 95 % TiO₂) with low CaO levels, but generate a large amount of iron oxide waste. Thus, there is a

need for a low cost beneficiation process to produce a high grade TiO_2 feedstock (> 90 % TiO_2) with minimal production of waste.

In an effort to develop a superior beneficiation process, a variety of molten salt routes have been investigated. In 1956, a patent was granted to Columbia-Southern Chemical Corporation for a process in which molten NaOH was used to convert ilmenite to a solid phase enriched in iron and a liquid phase enriched in TiO_2 (10). However, the process resulted in the formation of sodium titanates, resulting in high NaOH consumption and an unacceptably high Na-content in the TiO_2 product. In 1989, Heikel received a U.S. patent (11) for a process in which NaOH was used to produce sodium titanate which was then leached with HCl to form an amorphous $TiO_2 \cdot nH_2O$ product. The amorphous titania could be calcined to produce a high grade TiO_2 product; however, the high NaOH consumption and the need to treat the resulting acid stream make this a very expensive process. A substantial amount of effort has also been focussed on molten salt chlorination processes in which the ilmenite ore is reacted with Cl₂ in a molten chloride bath (12-15). However, such processes do not eliminate the chloride waste problem.

A molten salt extraction/electrolysis process could potentially avoid the problems of high salt consumption and waste generation. In this process, the iron fraction would be selectively extracted from the ilmenite and deposited as metallic iron at the cathode. Such a process should be capable of making a 90 - 95 % TiO₂ product similar to that obtained from the reduction-rust and reduction-leach processes. However, unlike the latter two processes, a valuable iron coproduct would be produced instead of an iron oxide waste.

Choice of Molten Salt System

A distinct advantage of molten salt systems over aqueous systems for electrolytic deposition of metallic iron is the high decomposition voltages associated with molten salt systems which makes it possible to control the cathode at a potential sufficiently negative to produce iron at reasonable rates without decomposing the salt. A number of molten salt systems may be envisioned; the specifications for an ideal salt system are listed below.

- 1) The solubility of the iron fraction of ilmenite in the melt should be high at relatively low temperatures while the TiO_2 fraction is insoluble.
- 2) The molten salt should be non-viscous and allow for high transport rates of the dissolved species to the electrodes, as well as allow rapid evolution of CO and/or CO₂ from the anode.
- 3) The salt should not react with the metallic iron product and should be easily washed free from both the iron and TiO₂ products.
- 4) For a low-cost process, the salt needs to be economically recovered and recirculated back to the process with minimal consumption.

EXPERIMENTAL

Ilmenite

Two different ilmenite sources were used in this investigation: 1) synthetic ilmenite, FeTiO₃, containing 53 weight % TiO₂, and 2) partially reduced Florida Ilmenite (PRFI) containing 67 % TiO₂. In both cases, the iron is predominantly present as Fe⁺². The synthetic ilmenite was prepared by heating a stoichiometric ground mixture of Fe₂O₃ and TiO₂ under a helium atmosphere to 1150 C for 12 hours, cooling, grinding, heating for 24 hours at 1150 C, cooling, grinding, and heating an additional 12 hours at 1150 C. Only ilmenite was present in the X-ray diffraction pattern. The PRFI sample was prepared by heating Florida Ilmenite (65 % TiO₂) for 8 hours at 1000 C under an atmosphere with a CO/CO₂ ratio of 0.1 to convert the iron to the Fe⁺² state.

Solubiity Studies

A schematic of the apparatus used for conducting the solubility experiments is shown in Figure 1. In a typical experiment, 300 - 400 grams of salt were added to an Al₂O₃ crucible inside a quartz tube. A pyrex cap equipped with two ports for gas inlet and exit, as well as a sampling port was attached to the top of the quartz tube via a 75 mm joint. The system was purged with either 200 sccm of helium or 10 % CO in helium, and heated to the desired temperature over a 2 hour period with a crucible furnace. The gas entered the reactor through a hollow Al₂O₃ tube which could be raised or lowered. Once the salt was melted, the Al₂O₃ tube was lowered into the melt, and the salt was sparged for 1 hour. Then the Al₂O₃ tube was lifted out of the melt, and a nickel crucible was lowered into the melt through the sampling port. Approximately 25 g of the melt were removed and poured into a dry stainless steel beaker. The beaker was placed in cold water to quench the melt, and the frozen salt was broken up and placed in a sample bottle which was immediately weighed and then placed in a dessicator. This sample served as the control sample.

After taking the control sample, 30 - 40 grams of ilmenite ore were poured into the melt through the sampling port. The melt was sparged for 1 hour, and then the solids were allowed to settle for 20 minutes before taking a sample of the melt. Once the sample was taken, the system was heated over a hour period to the next desired temperature. After sparging for 1 hour at temperature and then allowing the solids to settle for 20 minutes, another melt sample was taken. This procedure was repeated until a sample was taken at each desired temperature. The next day, a small portion of each sample was weighed, dissolved in HCl, and then analyzed by ICP (Inductively Coupled Plasma Spectroscopy).

Electrochemistry Experiments

A schematic of the apparatus used for the electrochemistry experiments is shown in Figure 2. 100 grams of salt were added to an Al_2O_3 crucible which was placed inside a quartz tube. The quartz tube was covered with a pyrex cap containing 2 ports for electrodes and a third port for gas inlet. The cathode consisted of an 8 cm long piece of 0.5 mm diameter Pt wire folded in a tight loop around a Pt lead wire so that the total length of the electrode was 4 cm. The Pt lead wire was passed through a hollow Al_2O_3 tube up through the port on the pyrex cap and connected to the potentiostat lead via an alligator clip. The anode consisted of a 4 cm long, 6 mm o.d. graphite rod. A spiral groove was cut at the top of the rod, and the Pt lead wire was wound tightly into the groove to hold the electrode. A 2 mm Ag wire was used as a quasi-reference electrode in each case. The Ag wire was also attached to a Pt lead wire. The Pt lead wires for the anode and reference electrode passed through 2 separate holes in an Al_2O_3 disk, and then up through separate holes in the same piece of 4-hole Al_2O_3 tubing as shown in Figure 2.

The salt was heated to the desired temperature under a He or CO/He purge, and sparged for 1 hour. The electrodes were then inserted into the melt to a depth of 4 cm, corresponding to approximate electrode areas of 1.3 cm^2 for the Pt electrode, and 7.5 cm^2 for the graphite electrode. Several cyclic voltammograms were run to characterize the melt in the absence of any ore. Then after removing the electrodes 20 grams of ore were poured into the melt. After sparging 1 hour and allowing the solids to settle for 20 minutes, the electrodes were immersed in the melt, and the electrochemistry experiments performed.

An EG&G PARC Model 270 Electrochemial Analysis system was used to conduct the electrochemistry experiments. This system consisted of a Model 273 Potentiostat/Galvanostat interfaced to an IBM PS/2 Model 30 computer.

RESULTS AND DISCUSSION

LiCl-KCl System

In beginning an investigation of a molten salt extraction/electrolysis process it was desirable to start with a system that was relatively well understood in order to gain some confidence with respect to the results obtained. The chemical and electrochemical properties of Ti-O and Fe-Ti-O compounds in the molten LiCl-KCl eutectic (44.4 weight % LiCl) at 470 C have been described by Ferry, et al. (15) and by Picard, et al. (16). An interesting property of this system is that Fe⁺² is far more soluble in the chloride salt than Fe^{+3} or Ti⁺⁴. Thus, it was felt that partial reduction of the iron fraction of ilmenite to Fe⁺² would allow selective extraction of the iron. However, a disadvantage of this system is that the solubility of Fe⁺² oxides is not very high in chloride salts.

The measured solubility of the iron fraction of ilmenite as a function of temperature

is shown in Figure 3 for both synthetic ilmenite and the partially reduced Florida Ilmenite (PRFI). For these experiments, the system was constantly purged with a mixture of 10 % CO in He to maintain a low oxygen activity in the melt. For both ilmenites the solubility of the iron fraction increases exponentially with temperature. In each case, less than 1ppm of titanium was detected in the salt indicating high selectivity for iron over titanium. Due to the higher solubility of Fe⁺² from the PRFI sample at 800 C, the electrochemistry experiments were conducted using this ilmenite sample.

Cathodic cyclovoltammograms (CV's) for PRFI in LiCl-KCl at 800 C are shown in Figure 4 for a platinum working electrode at sweep rates of .02 and 1.0 V/s. For reference, the CV for the LiCl-KCl in the absence of any ore is also shown. A reduction peak was observed between -0.2 and -0.4 V vs. the Ag quasi-reference electrode. The location of this peak was right where the reduction peak for the conversion of Fe⁺² to Fe⁰ was expected to occur (15). This peak assignment was confirmed as follows. The cathode potential was stepped to -0.25 V and held there for 1 hour. The cathode was then removed, and a black, highly magnetic material resembling iron filings was removed and analyzed by SEM/EDAX (Electron Diffraction Analysis of X-rays using a Scanning Electron Microscope). The material analyzed as 81 % Fe, 1 % Ti, 9 % K, and 9 % Cl. The K and Cl were due to the fact that the iron was not washed well before analyzing. The titanium was most likely due to the presence of a small amount of ore in the iron deposit.

An anodic cyclovoltammogram (CV) for PRFI in LiCl-KCl at 800 C using a graphite working electrode is shown in Figure 5 for a sweep rate of 0.1 V/s. This CV was virtually identical to what was obtained for LiCl-KCl in the absence of ilmenite. The break at approximately 1 V corresponds to where the oxidation of Cl⁻ to Cl₂ would be expected to occur (15). The lack of any peaks attributable to the reaction of oxyanions with the carbon electrode suggests that during deposition of metallic iron at the cathode, the corresponding anodic reaction is most likely the conversion of Cl⁻ to Cl₂. This may explain the secondary cathodic reaction that is evident in Figure 4 at potentials more negative than about - 0.25 V.

As the potential at the cathode becomes more negative, the deposition rate of iron increases, as does the evolution rate of Cl_2 at the anode. It is possible (although not confirmed) that the Cl_2 generated at the anode diffuses to the cathode where it is either reduced, or reacts with the metallic iron to form FeCl₂ which dissolves in the melt. In the latter case, the reaction with Fe would replenish the level of Fe⁺² in the boundary layer near the cathode and prevent the reduction reaction from becoming completely mass transfer-limited. As a result, a definitive peak would not be obtained. Similarly a definitive peak would not be obtained if the Cl_2 were just being reduced directly at the cathode. Instead, the cathodic current would continue to rise as the overpotential was increased. The higher reduction rate at the cathode would be largely balanced by a higher production rate of Cl_2 at the anode. Thus, at potentials more negative than -0.25 V, the apparent current density increases, but the net production of metallic iron at the cathode does not increase. This hypothesis is supported by the experimental observation that deposition of iron at potentials more negative than -.25 V vs. the Ag quasireference electrode, the measued current density was approximately 0.01 A/cm², of which only about half corresponded to the net reduction of Fe⁺² to Fe⁰.

The results presented above show that for ilmenite in the LiCl-KCl system, the iron deposition rate at the cathode is relatively low, and the reaction rate of oxyanions with the carbon anode is extremely low. These low rates can be attributed to the low solubility of oxides in chloride systems. Thus, it was decided to investigate the use of oxygen-containing salts. One class of oxygen-containing salts which also can easily be washed from the products and recovered are the alkali hydroxides. An added benefit of the hydroxide systems is that they are low melting. Therefore, it was decided to investigate the electrochemical behavior of ilmenite in the NaOH-KOH eutectic.

NaOH-KOH System

An interesting property of the alkali hydroxides is that the chemical properties of these melts are a strong function of the water content, or acidity (17-20). In general, under wet (acidic) conditions, metallic oxides react with the water and dissolve as cations plus hydroxide ions (e.g. FeO + $H_2O = Fe^{+2} + 2 OH^-$). As the melt is dried, the solubility decreases due to the lack of availability of water for reaction. When the melt is dehydrated still further, the solubility goes through a minimum and then increases again. Under dry (basic) conditions, the metal oxides generally dissolve as alkali-metal-oxide salts (e.g. $Fe_2O_3 + 2 NaOH = 2 NaFeO_2 + H_2O$) which are usually highly soluble.

The simplest way to vary the water content of the hydroxide melt is to start with a hydrated melt and heat it to drive off the water. As the temperature is raised, the melt becomes more dehydrated and thus, more basic. The solubility of synthetic FeTiO₃ in NaOH-KOH was measured under acidic (wet) and basic (dry) conditions. In these experiments, a mixture of 185 g KOH·0.5H₂O and 115 g of NaOH was heated to 250 C, during which time some steam was observed in the exit from the reactor. After taking a "blank" sample, 30 g of synthetic FeTiO₃ were added to the melt and sparged with 200 cc/min of dry helium for 1 hour. After settling for 20 minutes a sample was taken as described above. The melt was then heated over 1 hour to 350 C, during which time a substantial amount of steam was observed in the reactor effluent. After 30 minutes, no more steam was evident, and the melt was considered relatively dry. After an hour, another sample of the melt was taken. The measured solubility of FeTiO₃ in the NaOH-KOH mixture is shown in Table I for 250 C (wet) and 350 C (dry).

Table I Solubility of FeTiO₃ in NaOH-KOH

Temperature (C)	<u>Fe</u>	<u>Ti</u>	
250	0.7 %	0.4 %	
350	4.0 %	3.0 %	

As seen in Table I, unlike the LiCl-KCl system, iron is not selectively dissolved vs. titanium in this system. However, an extraction/electrolysis system could still be

envisioned where the melt is saturated with titanium such that no more titanium dissolves, while iron is continuously dissolved and then deposited on the cathode. Because of the high soluble titanium loss at 350 C, it was decided to investigate the electrochemistry of this system at 250 C (wet conditions) where the soluble titatium loss is minimized. One possible problem which was anticipated with this system is that metallic iron is known to be oxidized by water and/or hydroxyl ions in aqueous hydroxide systems (21). Thus, it was expected that metallic iron might be oxidized in a wet (acidic) NaOH-KOH melt. However, it was hoped that by maintaining a sufficiently negative potential on the cathode, this reaction of metallic iron with the melt could be minimized.

Cathodic CV's for synthetic FeTiO₃ in wet NaOH-KOH at 250 C are shown in Figure 6 for sweep rates of .02 V/s and 2 V/s. For comparison, the CV for the wet NaOH-KOH in the absence of ilmenite is also shown (sweep rate = 1 V/s). There is clearly a marked difference between the CV's with and without ilmenite present. However, the fact that the CV's with ilmenite present were nearly straight lines with no peaks, and that the sweep rate does not have a significant impact on the curves suggested that something was wrong. Initially, a short circuit was suspected, but it was quickly verified that this was not the case.

The strange appearance of the CV's in Figure 6 for ilmenite in wet NaOH-KOH may be explained as follows. As the iron species were reduced to metallic iron at the cathode, the freshly reduced iron was then reoxidized by reaction with the melt. As a result, there was no depletion of iron cations in the boundary layer near the electrode. Therefore, the current was solely determined by the electrode potential, and not subject to mass transfer limitations. This explanation is consistent with the obervation that after holding the cathode at a potential of -0.4 V relative to the Ag quasi-reference electrode for 30 minutes, no iron was observed on the cathode despite the fact that a steady current of 0.23 Amps was maintained.

The high reactivity of metallic iron with alkali hydroxides under acidic (wet) conditions makes it extremely difficult to develop an economical extraction/electrolysis process for this system. While the reactivity of metallic iron with the melt should be much lower under dry (basic) conditions, the high solubility of the titanium fraction in the melt under these conditions presents a problem. However, if a high steady-state level of titanium can be maintained in the melt without impacting the iron quality, this system may be worth investigating further.

LiBO2-KBO2 System

The next salt system chosen for study was the $LiBO_2$ -KBO₂ (44 wt. % $LiBO_2$, 56 wt. % KBO₂) system. This system was chosen because it was expected to have a high solubility for oxides and a low solubility for metallic iron. The solubility of partially reduced Florida Ilmenite (PRFI) in the $LiBO_2$ -KBO₂ system was measured in the same manner as desribed earlier for the other salt systems. In this case a helium purge was used throughout the experiment. The measured solubility of PRFI in the $LiBO_2$ -KBO₂ melt at

850 C is shown in Table II.

Table II Solubility of PRFI in LiBO2-KBO2 at 850 C

<u>Fe</u>	<u>Ti</u>	<u>Mn</u>	<u>Mg</u>
1.13 %	512 ppm	1.15 %	87 ppm

It is clear from Table II that iron is not selectively dissolved relative to titanium to a high degree in this system. As a result, an extraction/electrolysis process using this system would either have to maintain a high steady-state level of titanium in the melt, or an additional processing step would be required for recovering the titanium values from the melt. Nevertheless, the solubility of ilmenite measured in this system was about an order of magnitude higher than in the LiCl-KCl system. This higher solubility was expected to be somewhat offset by a higher viscosity which would slow the mass transfer rate in the LiBO₂-KBO₂ system.

Cathodic CV's for PRFI in $LiBO_2$ -KBO₂ at 850 C are shown in Figure 7 for sweep rates of 0.02, 0.1, and 1 V/s. For comparison, the CV for $LiBO_2$ -KBO₂ in the absence of ilmenite is also shown (sweep rate = 0.1 V/s). In the absence of ilmenite, no significant amount of reduction was observed until about - 0.7 V vs. the Ag quasi-reference electrode. However, when PRFI was dissolved in the melt, a reduction peak was clearly evident between -0.4 and -0.6 V depending on the sweep rate. It was readily verified by examining the electrode deposit that this reduction peak corresponded to the deposition of metallic iron on the platinum electrode. The iron deposition rates observed in this system were substantially higher than those observed in the LiCl-KCl system.

Unlike the LiCl-KCl system, the anodic reaction between dissolved oxygen species appears to be favorable in the LiBO₂-KBO₂ system. Anodic CVs of LiBO₂-KBO₂ in the absence of ilmenite were performed at 850 C using either the platinum electrode or the graphite electrode as the working electrode; the results are shown in Figure 8. When platinum was used as the working electrode, no oxidation of the melt occurred until potentials above +0.7 V vs. the Ag quasi-reference electrode were reached. The nature of this reaction was not investigated, but may have been the reaction of oxygen anions in the melt to produce O_2 . In contrast, when graphite was used as the working electrode, oxidation began at potentials more positive than -0.3 V, and the current density was much higher than in the platinum system. Because this reaction involves the melt itself there is no peak in the CV since the reaction does not become mass transfer limited.

The results shown in Figure 8 suggested that a reaction was occuring between oxygen anions and the graphite electrode. This was verified by the fact that after prolonged reaction, the carbon electrode was clearly pitted. Since no measurements were made on the gas effluent, the nature of this reaction is not known for sure, but is believed to be the reaction of oxygen anions with the graphite to produce CO and/or CO₂. In the presence of ilmenite, the CV looked essentially identical. Thus, it is expected that in the LiBO₂-KBO₂ system the reduction reaction corresponding to the deposition of metallic iron at the cathode

could easily be balanced by an oxidation reaction to produce CO and/or $\rm CO_2$ at the graphite anode.

Despite the relatively high cathodic and anodic current densities exhibited by the $LiBO_2$ -KBO₂ system, there are several serious problems associated with using this system for an extraction/electrolysis process. The solubility of the titanium fraction of ilmenite is high in this system and there is a strong tendency to form titanates. X-ray diffraction analysis of the residue at the bottom of the crucible indicated that the major phase present was Li_2TiO_3 . Moreover, it is very difficult to wash the flux off the iron product.

LiCl-KCl + LiBO₂

The results presented above show that iron can be selectively extracted from ilmenite and electrolyzed to produce powdered iron using a LiCl-KCl flux. However, the low solubility of the iron fraction of ilmenite in the melt results in a low deposition rate of metallic iron. Moreover, the anodic reaction between dissolved oxygen species and the graphite electrode is very slow in the LiCl-KCl system. In the LiBO₂-KBO₂ system, the solubility of the ilmenite is relatively high, resulting in acceptable iron deposition rates. It also appeared as if the anodic reaction between oxygen anions and the graphite electrode to produce CO and/or CO₂ occurred at a moderate rate. However, the high solubility of titanium and the tendency to form titanates combined with the difficulty of washing the LiBO₂-KBO₂ melt off the iron product combined to make this system unattractive.

Based on these results, it was postulated that if the positive results from the two systems could be combined while minimizing the negative results, it might be possible to develop a commercially viable extraction/electrolysis process. The most obvious way to combine the benefits of both systems was to add varying amounts of LiBO₂ to the LiCl-KCl system.

The effect of LiBO₂ addition on the cathodic CV's of PRFI in LiCl-KCl at 800 C is shown in Figure 9. Adding just 5 % LiBO₂ to the LiCl-KCl melt resulted in an order of magnitude increase in the size of the peak corresponding to iron deposition. Increasing the LiBO₂ level to 20 % resulted in a further increase in the size of the reduction peak. It is interesting to note that the peak occurs at roughly the same potential vs. the Ag quasi-reference electrode as was observed in the straight LiCl-KCl system.

Anodic CV's for LiCl-KCl-LiBO₂ at 800 C as a function of LiBO₂ content are shown in Figure 10 for a graphite working electrode (sweep rate =0.1 V/s). The curves were essentially identical when the ilmenite was present in the melt. When 5 % LiBO₂ was added to the melt an oxidation reaction was observed starting near 0.1 V vs. the Ag quasireference electrode. The size of this oxidation peak increased substantially when the amount of LiBO₂ was increased to 20 %. It is believed that the oxidation reaction that is occurring is the same as that in the straight LiBO₂-KBO₂ system; namely the reaction between oxygen anions and the graphite electrode to form CO and/or CO₂. At first glance, it would appear that adding more $LiBO_2$ to the LiCl-KCl melt might yield even better results. However, when the $LiBO_2$ level reached 20 % in the melt, it began to become more difficult to wash the melt off the iron product. Also, X-ray diffraction analysis of the residue at the bottom of the crucible showned the presence of $Li_{0.8}Ti_{2.2}O_{4.8}$. Thus, lower titanates begin to from at a $LiBO_2$ level as low as 20 %. The problem increases as the $LiBO_2$ level increases.

SUMMARY

The results for the four salt systems investigated are summarized in Table III below. The best results were obtained for the LiCl-KCl mixture containing 5 to 20 % LiBO₂. In this system the positive aspects of both the LiCl-KCl and LiBO₂-KBO₂ systems were combined. These results suggest that with the right salt system, an economic molten salt extraction/electrolysis process for converting ilmenite ores to a high grade TiO₂ feedstock and a saleable iron coproduct may be feasible.

Salt System	Positive Aspects	Negative Aspects		
LiCl-KCl	Selective extraction of Fe ⁺²	Low solubility of iron Fe ⁺² leads to low Fe deposition rates		
	Salt is easily washed off products	Anodic reaction forms Cl_2 rather than CO and/or CO_2		
NaOH-KOH (acidic)	High ilmenite solubility at low temperature	Titanium is also dissolved		
	Salt easily washed off product	Electrodeposited iron is reoxidized by the melt.		
LiBO ₂ -KBO ₂	High ilmenite solubility	Titanium is also dissolved		
	High rates of Fe deposition and CO evolution	Extremely difficult to wash salt off products		
		Titanate formation		
LiCl-KCl+LiBO ₂	High Fe deposition rate	Anodic reaction to form CO/CO ₂ is still relatively slow		
	Salt easily washed off products	Tendency to form titanates at high LiBO ₂ levels		

 Table III

 Summary of Results for the Four Salt Systems Investigated

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Figure 1: Schematic of Apparatus Used for Solubility Measurements



Figure 2: Schematic of Apparatus Used for Electrochemistry Experiments



Figure 3: Solubility of the Iron Fraction of FeTiO3 and PRFI in LiCl-KCl



Figure 4: Cathodic CV's of PRFI in LiCl-KCl at 800 C. Also shown is the CV for plain LiCl-KCl without ilmenite (dotted line)





Figure 5: Anodic CV of PRFI in LiCI-KCl at 800 C. Scan Rate = 0.1 V/s.

Figure 6: Cathodic CV's of FeTiO3 in NaOH-KOH at 250 C. Also shown is the CV for plain NaOH-KOH (1V/s).







 Figure 9: Effect of LiBO2 Addition on Cathodic
 Figure 10: Effect of LiBO2 Addition on Anodic

 CV of PRFI in LiCI-KCI at 800 C.
 CV of LiCI-KCI at 800 C.

 Scan Rate = 0.1 V/s.
 Electrode = graphite,

 scan rate = 0.1 V/s.
 scan rate = 0.1 V/s.

NEW PRINCIPLES FOR THE PROCESSING OF CARNALLITITES IN THE DOMAIN OF MOLTEN SALT HYDRATES

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New concepts stimulated by environmental problems have been developed for the processing of carnallite (KCI•MgCl2•6H₂O) and of complex composed MgCl₂ solution at elevated temperatures in the concentration range of molten salt hydrates. The main idea of the processes proposed is the separation of MgCl₂ as MgCl₂•4H₂O from the multi component salt-water mixture at temperatures around 160°C. Although the temperature is relatively high the processes are designed in a way, that the water vapor pressure does not exceed 0.1 MPa in any of the different manufacturing operations.

INTRODUCTION

The conventional processes for the manufacturing of KCl are based on the stable and metastable solid-liquid phase equilibria of the five-component sea water system Na+, K+, Mg2+/Cl-,SO42-//H₂O at temperatures up to about 110°C. If starting materials are used, which consists mainly of carnallite MgCl₂ is introduced into the process, which has than to be removed from the process by special procedures. Environmental problems can be caused if the concentrated MgCl₂ solution is discharged to waste.

On the other hand MgCl₂ is an interesting starting material for the production of MgO or magnesium metal. The processing of the MgCl₂ solution is expensive and inefficient, because of the large amount of water, which have to be evaporated. Moreover the conventional procedures for processing this solutions are faced with special problems which are mainly the result of supersaturation phenomena.

To overcome this general disadvantage carnallite should be processed at elevated temperatures in a hydrate melt without additional water. To derive an efficient process under these conditions the appropriate solid-liquid-vapor phase equilibria have to be known in detail at elevated temperatures (above 100°C).

Processes which proceed at elevated temperatures in the region of molten salt hydrates offer several advantages in comparison with conventional processes. These are

- significantly smaller solution volumes during the processing
- technologies producing less waste and
- high efficiency for the recovery of heat (because of the high temperature level).

On the other hand, disadvantages should also be considered such as increased corrosion and higher pressure.

Starting from the results of a comprehensive study of the solid-liquid-vapor equilibria of the five-component sea water system Na+, K+, Mg2+/Cl-,SO42-//H2O at elevated temperatures (up to 250° C) new concepts for the processing of carnallite and of complex composed solutions of MgCl₂ have been derived.

PHASE EQUILIBRIA

Solid-liquid equilibria

The solid-liquid phase equilibria of the five-component sea water system Na+, K+, Mg2+/Cl-, SO_42 -//H₂O have been studied at elevated temperatures (above 100°C) by using an analytical method. The results are published elsewhere (1-5).

The subsystem KCl-MgCl₂-H₂O, which is of particular interest was investigated in detail in the temperature range 120-250°C. A projection of the solid-liquid phase diagram of this system in the range of high MgCl₂-content is plotted in Figure 1. The plain lines represent the bivariant equilibria solid-liquid-vapor (isotherms), while the bold lines are the monovariant equilibria (2 solid phases are in equilibrium with the liquid and the vapor phase).

At temperatures above 120°C the following solid phases are stable:

- KCl
- carnallite (KCl*MgCl2*6H2O)
- 1.5KCl*MgCl2*2H2O
- MgCl2*4H2O and
- solid solutions $KCl_x MgCl_2 2H_2O$ ($0 \le x \le 1$).

Carnallite and MgCl2*4H2O are melting incongruently at 167°C and 181°C, respectively. Three invariant equilibria (3 solid phases are in equilibrium with the liquid and the vapor phase) are stable within the temperature range 120-250°C. From the phase diagram the following solid phase combinations with the appropriate temperatures can be deduced for the invariant equilibria:

- KCl*MgCl2*6H2O / MgCl2*4H2O / 1.5KCl*MgCl2*2H2O	(153°C)
The many of the second of the second s	(155 C)

- KCl / KCl*MgCl₂*6H₂O / 1.5KCl*MgCl₂*2H₂O (157°C)
- MgCl2*4H2O / 1.5KCl*MgCl2*2H2O / KCl*MgCl2*2H2O (solid solution) (165°C)

Vapor Pressure

The vapor pressure of the saturated liquid phase was calculated by using a modified BET equation and the parameters which have been deduced from the results of vapor pressure measurements in the system KC1-MgC12-HyO at high temperatures and in the range of molten MgCl2-hydrates (6). The intersection curve between the liquidus surfaces and the surface for pH₀O=0.1 MPa is plotted in Fig. 1 as dashed line. Obviously, saturated liquid phases with vapor pressures pH₀OS.1 MPa are also stable at relatively high temperatures in a relatively large concentration interval. The temperature maximum is located at about 193°C in the stability region of the solid solutions. In particular all liquid phases which are in equilibrium with MgCl2⁺4H₂O have lower vapor pressures than 0.1MPa, which should be a very interesting feature for the processing of Camallite and of complex composed solutions of MgCl2.

NEW PROCESSING PRINCIPLES

The processing principles will be explained by means of two examples. The balances for the different substances have been calculated by taking into account the phase equilibria of the five-component sea water system. For a better illustration the processes are discussed by means of the phase equilibria of the ternary system KCl-MgCl₂-H₂O. In general the temperatures as well as the compositions of the liquids in the appropriate steps of the processes given can be altered in a certain range.

Processing of Carnallitites in the range of molten salt hydrates

All proposals for the processing of carnallite in the range of molten salt hydrates made in the past have a common idea. The carnallite is decomposed in its own water of hydration at about 167°C (incongruent melting point of KCl*MgCl₂*6H₂O). The forming solid KCl is separated from the hydrate melt. From this hydrate melt synthetic carnallite is crystallized by cooling it down to about 120°C. The synthetic carnallite can be recycled. It remains a hydrate melt of MgCl₂*6H₂O with dissolved KCl and other contaminants, for example NaCl (if the mineral carnallitie is used as the starting material, which always contains NaCl). The whole process has two important disadvantages:

- The vapor pressure of the hydrate melt at the incongruent melting point of carnallite is larger than atmospheric pressure (ph,0=0.13 MPa) according to the phase diagram. Hence the decomposition of carnallite and the separation of the solid KCl have to be done in a pressure vessel, which makes the processes complicated and expansive.
- The content of the alkaline chlorides in the MgCl₂*6H₂O is to large for the production of MgO or magnesium without further purification. In addition it is not possible to utilize the relatively large melting enthalpy of MgCl₂*6H₂O energetically.

To avoid this disadvantages we propose the following process. The different steps of the process are summarized in the flow sheet in Fig.2 and illustrated in Fig.1 by the dot-anddashed lines. Carnallite or the appropriate mineral carnallitie is decomposed within a molten hydrate of MgCl₂ of the composition A at about 165°C (Fig. 1). For it, carnallite and melt are mixed in an appropriate ratio to form a molten hydrate of composition B and solid KCl as a result of the decomposition. After removing the KCl a synthetic carnallite is crystallized by cooling the liquid phase down to 150°C. The synthetic carnallite is separated and recycled. At this step the liquid phase composition has reached point C in the phase diagram. This liquid is concentrated by evaporation up to point A and returned to the decomposer. The MgCl₂'4H₂O crystallized during the evaporation represents the second final product.

Hence this process has the following advantages:

- 1. All stages of the process can proceed at vapor pressure pH₂O≤0.1 MPa.
- 2. The amount of waste produced, is as low as possible.
- The level of the impurities of both final products KCl and MgCl₂*4H₂O depends only on the efficiency of the solid-liquid separation.
- 4. A major part of the heat of fusion of the molten salt hydrate can be utilized energetically by using the high temperature level of the water vapor while concentrating the hydrate melt and crystallizing MgCl⁺₂4H₂O, respectively.

Processing of a complex composed solution of MgCl₂

The main feature of the conventional technologies for the processing of complex composed solutions of MgCl₂ is the removing of the impurities from the solution, which is in

general more disadvantageous than the separation of the final product from the mixture. The solution is concentrated by evaporation. During this process a mixture of NaCl and MgSO4*H₂O is precipitated at temperatures of about 120°C and removed from the solution. In some cases the SO₄-content of the solution is reduced by precipitation of K₂SO₄*2MgSO₄ (Langbeinite). During the cooling of the concentrated solution synthetic carnallite is crystallizing and removed from the cold solution. The resulting solution contains - besides MgCl₂ - various contaminants as MgSO₄, KCl and NaCl depending on the initial composition and concentration. The most important disadvantage of this procedure is the resulting MgSO₄ level of the MgCl₂ solution because of supersaturation, which makes further purification - usually by different steps of precipitation - essential. This additional purification process is not very efficient and cases considerable loss of MgCl₂.

The idea of the process proposed in this contribution is the separation of the final product - MgCl₂ - from the complex composed solution. MgCl₂*6H₂O and MgCl₂*2H₂O are not suitable for this purpose as we can learn from the phase diagram of the system KCl-MgCl₂-H₂O. The concentration interval of KCl of the stabilization area of MgCl₂*6H₂O is too small for an efficient separation process and MgCl₂*2H₂O. Suitable for the separation of MgCl₂ thydrate but it forms solid solution with KCl*MgCl₂*2H₂O. Suitable for the separation of MgCl₂ from a complex composed solution should be MgCl₂*4H₂O.

The different steps of the process proposed are illustrated in Fig. 1 by the dotted lines and are summarized in a flow sheet in Fig. 3. The complex composed solution of MgCl₂ is concentrated by evaporation in a first step as far as close to the saturation of MgCl₂*4H₂O (point G in Fig.1) by increasing the temperature to about 160°C. During this step a thermal desulfatization and in some cases a crystallization of NaCl occurs (if the concentration of NaCl in the primary solution is high enough). After removing the solids in a second evaporation process MgCl₂*4H₂O is crystallized and separated. The remaining hydrate melt of composition A is mixed with one part of the primary solution (composition D) in an appropriate ratio to allow the crystallization of synthetic carnallite at 120°C which is separated. The remaining liquid phase of composition F is mixed with the other part of preheated primary solution. The resulting solution is given to the evaporation process.

The following advantages are gained by application of the process proposed in comparison to conventional processes:

- The supersaturation of MgSO₄ has no negative influence on the quality of the final product. The separated MgCl₂*4H₂O can be used directly for the production of MgO or magnesium metal without additional purification.
- The water vapor pressure is lower than 0.1 MPa in all steps of the process, which is of particular importance for the different separation procedures.
- A large part of the heat can be recovered because of the high temperature level in the process.

The larger amount of energy which is necessary because of the higher degree of evaporation in comparison with conventional processes is not significant, if the overall process for example for the production of MgO is taken into account.

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Fig. 1: Projection of the MgCl2-rich part of the phase diagram of the system KCl-MgCl2-H2O at 120-200°C. — boundaries between the liquidus surfaces; — isotherms; ------ water vapour pressure pH,0=0.1 MPa.



Fig. 2: Flow sheet for the processing of carnallite.




MOLTEN CARBONATE FUEL CELL REACTION MECHANISMS

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Abstract. An overview will be presented of our research on the reaction mechanisms in a molten carbonate fuel cell (MCFC) of the last four years. Chronoamperometry and impedance measurements were performed on Au, Ni and Cu flag electrodes in a half cell setup and on porous anodes and cathodes in small laboratory-scale fuel cells. The gas composition was varied over a wide range to determine the reaction orders accurately. The research is described in detail in two Ph.D. theses.

INTRODUCTION

A fuel cell is an electrochemical system in which the chemical energy present in a fuel like hydrogen, methane, carbon monoxide or methanol is transformed directly into electrical energy. In the past, different types of fuel cells have been developed, differing mainly in the electrolyte composition and working temperature. Fuel cells are characterized by a high efficiency and neglectable emission of SOx and NOx. Due to the high efficiency also CO₂ emission is reduced when carbon containing fuels are used.

The Molten Carbonate Fuel Cell (MCFC) operates at a temperature of 650 °C and consists of a porous Ni/5-10%Cr anode and a porous Ni cathode, which is in situ oxidized and lithiated to become a semi conducting Ni(Li)O electrode. The molten carbonate electrolyte, presently an eutectic mixture of 62 mol% lithium and 38 mol% potassium carbonate, is contained in a porous matrix of lithium aluminate. Standard gas mixture of hydrogen, carbon dioxide and water is fed to the anode to simulate reformed methane, and a mixture of air with 30% carbon dioxide is fed to the cathode.

Since 1988 we have been involved in MCFC research in the framework of the Dutch National fuel cell program. The work resulted in two Ph.D. theses in Nov. '91 [1,2].

It is the aim of this presentation to give an overview of this work. For detailed information the reader is referred to the theses. Findings that might be useful for molten salt researchers in general are given in more detail.

EXPERIMENTAL

Potential steps of 10 to 100 mV anodic from the equilibrium potential were imposed using a EG&G PAR 273 potentiostat. During the measurements the potentiostat was kept in the 1 Amp current range to minimize the measurement resistance (1 Ohm) and thus the RC time of the double layer charging. The current was measured externally using a Philips PM9355 current probe placed around the counter electrode lead wire and recorded with a Philips PM3350 Digital Storage Oscilloscope IEEE connected to a PC. The experimental set-ups are described in detail in the theses.

Data evaluation

We have also payed much attention to the chronoamperometry data evaluation method. For a simple one step redox mechanism the well known Gerisher Vielstich relation has been derived:

$$i(t) = i(t=0) \exp(\lambda^2 t) \operatorname{erfc}(\lambda \sqrt{t})$$
(1a)

with λ a parameter containing the products $C_{OX}\sqrt{D_{OX}}$ and $C_{red}\sqrt{D_{red}}$ At time zero the current is purely charge transfer controlled. At short times, (t<<1/ λ^2) the response can be linearised:

$$i(t) = i(t=0) \left(1 - \frac{2\lambda}{\sqrt{\pi}} \cdot \sqrt{t}\right)$$
(1b)

thus a plot of i(t) vs \sqrt{t} should be linear for short times, and extrapolation to zero time yields a value for i(t=0). However we have shown that in the time region of the double layer charging decay this linear relation is not valid, hence \sqrt{t} extrapolation will yield systematic errors as is indicated in fig.1.

In these cases fitting of the full expression is a better method. However, there are situations where the fits are not successful or not even possible. An easy check on those situations is provided by Johnson and Barnartt[3]. A 'master curve' can be constructed:

$$R = \frac{i(t)}{i(2t)} = \frac{\exp(\lambda^2 \cdot t) \cdot \operatorname{erfc}(\lambda \cdot \sqrt{t})}{\exp(2\lambda^2 \cdot t) \cdot \operatorname{erfc}(\lambda \cdot \sqrt{2t})}.$$
(2)

It is shown that this function is always smaller than $\sqrt{2}$. From a current response we calculated R= i(200 µsec)/i(400 µsec). So whenever the data does not fulfil the requirement R < $\sqrt{2}$, the G-V relation does not hold. This proved to be the case for current responses on Ni and Cu in anode gasses and for Au in O₂/CO₂.

PART I: ANODE REACTION MECHANISM

The aim of our research was to obtain more knowledge on the fundamental processes that occur in a MCFC, with emphasis on reaction mechanisms and kinetics. An important method to determine the reaction mechanism is by determining the reaction orders of the reaction.

In general the exchange current density is given by a power law of the partial gas pressures involved in the anode or cathode reaction.

$$i_0 = i_0^0 [A]^a . [B]^b . [C]^c ... [Z]^z$$
 (3)

with i_0^0 the standard exchange current density i.e. the c.d. when all partial pressures [A], [B] etc. are 1 atm. The exponents a,b,c... are called the reaction orders that can be calculated theoretically. In general they are different for different reaction mechanisms however, there does not exists a unique relation between the reaction orders and the mechanism.

The MCFC anode is a porous structure made of Ni with 5 to 10% Cr or Al added for creep resistance. However to study the fundamental processes a large part of the work in half cells was concentrated on gold electrodes, since Au is more stable than Ni or Cu allowing a wide range of potentials to be used in cyclic voltammetry.

The experimental research on the anode kinetics was seriously hindered by the presence of water in the anode gas. Condensation of water on colder spots of the set-up has to be avoided. Another point of concern specific for the anode is the occurrence of chemical reactions in the gas phase. We have a.o. the shift reaction and the methane reforming or methanation reaction.

shift:	$CO_2 + H_2$	= H ₂ O + CO	(4)
methanation:	3H2 + CO	$= CH_4 + H_2O$	(5)

Whether or not these reactions are in equilibrium in a given experimental set-up cannot easily

be tested. However, frequently one does assume equilibrium. We have analysed our results for three cases: equilibrium of the shift reaction, no shift and the average gas composition and the methanation reaction was assumed to be neglectable (no methane formation from input gasses CO₂ and H₂. Hence we could indicate the influence of the assumption on the results. The uncertainty in gas composition is indicated by 'error' bars in the data plots. In other words those bars indicate a possible systematic error and not a random error of measurement. By following this approach i.e.; use a large range of gas compositions, use of gold electrodes as a model system and examine the influence of the shift reaction we were able to determine the reaction orders for the hydrogen oxidation reaction on gold relative accurately, excluding many proposed reaction mechanisms and suggesting a Volmer-Heyrovski type of mechanism. Using the model system with a gold electrode allowed us to give a critical evaluation of our measurements and results in literature on the more practical anode materials Ni and Cu. State of the art porous anodes of Ni with 10% Cr were tested mainly using impedance spectroscopy.

RESULTS ON GOLD

Chronoamperometry and Impedance spectroscopy.

We have used two techniques to determine the exchange current density i0 as a function of gas composition; Chronoamperometry (CA) and Impedance spectroscopy (IS). Both yielded comparable results for the i0 and the so determined reaction orders. The standard exchange current density was found to be between 40 and 120 mA/cm² depending on the assumption for the shift reaction and whether (the number of electrons transfered) is 1 or 2.

Based on the high reaction order found for H₂ (0.75) we concluded that the hydrogen oxidation on gold proceeds according to a Volmer-Heyrovski mechanism:

$$H_2 + CO_3^{2-} \leftarrow H_{ads} + OH^- + CO_2 + e rds$$
 (6)

$$H_{ads} + CO_3^{2-} \xleftarrow{} OH^- + CO_2 + e$$
 (7)

$$2 \text{ OH}^- + \text{CO}_2 \xrightarrow{\leftarrow} \text{H}_2\text{O} + \text{CO}_3^{2-}$$
 (8)

For this scheme, the theoretical reaction orders for carbon dioxide and water are $\alpha/2$ (hence

between 0.2 and 0.3 when $0.4 < \alpha < 0.6$.).

A negative reaction order for water can only be explained by a high surface coverage of hydroxyl ions. This would yield a reaction order of -0.25 for water, and 0.75 for carbon dioxide, while no coverage would yield 0.25 for both water and carbon dioxide. The experimental reaction orders therefore indicate the Volmer-Heyrovski mechanism with "intermediate" surface coverage of hydroxyl ions to be the most probable reaction mechanism for the hydrogen oxidation on gold in molten carbonate. The more or less accepted mechanism by Ang and Sammells for Ni that predicts three equal reaction orders of 0.25 is not valid for the hydrogen oxidation on gold.

Fit results of the impedance data support this conclusion since the best fit was obtained with a simple Randles circuit representing a charge transfer reaction and a diffusion process only, while equivalent circuits based on mechanisms with an dissociative adsorption step $(H_2 = 2 H_{ad})$ as in the Ang and Sammells mechanism were much worse.

Because the charge transfer resistance is inversely proportional to exchange current density the reaction orders can also be determined from the impedance measurements under the various gas atmospheres. As mentioned above both techniques yielded analogous results.

By thoroughly analysing CA and IS results also the products $C_{OX}\sqrt{D_{OX}}$ and $C_{red}\sqrt{D_{red}}$ could be determined yielding reasonable values. From the slope of the linear relation between $C_{red}\sqrt{D_{red}}$ and the partial pressure of hydrogen in the feed gas the Henry constant could be determined at 5±1 * 10⁻⁷ mol/atm.cm³. (see figure 2)

In Figure 3 an Arrhenius plot is presented for the exchange current densities determined at a gold electrode, for the two gas compositions 820 and 640.

From the Arrhenius equation the activation energy for the hydrogen oxidation can be calculated.

$$i_0 = i_0^* \cdot \exp(-\frac{E_{act}}{RT})$$
(9)

The activation energy is an important input parameter for integral fuel cell performance models, like the PSI model. The activation energy for gold in this temperature region is calculated to be $95 \pm 10 \text{ kJ} \cdot \text{mol}^{-1}$ for gas composition 820, and $61 \pm 12 \text{ kJ} \cdot \text{mol}^{-1}$ for gas composition 640. Assuming the reaction mechanism to be identical for these two gas compositions, a rough estimate for the activation energy can be determined from the average of these gas compositions: E act = $78 \pm 17 \text{ kJ} \cdot \text{mol}^{-1}$. For nickel, determination of the activation energy can only be estimated on account of the exchange current densities determined using the extrapolation technique, since it was not possible to perform the direct fit at 923 K. A rough estimate can be made from the extrapolation values: $55\pm 2 \text{ kJ} \cdot \text{mol}^{-1}$.

These values are somewhat higher than those reported by Ang and Sammells for nickel and cobalt (28 kJ·mol⁻¹ and 31 kJ·mol⁻¹ respectively). A paper on CA measurements mainly concentrated on solid gold samples will be submitted to the J.E.S.

Cyclic Voltammetry and Polarisation curves on gold

The electrochemical spectrum of gold in a Li/K ($62/38 \mod \%$) eutectic carbonate mixture has been evaluated under pure N₂, CO₂ and CO and in mixtures of H₂, CO₂ and H₂O. C.V.'s that were measured within the first two weeks after start up of the half cell on a 'fresh' gold electrode showed an extra anodic current peak that later disappeared. We ascribed this to the surface condition of the gold flag electrode. Etching of the grain boundaries was not only observed on gold, but also on Ni and Cu electrodes. This feature is important since it may partly account for the spread in the data and in the differences found between researchers.

Another diagnostic use of CV proved to be a test whether or not the electrode is fully submerged in the melt. In our first half cell set-ups made of alumina crucibles it is impossible to make a visual inspection of the electrodes in the melt. In improved cells we later used a quarts cover on the crucible. If the electrode was deliberately improperly submerged, the cathodic peak almost completely disappeared (see figure 4)

The mechanistic information from cyclic voltammetry (c.v.) experiments is limited due to the lack of theoretical background for complicated electrode processes like the hydrogen oxidation. Semi-quantitative analysis of the c.v. results offered some evidence for an adsorption step or a chemical reaction in the overall electrode process.

Using a low scan rate quasi stationary polarisation curves were measured as a function of gas composition and temperature. A limiting current density was observed in the anodic branch but not in the cathodic direction.

Averaging over three gas compositions the activation energy of the limiting current density was determined at 16 ± 6 kJ/mol from an Arrhenius plot in the temperature range of 550 to 800 °C. This activation energy of diffusion is smaller by a factor 2 or 3 than the activation energy for the exchange current density (80 kJ/mol) indicating that the relative contribution of kinetics to the anode polarisation becomes more important at lower temperatures while the contribution of diffusion to the polarisation does not increase as rapidly when the temperature is lowered. Because an MCFC suffers from severe corrosion problems one aims for an operating temperature as low as possible. The strong increase of the polarisation at lower T does not permit very low temperatures and an average stack temperature of 650 °C is a generally accepted compromise today.

RESULTS ON NICKEL AND COPPER

Impedance measurements and chronoamperometry experiments on Ni and Cu at 650 °C confirm the literature in the sense that the kinetics of the hydrogen reduction is fast. We have shown in fact that it is too fast to be determined (accurately) by CA or IS. Namely in a Nyquist representation of the impedance data no semicircle can be observed as for gold but only a Warburg element; characteristic for a diffusion process. The faster kinetics is also indicated by the higher current density of the response, although this can also be partly caused by dissolved hydrogen in the Ni and Cu electrodes. Also Pt and Pd electrode materials well know for there capability of storing hydrogen are found to give even larger current responses in a CA experiment.

Also in contrast with the CA results on gold the Ni and Cu data could not be described by the theoretical Gerisher Vielstich relation. This could be partly due to the double layer charging current that has not fully died out in the time range we analysed but also to the dissolved hydrogen in the electrodes.

In either case analysing the results using a simple linear or \sqrt{t} extrapolation to t=0 based on a linearisation of the Gerisher Vielstich relation as frequently applied will yield systematic errors and possibly wrong estimates of the reaction orders. As long as there is no theoretical relation available the extrapolation technique is the only possibility. So we have analysed the results with the \sqrt{t} extrapolation. Although a large spread in the so determined reaction orders was found we could conclude that they changed as a function of electrode material and temperature so that in contrast to gold no particular reaction mechanism manifests itself clearly. Further it cannot be excluded that two or more parallel mechanisms occur which contribution depend on gas composition or temperature. Hence we conclude that the question of the hydrogen oxidation mechanism (on Ni) is again open for discussion and more sophisticated methods have to be applied to determine the mechanism.

Porous NiCr anode

A Nyquist diagram of the impedance spectrum of a NiCr anode in general showed three semi-circles. The high frequency circle is ascribed to charge transfer. Dependant on the long or short film approximation of the thin film model for a porous electrode the activation energy of this kinetic process was determined from the size of the semi circle to be between 50 and 75 kJ/mol. One of the two low frequency semi circles had an activation energy of 16 to 25 kJ/mol and is ascribed to a diffusion process. These values are in agreement with the activation energies determined in half cells mentioned above. A sound explanation for the

third semi circle could not be given. A negative activation energy between -14 and -40 kJ/mol was found for this semi circle.

Wetting

We have also studied the wetting of anode materials by molten carbonate. Since this subject is not within the scope of this paper the reader is referred to an earlier paper [4]

PART II: CATHODE REACTION MECHANISM

The oxygen reduction in molten carbonate has been studied on a plane gold electrode submerged in a molten carbonate melt and on three different porous electrodes, made of NiO(Li), LiFeO2 (doped with either Mg or Co) and LiCoO2.

Impedance measurements on gold

From impedance measurements obtained on a plane gold electrode in a half cell set-up it is concluded that two parallel reaction mechanisms (I and II) are involved in the oxygen reduction. It was shown that it necessary to measure in the extreme low frequency range as low as 1 milliHz since it is in this regime that the chemical reaction step in the mechanism shows its influence in the form of a Gerisher impedance. In the higher frequency domain the impedance of the Gerisher resembles the 'normal' Warburg diffusion impedance (figure 6). The reaction steps constituting to mechanism (I) have been resolved, for mechanisms (II) the steps could not be unraveled due to conflicting results for this mechanism. However, since the impedance of I is much smaller than that of the second branch the first will dominate the process and determine the current and polarisation. The standard exchange current density for reaction mechanism I is 13.3 ± 1.5 mA/cm², with oxygen and carbon dioxide reaction orders of 0.40 ± 0.05 and 0.42 ± 0.17 respectively. The standard exchange current density for reaction mechanism II is much smaller: $10.8 \pm 0.7 \mu$ A/cm², with oxygen and carbon dioxide reaction orders of 0.85 ± 0.05 and -1.11 ± 0.14 respectively. So also in CA experiment the first branch will dominate. Mechanism I consists of following steps:

1) Formation of peroxide at the gas/electrolyte interface:

$$\frac{1}{2}O_2 + CO_3^{2-} \xrightarrow{\rightarrow} O_2^{2-} + CO_2 \tag{10}$$

2) Peroxide diffuses into the melt and interacts with dissolved carbon dioxide forming peroxycarbonate:

$$O_2^{2^2} + CO_2 \quad \stackrel{\rightarrow}{\leftarrow} CO_4^{2^2} \tag{11}$$

3) The peroxycarbonate reacts in two one-electron transfer steps at the plane gold electrode, partly covered with adsorbed oxide :

$$\operatorname{CO}_4^{2-} + e \xrightarrow{\rightarrow} \operatorname{CO}_3^{2-} + O^- \operatorname{r.d.s}$$
 (12)

$$O^- + e \xrightarrow{\rightarrow} O^{2-}_{ad}$$
 (13)

4) At the electrode surface the adsorbed oxide reacts with carbon dioxide forming carbonate:

$$\operatorname{CO}_2 + \operatorname{O}_{\operatorname{ad}}^{2-} \xrightarrow{\rightarrow} \operatorname{CO}_3^{2-}$$
 (14)

The equivalent circuit representing the super oxide/peroxide model also describes the impedance data very well. However the oxygen and carbon partial pressure dependencies do not agree with the expected theoretical dependencies based on this model.

Chrono-amperometry

The results of the chrono-amperometry indicate that the reduction mechanism is not a simple charge transfer reaction with diffusion of reactant and product since the ratio R=I(t)/I(2t) was larger than $\sqrt{2}$ as explained above. This is in agreement with the proposed more complicated peroxycarbonate reaction mechanism.

The partial pressure dependencies of the limiting currents observed in the quasi-steady state polarisation measurements can also be explained by this peroxycarbonate mechanism.

Addition of 1wt% BaCO₃ to the Li/K eutectic melt will result in an improved cathode performance since the limiting current and the inverse polarisation resistance measured in a polarization curve did increase after addition of BaCO₃.

Porous cathodes

Impedance were performed on three different porous electrodes, made of the standard NiO(Li) and alternatives LiFeO₂ (doped with either Mg or Co) and LiCoO₂. In general two semi circles are observed in the Nyquist representation of the data, although frequently the

two interfere with each other yielding the appearance of only one arc (see figure 7). The partial pressure dependencies of the low frequency (diffusion) arc indicate that both O₂ and CO₂ are physically dissolved and diffuse in molecular form. Two mechanisms can explain the reaction orders of the high frequency (kinetic) arc.

1) the dissociation oxygen followed by the reduction of the oxygen atom with the first electron transfer reaction as the r.d.s.

or 2) the reduction of peroxycarbonate also with the first electron transfer reaction as the r.d.s.

The dissociation of oxygen respectively the formation of peroxycarbonate must take place at the electrode surface if indeed O₂ and CO₂ are physically dissolved and diffuse in molecular form. Further it follows from the reaction orders determined that for either of the two mechanisms the NiO(Li) and the LiCoO₂ should have an intermediate coverage of adsorbed oxide while for Co-doped LiFeO₂ one of the two mechanisms being valid it must take place at a surface with no or low oxide coverage.

Assuming the same diffusion resistance for all cathodes the ratio of the maximum height of the diffusion arc and the kinetic arc is a measure for the catalytic activity of the electrode materials. From an analysis of these ratio's it is concluded that the catalytic activities of the three materials do not differ significantly. The larger impedance (and polarisation) of the LiFeO2 cathode must be due to the larger specific resistance compared to NiO and LiCoO2. A paper on the impedance measurements on porous cathodes is in preparation and will be submitted to the J.E.S.

NiO dissolution

The now widely used NiO cathode slowly dissolves into the melt. Together with the corrosion problem these severely reduce the life expectations of an MCFC.

Nickel ions diffuse to the anode side through the matrix where they are reduced to metallic Ni and deposited whenever the hydrogen concentration is large enough. The Ni deposition is explained with a flux model taking into account the transport of nickel ions, peroxide, superoxide and hydrogen in the matrix. The experimentally observed displacement of the deposition plane somewhere between the anode and the cathode is explained by a change in the tortuosity of the matrix that is slowly pressed together in an operating fuel cell. The work was performed in close cooperation with the Dutch Energy Research Centre (ECN) and a joint paper on the NiO dissolution model has been published [5].

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Figure 1: Current response to a 100 mV potential step, recorded at a gold electrode. Temperature: 923K. Gas composition 80% H₂ +20% CO₂ humidified at 60°C. The Faraday current (IF) as a result of a) a linear extrapolation and b) a direct fit of the G-V relation (1).

Simulations of the double layer charging current (IC) 1) using values for C_{dl} (50 μ F) and R_u (0.7 Ω) obtained from impedance measurements and 2) as obtained from an exponential fit of the resultant current after subtraction of the erfcexp fit result from the measurement (RC=12 μ s)



Figure 2 $C_{\text{Red}}\sqrt{D_{\text{Red}}}$ as a function of the average partial pressure of hydrogen in the gas phase, for gold at 923K.



Figure 3: Arrhenius plot for the exchange current densities of two gas compositions 80% H₂ + 20% CO₂ and 60% H₂ + 40% CO₂ measured at a gold electrode.



Figure 4: Cyclic voltammograms recorded at a gold flag electrode in a 80% H₂ + CO₂ gas atmosphere humidified at 60° C at 923 K. Scan rate: $100 \text{ mV} \cdot \text{s}^{-1}$.

1: correct electrode submersion ; 2: scattery cyclic voltammogram sometimes observed 3: electrode improperly submerged.



Figure 5: The variation of impedance behaviour with gas composition in frequency range: 96 kHz-1Hz measured at 923 K on:

a) gold Inlet gas composition 80% H₂ + 20% CO₂ (=820);

(legend: humidifier temperature)

b) nickel flag electrode (legend; gas composition)



Figure 6 Measured and calculated impedance data on gold flag electrode Gas atmosphere: 10% O2/30% CO2/60% N2.



IMHEX[®] 70-CELL SUBSCALE STACK TEST

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ABSTRACT

The IMHEX[•] (Internally Manifolded Heat Exchanger) Molten Carbonate Fuel Cell (MCFC) concept was verified in a 70cell subscale stack fabricated, assembled, and operated at M-C Power Corporation (MCP). An average specific power of 100 mW/cm² and 75% fuel utilization on simulated reformed natural gas. The stack operated more than 1200 hours with an average output of 5.5 kW.

The IMHEX[®] MCFC stack concept was developed at the Institute of Gas Technology (IGT). M-C Power Corporation was formed in 1988 with the sole mission to commercialize the IMHEX[®] MCFC technology.

As a part of the $IMHEX^{\bullet}$ MCFC technology transfer from IGT, two subscale (20- and 70-cell) stacks were fabricated and assembled at MCP.

The main objective of the 70-cell stack (MCP-2) was to prove the design. Stack MCP-2 was successfully tested at MCP's testing facility in the summer of 1991. No electrolyte migration was observed. Other objectives were to verify the ability to stack up a large number of IMHEX[®] cells and to verify the performance of components fabricated on MCP's commercial-scale equipment.

STACK ASSEMBLY AND INSTRUMENTATION

Stack MCP-2 consisted of 70 fuel cells (active area 1028 cm^2) with a Ni-Cr anode, an *in situ* oxidized NiO cathode, and carbonate electrolyte within a LiA102 matrix. This is the tallest internally-manifolded stack operated to date.

The electrode backing current collectors were made of perforated metal sheets: the anode current collector, of nickel; the cathode current collector, of stainless steel 316 SS. To inhibit corrosion, the wet seal area of the bipolar plates was aluminized.

To monitor internal stack temperature distribution, 34 thermocouples were installed inside the stack, in the active area of individual cells and in the gas manifolds.

A modified ABB Kent-Taylor MOD30/PC30 distributed control system was used for process control and data acquisition.

To determine the internal cell resistance, a repetitive interrupter technique (Hewlett Packard HP8116A, 50 MHz pulse generator) was used. Waveforms were acquired and analyzed on a Tektronix 11401 digitizing oscilloscope with an 11A33, 150 MHz differential comparator amplifier.

STACK PERFORMANCE

During the first 1000 hours, the stack operated with an average power output of 5.5 kW. Stack performance continued to improve after several hundred hours of operation. The summary of the stack performance is presented in Figure 1.

Internal resistance measurements were made after 350, 640 and 1045 hours of stack operation. The data are presented in Figure 1. Average cell resistance was 0.71 Ohm cm^2 for all 70 cells and 0.62 Ohm cm^2 for the best 60 cells. Twenty-five cells showed performance at the level of a bench-scale "twin" cell (resistance 0.4 Ohm cm²).

The polarization curve for 75% fuel utilization and 20% oxidant utilization is shown in Figure 2, after 1100 hours of operation.

POST-TEST OBSERVATIONS AND ANALYSIS

After 1250 hours of stable performance and an additional 350 hours of diagnostic testing, the stack was terminated.

Post-test analysis showed the same electrolyte amount and composition (K/Li ratio) in the cells located in the bottom, in the top and in the middle of the stack.

The relatively lower cell-to-cell uniformity, compared with previous IMHEX[•] stacks tested by IGT, was the result of imperfect sealing near the top of the stack, insufficient uniformity of gas distribution for the two bottom cells, and differences in the internal resistance. These issues can be solved by the expected tighter control of the component tolerances.

BENCH-SCALE TWIN CELL PERFORMANCE

In parallel to the operation of Stack MCP-2, a 100 cm^2 bench-scale cell test was performed at IGT. The objective of this test cell, having similar active components as Stack MCP-2, was to establish baseline performance for the components.

The cell operated approximately 1500 hours. During the test, for diagnostic purposes, the cell was operated on two different fuel gas compositions: standard reference gas (75% H_2 and 25% CO_2) and gas diluted with nitrogen (30.6% H_2 , 8.1% CO_2 and 61.3% N_2). In both cases, the fuel utilization was 75%. The performance of the cell is shown in Figure 3. The twin cell performance was at the level of the best IGT bench-scale cells, establishing the quality of components manufactured on MCP's full-scale equipment.

TEST RESULTS

The major results of the Stack MCP-2 test are summarized below:

- 1. The IMHEX[®] MCFC concept was verified in the 70-cell stack test. The stack demonstrated "stackability" of the IMHEX[®] design. The stack operated more than 1500 hours under load, surpassing the test objective of 1000 hours of operation, with components manufactured to M-C Power specifications.
- 2. No carbonate migration has been observed.
- 3. The stack exceeded projected power (7.2 kW) and attained 8 kW at 160 mA/cm² and 75% fuel utilization. Voltage of 58 cells (83% of all cells) was higher than 640 mV and 30 cells higher than 700 mV at these conditions.

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MCP-2 STACK PERFORMANCE









MCP-2 BENCH-SCALE TWIN CELL PERFORMANCE





COMPARATIVE BEHAVIOUR OF OXYGEN ELECTROCHEMICAL SYSTEMS IN MOLTEN ALKALI CARBONATES AT 500-750°C

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ABSTRACT

The behaviour of reduced oxygen species in Na-K, Li-K, Li-Na and Li-Na-K molten carbonate eutectics, is investigated thermodynamically and by the means of electrochemical methods.

Thermodynamic predictions are in good agreement with experimental results. It is shown that, in all the studied melts, peroxide ions are stabilized in basic media $(O_2^{2-}/O^2$ - system is characterized). Superoxide species is never stabilized in lithium-containing carbonate melts whatever the selected conditions. This species is stabilized in Na-K melt, in slightly basic media. O_2^{-}/O_2^{2-} system is evidenced and characterized. CO₂ species never participates in the rate-determining reduction steps.

STATE-OF-THE-ART

Chemical properties of molten alkali carbonates, generally used in fuel cells, are influenced by the existence of reduced oxygen species and their electrochemical behaviour. Catalytic effects of these media in the oxidative transformation of methane into ethane and ethylene are correlated with the stability of peroxide and superoxide species (1-5).

An abundant literature has been dedicated to oxygen reduction in molten alkali media (6-17). It is well admitted now that, according to the considered molten carbonate, O_2^{2-} and/or O_2^{-} species are involved in the reduction process. Several and controversial hypotheses have been formulated on the reduction mechanisms and in particular, whether or not CO₂ species participates in the rate-determining step of this process. In Li-K molten carbonate, the most investigated alkali carbonate melt, Appleby et al (6) postulated, on the basis of reaction orders, the reduction of peroxide species with carbon dioxide, followed by the direct reduction of superoxide. In the same melt, Vogel et al observed a single wave that they ascribed to a 3-electron reduction of superoxide species (11). In Na-K carbonate melt, Appleby et al (6) attributed the two reduction currents observed to: $O_2^{2-} + 2 CO_2 + 2e^- \Leftrightarrow 2 CO_3^{2-}$ and $O_2^{-} + e^- \Leftrightarrow$ O_2^{2-} respectively. In the same eutectic, Uchida et al (9) proposed a first superoxide path: $O_2^- + 2 CO_2 + 3e^- \Leftrightarrow 2 CO_3^{2-}$ followed by the direct reduction of superoxide species: $O_2^- + e^- \Leftrightarrow O_2^{2-}$. Other interpretations have been given by us for the two mentioned eutectics (14,15). In the case of Na-Li-K (12,16) and Li-Na (13,17) molten carbonate eutectics, it has been shown that, in basic media, peroxide is the only stable reduced oxygen species and that the reduction reaction is: $O_2^{2-} + 2e^- \Leftrightarrow 2 O_2^{2-}$.

In this paper, a synthetic study, partially based on previous works (14-17), was developed to elucidate the redox mechanisms of oxygen reduction in different molten carbonates and compare the behaviour of these melts, according to the nature of alkaline ion. A thermodynamic study allowed to describe the stability of reduced oxygen species at different temperatures and acidity levels. Electrochemical techniques were used to investigate oxygen redox systems and determine different experimental parameters (solubilities, diffusion coefficients, reaction rates etc.).

THERMODYNAMIC APPROACH

Thermodynamic data concerning the molten carbonate melts presented in Table I are deduced from thermochemical tables (18,19) and from Andersen's experimental data (20).

Eutectic	composition mol.%	melting point °C
Li2CO3_Na2CO3	53.3-46.7	496
Li ₂ CO ₃ K ₂ CO ₃	50-50	504
Na2CO3_K2CO3	56-44	710
Li2CO3-Na2CO3-K2CO3	43.5-31.5-25	397

Table 1- Composition and melting points of the alkali molten carbonates investigated.

Characteristic dissociation equilibria and thermodynamic selfionization constants have been described elsewhere (14-17). Na-K carbonate eutectic is an ideal mixture (21). In the case of Li-K, Li-Na and Li-Na-K melts, which do not form ideal liquid solutions, the activity coefficients were determined on the basis on Lumsden data (21). The accessible acidity domain, defining the limits between the most acidic medium ($P(CO_2)$ set at one atm.) and the most basic medium (molten salt saturated with oxide species) is defined by the constant pK_d^* :

$$pK_d^* = -\log a(M_2O) - \log P(CO_2)$$

(where $a(M_2O)$ is the activity of the oxide ion and $P(CO_2)$ the carbon dioxide vapour pressure). The values of pK_d^* at different temperatures are reported in Table II. At a given temperature, the acidity domain increases with the cation radius. It can be observed that the Na-K melt, with a large acidity range, is the less dissociated molten carbonate and therefore, the most stable.

T(°C)	Na-K	Li-K	Li-Na	Li-Na-K
450				7.44
500		6.56	6.56	6.56
550		5.83	5.84	5.84
600		5.18	5.22	5.23
650		4.71	4.73	4.74
700		4.30	4.33	4.34
750	9.09	4.18	3.89	3.91
850	7.80	3.43	3.16	3.18
927	6.98	2.93	2.68	2.70

Table 2- Evolution of the accessible acidity range (pKd^{*}) with temperature for the molten carbonate eutectics investigated in this study (18).

Acidity-potential diagrams have been established as previously described (the oxygen electrode was taken as a reference) (14,16). The oxidation of the molten eutectic is characterized by the following electrochemical systems: O^2/O_2 ; O^2/O_2^- and O^2/O_2^{2-} . Electrochemical stability diagrams have been contructed for the different eutectics. Figure 1 shows, for instance, the diagram of Li-Na-K melt at 550°C, with the oxidation reactions (O₂ or O₂²⁻ formation), the reduction reactions with (K, CO or C formation), the acidity limit (CO₂ set at one atm.) and the basicity limit (Li₂O precipitation). Under the experimental conditions given (even at very low oxygen pressures, $P(O_2) = 10^{-3}$ atm.), O_2^{2-} , stabilized in basic media, is the only reduced oxygen species present in this molten eutectic. O_2^- species is never present in significant amounts. The same behaviour has been observed for Li-Na and Li-K carbonate eutectics containing lithium ions. In the case of the Na-K melt, peroxide species is stabilized in basic media, whereas superoxide species can be stabilized in moderately basic or moderately acidic media. These interpretations are in agreement with the results obtained by Andersen in his experimental thermodynamic study of molten alkali carbonates.

ELECTROCHEMICAL STUDY

All the molten carbonate eutectics mentioned in Table I and sodium oxide were Merck reagents of analytical grade (>98% purity). Sodium peroxide was a Prolabo reagent (94% purity) and lithium oxide was a Johnson Matthey reagent (95% purity). The working electrodes were gold planar and gold wires. The auxiliary electrode was a gold wire. The reference electrode was a silver wire dipped into an Ag₂SO₄ (10⁻¹ mol./Kg) eutectic melt. The electrochemical apparatus, cell and conditions used in this investigation were described in previous works (15).

Reduced oxygen systems were characterized by the means of different electrochemical techniques at a gold electrode: hydrodynamic and cyclic voltammetry, chronoamperometry, chronopotentiometry and convolution potential sweep methods. In all the molten carbonates studied, the formation of peroxide or superoxide species is due to the reaction of molecular oxygen with oxide or carbonate ions (6). The instability of molecular oxygen in such media was pointed out in most of the electrochemical publications (6-17), as well as in experimental thermodynamic studies (20).

The behaviour of molten carbonates is greatly dependent on the acidity of the medium. No reduction currents representative of reduced oxygen species were observed in acidic media. Reduction currents of these species appeared in slightly basic or basic media, according to the nature of the molten eutectic.

In the case of the Na-K eutectic, a two-electron reduction current attributed to peroxide species was observed:

$$O_2^{2-}$$
 + 2e⁻ \Leftrightarrow 2 O²⁻

This system was analyzed in a previous study (14). When the acidity of the melt increased, the reduction current of peroxide species progressively disappeared and another reduction current corresponding to superoxide species was observed at a higher potential:

$$O_2^- + e^- \Leftrightarrow O_2^{2-}$$

Fig. 2 shows these reduction currents at two acidity levels.

In Li-K, Li-Na and Li-Na-K eutectics, experimental evidence was given for the existence of O_2^{2-} species in basic media, as predicted thermodynamically. O_2^- species was never observed whatever the selected conditions. Cyclic voltammetry and convolution potential sweep techniques were performed to describe the O_2^{2-}/O^2 - system. Theoretical equations describing the convolutive transformation of cyclic voltammograms were developed for non-unity systems (16).

The voltammogram obtained after addition of sodium peroxide in Li-K melt at 650°C is given in Fig. 3. Cathodic and anodic peaks are attributed to O_2^{2-}/O^2 - system.

In the case of Li-Na carbonate eutectic, peroxide reduction was evidenced by cyclic voltammetry (Fig. 4) and convolution potential sweep voltammetry at 750°C, confirming the results of Tomczyk et al (13). No oxidation current relative to oxide ions was detected, probably because it occured at a potential very close to the anodic limit of the medium. Fig. 5 shows a stationary voltammogram at 750°C, obtained by transformation of the cyclic voltammogram of Fig. 4. This result is in agreement with that of White et al (12). Fig. 6 shows the evolution of the solubility of Na₂O₂.

In all the molten eutectics, it was shown that there was no potential shifts corresponding to the reduction of peroxide or superoxide species with the acidity of the medium (important shifts are predicted thermodynamically when CO_2 species is included in the reduction paths) (14-17). This observation was confirmed, in the case of Li-Na and Na-K melts, by the determination of very low rate constants of neutralization reactions of CO_2 by oxide or peroxide species. Therefore, it can be concluded that CO_2 did not participate in the rate-determining reduction steps.

Table III summarizes all the results obtained with the four molten carbonate eutectics.

Parameters	Na-K 750°C	Li-K 650°C	Li-Na 750°C	Li-Na-K 500°C
O2 ²⁻ stability	basic media	basic media	basic media	basic media
O2 ⁻ stability	intermediate acidity	unstable	unstable	unstable
02 ²⁻ /0 ²⁻	rapid E ₀ = -0.25 V/(Ag ⁺ /Ag)	rapid E ₀ = -0.70 V/(Ag ⁺ /Ag)	rapid E _{1/2} = - 0.38 V/(Ag ⁺ /Ag) (only O2 ²⁻ +2e ⁻ → 2 O ²⁻)	rapid E _{1/2} = - 0.23 V/(Ag+/Ag)
O2 ⁻ /O2 ²⁻	$E_{1/2} = -0.21$ V/(Ag ⁺ /Ag) (only O2 ⁻ +1e ⁻ \rightarrow O2 ²⁻)			
S(Na2O) or S(Li2O)	3.0 10 ⁻² mol/Kg	8.0 10 ⁻² mol/Kg		
S(Na ₂ O ₂)	6.7 10 ⁻² mol/Kg		6.8 10 ⁻² mol/Kg	
D(O2 ²⁻)	1.5 10 ⁻⁵ cm ² /s	1.1 10 ⁻⁵ cm ² /s	1.2 10 ⁻⁵ cm ² /s	
D(O ²⁻)	6.8 10 ⁻⁵ cm ² /s	1.2 10 ⁻⁵ cm ² /s		
δ(O2 ²⁻)	1.2 10 ⁻² cm			
Rate constant $O^{2-} + CO_2 \rightarrow$	1.45 10 ⁻³ atm ⁻¹ s ⁻¹		1.4 10 ⁻³ atm ⁻¹ s ⁻¹	
Rate constant $O_2^{2-} + CO_2 \rightarrow$	4.4 10 ⁻³ atm ⁻¹ s ⁻¹		2.4 10 ⁻³ atm ⁻¹ s ⁻¹	

Table III- Electrochemical study of oxygen systems in different molten alkali carbonates: summary of the principal experimental results. S is the solubility, D the diffusion coefficien, δ the thickness of the diffusion layer.

CONCLUSION

The results obtained with molten alkali carbonates by electrochemical methods are in accordance with thermodynamic predictions and Andersen's experimental data.

Peroxide species can be stabilized in basic media in all the investigated melts. According to thermochemical data it appears that the stabilization of peroxide species is easier in alkali molten carbonates containing lithium ions (the stability of peroxide species decreases in the following order: $Li_2O_2>Na_2O_2>K_2O_2$).

Superoxide species are not present in significant quantities in molten carbonates containing lithium ions (KO₂>NaO₂>LiO₂). This species can be stabilized in molten Na-K melt, in slightly basic media.

The rate constants of the neutralization reactions of CO_2 by oxide or peroxide species are low enough to consider that CO_2 does not participate in the rate-determining reduction steps of O_2^{2-}/O^{2-} and O_2^{-}/O_2^{2-} systems.

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Figure 1. Stability range of Li₂CO₃-Na₂CO₃-K₂CO₃ eutectic at 550°C from Janaf Thermochemical Tables (18) under the following conditions: (1) a(i) = 1; (2) a(i) = 10^{-1} ; (3) a(i) = 10^{-2} ; (4) a(i) = 10^{-3} . (A) P(i) = 1 atm.; (B) P(i) = 10^{-1} atm.; (C) P(i) = 10^{-2} atm.; (D) P(i) = 10^{-3} atm. a(i) and P(i) represent respectively the activity and the partial pressure of species (i).



Figure 2. Voltammograms of molten Na₂CO₃-K₂CO₃ at a gold electrode at 750°C under $P(O_2) = 1$ atm. for 25 h and [Na₂O] = 0.4 mol./Kg. Bubbling $P(CO_2) = 0.1$ atm. + $P(O_2) = 0.5$ atm. for (a) t = 0; (b) = 3h.



Figure 3. Voltammogram of molten Li₂CO₃-K₂CO₃ at a gold electrode at 650°C, after addition of sodium peroxide (C = 1.35 10^{-2} mol./Kg). Ref. Ag*/Ag; v = 200 mV/s; P(argon) = 1 atm.; A = 0.125 cm².



Figure 4. Voltammogram of Li₂CO₃-Na₂CO₃ at a gold electrode at 750°C. $P(O_2) = 1$ atm. for 48 h; $[Na_2O_2] = 1.77 \ 10^{-3} \ mol/Kg + [Li_2O] = 0.53 \ mol/Kg;$ Ref. Ag⁺/Ag; v = 200 mV/s; A = 7.8 $10^{-2} \ cm^2$.



Figure 5. Convolution transformation of the cyclic voltammogram of Figure 4.



Figure 6. Plot of cathodic peak current vs $[Na_2O_2]$ (concentration of Na_2O_2 added), obtained from voltammograms of Li₂CO₃-Na₂CO₃ at a gold electrode at 750°C. Ref. Ag⁺/Ag. Argon pressure 1 atm.; v = 100 mV/s.

HIGH TEMPERATURE CORROSION OF NICKEL COATED WITH MOLTEN ALKALI CARBONATES

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ABSTRACT

The materials durability should be improved in order to develop the molten carbonate fuel cell. The corrosion of Ni alkaline carbonate coating were measured in CO₂/O₂ atmosphere at 873 K~1173 K. The corrosion of Ni with carbonate coating usually obeyed the parabolic rate law in CO₂/O₂ atmosphere. the parabolic rate constant decreased with the increase of the temperature with (Lio.62K0.38)₂CO₃ coating. At 1073 K the hot corrosion was observed several times with (Lio.62K0.38)₂CO₃ coating under low CO₂ pressure. The hot corrosion might take place by the dissolution/reprecipitation mechanism of the NiO scale owing to the solubility gradient in the carbonate film.

INTRODUCTION

The molten carbonate fuel cell(MCFC) is favored by the fact that wide variety of fuels, such as hydrogen, hydrocarbons, carbon monoxide, and their mixtures(coal gas) can be used. The exhaust heat of the MCFC is more valuable than that of the phosphoric acid fuel cell(PAFC), since the operating temperature of the MCFC is high. The MCFC can serve as a cogeneration system. However, the durabilities of the components of the MCFC cause big problems for long time operation(1). The corrosion of the metallic materials caused by the molten carbonate is one of them. Metals are easily attacked by molten salts at high temperature and the catastrophic corrosion occasionally occurs with the presence of the thin film of molten salt on the metal that is called "hot corrsion". The hot corrosion is mostly studied with the presence of Na2SO4 melt(2). The fluxing model is the predominant theory for the hot corrosion, where the solubility of the metal oxide that is formed by the corrosion reaction and the dissolution mechanism of the oxide are the important factors(2). Although the hot corrosion have been reported with the presence of molten carbonate(3-6), no paper discussed in relation to the solubility of the corrosion product that is the key factor to realize the effect of molten salt. In this study Ni was selected to the metallic material since Ni is a important component for high temperature alloys and also used as the electrode and the separator material for MCFC. The corrosion of Ni with the presence of molten

melt under $67\%CO_2-33\%O_2$ atmosphere. The corrosion reaction obeyed the parabolic rate law and the parabolic rate constants were very close to that obtained in air by Gulbransen(11). Since the results were very close to that obtained without CO₂ and the corrosion rate of Ni in 100%CO₂ atmosphere was so small that the weight gain could not be measured at these temperatures, the major oxidant in gas is O₂ and CO₂ gas does not directly affected the corrosion reaction without the presence of the carbonate melt.

1. Corrosion with Li2CO3 coating

With the presence of carbonate film, the corrosion reaction proceeded faster. Figure 2 shows the parabolic plots of the corrosion of Ni with Li₂CO₃ melt coating under 67%CO₂-33%O₂ atmosphere at 1073 K. Except the initial period the reaction obeyed the parabolic law. The parabolic rate constants depended on the amount of coating.

Figure 3 shows the relation between the parabolic rate constant k_{P} and the coated amount of carbonate melt at 1073 K. The reaction rate k_{P} increased with the small amount of the carbonate melt coating and gave a maximum of 0.12 mg²cm⁻⁴h⁻¹ at 4 mgcm⁻² coating. The reaction rate did not depend on the coating amount if the amount was larger than 10 mgcm⁻².

Figure 4 shows the parabolic plot of the weight gain of the corrosion of Ni with Li₂CO₃ coating of 30 mgcm⁻² at the temperature range from 1023 K to 1173 K. Clearly the corrosion reaction obeyed the parabolic law from the initial period of the reaction at 1023 ~ 1123 K. At 1173 K the parabolic law was observed after 10 h.

Figure 5 shows the cross section of the specimen after corrosion for 100 h at 1073 K. The corrosion scale had double layer and the outer layer was relatively porous.

2. Corrosion with (Lio.62K0.38)2CO3 coating

Figure 6 shows the parabolic plot of the corrosion of Ni with (Li0.62K0.38)2CO3 coating. Other reaction conditions were same as those of Fig.2. During the initial several hours the reaction did not obey the parabolic law. During this period the amount of corrosion was 2 or 3 times larger than that with Li2CO3 coating. This might be caused by the difference of the solubilities of NiO in the carbonate melts. At this condition the solubilities of NiO are $4x10^{-6}$ (mole fraction) in Li2CO3 melt and $13x10^{-6}$ in (Li0.62K0.38)2CO3 melt(10). Since the solubility of the oxide scale is higher in (Li0.62K0.38)2CO3 melt, the oxide scale that was formed during the corrosion was unstable and the corrosion reaction proceeded faster. After 60 h

carbonate was reported in few papers(7~9). Ting reported that the corrosion of Ni was accelerated with the molten carbonate coating and in O₂ atmosphere(8). He also reported that the molten carbonate penetrated through the oxide scale and reached the metal/oxide interface(7,8). Their results were obtained only at 923 K. In order to elucidate the hot corrosion mechanism of Ni with carbonate coating, more wide reaction conditions, such as temperature, amount of melt, gaseous compositions, etc. should be studied. In this paper the corrosion of Ni with molten carbonate coating has been studied in CO_2/O_2 atmosphere. The results were compared with the solubility of NiO(10).

EXPERIMENTAL

Ni specimens 6x12 mm were cut from sheet Ni (1 mm thickness, 99.7% purity. Impurities are given in Table 1) and were polished successively with #600 - #1500 SiC abrasive papers, followed by degreasing with a neutral detergent, washing with ethanol, and drying and weighing before test.

The Ni specimens were coated with 0~60 mg/cm² of (Li0.62K0.38)₂CO₃ or Li₂CO₃ by dipping the carbonate-ethanol mixture on the metal and drying. The amount of carbonate on the metal was obtained by the weight change of Ni specimen before and after the carbonate coating. The coated specimen was placed in a reaction vessel. Before starting the corrosion test, the specimen was held at 463 K for 20 min in order to remove the remaining moisture. The weight gain of the specimen was measured and monitored continuously by TGA(Shimazu DT-40). The atmosphere was normally 67%CO₂-33%O₂ gas mixture with the flow rate of 75 cm³/min. To see the effect of gaseous composition, CO₂ pressure was changed from 10⁻⁵ to 0.85 atm and O₂ pressure was changed from 0.1 to 0.3 atm. The reaction temperature was from 873 to 1173 K. The reaction time was normally 100 h. After the weight measurement, the specimens were analyzed by SEM and EPMA.

RESULTS AND DISCUSSION

Before the corrosion study, the vaporization and the weight loss of the carbonate melt was checked. 0.238 g of (Li0.62K0.38)2CO3 was placed in a test cell and the weight change was measured for 100 h under 67%CO2-33%O2 at 1073 K. The observed weight loss was less than 0.1 mg. Since the vapor pressure of Li2CO3 is smaller than (Li0.62K0.38)2CO3, the vaporization loss of Li2CO3 was estimated to be also smaller than that of (Li0.62K0.38)2CO3. Since the weight loss could not be detected below this temperature, the weight loss owing to the vaporization of the carbonate was neglected in this study.

Figure 1 shows the parabolic plots of the weight gain of Ni without carbonate

the corrosion reaction obeyed the parabolic law.

Figure 7 shows the dependence of the parabolic rate constant on the amount of the carbonate on the specimen. The maximum reaction rate was 0.12 $mg^2cm^{-4}h^{-1}$ at 5 mgcm⁻² coating. Although this maximum reaction rate with (Lio.62K0.38)2CO3 coating is higher than that with Li2CO3 coating, the difference was very small compared to the difference during the initial period. Since the corrosion reaction obeyed the parabolic law, the reaction was controlled by the diffusion of the ionic species through the oxide scale. At this stage the oxide scale was NiO for both melt coating and the diffusion rate should be same for both cases. The reaction rate did not depend on the coating amount if the coating was larger than 20 mgcm⁻². If the large amount of the carbonate was placed on the metal, the total carbonate could not hold on the metal since the melt could easily flow away from the metal specimen. From these data the maximum amount of the melt that could hold on the metal was estimated to be 20 mgcm⁻² in this experiment.

Figure 8 shows the parabolic plot of the corrosion of Ni at the temperature range from 873 K to 1073 K. Although the reaction obeyed the parabolic law after 60 h, something curious is the temperature dependence. In the very initial period of the reaction (<2h), the corrosion rate became larger at higher temperatures. However, the temperature dependence was reversed as the reaction proceeded and the parabolic rate constant decreased as the temperature increased. Usually the reaction rate should increase at higher temperatures. Since the reaction obeyed the parabolic law, the rate determining step is the diffusion of the ions through the scale. The diffusion path or the mechanism might be changed as the temperature changed.

Figure 9 shows the surface of the specimen after the corrosion test. At 1073 K the surface of the scale was covered by the fine crystals. On the other hand the surface of the specimen after corroded at 873 K was covered by the large crystals and the scale was looked porous. This difference might be caused by the solubility of the oxide scale. The solubility of NiO is $14x10^{-6}$ and $46x10^{-6}$ (mole fraction) at 1073 K and 873 K, respectively, in $67\%CO_2$ - $33\%O_2(10)$. Since the solubility of the scale is high at 873 K, the large crystal can be easily formed by the dissolution-recrystallization mechanism. If the scale is porous, the oxidant(O_2) can easily diffuse through the pore that is filled with carbonate melt. This might be the reason for the inverse temperature dependence of the corrosion rate.

Figure 10 shows the Arrhenius plot of k_p for the corrosion of Ni with and without carbonate melt coating. Clearly the negative dependence of k_p on temperature is observed for (Li0.62K0.38)2CO3 coating. The activation energy of k_p for Li2CO3 coating was 156 kJ/mol that is same as that without carbonate coating. Since the solubility of NiO in Li2CO3 melt is very low compared to that in (Li0.62K0.38)2CO3 (10), the oxide scale that is formed during the corrosion is very similar to that

without carbonate. The corrosion reaction depended on the gaseous atmosphere, namely CO₂ pressure and O₂ pressure.

Figure 11 shows the corrosion curves under the several CO₂ pressures at 1073 K. At the CO₂ pressure above 8.5×10^{-3} atm the corrosion reaction obeyed the parabolic law and the catastrophic corrosion could not be seen. However, at the CO₂ pressure below 10^{-3} atm the corrosion reaction proceeded tremendously after the initial induction period and the hot corrosion was observed.

Figure 12 shows the dependence of the corrosion amount on the CO₂ pressure. At 1073 K the amount of corrosion becomes larger under lower CO₂ pressure because the hot corrosion takes place more easily. On the other hand the corrosion reaction obeyed the parabolic law and the hot corrosion could not be seen at 923 K.

Figure 13 shows the cross section of the corroded specimen for 100 h under CO2 pressure of 8.5x10⁻⁵ atm at 1073 K. At this condition the hot corrosion took place and the most metal was consumed. According to the EPMA study, K was detected throughout the whole scale formed. Since K compound was not formed with Ni, the carbonate melt penetrated through the scale. This observation was same as that of previous papers(7,8). If the carbonate melt was present through the scale, the dissolution and the deposition of the oxide scale could take place throughout the scale. The hot corrosion took place more easily at higher temperature and lower CO2 pressure. This phenomenon is closely related to the dissolution of the NiO scale to the carbonate melt. At low CO₂ pressure NiO showed the basic dissolution and the solubility increased at lower CO₂ pressure(10). In the basic dissolution region the solubility increased at higher temperatures(10). At 1073 K and low CO2 pressure the solubility of NiO scale to the carbonate melt is larger than that at 923 K. If the dissolution reaction obeyed the basic dissolution, the solubility of NiO at the scale/gas interface was smaller than that of the metal/scale interface. At this condition the basic fluxing of the oxide scale could easily take place(2). This might be the reason for the hot corrosion at 1073 K under low CO2 pressure. At 923K the corrosion reaction obeyed the parabolic law.

Figure 14 shows the dependence of k_p on CO₂ pressure. k_p clearly increased as the increase of CO₂ pressure at the pressure higher than 0.1 atm(10). At this condition the acid dissolution of NiO takes place and the solubility of NiO increased as the CO₂ pressure increased. This solubility might affect the corrosion reaction and the corrosion rate increased owing to the increase of the solubility. The corrosion rates at PO₂=0.15 are larger than those at PO₂=0.3. Usually the parabolic rate constant becomes smaller or keeps constant at the lower PO₂, since the oxidant activity decreases(12). The results of Fig.14 are reversed. Since the solubility of NiO does not depend of the O₂ pressure(10), the results can not be explained by the solubility of the oxide scale. Since k_p represents the diffusivity of the ions through the oxide scale, the oxide scale that is formed at low O₂ pressure might be more defective. In other words, the stable oxide scale could be formed more easily at higher O₂ pressure.

CONCLUSION

The high temperature corrosion of Ni with alkaline carbonate coating was deeply affected by the solubility of NiO that was formed on metal. In this study the parabolic rate law was observed except 1073 K under low CO₂ pressure. This tendency is different from that of Shores(7). Although the reason is not clear, the metallic characteristics such as impurities, grain size may affect the corrosion reaction.

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 Table 1 Chemical composition of specimen

Fig.1 Parabolic plots of the corrosion of Ni without molten carbonates at 923 K~1173 K under 67%CO2-33%O2 for 100 h.



Fig.2 Parabolic plots of the corrosion of Ni coated with Li2CO3 under 67%CO2-33%O2 at 1073 K.







Fig.4 Parabolic plots of the corrosion of Ni coated with 35 mg/cm² of Li₂CO₃ at 1023 K~1173 K under 67%CO₂-33%O₂.



Fig.5 SEM micrograph of the cross section of the corroded Ni coated with 22 mg/cm² of Li₂CO₃ under 67%CO₂-33%O₂ at 1073 K for 100h.



Fig.6 Parabolic plot of the corrosion of Ni coated with (Li0.62K0.38)2CO3 under 67%CO2-33%O2 at 1073 K.



Fig.7 Relation between the parabolic rate constant k_p and the coated amount of (Li0.62K0.38)2CO3 at 1073 K under 67%CO2-33%O2.



Fig.8 Parabolic plot of the corrosion of Ni 32 mg/cm² of (Lio.62K0.38)2CO3 at 873 K~1073 K under 67%CO2-33%O2.



1073 K



873 K

Fig.9 SEM micrograph of the surface of the corroded Ni coated with 32 mg/cm^2 of (Lio.62K0.38)2CO3 under 67%CO2-33%O2 for 100 h.



Fig.10 Arrhenius plots of k_P for the corrsion of Ni with and without molten carbonate.



Fig.11 TGA curves for the corrosion of Ni coated with 35~41 mg/cm² of (Li0.62K0.38)2CO3 under several CO2 pressure at 1073 K.



Fig.12 Corrosion amount of Ni coated with $35~41 \text{ mg/cm}^2$ of (Lio.62K0.38)2CO3 at 1073 K and 923 K as a function of CO2 pressure for 100 h.



Fig.13 SEM micrograph of the cross section of the corroded Ni coated with 37 mg/cm² of (Li0.62K0.38)2CO3 at 1073 K under $Pco2=8.5 \times 10^{-5}$ for 100 h.



Fig.14 Parabolic rate constant kp of the corrosion of Ni coated with 35 mg/cm^2 of (Li0.62K0.38)2CO3 at 923 K as a function of CO2 pressure for 75 h.

DEVELOPMENT OF CATHODES FOR AN ALUMINUM-CHLORINE FUEL CELL IN HIGH TEMPERATURE CHLORIDE MELTS

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ABSTRACT

An aluminum-chlorine fuel cell for manufacturing aluminum chloride was proposed as one process of an electrochemical cycle for production of high-purity aluminum from aluminum To develop cathodes for the fuel cell, several scraps. graphite electrodes with many holes of the same size were tested by changing the hole sizes and numbers, and the performance for the reduction reaction of chlorine was estimated in terms of the discharge characteristics of the cell in a mixture of MgCl₂ 25 mol%-NaCl 75 mol% at 750 °C. The voltage drops due to the resistance of the reduction reaction decrease with the decrease in the size of the holes. but in small holes such as those 2 mm in diameter hardly all holes worked equally, showing the difficulty of enlarging the reaction zone. To overcome this disadvantage of drilled electrodes, grooved electrodes were developed and an output current of 4 A at an output voltage of 1.5 V was attained using electrodes with a diameter of 68 mm.

INTRODUCTION

Manufacturing aluminum with a purity over 99.999% from aluminum scraps is significant from the view-point of saving natural resources and energy. For this production, three stepwise processes should be considered. The processes are described in the flow chart in Fig. 1: (1) a process for manufacturing aluminum chloride by chlorination of aluminum scraps, (2) a process for refining crude aluminum chloride, and (3) a process for electrowinning high-purity aluminum from the purified aluminum chloride. If, as the first process, an aluminum-chlorine fuel cell is constructed to produce aluminum chloride from aluminum scraps, much electric energy can be produced in contrast to the usual direct chlorination of aluminum, and by applying this energy to step (3) a very advantageous electrochemical cycle for high-purity aluminum production can be constructed in a molten salt system.

In this cycle, (2) and (3) have been investigated in our laboratory for over a decade and most of the problems in these processes have been solved.¹⁻⁵) The fuel cell is composed of a chlorine/graphite electrode as the cathode and aluminum scraps as the anode; chlorine is reduced to

chloride ions on the cathode and aluminum is oxidized to aluminum ions on the anode. The chlorine gas can be supplied from step (3), the aluminum electrowinning process, and the electric power generated in the fuel cell, about 1.5 V, can be allotted for the input power of the electrolysis process, about 2.5 V. In the fuel cell, the reduction reaction of chlorine gas occurs around a three-phase boundary layer where chlorine gas, fused salts and the graphite electrode coexist. The performance of the cell greatly depends on the cathode characteristics, especially on those of the three-phase boundary layer. The present work is concerned with the development of the cathodes of the fuel cell. Several graphite electrodes with many holes of the same size were tested by changing the hole sizes and numbers. Several grooved electrodes with different reaction-zone areas were also investigated and the results were compared with those from the drilled electrodes.

EXPERIMENTAL

The experimental apparatus is schematically described in Fig. 2. A transparent quartz tube with an inner diameter of 95 mm and a length of 500 mm was used as a reaction cell. The bottom of the tube was stopped up with frozen salts to contain fused salts as a test electrolyte. In the center part of the cell, a graphite electrode as a cathode and a pure aluminum pool in a graphite crucible as an anode were set facing each other. Chlorine gas in a cylinder was led through a pyrolytic carbon tube or a quartz tube to the bottom of the cathode electrode. The anode was prepared from tips of pure aluminum metal which were preliminarily melted down and solidified in a graphite crucible with a diameter of 50 mm.

A mixture of MgCl₂ 25 mol% - NaCl 75 mol% was employed as a supporting electrolyte. First, in order to remove impurities contained in the melts, the mixture was pre-electrolyzed at 30 A for 2 hours in the Next, electrolysis was carried out and presence of aluminum chloride. the current-voltage curves were measured to estimate the resistance of the melts. Then the output characteristics of the fuel cell were determined as voltage-current relations by short-circuiting both electrodes with seven kinds of resistances mounted in an outer circuit. The circuit was connected with two graphite leads from the top of the chlorine electrode and with two graphite leads from the bottom of the aluminum electrode; one was for measurement of output voltage and the other for output current at both electrodes. The experimental temperature was 750 °C.

Both drilled and grooved electrodes were tested by changing the area of the reaction zones around peripheries of holes for the former electrodes and around grooves for the latter electrodes. The side view and the bottom of an electrode with holes are schematically illustrated in Fig. 3 and those of a grooved electrode in Fig. 4. As seen from Fig. 3, chlorine gas led through the pyrolytic carbon tube to the center of the cathode was introduced to the holes at the bottom through branched paths. The hole diameter, d, was changed from 2 to 11 mm and the number, n, from 6 to 186. Now we define the total length of reaction zones as the total length of the peripheries of the holes, ℓ . Chlorine gas was supplied to the grooved surfaces by a quartz tube, the open end of which was set directly under the center of the bottom surface (the tube is not shown in Fig. 4). The length of the reaction zones, ℓ , that is, the gross length of the circumferences of the square pillars, was changed from 51 to 210 cm.

RESULTS AND DISCUSSION

Electrodes with holes

While changing resistances of the outer circuit, variations in output voltage, V_B , and output current, I_T , were recorded on a chart. One such chart is presented in Fig. 5. As seen from the figure, the output voltage and output current reached steady state values corresponding to the resistances and returned to an open-circuit state within the experimental time duration, 5 minutes. It shows that the reversibilities of the reactions of the fuel cell is are fairly high.

Typical relations between output voltage, V_B and output current, I_T , (characteristic curves of the fuel cell) are shown in Fig. 6. Both curves in the figure show linear relations in the region of relatively small currents, and the extrapolation of the curves to the output voltage axis give the same value, the open-circuit voltage, V_d , of 1.91 V.

The output voltage-current relation for the fuel cell is presented in Fig. 7 with the voltage-current relation under electrolysis in the same The dashed, dotted line in the figure indicates the opensystem. circuit voltage which corresponds to the electromotive force of the As the circuit is connected with a certain resistance, some cell. output current flows and the output voltage changes to V_B. Since the voltage drop due to anodic dissolution of the aluminum is negligible in the present experimental conditions, the difference between V_d and V_B is the voltage drop caused by the resistance of the melts, R_M, and some resistance attributed to chlorine reduction. We refer to the resistance as the reaction resistance of the chlorine electrode, R_{p} , though its origin is not yet clear. The relation between them is written as $V_B = V_d - (R_M + R_R) \cdot I_T$. An investigation on the electrowinning of aluminum using the same melt composition as in this work showed that the cell voltage for electrolysis was composed only of Ohmic drop in the melts and that the resistance of melts could be calculated from the gradient of voltage-current relations obtained under electrolysis.⁶⁾ If the resistance of the melts obtained in this manner is nearly the same as R_M , the voltage drop due to the resistance of the melts, $R_M I_T$, can be estimated as shown by the broken line in the figure and, as a result, the voltage drop due to R_R , R_RI_T , can be obtained. To create a high-quality fuel cell the voltage drop caused by ${\rm R}_{\rm R}$ should be lowered as little as possible.

The relations of output voltage-current were determined at several electrodes by changing their diameters and the numbers of holes. The voltage drops for reaction resistance estimated from the above relations are presented as a function of output current in Fig. 8. The hole diameters and numbers of electrodes were changed from 4 to 9.6 mm, from 7 to 40, respectively, and they are shown with the total length of the circumference of the holes, ℓ , in the figure. The figure shows that the voltage drops decrease with increases in ℓ .

Since it is difficult to specify the real reaction areas around the peripheries of menisci, we introduce an output current per length of the reaction zone, $I_{\rm T}/\ell$, to estimate the effectiveness of the holes for chlorine reduction (the value is equal to current density at a unit width of the reaction zone). The voltage drops in Fig. 8 are replotted against $I_{\rm T}/\ell$ in Fig. 9. The figure shows that the voltage drops against $I_{\rm T}/\ell$ only slightly depend on hole diameter and the number of holes. It is suggested that the width of reaction zones is not much different for all holes focused in the figure.

The gradient of the $R_R I_T - I_T/\ell$ curve, R_R , indicates a special value such as specific resistance of the reaction zone; the unit of the gradient is ohm·cm. The value is a function of the specific resistance for chlorine reduction and the width and thickness of the reaction zone: both width and thickness cannot be constant throughout the reaction zone and we suppose here an average width and thickness for the effective reaction area. The chlorine gas dissolution into the melts or the diffusion of dissolved chlorine to graphite surfaces must control the rate of the reduction reaction. Supplementary experiments showed that the voltage drops due to reaction resistances did not change with the flow rates of chlorine gas and the vibration of the chlorine electrodes so that effective agitation against the diffusion layer might not be produced.⁽⁷⁾ It is, in any case, reasonable to consider that the thickness of the reaction zones was nearly equal for all kinds of holes in our experimental conditions, and that R_R became a parameter for the width of the reaction zone.

In many cases R_R showed a linear relation with I_T/ℓ in the small output current range as seen in Fig. 9, and the gradients of $R_R I_T - I_T/\ell$ relations are calculated and plotted against diameters of holes in Fig. 10. As seen from the figure, R_R decreased with the decrease in the diameter of the holes and had a minimum value at about 3 mm. This suggests that small holes have wide reaction zones which should depend on the shapes of the menisci. In small holes with a diameter such as 2 mm, hardly all holes work in the same way, because even small differences in the contact angle of chlorine gas with the electrode. It was also confirmed from experiments that the fuel cell could work steadily for a long time as long as excess chlorine gas was supplied.

Grooved electrode

As explained above, to create a homogeneous flow of chlorine gas through all holes of small sizes is difficult and it leads to a limitation of the area of the reaction zone for drilled electrodes. In order to enlarge the area in a particular electrode, electrode surfaces were grooved and a length of 210 cm for the reaction zone was attained. The same experiments as at the drilled electrodes were carried out using grooved electrodes and the obtained relations between voltage drop and output current per length of reaction zone are presented in Fig. 11. The voltage drops for reaction zones with different lengths were not much different from each other as those of the drilled electrodes shown The values were slightly larger and, as a result, the R_R in Fig. 9. became a little larger than with the drilled electrodes, but the gross drop of the output voltage became smaller than that of the drilled electrode, because of its large reaction area.

Figure 12 shows the output voltage for a grooved cathode with a reaction zone of 210 cm in comparison with that for a drilled cathode with a reaction zone of 117 cm. As shown in the figure, the grooved electrode was superior to the drilled electrode and the former could supply 4.0 A at 1.5 V for the electrowinning process, in contrast to 1.4 Å at 1.5 V for the latter.

CONCLUSIONS

In order to develop cathode electrodes for an aluminum-chlorine fuel cell, electrodes with chlorine-supply holes were tested by changing the The discharge characteristics showed that the hole sizes and numbers. voltage drops due to resistance of the reduction reaction decreased with the increase in the length of the reaction zone and with the decrease in the size of holes. However, when the hole became as small as 2 mm, the holes did not function evenly. The grooved electrodes made it possible to enlarge the length of the reaction zone to 210 cm and to produce 4 A at 1.5 V.

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Fig. 1 Flow chart for production of high-purity aluminum from aluminum scraps.



Fig. 2 Schematic diagram of experimental apparatus.













Schematic diagram of a grooved cathode. Top: side view, bottom: bottom view.



Fig. 5 Output voltage and output current responses to changes of resistances of the outer circuit. Electrode: d=6 mm and n=40.







Fig. 7 Output voltage-current relation for the fuel cell in a shortcircuiting cathode and anode for certain resistance and voltagecurrent relations in electrolyzing.



Fig. 8 Output voltage-current relations of various drilled cathodes.



Fig. 9 Voltage drops as a function of output current per length of reaction zone. Electrode: drilled type.



Fig. 10 Dependency of reaction resistance on the diameter of chlorine-supply holes.



Fig. 11 Voltage drops as a function of output current per length of reaction zone. Electrode: grooved type.



Fig. 12 Comparison of output voltage of the grooved cathode to that of the drilled cathode.

APPLICATION OF MOLTEN SALTS IN PYROCHEMICAL PROCESSING OF REACTIVE METALS

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ABSTRACT

Various mixes of chloride and fluoride salts are used as the media for conducting pyrochemical processes in the production and purification of reactive metals. The direct oxide reduction [DOR] process for the extraction of certain reactive metals utilizes calcium as the reductant which produces calcium oxide saturated calcium chloride salt as the waste product. A method has been studied to recover calcium by electrowinning it from the molten salt-mix. The recovery of calcium is characterized by the process efficiency to overcome back reactions in the electrowinning cell. A need to enhance the deposition rate by controlling the cell design and process parameters has been identified. Therefore, a theoretical analysis, based on fundamental rate theory, has been performed to understand the process parameters controlling the metal deposition rate, behavior of the ceramic anodesheath and influence of the back-reactions. It has been observed that the deposition of calcium is dependent on the ionic diffusion through the sheath. It has also been evidenced that the recovered calcium is completely lost through the back-reactions in the absence of a sheath. The importance of anode/cathode area ratio has been highlighted. A practical scenario has also been presented where the electrowon metal can be used in situ as a reductant to reduce another reactive metal oxide.

INTRODUCTION

Direct oxide reduction, molten salt extraction, electrorefining and salt scrub reduction are some of the pyrochemical processes that use molten salt medium in the production and purification of certain reactive metals. Various salt mixtures of chlorides with additions of fluorides are used as the media which generates a considerable amount of contaminated waste that has to be processed before recycling or disposal. The commercial production of reactive metals often utilizes the direct oxide reduction (DOR) process, according to the following reaction (1):

$$MeO_2 + 2Ca \neq Me + 2CaO$$
 [1]

Reactive metal oxide is reduced with calcium to produce reactive metal and calcium oxide. The calcium oxide is dissolved by molten calcium chloride as it forms at the operating process temperatures between 850 and 900 °C. The present investigation focuses on separating the salt into calcium metal and calcium oxide-free calcium chloride, both of which can be recycled in the process.

In 1954, Threadgill (2) developed a process for electroreducing calcium from calcium chloride/ calcium oxide electrolytes. Calcium oxide levels studied in this early investigation were below 2 wt. pct., and calcium electrowinning was achieved with the rising cathode technique. This technique was based upon continually pulling an electrolyte-covered calcium 'carrot' out of the molten salt. Threadgill reported that calcium electrowinning at calcium oxide concentrations higher than two wt. pct. was not possible because the viscosity of the salt decreases with increased calcium oxide levels. With lower viscosity levels, electrolyzed calcium does not remain covered with frozen electrolyte and ignites in air. Also, lower viscosity levels produce convection currents which were believed to wash calcium back into the bath. The optimal electrowinning conditions, for that system, therefore were calcium oxide content between 0.5 and 1 wt. pct., and electrolyte temperature between 788°C and 816°C.

Lukasko and Murphy (3) have recently developed a method for electrolytically producing calcium metal using an electrowinning/electrorefining sequence. In the initial electrowinning step, a calcium-tin alloy is produced in a molten cathode type of cell using a potassium chloride/calcium chloride electrolyte at 650°C. Tin was chosen as the cathode material due to its high solubility for calcium. The calcium-tin product (~7.5 wt. pct. Ca) of electrowinning is then used as the anode in the subsequent electrorefining step. Electrorefining was done in a calcium chloride/calcium fluoride electrolyte at 850°C. One of the advantages of producing calcium by this two-step method is a lower energy requirement, compared with present commercial production methods (3). The major advantage of using a liquid tin cathode is that free calcium is not available to reoxidize or form other compounds in the system, thus improving the efficiency and enabling the use of graphite as an anode.

Poa, Mulcahey and Johnson (4) have reported the results of calcium oxide dissociation experimentation from calcium chloride electrolyte with 15 wt. pct. calcium fluoride, using a liquid zinc cathode and a consumable graphite anode at $785 \,^{\circ}$ C. Calcium fluoride is present in certain reactive metal oxide reduction fluxes, since it lowers the melting point of calcium chloride and thereby lowers the necessary operating temperature. Preliminary results indicate that calcium oxide dissolved in molten calcium chloride/calcium fluoride can be electrolyzed to produce calcium dissolved in a liquid zinc cathode. Oxygen gas reacts with the consumable graphite anodes, and is driven out of the cell as carbon dioxide and carbon monoxide. Final calcium weight percentages in the zinc cathode range between 0.27 and 2.28 wt. pct.

Kipouros and Sharma (5) have studied electrolytic regeneration of neodymium oxide (Nd_2O_3) reduction salt, and have reported successful calcium oxide dissociation with calcium recovery in the range of ten to twenty wt. pct. The investigation involved the use of calcium chloride with calcium fluoride levels near fifteen wt. pct.. Calcium oxide levels ranged between 4.74 and 8.38 wt. pct. According to the investigators, low calcium recovery levels were due to calcium carbonate and calcium carbide formation at the anode.

Steele (6) has reported the results of calcium oxide electroreduction using a calcium chloride-based electrolyte with 35.4 wt. pct. lithium chloride (LiCl) and 8.4 wt. pct. calcium oxide. Steele concludes that although this electrolyte has several advantages over pure $CaCl_2$, as a flux for a calcium electroreducing cell, the advantages do not outweigh the major disadvantage of anodic corrosion. The advantages of calcium chloride/lithium chloride-type electrolytes, relative to pure calcium chloride, include lower calcium solubility levels, slower reaction rates for recombination, and lower vapor pressure levels for calcium chloride above the melt.

The solubility of calcium in calcium chloride-based systems at temperatures between 760 and 950 °C has been well characterized (7). The reported calcium solubility at these temperatures ranges between 2.1 and 16 wt. pct. Peterson and Hinkelbein (8), Sharma (9), Dworkin, et al.(10), Shaw and Perry (11) and Staffanson (12), however, report a maximum solubility level of about 3 - 4 wt. pct., indicating that the early reported value of 16 wt. pct by Cubiciotti and Thurmond (13) is high due to the influence of other calcium products in the salt. Figure 1 shows the collective plot for the available calcium solubility data.

A comprehensive survey of the calcium electrowinning work done in the past and its limitations has been described (14). The analysis of this earlier work indicates that two systems have been successfully used: (1) rising cathode technology, and (2) liquid cathode technology. Both of these methods suggest that calcium should leave the system either through a physical withdrawal, or by using a molten metal cathode. These methods have the advantage of enhancing the recovery rate by lowering the activity of calcium in the cell. The attempts to deposit calcium in the elemental form within the system, using graphite anodes, have met with little success in the past (6), essentially due to its reactive nature and readiness to form very stable compounds with other components in the system, such as carbon, oxygen and carbon dioxide. This work describes the modelling of the various reaction rates involved in the cell for electrowinning calcium from the waste salt, to achieve expressions which relate rates to physical and chemical parameters, such as the voltage, current density and activities of various liquid and gaseous species. The study has identified the controlling factors and attempted to overcome the back reactions by enhancing the calcium deposition rate, removing the anodic gaseous products quickly and by placing a ceramic diaphragm between the electrodes which provides the ionic conductivity but keeps the deposited calcium away from the anode. One of the goals of the present investigation is to develop a technology to allow for simultaneous calcium metal oxide would be chemically reduced to metal by calcium in a cell which electrolyzes the resulting calcium oxide back into calcium metal and oxygen gas.

EXPERIMENTAL

The following sections describe the materials, apparatus, and procedures used in the calcium electrowinning trials completed thus far (15). The objective of these trials was to demonstrate the process of depositing calcium on the cathode by electrolytically dissociating calcium oxide, to determine the operating parameters (temperature, voltage, current densities, electrolyte composition) necessary to dissociate calcium oxide, and to investigate the problem areas in calcium recovery.

Materials

Calcium chloride and calcium oxide used in the experiments were received in pellet and powder form, respectively. To ensure that moisture was not present, calcium chloride and calcium oxide were dried at $250 \circ C$ and $900 \circ C$ respectively, both for twelve hours under a nitrogen cover. The presence of water (from hydrated CaCl₂) in some of the earlier experiments essentially changed the primary cathodic reaction from calcium deposition to hydrogen evolution. After drying, these materials were kept in an inert atmosphere until ready for use.

Consumable graphite anodes and a stainless steel cathode have been used for electrolysis. The anodes were of AGKS (moderate) purity, and had dimensions of 6 mm diameter and 305 mm length. The cathode was cylindrically shaped, with dimensions of 102 mm diameter and 1.6 mm thickness. The immersion depth in the salt for the cathode ranged between 32 mm and 108 mm, in order to vary the active cathodic area.

Magnesium oxide crucibles were used to contain the molten salt. The crucibles had dimensions of 130 mm diameter, 305 mm height, and 3 mm wall thickness. Alumina sheaths were used to protect the thermocouple. Alumina and magnesia sheaths were used to protect the anode, in several configurations. Porous and dense sheath materials were tried in both closed- and open-ended sheath configurations. The arrangement of the cell components in a typical cell is shown in figure 2.

<u>Apparatus</u>

The furnace and the cell were contained within an argon atmosphere glovebox with a slightly positive argon pressure. The atmosphere was circulated and kept within acceptable purity limits with a Vac Systems model MO40-H Dri Train.

The temperature of the resistance furnace was controlled with a temperature controller, and a current limiting SCR power controller. Furnace temperature was measured with a chromel-alumel thermocouple placed next to the elements. The temperature of the salt was also monitored with a chromel-alumel thermocouple immersed in the salt bath and contained within an alumina sheath. The graphite anode and stainless steel cathode were connected to a 10 V-50 A max. controllable DC power supply. A stainless steel backup liner was used to protect the furnace well in the event of a crucible failure.

Dense open-ended alumina sheaths were used to shield the anode in certain trials. The sheaths had an outside diameter of 22 mm, wall thickness of 2.6 mm, and the lengths ranged between 229 mm and 413 mm. A flared-end version of the tube was also tried to enhance oxygen gas collection at the anode. The maximum outside diameter of the flared end of these sheaths was 35 mm.

Porous alumina and magnesia closed-end anode sheaths with the same size as the dense sheaths were tried on various trials as the open-ended sheaths were found to be ineffective in maintaining the ionic flow or in preventing the graphite from mixing in the salt. Porosity levels ranged near 20 percent. Sheaths were evaluated for their ability to allow molten salt to infiltrate, to prevent graphite contamination of catholyte and their ability to enable electrolysis in the cell by providing a conductive path for the ions.

Based on the observations made on the first set of trials with the 6 mm dia. anode rods and narrow sheaths, the sheath and anode configurations were modified to accommodate wider sheaths (50 mm dia.) and 13 mm dia. anode [Figure (3)].

Procedure

All operations were performed in an argon atmosphere glovebox. Calcium chloride and calcium oxide were mixed in a magnesium oxide crucible, to make a simulated DOR salt mixture. The salt mixture was melted in the crucible, and then held at the desired electrolysis operating temperature.

Cathodic current density ranged between 0.40 KA m^{-2} and 1.44 KA m^{-2} for the electrolysis trials conducted. Current was held constant at 25 Amperes during these trials, while the voltage varied between 5 and 25 V. The voltage started to fluctuate once the anode surface area in the salt changed due to thermal erosion and reaction with oxygen. The voltage was around 25 V when the anode rod reduced to a pin.

Electrowinning times ranged between 1.0 and 10.6 hours, and integrated current for the trials ranged between 25.0 A·h and 265.8 A·h. Average anode life was 84 minutes. The criterion for replacing an anode during cell operation was the cell voltage level ranging between 10 and 15 volts, to maintain a constant current level of 25 Amperes. Cell operating data for the electrolysis trials are listed in Table I.

After electrolysis, salt samples from different regions of the solidified salt were analyzed for calcium and calcium oxide. Analytical methods similar to those reported by Threadgill (2) and Axler (7) were used for these analyses. Hydrogen evolution and alkalinity determination (titration with hydrochloric acid) were used as techniques to establish the respective amounts of calcium and calcium oxide in each sample.

RESULTS AND DISCUSSION

The electrowinning trials with 6 mm dia. anode were performed to determine the parameters necessary to dissociate calcium oxide and to win calcium metal. The results indicate from current and time measurements that calcium was present at the cathode during electrolysis for several of the trials, but was not recoverable. Calcium at the cathode has the possibility of reacting with oxygen, carbon dioxide, or carbon to form calcium carbonate or calcium carbide if the anodic and cathodic products are allowed to come in contact. Some pertinent observations have been made:

Proper handling of the graphite anodes, ceramic sheaths and the crucible are of utmost importance, particularly under high temperature conditions, since many trials had to be terminated due to component breakage during the melting or electrowinning. Since the salt is in a pellet form, subsequent additions of cold charge became necessary during melting to have an adequate level of molten salt. These additions caused thermal shock to the crucible in some experiments which had to be terminated.

The dissolution of calcium oxide in calcium chloride has an extremely slow kinetics at temperatures below 900°C, although 18 wt. pct. solubility is predicted by the phase diagram at the temperature. The salt-mix needs to be molten at 1000°C to take the oxide completely into solution. The experiments done at lower temperatures showed an incomplete solutionizing and had high concentrations of calcium oxide in the bottom of the crucible. The cell operating temperature should be maintained around 850°C due to various reasons:

- (1) lower the solubility of calcium in the salt
- (2) slow down the kinetics of other chemical reactions within the cell.
- (3) lower the thermal stress on the cell components and the furnace.

A temperature of 850°C is sufficient to keep the molten salt fluid and produce liquid calcium. However, a higher temperature has distinct advantages of faster kinetics of oxide dissolution and lowers thermodynamic dissociation potential for the

oxide which can improve the cell efficiency. Calcium carbonate is also unstable preventing the reaction between calcium oxide and carbon dioxide. However, dissolution of calcium oxide can also be enhanced by stirring or sparging the molten salt by an inert gas (11).

Since it was determined that calcium is getting deposited on the cathode and subsequently participating in back reactions, three distinct possibilities existed besides dissolution in the salt, viz. calcium oxide, calcium carbonate and calcium carbide. Therefore, qualitative tests were performed and the presence of calcium carbonate was confirmed. There is also a known solubility of carbon dioxide (16) in similar salt systems, which supports at least the concept of calcium carbonate formation. Also, in the absence of hydrogen evolution on the cathode, the presence of calcium carbonate confirms the dissociation of calcium oxide and, therefore, the winning of calcium (15,17).

Besides calcium oxide and calcium carbonate, it is possible that calcium and carbon are reacting to form calcium carbide. Although the salt was not specifically analyzed for calcium carbide, previous investigations have shown that this compound may form under similar conditions (5).

The solubility of calcium in the salt, shown in figure (1), accounts for the poor recovery efficiencies observed. The aspect of calcium solubility in the salt mix is of utmost importance, since it not only affects the electrolyte characteristics in terms of ionic conductivity, transport and salt viscosity, etc., it also interferes with the electrode processes by altering the established double layers and concentration gradients. The solubility of calcium in calcium chloride is a strong function of calcium oxide in the salt and has been found to vary inversely (7). The solubility is also affected by the use of graphite as the anode where oxygen is released as a result of the anodic reaction and causes the formation of carbonates (11). The dissolved calcium, however, is useful in the in situ reduction.

Experiments were carried out using alumina (both close-end porous and openend dense) and magnesia (closed-end porous) sheaths around the 6 mm anode graphite rod. Alumina sheaths reacted with the salt and perhaps were reduced by calcium producing calcium oxide and aluminum, as significant erosion was observed on all the alumina components in the cell. The closed-end porous (20 pct. porosity) alumina sheaths took prohibitively long hours for the salt to infiltrate. The 33 pct. porous sheath had very poor mechanical strength and were damaged during or within short time of insertion.

It was demonstrated that molten calcium chloride at 900°C adequately infiltrates porous magnesia sheaths of thirty percent porosity, within an hour of immersion. Some electrowinning experiments were conducted with magnesia sheaths, where the following observations were made:

- (1) The cell voltage was higher in experiments with the sheath than without, for a given current supply.
- (2) Graphite anode did not erode and the salt outside the sheath was clean.

- (3) Calcium dissolved in the salt was detected by hydrogen evolution test.
- (4) Chlorine gas was also detected during these experiments.

Based on the above observations, it can be concluded that a high voltage is achieved in the cell which causes the calcium chloride dissociation and chlorine gas evolution, once the concentration of calcium oxide gets close to 500 ppm. The rate of flow of chlorine ions to the anode through the sheath configuration used, is faster than oxygen ions. Therefore, (a) chlorine gas is produced, (b) calcium is deposited on the cathode and (c) carbon anode does not oxidize. A wider and more porous sheath could, therefore rectify this situation and allow the cell to operate at lower voltage.

The analyses of the data obtained from the experiments with 6 mm dia. anodes and narrow sheaths show no evidence of any significant calcium recovery, either as a separate phase on top of the salt or in the dissolved form. It has been conclusively shown that electrowinning occurred, calcium oxide dissociated and transfer of ions took place. However, <u>calcium could not be recovered as a mass on</u> the cathode in its elemental form. Various possibilities exist for the absence of calcium, which provide an insight into the process in the cell and also direct the future course of research.

Back Reactions with oxygen, carbon and carbon dioxide

If it is assumed that calcium chloride does not participate in the chemical or electrochemical reactions in the cell and is only an inert electrolyte, then the only other chemical species present in the cell are calcium, carbon and oxygen. The source of calcium is the calcium oxide and of carbon is the graphite. Oxygen is present from the dissociation of the oxide and from the ingress into the cell through leakages and as an impurity in commercial argon gas. The various possible reactions in the cell in a complete absence of moisture are:

CELL REACTIONS

$$\begin{array}{ll} 2\text{CaO} & \rightarrow 2\text{Ca} + \text{O}_2 & [2] \\ \text{C} + \text{O}_2 & \rightarrow \text{CO}_2 & [3] \end{array}$$

BACK REACTIONS

Ca	+	CO_2	⇒ CaO + CO	[4]

- $\begin{array}{l} CaO + CO_2 \Rightarrow CaCO_3 \\ Ca + 2C \Rightarrow CaC_2 \\ Ca + CaCl_2 \Rightarrow Solution \\ 2Ca + O_2 \Rightarrow 2CaO \end{array}$

Calcium is produced through reaction [2] and is lost through reactions [4] through [8]. Reactions [3,4,5 and 8] involve gaseous phases and their rates can be controlled by (a) the removal of anodic gases efficiently, (b) use of a lower cell temperature and (c) prevention of oxygen ingress in the cell. The presence of calcium carbonate has been confirmed by silver nitrate test which also confirms the existence of reactions [3-5]. There is also a solubility of carbon dioxide in the salt which can readily form carbonate in the presence of calcium oxide (16). Reaction [6], which is simply a measure of the calcium solubility in calcium chloride, is known to be a function of temperature and calcium oxide content and is found to range between two to four weight percent (8-12). The solubility of calcium can only be lowered by a decrease in the process temperature. The formation of calcium carbide (reaction [6]) can also potentially cause the absence of calcium at the end of the experiments. The formation of calcium carbide can be prevented by placing a sheath around the graphite anode and keeping the calcium and carbon apart. A sheath around the anode is also necessary to prevent the carbon from disintegrating and floating over the salt layer, creating a short-circuiting situation. Disintegration of the graphite anode also causes the voltage to fluctuate as the tip of the anode reduces to a pin.

Thus, to be able to produce calcium it is necessary that the rate for reaction [2] (the electrochemical cell reaction) is maximized, which can be done by increasing the cathodic current density. This practice can be achieved in three ways:

- (1) Increase the cell current, which will also require an increase in the cell voltage for a given resistance.
- (2) Decrease the cathodic area.
- (3) Increase the anodic area, since the anode is consumable and reduction in area to a large extent causes the anodic current density to surge very high.

The cell configuration was modified to allow the above changes [Figure (3)]. An optimum anode to cathode area ratio has to be maintained before the current can be increased. Experiment conducted with the 13 mm dia. anode and 50 mm dia. porous magnesia sheath has shown that metallic calcium is collected on the cathode and is recoverable as a mass. The porosity of the anodic sheath, however, has to be optimized to maintain an ionic flow through the sheath. The rate of flow determines the cell efficiency since the sheath acts as an additional resistance in the cell.

The rate of reactions [4-8] can be effectively lowered by lowering the temperature, quickly removing the anodic gases and using an appropriate sheath around the anode as observed during the trial with 50 mm dia. sheath. An analysis based on the fundamental rate theory shows the critical parameters that control the electrode reactions and the metal deposit.

Theoretical Rate Expression

Fundamental reaction rate theory can be applied to predict the rate of calcium deposition rate on the cathode for a given current density and to determine the cell

potential required. As discussed earlier, the deposited calcium can be lost within the system through a series of backward reactions.

FORWARD REACTIONS IN THE CALCIUM ELECTROWINNING CELL:

Boundary Condition: $r_{Ca} = 2r_{O2} + r_{Cl2}$				
$CaCl_2 = Ca$	$+ Cl_2$	(cell reaction)	[17]	
$2Cl^{-} = Cl_2$	$+ 2 e^{-1}$	(anode)	[16]	
$Ca^{++} + 2e^{-}$	= Ca	(cathode)	[15]	
$CaCl_2 = Ca$	$^{2+}$ + 2Cl ⁻	(electrolyte)	[14]	
2CaO + C	$= 2Ca + CO_2$	(cell reaction)	[13]	
$C + O_2 =$	= CO ₂	(reaction at anode)	[12]	
$2O^{-} = O_2$	+ 4 e ⁻	(anode)	[11]	
$2Ca^{++} + 4e$	e ⁻ = 2Ca	(cathode)	[10]	
2CaO = 2C	$a^{2+} + 2O^{2-}$	(electrolyte)	[9]	

where all the rates are in moles/sec.

Figure (4) shows the dependence of equilibrium cell potential on the calcium oxide content of the salt. The dissociation of calcium chloride (Reaction [14]), an undesirable reaction in the present cell, is thermodynamically feasible only below a calcium oxide content of 0.04 wt. pct. in the salt, when an inert anode is used for oxygen evolution. However, the use of carbon anode makes it even more difficult for the chloride to dissociate, since the equilibrium potential of reaction (13) is significantly lower than the potential for reaction (14) if an infinitely small amount of calcium oxide is present in the salt. Therefore, it is possible to dissociate all the calcium oxide in an inert calcium chloride salt medium. Accordingly, the boundary condition would reduce to:

$$r_{Ca} = 2r_{O2}$$
 [19]

<u>Calculation of r_{Ca} :</u> (Based on equation 10 and 15)

$$\mathbf{v}_{\text{fwd}} = \mathbf{v}_{\text{o}} \bullet e^{-(\Delta G^* + \Delta G')/\text{RT}}$$
[20]

$$\mathbf{v}_{bkwd} = \mathbf{v}_{o} \bullet e^{-\Delta G^{*}/RT}$$
[21]

where υ_o is the atomic vibrational frequency, $\text{sec}^{\text{-1}}$

$$\mathbf{v}_{\text{net}} = \mathbf{v}_{\text{fwd}} - \mathbf{v}_{\text{bkwd}} = \mathbf{v}_{\text{o}} \cdot \mathbf{e}^{-\Delta G^*/RT} \left[\mathbf{e}^{-\Delta G^*/RT} - 1 \right]$$
 [22]

$$\mathbf{v}_{\text{net}} = \mathbf{v}_{\text{o}} \cdot \mathbf{e}^{\Delta S^*/R} \cdot \mathbf{e}^{-\Delta H^*/RT} \left[\mathbf{e}^{-\Delta G'/RT} - 1 \right]$$
[23]

where v_{net} is the net jump frequency of calcium ions that produce metal on the cathode [Figure (5)] and ΔG^* is the Free energy activation barrier/mole. The driving force/mole, ΔG^* , can be expressed as:

$$\Delta G' = + nF\eta_{Ca} + RT \ln ([Ca]/[Ca^{++}])$$
[24]

$$\eta_{\rm Ca} = {\rm E}^{\rm c}_{\rm appl.} - {\rm E}_{\rm Ca}$$
[25]

$$E_{Ca} = E_o^{Ca} - [RT/nF] \ln ([Ca]/[Ca^{++}])$$
 [26]

where η_{Ca} is the cathodic over-potential in (-) volts [Figure (6)]; $E_{appl.}^{c}$ is the cathodic applied potential; E_{o}^{Ca} is the Standard calcium half-cell potential (-2.87 volts) and E_{Ca} is the Equilibrium calcium half-cell potential.

$$e^{-\Delta G'/RT} = e^{-nF\eta} c_a/RT} \cdot e^{\ln ([Ca++]/[Ca])}$$
[27]

$$= [Ca^{2+}]/[Ca] \cdot e^{-nF\eta} ca/RT$$
[28]

where nF is 2 x 96500 amp-sec/mol, R is the Universal Gas Const. (8.314 joules/K-mole) and T is the cell temperature at 950 °C [1223 K].

$$\mathbf{r_{Ca}} = \text{mole/sec} = \mathbf{v}_{\text{net}} / \text{Av. No.}$$

$$= 1.66 \text{ x } 10^{-24} \cdot \mathbf{v}_{\text{net}}$$

$$= 1.66 \text{ x } 10^{-24} \cdot \mathbf{v}_{0} \cdot e^{-\Delta S^{*}/R} \cdot e^{-\Delta H^{*}/RT} [e^{-\Delta G'/RT} - 1]$$

$$= 1.66 \text{ x } 10^{-24} \cdot \mathbf{v}_{0} \cdot e^{-\Delta S^{*}/R} \cdot e^{-\Delta H^{*}/RT} [[Ca + +]/[Ca]] \cdot e^{-nF\eta} c_{e}^{/RT} - 1]$$

$$\mathbf{r}_{\mathrm{Ca}} = \underline{\mathbf{A}' \bullet \mathrm{e}^{-\mathrm{n}\mathrm{F}\eta} \mathbf{e}_{\mathrm{c}}^{/\mathrm{R}\mathrm{T}}}$$
[29]

where A' is a coefficient = $1.66 \times 10^{-24} \cdot v_0 \cdot e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT} \cdot [Ca^{2+}]/[Ca]$ in moles/sec. and $-nF\eta_{Ca}/RT > 1$.

For a cell current efficiency of 100 percent and a given current of I amperes:

$$\mathbf{r}_{Ca} = \underline{5.2 \times 10^6 \bullet I \text{ mole/sec}}$$
 [30]

$$\mathbf{r}_{Ca} = \underline{5.2 \times 10^{-6} \bullet i_c \bullet C_{area}}$$
[31]

where i_c is the cathodic current density in amps/cm² and C_{area} is the cathodic area.

Combining equations [29] and [31]:

$$\mathbf{i}_{\mathbf{c}} = \underline{\mathbf{A}^{\bullet} \mathbf{e}^{-\mathbf{n}\mathbf{F}\boldsymbol{\eta}}\mathbf{c}\mathbf{a}^{\mathbf{R}\mathbf{T}}}$$
[32]

where A^* , in amperes/cm², is a new coefficient and incorporates the cathodic area. Equation (32) is the familiar Tafel Equation and can be expressed in the form:

$$\log i_{c} = \beta - nF\eta_{Ca}/RT$$
[33]

where $\beta = \log A^*$. Equation (33) can be rearranged as:

$$-\eta_{\rm Ca} = \alpha \log i_{\rm c} + \beta'$$
[34]

where α is RT/nF = 0.0527 volt, β ' is $-\alpha \bullet \beta$ and β is dependent on the atomic jump frequency of calcium ions, the free energy activation barrier, $\Delta G'$, and the cathodic area. Thus, β is a constant at a given temperature and cathode area. For a given cathodic current density, i_{σ} (i.e rate of calcium deposition), η_{Ca} can be thus calculated.

<u>Calculation of \mathbf{r}_{02} : (based on equation [11])</u>

A similar analysis can be done to develop a rate equation for the anodic reaction of oxygen evolution and an equation similar to equation (29) can be obtained:

$$\mathbf{r}_{02} = \mathbf{A}'' \bullet \mathbf{e}^{\mathbf{n} \mathbf{F} \eta} \mathbf{o}_2^{/\mathrm{RT}}$$
 [35]

where A" is a coefficient = 1.66 x $10^{-24} \cdot v_0 \cdot e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT} \cdot ([O^2]^2/pO_2)$ in moles/sec.

For a cell current efficiency of 100 percent and given current of I amperes:

$$r_{02} = 2.6 \times 10^{-6} \bullet I \text{ moles/sec}$$
 [36]

$$r_{02} = 2.6 \times 10^{-6} \bullet i_a \bullet A_{area}$$
 [37]

where i_a is the anodic current density in amps/cm² and A_{area} is the anodic area.

Combining equations [35] and [37]:

$$\mathbf{i}_{\mathbf{a}} = \underline{\mathbf{A}^{**} \bullet \mathbf{e}^{\mathbf{n} \mathbf{F} \boldsymbol{\eta}} \mathbf{o}_{\mathbf{2}}^{/\mathbf{R} \mathbf{T}}}$$
[38]

where A^{**} , in amperes/cm², is a new coefficient incorporating the anodic area. From equation (38):

$$\log i_a = \beta^* + nF\eta_{\Omega^2}/RT$$
[39]

where $\beta^* = \log A^{**}$. Equation (39) can be rearranged as:

$$\eta_{O2} = \alpha^* \log \mathbf{i_a} + \beta''$$
[40]

where α^* is RT/nF = .0263 volt, $\beta^{"}$ is $-\alpha^* \bullet \beta^*$ and β^* is a function of the atomic jump frequency of oxygen ions, the free energy activation barrier, ΔG^* , and the anodic area. Thus β^* is a constant at a given given temperature and anode area. For a given anodic current density, i_{α} (i.e rate of oxygen evolution), $\eta_{\Omega 2}$ can be thus calculated.

Equations (34) and (40) have been plotted in Figure (6). The required applied potential of the cell can be calculated for a given applied current density for the two electrodes [figure (6)].

Total applied potential,

$$E_{appl.} = E_{Ca} + E_{O2} + \eta_{Ca} + \eta_{O2} + IR_{drop}^{salt} + IR_{drop}^{sheath}$$
[41]

where $E_{Ca} + E_{O2} = E_o^{Ca} + E_o^{O2} + 0.029 \log Q$ and η_{Ca} and η_{O2} are given by equations [34] and [40].

$$\eta_{Ca} + \eta_{O2} = \log (i_a^{a^*} / i_c^{a}) + (\beta'' - \beta')$$
 [42]

The current densities, i_c and i_a , and, therefore, the cell efficiency or the calcium deposition rate is not only driven by the applied over-potentials, η_{Ca} and η_{O2} , but the respective anodic and cathodic areas, A_{area} and C_{area} . In other words, the cell behavior can be controlled by controlling the electrode configurations, sheath porosity and applied potential. Under standard condition, i.e. $\mathbf{Q} = 1$; the applied cell potential can be accurately calculated by equation [41]. The term, $\log(i_a / i_c)$ in equation [42] translates to a function of the ratio of cathode to anode areas for a given applied current, **I**. However, as discussed earlier, $\beta^{"} - \beta^{"}$, also has an equal but opposite dependency on the respective electrode areas and, therefore, the over-potentials are independent of the electrode areas. In a practical situation in a cell, where the electrode areas are different, the over-potential can be determined by using Figure (6). Equation (41) completely describes the cell reactions. It illustrates the importance of individual voltage components and criticality of the sheath behavior in not only controlling the cell potential but the flow of ionic species to the anode. The voltage components can be described separately for the two conditions of inert anode application and a graphite anode application:

Inert anode: [950 C]

$$E^{oCa} + E^{oO2} = 2.65 \text{ volts}$$

$$Q = (a_{Ca} \bullet p_{O2}^{1/2} / [Ca^{2+}] \bullet [O^{2-}])$$
[43]

Carbon anode: [950 C]

$E^{oCa} + E^{oO2} = 1.62 \text{ volts}$ $Q = (a_{Ca} \bullet p_{CO2}^{1/2} / [Ca^{2+}] \bullet [O^{2-}])$ [44]

It is evident from the above analysis that the rate of flow of ions through the sheath will have a major influence on the cell potential, since it will determine the values of IR_{drop}^{sheath} and Q. The activity of calcium ions can be assumed as unity, since both the oxide and chloride electrolyte provide the source for calcium ions. The activity of calcium metal will be determined by the solubility of the metal in the salt which is found to be 2 - 4 wt. pct. (7), depending on the oxide content and the cell temperature. Beyond the solubility limit of calcium in the salt, the metal will have an activity of unity. It is important to note that the dissolution of calcium in the electrolyte is the only feasible back reaction in the presence of a sheath. Therefore, the constitutive constant, Q, will depend on the flow of oxygen ions through the sheath and the efficiency of removal of oxygen or carbon dioxide gas from the anode and will be a function of time. The removal of the anodic gases is controlled by the flow of argon gas within the cell enclosure at one atm. pressure. This discussion, therefore, suggests that a near total depletion of oxygen ions within the sheath (lack of flow of oxygen ions through the sheath) can raise the equilibrium potential of the cell to a level where the evolution of chlorine becomes feasible thermodynamically and chlorine gas would then start to evolve on the anode [Figure (6)]. In an event, where chlorine depletion also takes place within the sheath, the cell will effectively shut off.

In situ electrowinning and direct oxide reduction

If calcium metal is electrowon and back reactions are minimized by the steps mentioned above, then it will be possible to carry out an in situ direct oxide reduction of the metal oxide by the following reaction:

$$\begin{array}{ll} \text{MeO}_2 + 2\text{Ca} \Rightarrow 2\text{CaO} + \text{Me}^{\ddagger} & [1]\\ 2\text{CaO} &= 2\text{Ca} + \text{O}_2 & [2] \end{array}$$

Reactions [1] and [2] give a net reaction of:

$$MeO_2 = Me + O_2$$
 [45]

The rate of reaction [45] is directly linked with reaction [2]. If the rate for reaction [2] is increased, the rate for reaction [45] will increase significantly as the reduced high density metal will settle in the bottom of the cell. The rates for back reactions will also be lowered by the presence of in situ reduction using calcium. Calcium oxide will be continuously generated keeping its concentration in the salt at near constant level, which will aid in keeping the salt density and fluidity as well as the calcium solubility constant. Such a process has been successfully developed for producing neodymium from its oxide (5).

The present results suggest that the in situ cell is feasible, since electrolytic dissociation of calcium oxide is observed. Cell improvements have been incorporated to design a system which allows for calcium recovery. Such a cell system has been tested with 50 mm dia. ceramic low-density Magnesia flat-bottom crucible as anode sheath stock (Figure 3). The outside diameter of these crucibles is in the range of 50 mm which will allow the use of up to 25 mm round graphite anode rods. The results show that metallic calcium can be deposited and maintained at the cathode.

These investigations offer potential improvements in waste management in the reactive metal production and provide an accurate mechanistic understanding of the electrolytic calcium metal production process.

Future Directions

To recover calcium, under DOR conditions with 10 wt. pct. calcium oxide, it is apparently necessary to remove electrowon calcium away from the system immediately after its formation. Since calcium has a strong thermodynamic driving force to react with other species in the system, it is necessary to design the cell and operating parameters to allow for winning the calcium faster than it is being lost. Possible ways of overcoming the fast kinetics for back reactions include using a high cathode current density or a high active anode area, or both. For example, arranging the anode and cathode in such a manner as to achieve a high anode area to cathode area ratio, as well as operating at a relatively high current level, may result in a net accumulation of calcium. Also an optimization of the porosity and evaluation of the closed-end porous anode sheaths and reduction in the cell operating temperature needs to be investigated.

CONCLUSIONS

(1) Calcium can be electrowon from 10 wt. pct. calcium oxide-calcium chloride salt mixture by the dissociation of calcium oxide. However, the recovery as a mass requires cell modifications to control the back reactions. The modifications are:

- [a] Use of 30-40 vol. pct. porous close-end MgO anodic sheath.
- [b] Quick removal of anodic gases.
- [c] Complete isolation of cell atmosphere.
- [d] Optimization of temperature.
- [e] Increase in the cathodic current density.

(2) The electrode reaction rates have been analyzed to derive a constitutive process equation which shows the importance of anodic sheath and the electrode areas in controlling the cell potential.

(3) The application of electrowon calcium to perform an insitu reduction of another reactive metal oxide has been analyzed.

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Electrolyte	CaCl ₂ , 0-10 wt. pct. CaO		
<u>Cell</u>	atmosphere: crucible: operating temp.: current: voltage: time:	argon magnesium oxide 850-970 °C 25 A 5 - 25 V 3.5 - 10.6 h	
<u>Anode</u>	material: size, cm: active area: current density:	graphite 6.4 mm dia x 305 mm length 0.0005 - 0.0011 m^2 20 - 50 KA m^{-2}	
Cathode			
-	material: size, cm: active area: current density:	stainless steel 273 x 152 mm 0.0173 - 0.0312 m ² 0.40 - 1.44 KA m ⁻²	

Table I - Cell Operating Data Calcium Electrowinning Trials.



Figure 1 - Solubility of calcium in calcium chloride



Figure 2 - Schematic diagram of the cell configuration with a ceramic anode sheath.



Figure 3: Schematic diagram of the cell showing the arrangement for 13 mm diameter anode rod and 50 mm diameter sheath



Figure 4: Dependence of equilibrium cell potential on calcium oxide content





Figure 5: Activation energy barrier for the ionic jump



log i (A cm⁻²)

Figure 6: Cell potential Vs. applied current density
INVESTIGATIONS AT LOS ALAMOS NATIONAL LABORATORY OF CALCIUM CHLORIDE BASED MOLTEN SALTS SYSTEMS

by

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Key Words- Pyrochemistry, Calcium Chloride, Plutonium, Molten Salt Processing

ABSTRACT

Calcium chloride has been in service at Los Alamos National Laboratory as a media for the reduction of plutonium oxide to metal and for the molten salt extraction of americium from aged plutonium metal. To provide data for the optimization of plutonium oxide reduction, the solubility of calcium metal has been measured in solutions comprised of varying amounts of calcium oxide in calcium chloride. Additionally, recent work has demonstrated the viability of calcium chloride as an electrolyte for plutonium electrorefining and the benefits of oxygen sparging the calcium chloride salt to reduce the bulk requiring aqueous plutonium recovery.

INTRODUCTION

Los Alamos National Laboratory (LANL) employs a pyrochemical purification scheme for plutonium consisting of three main processes. The first is Direct Oxide Reduction (DOR) which converts impure plutonium oxide to plutonium metal. The second is Molten Salt Extraction (MSE) which extracts ingrown americium from aged plutonium metal. The third is electrorefining (ER) which refines impure plutonium metal to 99.96% purity.

Calcium chloride has been in use as the solvent salt in DOR for more than 10 years and LANL has proven the ability to regenerate and then reuse the calcium chloride salt. LANL has experimented with different solvent salts in MSE and found that calcium chloride maximized americium extraction. With two of the three LANL processes

operating in calcium chloride the use of a common salt system for the pyrochemical processes was attractive. This would allow for the design of a future multiprocess cell. In an effort to see if a common salt was viable, $CaCl_2$ was substituted for the traditional NaCl/KCl system in the ER process. Figure 1 shows a current processing flowsheet for plutonium purification at LANL. All the operations in this flowsheet have been performed in CaCl₂ in the temperature regime of 850°C with plutonium quantities in the kilogram scale.

DIRECT OXIDE REDUCTION Principal Investigator Greg Bird

Conversion of PuO_2 to metal is accomplished via the Direct Oxide Reduction (DOR) process.¹ PuO_2 is reduced to metal with Ca^o dissolved in a molten CaCl₂ media according to the following reaction:

$$PuO_2 + 2Ca^{\circ} \xrightarrow{CaCl_2} 2CaO + Pu^{\circ}$$

As the PuO_2 is reduced, CaO is generated and dissolves within the salt solution. As the reaction proceeds, CaO content increases within the salt solution phase and the plutonium produces a separate metal phase below the salt.

Spent DOR salts are regenerated by a high temperature reaction with Cl_2 gas which converts the CaO reaction product and excess Ca^o to CaCl₂.² Several chlorinating reagents have been studied.³ This procedure has proven highly successful in full scale application at LANL and has dramatically reduced radioactive waste volumes. Chlorine appears in the off-gas stream when the CaO conversion in the salt is completed so an inline spectrophotometer is being developed for DOR which can be used to optimize the salt rechlorination process.

PHASE BEHAVIOR OF CALCIUM CHLORIDE BASED SYSTEMS Principal Investigator Keith Axler

The phase behavior of the system Ca-CaO-CaCl₂ has been studied for optimization of pyrochemical operations and the interdependence of Ca^o and CaO solubilities within the CaCl₂-based system have been characterized.⁴ This work has extended the previously available data on the system^(5,6) by establishing the behavior of the intersolubilities over a range of temperatures significant to processing. The work has shown the suppression of the Ca^o solubility limit with increasing CaO content. The compositional interdependence of these species has strong significance as the efficiency of the process is related to the amount of Ca^o which can be maintained in solution.

The cited study by Perry and Shaw has reported a 2.7 wt% Ca^o solubility limit in CaCl₂ at 800°C. They also reported the Ca^o solubility limit to be suppressed to 0.4 wt% when the CaO content was increased to 9.1 wt% in the CaCl₂-based system. The current work has shown that at 850°C, the Ca^o solubility decreases from 2.8 wt% to 1.8 wt% as

the CaO content increases from zero to 3.4 wt%. At 900°C, the Ca^o solubility ranges from 3.7 wt% (zero CaO) to 1.9 wt% (6.0 wt% CaO in solution). The dissolution of CaO in the system was found to be kinetically limited and samples of the solutions of higher CaO compositions required greater than 24 hours to equilibrate. The system behavior is further complicated by the differences between Ca^o and CaO dissolution rates. The availability of both undissolved Ca^o and CaO is a viable condition during the reduction process. By increasing the system temperature, the Ca^o solubility is increased but the accelerated CaO dissolution could effectively reduce the amount of dissolved Ca^o. The optimum process time and temperature reflects this consideration as well as other factors such as crucible interactions which provide an additional source of CaO to the system independent of the PuO₂ reaction with Ca^o.

MOLTEN SALT EXTRACTION Principal Investigator Mary Ann Reimus

The Molten Salt Extraction process is used to extract ingrown Am from Pu metal. The Pu is placed in a furnace along with a solvent salt and oxidant. The Am, initially present in its reduced state in the Pu metal, is oxidized and then dissolves into the solvent salt. Work was conducted in Fiscal Years 88 and 89 that investigated the effect of various alkali metal-calcium chloride binary salt systems on MSE at Los Alamos National Laboratory. The alkali metal chlorides studied included NaCl, KCl, CsCl and LiCl. Calculated distribution coefficients indicated that CaCl₂ was the best solvent system for MSE. Currently, MSE is run at LANL using CaCl₂ as the solvent salt and PuCl₃ as the oxidant. The process is extremely efficient with an average of 94% of the Am initially present being removed from the Pu metal in one extraction.

ELECTROREFINING Principal Investigator Sammi Owens

The traditional plutonium electrorefining process at LANL is performed in NaCl-KCl.⁷ In 1988 LANL started experimenting with CaCl₂ and CaCl₂/CaF₂ systems for ER.⁸ The design of the current LANL cell is restricted information.

Twenty-five full-scale electrorefining runs have been completed using $CaCl_2$ with $PuCl_3$ oxidant.⁹ Nineteen of those runs produced plutonium metal and all of that metal met purity requirements. Fourteen runs successfully shut off using the back *EMF* measurement used in the NaCl/KCl system. Table 1 shows the average feed and product analysis of the nineteen successful runs. (Note: Successful is defined by having a greater than 0% Process Yield.) The product metal is high quality and is comparable to the metal produced with the NaCl/KCl salt system. These average decontamination factors do not represent the possible decontamination factors since many impurities were below detection limits in the feed and/or in the product. A few feeds had individual impurity levels high enough to get a significant decontamination factor and in Table 2 the highest obtained decontamination factors are given.

Table 3 provides the process, collection and dissolution yields for all 25 calcium chloride ER runs. Six runs were defined as failures due to the 0% process yield: three were early runs at excessive temperatures resulting in cell equipment breakage; the other three were due to furnace element or thermocouple failures. The yields are calculated according to the following equations:

Process Yield = R / ICollection Yield = R / (I - A)Dissolution Yield = (I - A) / I

where R = grams Pu in product ring I = grams Pu in feed ingot A = grams Pu left in anode heel after run

Table 4 compares the yields for the calcium chloride runs with recent NaCl/KCl runs. The process yields are equivalent for the two salt systems. The average collection yield for calcium chloride of 87% seems to be significantly higher than the 82% for NaCl/KCl. Since collection yield is a measure of how much Pu is collected in the product compared with how much is dissolved from the feed, the electrorefining is working well. The dissolution yield for calcium chloride averages less than that for NaCl/KCl. The dissolution yield is a measure of how much of the anode metal gets dissolved and is really more a statement of the impurity of the starting feed. As the plutonium is removed from the anode, the percentage of impurities in the anode and cathode) increases. Once it reaches a preset measurement the electrorefining terminates in order to prevent the impurities from oxidizing into the salt.

After electrorefining, the $CaCl_2$ salt is easily sparged with oxygen to precipitate the Pu held up in the salt and minimize residues for aqueous recovery.

The major difficulties so far with calcium chloride are with the difficult breakouts and the possible high concentration of Am in the salt. Currently ER salts are of much greater volume than MSE salts and Am is handled easier in a smaller volume of salt. To ease breakout and minimize salt volume a new ER crucible designed by Peter Lopez is being tested.¹⁰

OXYGEN SPARGE Principal Investigator Ed Garcia

After pyrochemical processing, plutonium is held up in the processing salt as plutonium trichloride, plutonium oxychloride, plutonium oxide and plutonium metal shot. Mullins and Leary of LANL bubbled argon and oxygen through molten NaCl-KCl and used the differing precipitation rates of plutonium and americium species to separate the

two.¹¹ Plutonium oxide precipitated first, forming a Pu-rich bottom phase which could be physically broken away from the Am-rich top phase when cooled. Later work by West, Bird and Valdez concentrated on the recovery of Pu from these salts rather than the separation from Am.

In current work by Ed Garcia the process parameters and optimization of $CaCl_2$ and NaCl-KCl oxygen sparging are being investigated. The process chemistry is now well understood. Oxygen reacts with plutonium trichloride to form plutonium dioxide. In electrorefining salts there is a quantity of suspended metallic plutonium. Metallic plutonium and plutonium dioxide cannot coexist in chemical equilibrium and react to form plutonium oxychloride with the salt as a reagent in the reaction:

Pu + 3 PuO₂ + 2 CaCl₂ $\xrightarrow{850^{\circ}C}$ 4 PuOCl + 2 CaO

In the subsequent aqueous recovery process, plutonium oxychloride is easier to dissolve than plutonium oxide.

A by-product of the oxygen sparge process is chlorine. The in-line spectrophotometer being developed for DOR is also being used to detect chlorine in the off-gas stream and correlate the chlorine concentration with plutonium concentration in the molten salt. This will optimize sparging times and reduce radiation exposures.

LANL has a large number of old processing salts stored in the vault awaiting aqueous dissolution and Pu recovery. Oxygen sparging allows discard of the top Pu-lean phase. An oxygen sparge campaign was recently started to reduce the bulk of these salts. $CaCl_2$ salts resulting from DOR and the recent experiments in electrorefining, $CaCl_2/CaF_2$ salts and regular NaCl/KCl salts from electrorefining have all been successfully oxygen sparged. The bulk weight of salts has been reduced by an average of 68% and the discardable top salt has averaged 7.1 g Pu/ kg Net Wt. We expect to get even greater bulk reductions and lower discard concentrations as the process is fine tuned and reusable crucibles are implemented.

This reduction in bulk provides an even greater savings in aqueous generation of waste. Every kilogram of salt not sent to aqueous recovery saves 70 liters of low level liquid waste solution.¹² This work has great significance when trying to decide how to process the waste salt inventory currently stored at the EG&G Rocky Flats Plant.

SUMMARY

LANL's recent development work has shown that it is possible to run a successful pyrochemical purification scheme for plutonium in calcium chloride molten solvent salt. Rechlorination of the calcium oxide built up in the calcium chloride DOR salt greatly reduces the amount of salt discarded and may allow the rechlorinated salt to be used in ER. Recent improvements in LANL's offgas analysis capabilities allow optimization of the DOR process, subsequent salt rechlorination and oxygen sparging. Studies of the phase behavior of the Ca-CaO-CaCl₂ system have allowed for further optimization of DOR by defining the optimum process time and temperature for maximizing Ca^o solubility and minimizing crucible reactions. Americium removal in the MSE process

has been shown to be greatly improved using calcium chloride with a $PuCl_3$ oxidant. Electrorefining in calcium chloride has been shown to be successful on a full-scale, producing pure plutonium metal products and having process and collection yields similar to the traditional NaCl/KCl process. Oxygen sparging of calcium chloride salts has been very successful and process parameters are being optimized based on the newly gained knowledge of the process chemistry and installation of off-gas detection equipment. The current oxygen sparge campaign of old LANL salts has shown that oxygen sparging can reduce the bulk salt volume requiring further processing by 68%.

The future directions for LANL's work include investigation of reusable crucibles, installing at-line analytical capabilities, increasing electrorefining equipment reliability, and designing a multiprocess cell.

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TABLE 1

Calcium Chloride Electrorefining- 19 Runs (impurities in ppm unless stated otherwise)

	-	DODUICT	ALTER LOT	
	HEED	PRODUCT	AVERAGE	
	AVERAGE	AVERAGE	DEUN	
Pu	99.03%	99.94%	FACTOR	
Am	769	53	14	
Ga	3429	34	101	
NI	100	3	48	
Ве	5	0.13	42	
Ca	911	24	37	
Cr	212	/	29	
Y	70	5	20	
Mn	15	1	19	
Ві	10		10	
U	165	10	16	
Mg	472	41	11	
Fe	278	30	9	
C	237	33	7	
SI	155	24	7	
Cu	27	4	6	
Zr	12	2	6	
Th	38	8	5	
Al	142	29	5	
T2*, uci/g	9.86	3	4	
в	13	4	3	
Ti	9	3	3	
Sn	24	9	3	
Zn	6	3	2	
Np 237	121	54	2	
РЬ	42	25	2	
v	7	4	2	
Ta	129	94	1	
Мо	18	14	1	
к	68	60	1	
Ba	1	1	1	
Co	5	5	1	
Li	3	3	1	
W	57	56	1	
Cd	1	1	1	
Nb	5	5	1	
Rb	9	9	1	
Sr	1	1	1	
Re	20	22	1	
Ce	75	90	1	
Hf	5	6	1	
La	20	24	0.83	
Na	56	73	0.76	
Ag	14	43	0.33	

* Tritium is reported as T2 and is in microcuries/gram

TABLE 2

Calcium Chloride Electrorefining Highest Obtained Decontamination Factor

	Highest		Highest
Element	DF	Element	DF
Am	62	Cu	55
Fe	39	В	53
U	162	Та	38
С	29	Si	34
Np	6	Zr	22
Ga	3100	Pb	15
Ca	5650	Sn	15
Be	450	Ti	14
Cr	333	v	14
Ni	327	Al	12
Y	270	Sr	10
Bi	250	w	10
Mg	172	Мо	9
Th	144	Rb	6
Mn	98	Re	5
Zn	58	Ce	5

TABLE 3

Run	Process	Collection	Dissolution
#	Yield	Yield	Yield
8361	92	92	100
8362	8 5	8 5	100
8363	56	92	61
8365	71	71	100
8366	0	0	2
8367	0	0	34
8368	0	0	13
1434	70	89	78
2373	56	91	62
9382	77	90	86
1435	0	0	1
1436	64	83	78
1437	89	98	91
2374	87	87	100
2375	56	93	60
2376	0	0	0
2377	40	63	63
1438	91	91	100
1439	72	84	85
1440	0	0	3
1441	75	75	100
2378	72	92	79
2379	78	92	85
2380	82	90	91
1442	91	91	100

Yields of 25 CaCl2 ER Runs

TABLE 4

Average Yields for NaCl/KCl runs vs. CaCl2 runs

# of		Process	Collection	Dissolution
	Runs	Yield	Yield	Yield
NaCl/KCl	323	73%	82%	89%
CaCl2	19	74%	87%	85%





VOLTAMMETRIC STUDY OF A PLANAR ELECTRODE WITH SUPERMENISCUS FILM IN MOLTEN CARBONATE

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ABSTRACT

Cyclic voltammetry with a variable scan window was applied to study the electrochemistry of oxygen reduction at a gold flag electrode in molten carbonate. To account for the effect of supermeniscus film formation, a modeling approach was combined with oxide addition and linear potential scanning at a wire electrode. Characteristic peaks are observed in the -0.3 V to -0.5 V range. These are due to a different reaction than oxygen reduction, which occurs at -0.1 V to -0.3 V. Most likely, they are associated with reduction of superoxide.

INTRODUCTION

In molten carbonate fuel cell operation, the porous cathode is likely to be covered by a film internally, similar to the supermeniscus film formed along the wire shown in Fig.1. Supermeniscus films have been observed also at planar and cylindrical electrodes in molten carbonate⁽¹⁾, and the effect on cyclic voltammograms (CV) has been discussed⁽²⁾. To analyze the effect of such a film at a planar electrode, mathematical modeling as well as an experimental comparison of cyclic voltammograms between flag electrode and wire electrode are used, with the objective to determine the overall impact of this effect on the study of kinetics by cyclic voltammetry.

MODELING RESULTS

When a supermeniscus is formed it may affect the mass transfer of reactants to the active surface of the electrode. To analyze this, different boundary value problems representing various mass transfer processes are analyzed, assuming a general CEC cathodic mechanism

$$Z \rightleftharpoons O + ne \rightleftharpoons R \rightleftharpoons Y$$
^[1]

At a planar electrode undergoing a potential scan the following cases can be distinguished: (Case I) semi-infinite diffusion, where $x \to \infty, C \to C^*$; (Case II) insulated-boundary finite diffusion or *leakage-film diffusion*, where $x = \delta$, $\frac{\partial C}{\partial x} = 0$; (Case III) diffusion-layer finite diffusion or *thin-film diffusion*, where $x = \delta$, $C = C^*$. The Laplace transforms of the surface concentrations in these three cases can be expressed as:

Case I:
$$C_o(s) = \frac{C^*}{s} - \frac{i(s)}{nFA} \frac{1}{D_o^{0.5} s^{0.5}}$$
 [2]

Case II:
$$C_o(s) = \frac{C^*}{s} - \frac{i(s)}{nFA} \frac{1}{D_o^{0.5} s^{0.5}} tanh(\sqrt{\frac{s}{D}}\delta)$$
 [3]

Case III:
$$C_o(s) = \frac{C^*}{s} - \frac{i(s)}{nFA} \frac{1}{D_o^{0.5} s^{0.5}} \operatorname{coth}(\sqrt{\frac{s}{D}}\delta)$$
 [4]

The current through an electrode in a stationary solution as a function of time, following a potential scan, is given by⁽³⁾:

$$i = -nFAC_o^* \sqrt{\pi D_o} Y(t)$$
^[5]

where A is the active surface of the electrode and the diffusivities of species O and R are assumed to be equal for numerical simplification. Therefore, the current function Y(t) for these three cases can be expressed as

$$Y_{I} = \frac{2}{\pi} [P'(0)\sqrt{t} + \int_{0}^{t} \sqrt{t - \tau} P'' d\tau] + \frac{P(0)}{\pi\sqrt{t}}$$
[6]
with $P = \frac{1}{1 + \theta S_{\lambda}(t)}$
 $\theta = exp[(\frac{nF}{R_{g}T})(E - E_{0})]$
 $S_{\lambda}(t) = e^{-at}$ when $t \le \lambda$
 $S_{\lambda}(t) = e^{at - 2a\lambda}$ when $t \ge \lambda$
 $Y_{II} = Y_{I} - \frac{1}{\sqrt{\pi}} \frac{\sqrt{D}}{\delta} \int_{0}^{t} [\int_{0}^{1} e^{-(\xi)^{2}\pi^{2}(t - \tau)D/4\delta^{2}} d\xi] P' d\tau$
 $-\frac{1}{\sqrt{\pi}} \frac{\sqrt{D}}{\delta} P(0) \int_{0}^{1} e^{-(\xi)^{2}\pi^{2}(t - \tau)D/4\delta^{2}} d\xi$ [7]
 $Y_{III} = Y_{I} - \frac{1}{\sqrt{\pi}} \frac{\sqrt{D}}{\delta} \int_{0}^{t} [2 \int_{0}^{1} e^{-(\xi)^{2}\pi^{2}(t - \tau)D/4\delta^{2}} d\xi - 1] P' d\tau$
 $-\frac{1}{\sqrt{\pi}} \frac{\sqrt{D}}{\delta} P(0) [2 \int_{0}^{1} e^{-(\xi)^{2}\pi^{2}(t - \tau)D/4\delta^{2}} d\xi - 1]$ [8]

Here a is the dimensionless scan rate ν ($a = nF\nu/R_gT$), and λ is the time at which the scan is reversed.

The numerical solutions are shown in Figs.2 and 3 for cases II and III with different δ/\sqrt{D} values. In case II, the case of insulated-boundary finite diffusion, the boundary condition at δ is $D(\frac{\partial C}{\partial x}) = 0$, not constant sink concentration C^* . Therefore, the driving force for mass transfer will be reduced by the applied scan. In that case, the oxygen reduction (cathodic) peak potential will be less cathodic when this film is thin; at the same time, the peak current due to the leakage film will also be small due to the limited reactants coming to electrode surface by mass transfer.

In case III, diffusion-layer finite diffusion, the boundary condition at δ is $C = C^*$, i.e., an unlimited source of oxidant species O with constant concentration C^* can be regenerated at the gas/liquid interface. Therefore, a high peak current and high cathodic peak potential will be expected if the supermeniscus film is thin. This characteristic is shown in Fig.3. The peak potential increases from cathodic 87 mV to cathodic 636 mV as the δ/\sqrt{D} values decreases from 10 to 0.1 $sec^{0.5}$. Two limiting cases are observed. One is that of overlapping polarograms of forward and reverse scans when $\delta \to 0$, i.e., cyclic voltammograms for very thin film situation. The other is $Y_{II}(t) = Y_I(t)$ when $\delta \to \infty$, i.e., a thick film has the same effect a the planar-surface, semi-infinite-diffusion case. Nevertheless, it is clear that one cannot easily observe two peaks (split peaks) on the polarogram when an electrolyte film is adjacent to a planar electrode as shown in Fig.1 (see Fig.4).

Figs.5 and 6 also indicate that the peak potentials will shift to more cathodic and less cathodic for cases II (*leakage-film diffusion*) and III (*thin-film diffusion*) respectively as the scan rate increases, and that this is not observed for the case of a planar electrode (case I).

From these simulation results it is concluded that: (1) Peak potential is dependent on scan rate for both leakage-film and thin-film diffusion. The peak shifts to more cathodic potentials for the case of leakage-film diffusion as the scan rate increases. The opposite applies to thin-film diffusion case. (2) A low peak current is observed in the leakage-film diffusion case, and a high peak current in the thin-film diffusion case. (3) No clear split-peaks can be observed for the same reaction if a film is adjacent to the planar electrode. (4) The characteristics of the CV's are strongly dependent on the film thickness and the reaction rate of preceding and following reactions. If the preceding reaction is slow, the CV response is similar to that for the case of insulated-boundary diffusion. If the preceding reaction is fast, the polarographic behavior of this film is like that of a thin-film layer. The same types of behavior also occur in the case of a following reaction. (5) The values obtained for the slope of i_p vs $\sqrt{\nu}$ may be artificially high if the effect of film formation is not accounted for.

EXPERIMENTAL RESULTS

A fully immersed gold flag (or wire) electrode in $62/38 \mod 10^{10} M_2 CO_3/K_2 CO_3$ electrolyte (see Fig.1) was polarized by potential scanning, under a variety of gas compositions, at $650^{\circ}C$ and 1 atm.

Various CV Window

Cyclic voltammograms have been recorded with different scan windows using a flag electrode, starting from open circuit voltage (OCV) in the cathodic direction to -1.3V. One of the results is shown in Fig.7. The correspondence of cathodic peaks with those in the reverse direction can be verified in this study.

Peak a occurs around -0.1 to -0.3 V. It has a positive trend with O_2 partial pressure, and a small negative trend with CO_2 . Either the reduction of peroxide or that of superoxide ions, or both, are the possible mechanisms corresponding to this peak. Peak b occurs around -0.5 to -0.7V, with no corresponding peak in the reverse scan, It can be observed clearly only at high O_2 partial pressure. Reduction of dissolved oxygen gas, of adsorbed oxygen and of superoxide with irreversible characteristics are possible reactions. However, peak b may also be due the supermeniscus effect.

Peak c occurs around -0.8 V to -1.0 V, and the dependence of peak c on O_2 or CO_2 partial pressure could not be established clearly. By increasing the reversal potential (switching potential) from one cycle to the next, anodic peak g was shown to correspond to the cathodic peak c. Peak g can be observed in reversal scan only after peak c is observed in forward scan as seen in Fig.7. However, it is to be noted that the reproducibility of the peak current c and g are not a good as that of peak a. It appears that reduction of adsorbed oxygen:

$$O_{ads} + 2e^{-} \rightleftharpoons O^{=}$$
^[9]

as a reversible charge transfer reaction is responsible for c and g. Consequently, these peaks depend on the previous history of the electrode surface and this should have a complicating effect on the cyclic voltammograms.

Effect of Supermeniscus Film

The effect of a supermeniscus film adjacent to a planar electrode is also dependent on the reaction rate of the preceding reaction and the following reaction. If the preceding reaction is slow, then the effect is similar to that in the case of insulated-boundary finite diffusion, as discussed above. The effect is negligible due to the smaller current function and the smaller surface area compared to those of the planar electrode. On the other hand, if the preceding reaction is fast, the CV behavior of the supermeniscus film will be like that of a thin-film finite diffusion; a negative shift of the peak potential and an increase in the peak current are expected. The same behavior is also observed in the case of a following chemical reaction.

Two auxiliary experiments were carried out to investigate the effect of a supermeniscus film on the cyclic voltammogram, by changing the ratio between the surface area of the supermeniscus film and that of the planar electrode. In one of these the depth of immersion was varied; in the other, a wire electrode was used for comparison.

Depth of Immersion of Flag Electrode

The peak current is proportional to the overall surface area, therefore a linear relation of peak current i_p and immersion depth x can be established to evaluate how much current is contributed by the supermeniscus film. The slope obtained is $18\mu A/cm$, and the current for complete immersion at x = 6mm is $138\mu A$. This is the current due to the circular flag and the supermeniscus film only, without immersion of the wire. The surface area of the circular flag is $0.58 \ cm^2$, so the effective surface area of the supermeniscus film, A_{film} , is related to the diameter of the electrode wire as follows:

$$\frac{138}{0.5844 + A_{film}} = \frac{18}{d * \pi}$$
[10]

The diameter of the wire can be measured directly or evaluated from the peak currents of the flag electrode and the wire electrode, at the same immersion depth of 2.0 cm. This yields:

$$\frac{i_p(flag)}{i_p(wire)} = \frac{163.2}{28.4} = \frac{0.5844 + A_{film} + 1.4 * d * \pi}{A_{film} + 1.4 * d * \pi}$$
[11]

From Eqs [10] and [11], the following values are obtained: $A_{film} = 0.014cm^2$ and d = 0.0248cm (compare the measured value: 0.025cm). The height of the supermeniscus film is estimated at approximately 0.18 cm. This is identical to the theoretical value of the electro-capillary height according to the Neumann relation⁽¹⁾, using surface tension 216.7 dyne/cm and wetting angle 60 deg.

From the above results, the peak current due to the supermeniscus film appear to be only 2% compared to the flag electrode. Since no appreciable peak current due to the supermeniscus film is observed, either the preceding or following reaction, or both, are slow. Consequently, it is concluded that chemical dissolution of oxidant species or oxide ion recombination, which are responsible for peak a, are slow reactions.

Comparison with Wire Electrode

The comparison of flag and wire electrode response also provides some information about which preceding reaction is fast, because the supermeniscus film will have a dominant effect on the CV, i.e., it will cause a more cathodic peak potential. Figs. 8 to 10 show the polarography of both flag and wire electrodes for different gas compositions.

Peak a indicates that either its preceding or following reaction is slow, as discussed before. Peak b is around -0.5V to -0.6 V. It is clearly observed at both wire and flag electrodes under O_2/CO_2 0.9/0.1 oxidant gas and at a wire electrode under O_2/CO_2 0.1/0.1. Comparing the difference between flag and wire electrodes, the supermeniscus film effect is seen to make a major contribution to peak b. One possible explanation is the reduction of superoxide (O_2^-) to peroxide $(O_2^=)$, while both the preceding and following reaction are fast:

$$O_2 + O_2^{=} \rightleftharpoons 2O_2^{-}$$
^[12]

$$O_2 + 2O^{=} \rightleftharpoons 2O_2^{=}$$
^[13]

It is also possible that the regenerated $O_2^=$ is reduced to oxide ions very quickly under such a high cathodic potential.

This implies that peak b will be observed only if the equilibrium concentration of superoxide ions is high. The oxidant gas O_2/CO_2 0.9/0.1 results show that this is the case for both flag and wire electrodes; they also indicate that the supermeniscus film contributes the major part of the peak current since superoxide ions are diffusing across a thin layer and must be generated rapidly by reactions [12] at the gas/liquid interface. However, in this case $(O_2/CO_2:0.1/0.9)$, the high CO_2 partial pressure implies a low equilibrium $O^=$ concentration. Therefore small peroxide and superoxide equilibrium concentrations occur at the G/L interface, and then no peak b can be observed clearly. Also, since peroxide is reduced to oxide ion in peak a of CV, the following scans at the flag electrode cannot generate a big b-peak due to the decrease in concentration of superoxide at the G/L interface (e.g., with 0.1/0.9 gas mixture).

In the case of the wire electrode, however, the supermeniscus film is exposed to oxygen gas and, in a $O^{=}$ rich environment, regeneration of superoxide ions contributes to the supermeniscus film peak b. That may be the reason why peak b is observed more clearly at a wire electrode than at a flag electrode in the case of 0.1/0.1 oxidant gas. The effect of a supermeniscus film at a partially immersed electrode which is suddenly raised, has been studied by White and Twardoch⁽²⁾. Their results can be adequate explained by this proposed mechanism. It is to be noticed that a high scan rate will also minimize peak b due to the large amount of oxygen reduction at peak a, which reduces the available concentration of superoxide by reaction [12]. This explains the absence of peak b in the CV's obtained by Nishina and Uchida⁽⁴⁾.

Peak c is considered to be due to following electrode reaction:

$$O_{ads} + 2e^- \longrightarrow O^-$$
 [14]

possibly in two steps with $(O)^-$ as intermediate. In the case of a wire electrode, the peak potential of peak c is anodically shifted, and this implies that the preceding reaction is not fast. Therefore, peak c is not likely to be carbon deposition since the physical dissolution of CO_2 is the preceding reaction. An abnormal case is that of a wire electrode under oxidant gas O_2/CO_2 : 0.1/0.1, which shows high peak current c and a type of adsorption-desorption CV. This may be the result of a mistake, for example, when the gas is sparged too vigorously and a film of electrolyte (supermeniscus film) forms along the wire. The latter is then covered completely by a thin layer of O_{ads} . However, this artificial error provides useful information for clarifying the reaction, involved in peak c, which is most likely reduction of adsorbed oxygen.

The peak g of reverse scans is observed at all flag electrodes. The formation of an adsorbed oxygen layer may be considered as an explanation:

$$O^{=} \longrightarrow O_{ads} + 2e^{-}$$
^[15]

In the case of the wire electrode, this adsorbed oxygen layer is easily kept in equilibrium with oxygen gas through the supermeniscus film, therefore peak g is not evident at most wire electrodes. The latter do not have a large surface available for adsorption, like the flag electrode in a bulk molten salt.

CONCLUSIONS

Combining the above analysis with the experimental results of oxide addition⁽⁵⁾, it is concluded that the supermeniscus film acts as an insulatedboundary diffusion layer in peak a, where the following recombination reaction is slow. However for reduction of superoxide ion, the supermeniscus film behaves as thin-film diffusion layer with constant concentration boundary condition. Peak b, which was observed in the present work using fully immersed gold flag or wire electrodes, and is expected to emerge more clearly in the case of a partially immersed gold flag electrode, is due to another reaction than that of peak a. Its CV response at a planar electrode may be overshadowed by peak a due to low surface concentration. However, when the area of the supermeniscus film increases, the current response increases and peak b becomes clear and dominant.

The most plausible mechanism for peak a is

$$O_2^{2-} + 2e^- \rightleftharpoons 2O^{2-} \tag{16}$$

with either dissolution of peroxide or oxide ion recombination being slow. Peak b may be assigned to reduction of superoxide ion

$$O_2^- + e^- \rightleftharpoons O_2^{2-} \tag{17}$$

preceded and followed by fast equilibrium reactions [12] and [13] (or [16] at high cathodic potential). From a comparison of wire and flag electrodes, peak c does not appear to be due to carbon deposition. A strong possibility is reduction of adsorbed oxygen atoms (equation [14]).

Both superoxide and peroxide reduction may contribute to the overall oxygen reduction kinetics. The role of CO_2 is enhanced by the intermediate production of $O^=$, which has a low rate of recombination with CO_2 and can react with O_2 or O_{ads} to form peroxide or superoxide ions. This complex behavior makes kinetic studies using CV a more or less semi-quantitative tool, because no clear dependence on CO_2 can be observed.

Finally, it is generally agreed that a film probably covers the agglomerates in the porous cathode of the MCFC. Therefore, further study of supermeniscus films with a suitable model would be very relevant, especially of current response in the -0.3V to -0.5V range, since this is expected potential range at high current densities.

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Fig.1 Schematic of flag electrode and wire electrodes.



Fig.2 Cyclic voltammetry polarogram of the insulated-boundary finite diffusion case where $\delta/D^{0.5}$ equals 10, 1 and 0.1 sec^{0.5} with scan rate = 20 mV/sec.







Fig.4 Cyclic voltammetry polarogram of a thin film adjacent to a planar surface with A'/A equaling 0.5, $\delta/D^{0.5} = 0.1 \ sec^{0.5}$ and scan rate = 20 mV/sec.







Fig.6 Cyclic voltammetry polarogram of the diffusion-layer finite diffusion case at various scan rates where $\delta/D^{0.5}$ equals 1 sec^{0.5}.



Fig.7 Cyclic voltammograms of flag electrode with scan rate = 200 mV/sec in molten carbonate for oxidant gas O_2/CO_2 :10%/10%.



Fig.8 Cyclic voltammograms of flag and wire electrodes in molten carbonate for O_2/CO_2 : 0.1/0.9 oxidant gas and scan rate = 200 mV/sec.







Fig.10 Cyclic voltammograms of flag and wire electrodes in molten carbonate for O_2/CO_2 : 0.9/0.1 oxidant gas and scan rate = 200 mV/sec.

MATERIAL-DEPOSITION PROCESSES IN THE SEPARATOR OF LI-ALLOY/FeS, THERMAL CELLS

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ABSTRACT

The deposition of Li_2S and Fe in the separator layer of Li-alloy/FeS₂ thermal cells during discharge was studied. The parameters having the most impact included: anode Li activity, (fused lithiated catholyte treatment vs. unfused, VS. unlithiated), and electrolyte composition. The quenched cells were subjected to detailed postmortem examination by optical microscopy to measure the distribution and amount of deposition products in the separator layer. Complementary examination of select cells was also conducted using scanning electron microscopy and energy dispersive spectroscopy.

INTRODUCTION

During the discharge of Li-alloy/FeS₂ thermal cells, a dark, sometimes-colored band is observed in the separator layer between the Li-alloy anode and FeS₂ cathode. This band has been analyzed to contain both S and Fe (1). The process of material deposition in the separator is believed to be the result of self-discharge reactions between dissolved species originating from the anode and cathode. In earlier work, it was shown that an open-circuit condition and temperatures of 500°C or more greatly accelerated the self-discharge processes (2). The band in the separator becomes most pronounced under these conditions. Careful examination under reflected light (polarized and nonpolarized) of cross-sectioned, discharged thermal cells revealed that the band contained large numbers of crystals. Analyses showed these crystals to be primarily Li₂S (3).

To obtain a better understanding of the mechanism responsible for the deposition of material in the separator, a study was undertaken to investigate the parameters believed to have the most impact. These include: FeS, particle size and purity, anode Li activity, catholyte treatment (fused vs. unfused, lithiated vs. unlithiated), and electrolyte composition. All the tests were conducted under open-circuit condition for times of one-half or one hour at a temperature of $500^{\circ}C$. The quenched cells were then potted in epoxy, cross-sectioned, and subjected to detailed postmortem examination by optical microscopy to measure the distribution and amount of deposition products in the separator layer. Complementary examination of select cells was also conducted using scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS).

EXPERIMENTAL PROCEDURES

Equipment

The cells tested in the study were circular in cross-section and 3.18 cm (1.25") in diameter. Each cell consisted of a separator pellet sandwiched between an anode and cathode pellet, with stainless steel current collectors on the ends. The cells were heated between stainless steel platens under a constant applied pressure of 55.2 kPa (8 psig) at a temperature of 500° C for either one-half or one hour. All of the opencircuit tests were conducted in an argon-filled glove box where the oxygen and moisture contents were maintained at <10 ppm each.

Encapsulation of samples was carried out in a dry room maintained at <3% relative humidity. Subsequent sectioning and polishing were conducted in either the dry room or an inert-atmosphere glove box. The optical microscopy was also performed in an inert-atmosphere glove box.

Materials and Processing

The composition of electrolytes that were used in the separators for the study are listed in Table I, along with their melting points and the amount of MgO binder needed for equivalent, effective immobilization of the salt when molten. The electrolytes were prepared by fusion of a mixture of the component halides at 600°C for 3 h in a quartz crucible in the dry room. The separator mixes were prepared by blending the electrolyte powders with Maglite S MgO (Calgon Corp., Pittsburgh, PA) and fusion of the mixture in a quartz tray at 400°C (500°C for the all-Li mix) for 16 h in the dry room. After cooling, the separator mix was granulated into a fine (-60 mesh U. S. Standard) powder. The anode materials used were: 44% Li/56% Si alloy (-100+325 mesh), 20% Li/80% Al alloy (-100 mesh), and pure Li (19% Li immobilized with 81% Fe). (Unless stated otherwise, all compositions are reported in weight percent.)

The catholytes were made by blending purified FeS₂ (>98.6% pure) and separator material together. (The same electrolyte was used in both separator and catholyte for a given test.) The compositions of the various catholytes and anodes used in the various cells examined in this study are summarized in Table II. The catholytes formulated with FeS₂ used -325+425 mesh (predominantly) or -425 mesh material. Both Li₂O and Li₂S were used for lithiation of the FeS₂-based catholytes. The fused mixes were heated at 400°C for 8 h under argon. Fusion and lithiation affect the initial voltage spike that occurs upon activation of the Li-alloy/FeS₂ thermal battery (4) and the extent of self-discharge (2). One cell was constructed with Li₃Fe₂S₄ which is the primary product that forms when FeS₂ is discharged at high temperatures in molten salts.

Each of the electroactive cell components was prepared by cold pressing of powders in a double-action die.

RESULTS

Cathode Effects

FeS₂ Particle Size. Changing the FeS₂ particle size from -325+425 mesh to -425 mesh or fusing the catholyte under argon had no noticeable effect upon the amount and distribution of Li₂S in the separator of cells based on LiCl-KCl eutectic. The coloration effects and maximum particle size of the Li₂S were identical for the two particle sizes of FeS₂. The banded structure of the deposited Li₂S is shown in Figure 1 for a cell with an unfused, unlithiated catholyte, held on open circuit at 500°C for 1 h.

Lithiation. Lithiation promoted the deposition of Li₂S in the separator. The type of lithiation agent and level of lithiation affected the morphology of the deposit. Similar results were observed when Li₃Fe₂S₄ was substituted for FeS₂ in the catholyte. This is not unexpected, since Li₃Fe₂S₄ is one of the products that forms during lithiation, as shown in Eq. 1:

 $55FeS_2 + 48Li_2O ----> 25Li_3Fe_2S_4 + LiFe_5O_8 + 10Li_2SO_4$ [1]

Low-level lithiation of the catholyte with Li₂O tended to cause extensive discoloration of the separator in cells under open-circuit conditions. When the same lithiated mix was fused, however, a banded structure of Li₂S in the separator was observed under the same conditions. This is shown in Figures 2 and 3 for samples lithiated with 1.5% Li₂O for the unfused and fused catholytes, respectively. (This is equivalent to a Li/FeS₂ atomic ratio of 0.164.) The separator discoloration was more pronounced for the unfused catholyte (Fig. 2). Under polarized light, a pronounced orange-colored band was observed, with the greatest intensity being associated with the band of Li₂S.

Fusion of the catholyte results in improved wetting of the FeS, particles by electrolyte and better distribution of it throughout the catholyte. This process may have enhanced the mass transport of the diffusion species through the cathode and into the separator during the open-circuit tests.

As shown in Figure 4, increasing the degree of lithiation to 3.0% Li₂0 (Li/FeS₂ of 0.335 a/a) caused pronounced discoloration in the separator, relative to 1.5% Li₂0.

The catholyte treatment affected the morphology of the Li₂S deposit as well as the relative location within the separator. A tight banded structure of fine Li₂S crystals was observed for cells with unlithiated catholytes (Fig. 1).² Lithiation with Li₂O caused larger crystals of Li₂S to form over a greater region of the separator, as shown in Figure 5. A bridging morphology, intermediate between these two extremes, was observed with catholytes lithiated with Li₂S, as shown in Figure 6.

The relative position of the band of Li₂S in the separator is shown in Figure 7. The narrowest band occurred with the unlithiated, unfused catholyte. In all cases, lithiation shifted the minima in the band closer to the anode, resulting in a broader band. Fusing the catholyte with 1.5% Li₂O caused the band to shift from both electrodes and become narrower. The broadest bands occurred with the fused catholytes lithiated with Li₂O. In general, increasing the time on open circuit shifted the band closer to the cathode, especially for the catholyte with Li₃Fe₂S₄.

The effect of catholyte treatment upon the volume of Li₂S in the separator is shown in Figure 8. Lithiation with Li₂S increased the amount of Li₂S much more than when Li₂O was used. Catholyte fusion increased the amount of Li₂S when Li₂S was used for lithiation but decreased the amount when Li₂O was used. More Li₂S formed at the higher levels of lithiation. Only a Small amount of Li₂S formed when Li₃Fe₂S₄ was used in the catholyte in place of FeS₂.

Fe Impurities. The addition of Fe_2O_3 and $FeSO_4$ impurities to the unfused, unlithiated catholyte reduced the amount of Li₂S deposition in the separator from 12 to 5-10 vol. % after the open-circuit tests. However, the use of highly impure FeS₂ resulted in comparable Li₂S deposition as for the purified material. The exact nature of the FeS₂ impurities is unknown but is thought to involve acid-soluble Fe species.

^{1.} The term "minima" used in this report refers to the edge of the separator band nearest to the anode, while "maxima" refers to the edge closest to the cathode.

A comparable orange coloration in the separator was observed after the open-circuit tests for cells with catholytes containing highly impure FeS₂ and those with added Fe-containing impurities. The coloration and Li₂S-deposition morphology were similar to those for cells with lithiated catholytes tested under the same conditions. SEM/EDS analysis showed Fe was associated with the areas of intense coloration. Larger concentrations of Fe were noted for the sharply defined orange-colored band relative to the gross coloration or darkening.

The cells with impure FeS₂ and FeSO₄ were the only ones in which elemental Fe particles were observed in the separator after the opencircuit tests. This suggests some source of soluble Fe is responsible. This was substantiated by adding FeCl₂ or FeCl₂ to a LiCl-KCl eutectic/MgO separator mixture and fusing at 400°C³ for 16 h. The separator pellet with the added FeCl₃ showed a concentrated orange band that constituted about 5% of the total pellet volume. In the case of the separator pellet with added FeCl₂, only a gross darkening was observed. When elemental Fe was also added to the separator pellet with FeCl₃, the orange band was eliminated and replaced with a slight darkening of the whole pellet. Elemental Fe also reduced the degree of darkening observed with the pellet with FeCl₂. This suggests that the coloration is due to a soluble Fe cation, with the observed color being dependent upon the oxidation state of the Fe. Addition of elemental Fe serves as reduction sites for these cations.

Anode Effects

The Li activity of the anode was varied by changing the composition. The location of the Li₂S band in the separator after open-circuit tests at 500°C for 1 h is shown in Figure 9 for Li-alloy/FeS₂ cells based on the LiCl-KCl eutectic. (The unfused, unlithiated catholyte was used for all these tests.) The maximum deposition front (edge of the band closest to the cathode) advanced as the activity of the anode was increased. The widest band was observed for the cell with the anode of highest activity (i.e., pure Li). Similar band widths were observed for the other anodes. There was no obvious trend in the Li₂S deposition morphology with anode activity. As shown in Figure 10, the volume of Li₂S in the separator was directly proportional to the Li activity (r^2 =0.989).

When the Li-alloy anodes were replace by LipFeS₄, no band formed in the separator. This was as predicted, since this material has little or no solubility in the molten salt, in contrast to the FeS₂ or the Li alloys. This supports the contention that the band formation is a consequence of chemical reaction in the separator of dissolved anodic and cathodic species.

Electrolyte Effects

The location of the Li₂S band was strongly influenced by the composition of the electrolyte, as shown in Figure 11. The volume of Li₂S tended to increase with increasing molar content of the Li halides in the electrolyte, as shown in Figure 12 ($r^2=0.71$).

In contrast to the cells with lithiated catholytes or catholytes with additives, most of the unfused, unlithiated electrolytes showed a lack of orange coloration in the separator after open-circuit tests. The exceptions were cells with the all-Li and KBr-LiBr-LiCl eutectic, where intense colored bands were observed under polarized light--one orange-colored band nearer the cathode and an adjacent black band. The coloration was more intense for the cell with the all-Li electrolyte. The bands were not consistent in relative location, being parallel in some instances and merging together in others. It was not possible to confirm the presence of Li₂S crystals in the separators for these two cells. They may have been present but may have been extremely fine in particle size.

The banded Li₂S deposition that occurred in cells with the unfused, unlithiated catholytes based on LiCl-KCl was also noted for cells with the CsBr-LiBr-KBr and LiCl-KCl-CaCl₂ electrolytes.

DISCUSSION

Several processes occur in the separator of Li-alloy/FeS, thermal cells under open-circuit conditions at 500° C. These are deposition of Li₂S and localized color changes. The relative degree to which these phenomena are manifested is sensitive to changes in the active materials used to construct the cells.

The amount and distribution of Li_2S is governed by the type of soluble species originating from the anode and cathode and their solubilities in the various electrolytes. Knowledge of the relative solubility of FeS, in these electrolytes would be very useful for understanding the deposition processes. (Work in this area is currently underway.)

The coloration in the separator is related to the presence of soluble-Fe species. This process appears to be in competition with the Li_2S deposition process. Higher concentrations of Fe-bearing impurities, for example, reduced the extent of Li_2S deposition. The presence of soluble-Fe species was promoted by lithiation, impurities in the FeS₂, or by the addition of Fe-containing additives to the cathode. The soluble-Fe species may be reacting with and tying up soluble-S species originating in the cathode before they can migrate into the separator.

The location and width of the band of Li₂S crystals in the separator and their morphology was influenced by the composition of the cathode, anode, and electrolyte used in the cells. Increasing the Li activity of the anode moved the band maxima closer to the cathode, while changes in the cathode composition tended to move the deposition minima closer to the anode. However, there was no clear trend in the location of the deposition band in the separator with changes in the electrolyte.

Reaction Mechanisms

The deposition processes requires the presence of soluble reactive species that originate at each electrode. This can be represented at the cathode by Eq. 2

$$FeS_{2(s)} \xrightarrow{----} FeS_{2(soln)} \xrightarrow{----} Fe^{+2} + S_2^{-2}$$
 [2]

and at the Li-alloy anodes by Eq. 3.

$$LiM_{(s)} \xrightarrow{\text{current}} xLi_{(soln)}^{o} + Li_{(1-x)}M$$
 (where M=Si,Al) [3]

Once in solution, the species will diffuse into the separator and deposition will occur when the two diffusion fronts meet and react. Possible reactions related to Li_2S deposition are:

$$S_2^{-2} + 2Li_{(soln)}^0 - - - > 2Li^+ + 2S^{-2}$$
 [4]
 $S^{-2} + 2Li^+ - - > Li_2S_{(s)}$ [5]

Deposition will occur when the solubility of Li₂S in the molten salt is exceeded which will depend strongly upon temperature and composition of the electrolyte. For example, the solubility of Li₂S in the all-Li electrolyte at 550°C is almost nine times as great as for the LiCl-KCl eutectic (5). The presence of MgO binder in the separator serves to increase concentration gradients by providing a tortuous path for the diffusing species. This will enhance localized concentrations of Li₂S, thus promoting deposition of crystals.

The deposition processes will be influenced by the steady-state concentrations of the reacting species which, in turn, will depend upon the rate of dissolution of the soluble species at each electrode, their solubility in the molten salt, and their rates of diffusion. The diffusion rates of the reactive solution species in the separator will be influenced by the binder (MgO) content. The morphology of the Li₂S deposition and the relative position of the band in the separator will be influenced by these processes which, in turn, will be affected by the composition of the anode, cathode, and electrolyte, as well as temperature.

The higher activity of Li in the anode will lead to a higher concentration of dissolved Li in the electrolyte which, in turn, would be expected to result in a higher concentration of Li₂S via Eq. 4. The data of Fig. 10 substantiate this argument. The effect² of Li activity upon the location of the deposition band, however, is not as clear. In general, the

higher Li activity resulted in greater advancement of the deposition front, which suggests a higher steady-state concentration of dissolved Li at the reaction zone. The greatest advancement occurred with the anode of pure Li, resulting in the widest deposition band. In contrast, the close proximity of the deposition band to the anode for the case of the 35% Li-Si and 20% Li-Al anodes (Fig. 9) indicates that the concentration of dissolved Li was low at the anode-separator interface and even lower in the bulk of the cathode progressed across 60-70% of the separator before encountering sufficient dissolved Li to react to form Li₂S crystals.

The composition of the electrolyte would be expected to have a significant effect upon the solubility of the Li and FeS₂. In general, the amount of Li₂S deposition was weakly correlated to the molar content of LiX of the electrolyte. Except for the case of the LiCl-KCl-CaCl₂ electrolyte, there was a tendency for the maximum in the reaction front to move closer to the cathode with decrease in LiX content of the electrolyte. The wide band for the RbCl-LiCl-KCl eutectic suggests a higher solubility of Li in this electrolyte. Detailed solubility data for the anodes and FeS₂ in the various electrolytes would be needed to explain the observed trends.

A possible reaction related to Fe deposition is:

The dissolution of FeS₂ will result in the formation of soluble Fe species that can be reduced to elemental Fe by the soluble Li originating from the anode. The fact that elemental Fe is not always found with the Li₂S crystals suggests that there is strong competition between the reactions of Eqs. 4 and 6. When other sources of soluble Fe are present in the cathode (e.g., highly impure FeS₂ and FeSO₄ additive), however, elemental Fe is readily formed.

The effect of lithiation upon the deposition of Li₂S was pronounced. The presence of Li₂O or Li₂S in the catholyte increases² the wetting of binder and FeS₂ by² the electrolyte phase and, therefore, impacts masstransport processes. This is evident in the dramatic widening of the Li₂Sdeposition band in the separator (Fig. 7). This suggests improved diffusion of the cathodic solution species for the lithiated catholyte. The same effect is evident in the self-discharge behavior of Li(Si)/FeS₂ cells as a function of catholyte treatment. Fusion or lithiation both resulted in increased rates of self-discharge (2).

While the deposition of material in the separator does not in itself impact the performance of the battery, it serves as an indicator of the past history of the battery. The deposition is minimal if the battery has been discharged under load, since the deposition processes are occurring in parallel with the normal electrochemical processes, and, under these conditions, the deposition processes will be secondary. However, if the battery has been subjected to open-circuit conditions for an appreciable length of time (e.g., one-half hour or more), the will be significant deposition of Li_2S in the separator or the separator will exhibit

noticeable coloration. This can be very useful for determining the past history of an activated thermal battery where there is some question as to the discharge history of the battery.

CONCLUSIONS

The deposition of Li₂S and Fe in the separator of Li-alloy/FeS₂ thermal cells at 500°C under open-circuit conditions appears to be due to self-discharge processes and involves species that originate in the anode and cathode. The most probable species are dissolved Li and Fe-S complexes resulting from dissolved FeS₂. These species diffuse into the separator layer where they chemically react to form a discontinuous band of Li₂S crystals. Deposition of elemental Fe occurs only when the concentration of soluble Fe species is enhanced by the use of highly impure FeS₂ or the presence of soluble-Fe additives such as FeSO₄.

The morphology, quantity, and relative distribution of the Li₂S crystals that are deposited are dependent upon the activity of the Li anode, the catholyte treatment, and the composition of the electrolyte. These parameters impact the dissolution and solubility of Li and FeS, in the melt and affect the diffusion of the reactive species through the separator. Increasing the Li activity of the anode results in increased solubility of Li in the melt and a corresponding increase in the volume of Li₂S crystals. A higher molar concentration of Li halides in the electrolyte also tends to promote Li₂S deposition.

The presence of Li₂S deposition in, or coloration of, the separator of activated thermal batteries provides valuable information as to the past discharge history of the batteries. Substantial time on open circuit will result in the presence of significant amount of Li₂S crystals in the separator or give rise to noticeable coloration in the separator.

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Table I. Compositions and Melting Points of Electrolytes Used in Study

Electrolyte Composition*	Electrolyte <u>Melting Point, ^OC</u>	% MgO <u>In Separator</u>
45% LiC1/55% KC1	352++	35
57.331% LiBr/42% KBr/0.67% LiF	313**	25
51.41% KBr/36.54% LiBr/12.05% LiCl	321	30
36% LiC1/53.8% KC1/9.6% CaCl,	340	35
42.75% CsBr/39.08% LiBr/18.17% KBr	238	30
58.91% RbC1/29.2% LiC1/11.88% KC1	265++	35
69.4% LiBr/22% LiC1/9.6% LiF	437	35

* All compositions are reported in weight percent. ** Measured by DSC; all others are literature values.

Table II. Composition of Catholytes and Anodes Used in Open-Circuit Separator Studies.

Cathode Description				
Active			Eutectic	
<u>Material</u>	<u>Additive</u>	Fused?	<u>Electrolyte</u>	Anode
*				
FeS,	None	No	LiCl-KCl	44% Li-Si
FeS5	1.5% Li ₂ 0	No	LiCl-KCl	44% Li-Si
FeS5	1.5% Li50	No	LiC1-KC1	44% Li-Si
FeS5*	1.5% Li50	Yes	LiCl-KCl	44% Li-Si
FeS	3.0% Li50	Yes	LiCl-KCl	44% Li-Si
FeS5	2.3% Li5S	No	LiCl-KCl	44% Li-Si
FeS5	2.3% Li5S	Yes	LiCl-KCl	44% Li-Si
FeS5	3.0% Fe ₂ 0 ₂	No	LiCl-KCl	44% Li-Si
FeS5#	3.0% Fe\$0⊿	No	LiCl-KCl	44% Li-Si
FeS5#	None 7	No	LiCl-KCl	44% Li-Si
FeS5	1.5% Li ₂ 0	Yes	LiCl-KCl	44% Li-Si
LisfesS	None 2	No	LiCl-KCl	44% Li-Si
FeS, 1	None	No	LiCl-KCl	35% Li-Si
FeS5	None	No	LiCl-KCl	20% Li-Al
FeS5	None	No	LiCl-KCl	19% Li(Fe)
FeS ²	None	No	LiC1-KC1	Li ₂ FeS ₂
FeS	None	No	l iBr-KBr-l iF	44% i-Si
FeSa	None	No	CsBr-LiBr-KBr	44% i-Si
FeSa	None	No	RbC1-LiC1-KC1	44% i-Si
FeS	None	No	LiCl-KCl-CaCl	44% i-Si
FeS	None	No	KBr-LiBr-LiC1 ²	44% Li-Si
FeSa	None	No	liCl-liBr-liF	44% i-Si
	none			11/0 21 01

* FeS, particle size was -425 mesh; all others were -325+425 mesh. # Unpurified FeS₂ with high level of Fe impurity.



Figure 1. Banded Li₂S Deposition for 44% Li-Si/feS_Cell with Unfused, Unlithiated Catholyte and LiCl-KCl Eutectic after 1 Hour on Open Circuit at 500°C.





Figure 2. Gross Discoloration (in Polarized Light) for 44% Li-Si/FeS, Cell with Unfused, Li₂O-Lithiated (1.5%) Catholyte and LiCl-KCl Eutectic after 1 Hour on Open Circuit at 500°C.



Figure 3. Banded Discoloration (in Polarized Light) for 44% Li-Si/FeS₂ Cell with Fused, Li₂O-Lithiated (1.5%) Catholyte and LiCl-KCl Eutectic after 1 Hour on Open Circuit at 500 C.


Figure 4. Gross Discoloration (in Polarized Light) for 44% Li-Si/FeS₂ Cell for Fused, Li₂O-Lithiated (3.0%) Catholyte² and LiCl-KCl Eutectic after 1/2 Hour on Open Circuit at 500°C.

Anode Epoxy

Figure 5. Scattered Li_2S Deposition for 44% $Li-S1/FeS^2$ Cell with Unfused, $Li_2O-Lithiated^2(1.5\%)$ Catholyte and LiCl-KCl Eutectic after 1 Hour on Open Circuit at 500°C.

0.5mm____



Figure 6. Bridged Li₂S Deposition for 44% Li-Si/FeS₂ Cell with Fused, Li₂S-Lithiated (2.3%) Catholyte and LiCl-KCl Eutectic after 1 Hour on Open Circuit at 500°C.



Figure 7. Effect of Catholyte Treatment upon the Location of Li₂S Band in the Separator of 44% Li-Si/FeS₂ Cells Based on LiCl-KCl Eutectic after 1/2 and 1 Hour of Open Circuit at 500 °C.



Figure 8. Effect of Catholyte Treatment upon the Volume of Li₂S in the Separator of 44% Li-Si/FeS₂ Cells Based on LiCI-KCl Eutectic after 1 Hour on Open Circuit at 500°C.



Figure 9. Effect of Li Activity of Anode upon the Location of Li₂S Band in the Separator of 44% Li-Si/FeS₂ Cells Based on LiCl-KCl Eutectic after 1 Hour on Open Circuit at 500°C.



Figure 10. Effect of Li Activity of Anode upon the Volume of Li₂S in the Separator of 44% Li-Si/FeS₂ Cells Based on LiCI-KCl Eutectic after 1 Hour on Open Circuit at 500°C.



Figure 11. Effect of LiX Concentration in Electrolyte upon the Location of Li₂S Band in the Separator of 44% Li-Si/FeS₂ Cells Based on LiCl-KCl Eutectic after 1 Hour on Open Circuit at 500°C.



Figure 12. Effect of LiX Concentration in Electrolyte upon the Volume of Li₂S in the Separator of 44% Li-Si/FeS₂ Cells Based on LiCI-KCl after 1 Hour on Open Circuit at 500°C.

PERFORMANCE OF A SODIUM-SELENIUM(IV) MOLTEN CHLOROALUMINATE CELL FOR AN ELECTRIC VEHICLE

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ABSTRACT

Performance of a molten salt cell, sodium/beta"alumina/selenium(IV) in a basic chloroaluminate melt, has been studied to develop the battery for electric vehicles. Results on the response to the load, the cell resistance and the current distribution in the positive current collector are presented.

INTRODUCTION

The development of advanced batteries for electric vehicles has recently a lot of attention. These batteries require several severe properties such as high power density, high energy density, quick response, long cycle life, maintenance free, capability at wide temperature range, rapid charging and low cost. A rechargeable cell, sodium/ beta"-alumina/tetravalent selenium in a basic chloroaluminate melt, is one of the most attractive batteries, since this shows high emf, 3.8V at 423-523K (1) and high energy density as high as 415Wh/kg based on the weight of active components (2). Although this cell possesses high potential, a lot of properties should be improved to apply for the electric vehicles. Recent results on the response to the load, cell resistance, and current distribution in the positive current collector are presented in this paper.

EXPERIMENTAL

Three kinds of cell design have been prepared to investigate the behavior of a single cell. Typical arrangements of experimental cells are shown in Figures 1 and 2. These cells consist of a Pyrex glass compartment filled with the positive melt which is separated from the liquid sodium electrode by means of a beta"-alumina tube.

The sizes of beta"-alumina tubes obtained from NGK Spark Plug or Mitsubishi Heavy Industry are 16mm or 15mm OD, 13mm ID, and 100mm length. A graphite felt (GF-20 from Nippon Carbon) is used in these cells as the positive current collector. Tungsten wire and sheet are used to get electric contact between the graphite felt and terminal. These three of cells have different design of the positive kinds electrode. Type-A shown in Figure 1 has two tungsten wire to eliminate the resistance of tungsten wire, of which one is used for current flow and the other is for voltage measurement. Type-B is similar to type-A, in which only one for current flow and voltage tungsten lead is used measurement. The other cell, type-C, shown in Figure 2 has four tungsten microelectrodes set in the graphite felt. The position of these microelectrodes is also shown in this figure. The inner one (I) is between the beta"-alumina and the graphite felt, and the outer one (0) is between the graphite felt and the tungsten sheet. The other two (MI and MO) are between graphite felt sheets. In this type cell the lower graphite felt was used as guasi-reference elctrode. The chemicals, AlCl₃, NaCl and Na, were used after purified with usual methods. SeCl₄ (4N) was used as received. Each experimental cell was prepared as fully charged state.

RESULTS AND DISCUSSION

The load curves of electric vehicles show the abrupt change of power, and the pulsed output power continues from several seconds to a few minutes. This load pattern requires the batteries to respond quickly and to supply constant power at least for a few minutes. To study the response to the quick change of the load, a type-B cell (No. CS-1002, theoretical capacity 20.1Ah) was discharged with high current pulses. Figure 3 shows typical transient observed in this cell with 5A (0.1 A/cm²-beta") pulses at the early stage of discharging at 433K. Quick response to the load was surely observed, and voltage change within 10s was negligible. This stable voltage could continued at least for several minutes except for the end of discharging. These results suggest that the charge transfer in both electrodes and ionic conduction in the solid electrolyte and molten salts must be fast enough for the response to the abrupt change of the load. The average voltage at discharging calculated from closed and open circuit voltage was little influenced by the value of pulsed current density, if the average discharging current density was the same. This suggests that the polarization mainly consists of the resistance of the components such as melts and beta"-alumina.

The resistance of this cell, No.CS-1002, at the early stage of the discharging was 15 $ohm \cdot cm^2$ -beta" at 433K and 7 ohm.cm²-beta" at 473K. This resistance at 473K is almost the same as those for previous cells with graphite felt current collector. This value is, however, larger than that estimated from the specific resistance of the cell components, such as beta"-alumina and molten salts, which might be at most 3 ohm.cm²-beta" at 473K. To study this discrepancy between the experimental and estimated values, type-A (No.HC-1109, theoretical capacity 30.1Ah) was precell pared, in which we can eliminate the resistance of tungsten lead as mentioned above. In our experimental cell made with Pyrex glass, long tungsten wire should be used to connect the current collector to the terminal. The resistance of long tungsten wire at 473K cannot be negligible. Figure 4 shows the typical charge and discharge curves observed for the cell No.HC-1109, where the solid and broken lines indicate the voltages measured with voltage terminals and current flow terminals, respectively. The difference measured with two methods, about 2 $ohm \cdot cm^2$, corresponds to the resistance of tungsten wires, which changes with the height of sodium and melt in the cell. The minimum cell resistance without tungsten wires was 3.6 ohm.cm²-beta" at the discharging at 473K, and similar values was observed at the charging as shown in Figure 4. The wall thickness of the beta"-alumina tube used in this cell was 1.5mm, which indicates the resistance of the ceramic tube is $1.7 \text{ ohm} \cdot \text{cm}^2$ beta" at 473K. Since the thickness of the graphite felt with positive mix was about 9mm, the rest of the cell resistance except the beta"-alumina is mainly due to the melt resistance. Therefore, we can conclude the polarization of the Na/Se(IV) battery must be ohmic. In the cell No.HC-1109 three layers of graphite felt was used, the another cell (type-A) with two layers of graphite felt was recently prepared. This cell showed lower resistance such as 3.0 ohm. cm²-beta" at 498K. On these grounds we have come to the conclusion that thin-wall beta"-alumina as 1.0 mm and two layers of graphite felt should be adopted for the practical cells of which resistance is lower than 3.0 $ohm \cdot cm^2$ -beta".

The effects of current density on the charge and discharge curves are depicted in Figure 5. The cell voltage even with 5A (0.1 A/cm²-beta") was flat at the discharging, which suggests high power density can be obtained from the Na/Se(IV) cell. At the charging, however, the voltage with high current densities often fluctuated as shown in Figure 5. The evolution gaseous compounds may cause these voltage fluctuation.

It is well known for Na/S battery that the electrochemical reaction rate is high at the solid electrolyte

surface and container surface, when one kind of graphite is used for the current collector. It is likely that similar phenomenon occurs in the sodium/molten chloride cells which use porous materials as the current collector. In order to estimate the reaction rate during charging and discharging, the potential of four microelectrodes in a type-C cell was measured. FIgure 6 shows the open circuit voltage just after the break of the current at the charging. The inner electrode (I) usually showed higher potential than those of other electrodes. The outer electrode (0) showed higher value at the first half of the charging. On the other hand, these electrodes showed lower potential during the discharging. The potential of these microelectrodes measured at the closed circuit also exhibited the similar tendency. The higher potential at the charging and lower value at the discharging of the inner and outer electrodes suggest that the electrochemical reaction rates near these two microelectrodes are high near the beta"-alumina surface and near the container surface. This ununiform current distribution in the graphite felt would cause the serious problem especially at the discharging. In sodium/molten chloroaluminate cells which utilize the basic melts, solid NaCl deposits on the current collector during the discharging. When the reaction rate is high near the solid electrolyte, deposited NaCl will fill up the pore of the graphite felt. This indicates the volume occupied by the melts becomes narrow, and the cell resistance increases with discharging. It is assumed that this ununiform current distribution may be one of the reason of an increase in the cell resistance with the number of cycles. We now plan to adopt the dual mat design for the current collector in order to suppress high rate near the beta"-alumina surface.

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Figure 1 Schematic Representation of a Type-A Cell







Figure 2 Schematic Representation of a type-C Cell



Figure 4 Charge and Discharge Curves for a Type-A Cell (No.HC-1109)

Charged State/%



Figure 5 Charge-Discharge Curves with Several Current Densities at a Type-A Cell (No.HC-1109)



Figure 6 Open Circuit Potential of Four Microelectrodes during Charging

THE MODIFICATION OF FLEMION MEMBRANES FOR USE IN ENERGY GENERATING DEVICES

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ABSTRACT

Flemion is a perfluorocarboxylated polymer somewhat similar to Nafion. The structure of Flemion was altered by converting the methylester functional group to an acyl group and then acylating the benzene ring of dibenzyl-18cr-6 ether thereby attaching it as a pendent to the polymer chain. Pyridinium heptachloroaluminate served as the reaction medium and as the Friedel-Crafts catalyst for the acylation reaction. The crown ether was complexed with LiCl to produce a solid electrolyte with mobile anions. A second solid electrolyte, in the fast ionic conductor range, was produced by saturating the lithium carboxylate form of the Flemion with crown ether and then complexing the dissolved ether with LiCl.

INTRODUCTION

In an earlier study, (1) we modified Nafion 901,(2) which is a perfluorinated polymer membrane that contains both sulfonic acid and carboxylic acid pendent groups, in an attempt to convert it from a cationic conductor to an anionic conductor whose mobile species is the Cl^- ion. As a Cl^- ion conductor the membrane would have many uses, one of which would be as the separator to prevent chlorine gas in the cathodic compartment from reacting with the methylethylimidazolium chloride electrolyte in the Al/Cl_2 molten salt battery.(3) A key step in the modification of the sulfonic and carboxyllic acid functional groups to sulfonyl and acyl chlorides

respectively. This was done by reacting the membrane with SOCl₂, but regardless of the conditions used, some of the sulfonic acid groups always remained unreacted. We therefore decided to completely avoid the sulfonic acid problem by switching to Flemion, (4) a membrane containing only methyl ester functional groups which could be readily converted to carboxyllic acids.

Flemion is a perfluorocarboxylated polymer membrane somewhat similar to Nafion. It is prepared by copolymerizing tetrafluoroethylene and carboxylated perfluorovinyl ether (5,6) and is manufactured by Asahi Glass Company Ltd. Because of its high ionic conductivity and comparative inertness, as well as its ability to reject anions such as OH⁻ and Cl⁻, Flemion has been widely used in the chlor-alkali industry as the membrane separating the anodic and cathodic compartments in chlor-alkali cells. The chemical structure of Flemion is shown schematically below:

 $-(CF_2-CF_2)_x-(CF_2-CF)_y-$ | $(OCF_2-CF)_m-(CF_2)_n-COOCH_3$ | CF_3

where m is 0 or 1 and n has values between 1 and 5.

The principal objective of the present research was to attach dibenzo-18-crown-6-ether (CE) as a pendent hanging from the polymer chain and then complex the crown ether with LiCl. The CE-LiCl complex was shown to be a fast ion conductor in the solid state with the mobile species being the Cl⁻.(7,8) The LiCl-CE complex is shown in Fig. 1. We thought that if all of the acyl chlorides could be converted to CO-CE s, and if the structure of the LiCl-CE complex was essentially the same in the membrane as it was in the solid, the membrane itself would become a Cl⁻ conductor and reject cations. Moreover, if the extent of several of the reactions could be controlled, it would be a relatively simple matter to produce a polymeric electrolyte with mobile cations and anions; in effect a polymeric molten salt. This material would also have many uses in energy generating devices and in electrolysis cells.

EXPERIMENTAL DETAILS

Flemion sheet, 0.145mm thick, was furnished by Asahi Glass Ltd. Coupons of this material, between approximately 1 and 2 cm², were used for most of the chemical reactions. The Flemion was converted to the carboxylic acid form by immersing the coupon first in concentrated sodium hydroxide for 16 hrs at 90 °C and then in 1 M HCl at room temperature for 24 hrs.

The carboxylic acid was next converted to an acyl group by refluxing the membrane in thionyl chloride for approximately 12 hrs. The FTIR spectrum of the acylated membrane (Fig. 2) together with a Mohr titration of the acidic solution formed by the membrane reacting with water:

 R_f -COCl + H_2O ---> R_f -COOH + HCl [1]

indicated that essentially all of the carboxylic acid groups were converted to acyl groups.

The Flemion acyl chloride membrane was immersed in pyridinium heptachloroaluminate, a room temperature molten salt, at 40 °C. Dibenzo-18-cr-6 was added to the melt and allowed to react with the membrane for as long as 36 hrs. After the allotted reaction time, the membrane was removed from the melt and thoroughly washed in water. In addition to quenching the reaction, this technique converted unreacted acyl sites to carboxyllic acids. The membranes were then dried under vacuum to constant weight.

The extent of the reaction of R_f -COCl with the crown ether was monitored by measuring the membrane's weight increase and by measuring the membrane's UV-vis spectrum with an HP-8452A diode array spectrophotometer.

A second series of CE acylations were carried out by first dissolving the CE in warm methanol and then immersing Flemion, whose methyl esters had been converted to carboxyllic acids, in this solution for approximately 24 hrs. The CE diffused into the Flemion saturating it. The methanol was removed by evaporating it under vacuum at 70 °C for approximately 12 hrs. The CE containing membrane was refluxed for approximately 12 hrs in SOCl₂ and subsequently treated as in the first series of experiments. The SOCl₂ did not react with the CE.

All molten salt and acylation reactions were carried out in a controlled atmosphere glove box, the atmosphere being the boil-off from liquid nitrogen. The acylated membranes were never exposed to the atmosphere because water in the air would eventually convert the acyl groups back to carboxylic acids.

The ac conductivities of the dry membranes were measured with a Jones bridge at 1000 hz.

Transference numbers for the mobile ions in the dry membranes were measured with a Tubandt cell similar to the one described by Bottelberghs (9), but with three Flemion coupons in place of the three solid electrolyte pellets. That is, one LiCl complexed piece of Flemion was the anodic compartment, a second piece of supposedly identical Flemion the central compartment and a third piece the cathodic compartment. Weight changes of the anodic and cathodic compartments along with chemical analysis of the copper electrodes allowed the Li⁺ and Cl⁻ transference numbers to be calculated.

RESULTS AND DISCUSSION

The chemical reactions necessary to convert the methyl ester form of Flemion to the acyl chloride form are:

R _f -COOCH ₃	3 +	NaOH	>	R _f -COONa	+	СH ₃ OH	[2]
R _f -COONa	+	HCl	>	R _f -COOH	+	NaCl	[3]
R _f -COOH	+	SOC12	>	R _f -COCl	+ S(0 ₂ + HCl	[4]

The reaction between the Flemion acyl chloride and the CE is:



The mechanism for this reaction is most likely:

 $R_{f}-COC1 + Al_{2}Cl_{7}^{-} ---> R_{f}-CO^{+} + 2AlCl_{4}^{-}$ [6]

 $R_{f}-CO^{+}$ + CE ---> $R_{f}CO-CE^{+}$

 $R_{f}-CO-CE^{+} ---> R_{f}CO-CE + H^{+}$ [8]

[7]

 H^+ + $AlCl_4^-$ ----> HCl + $AlCl_3$ [9]

 $AlCl_3 + AlCl_4^- ---> Al_2Cl_7^-$ [10]

In this mechanism, the pyridinium heptachloroaluminate serves as both medium and catalyst for the Friedel-Crafts reaction.

Reacting the Flemion acyl chloride directly with the CE in pyridinium heptachloroaluminate (Eq.5) produced membranes with a maximum of 5% of the acyl sites bonded to crown ethers. A shift of 12 nm in the absorption maximum in the CE's UV-vis spectrum from what it was when the CE was simply dissolved in the membrane, but not reacted, indicated a chemical bond had formed, almost certainly between the CE's benzene ring and the acyl group. Moreover, the acylated CE could not be removed from the membrane whereas the dissolved CE diffused out of the membrane when it was immersed in warm methanol. Fig. 3 and Fig. 4 show the spectra of the dissolved and bonded CE s respectively. Curiously enough, CE s would bind to nearly all of the acyl sites in Nafion 901 membranes under similar conditions.(1)

The CE bonded Flemion coupons were immersed in aqueous LiCl solutions. The LiCl diffused into the membrane and formed a complex with the CE similar to that shown in Fig. 1. Evidence for complexation took the form of a significant change in the FTIR spectrum of Flemion-CE after the LiCl was added and the membrane dried under vacuum. For example, the transmittance peak at 1566 cm⁻¹ disappeared after the CE was complexed. In addition, the electrical conductivity (Table 1) of the LiCl complexed membrane was considerably higher than that of the CE bonded Flemion alone or the Flemion carboxylic acid containing LiCl. A dc of ten volts was placed across this membrane which was held between a copper anode and a platinum cathode. After several hours, the copper turned green indicating the formation of CuCl₂ and confirming that the complexed CE in the Flemion had similar properties to the solid CE-LiCl complex. Some Li also plated out at the cathode and was detected by wetting it and measuring the pH of the water, which was always The transference numbers of this material were basic. not measured.

There are several possible explanations for the consistently low yields of bonded CE s, but the most plausible is that most of the reaction occurred at, or near, the surface of the membrane and not in the interior. The morphology of the membrane (10) is such that the carboxylic acid groups, and by inference the acyl groups, arrange themselves along the inner surface of cylindrical channels running through the membrane, as shown in Fig. 5a. The acylated CE s block the entrance to these channels thereby preventing further acylations in the interior of the channel, as shown in Fig. 5b. Since under all reaction conditions used to date, the acyl groups at the mouth of a channel reacted prior to the acyl groups in the channel's interior, high yields of bonded CE s could not be obtained.

Because immersing the Flemion acyl chloride in pyridinium heptachloroaluminate containing CE gave low yields of bonded CE's, and because it was assumed the reason for this low yield was that the mouths of the channels through the membrane were blocked by bonded CE s, it was decided to circumvent this problem by first saturating the Flemion carboxylic acid membrane with CE and then refluxing this membrane in SOCl₂ to produce an acylated material whose channels were already filled with CE's. This membrane would be expected to acylate both interior and surface CE s. Pieces of this material were then immersed in the molten salt to which a small quantity of CE was added to discourage diffusion of the CE out of the membrane. As a standard, neat Flemion acyl chloride coupons were also added to the same solution. After several minutes the pyridinium heptachloroaluminate solution turned purple, as did the membranes with incorporated CE. However, the blank acylated membranes remained clear, even after several weeks in the melt. After being removed from the purple melt, the clear membrane's UV-vis spectrum showed that the CE had bound to the membrane as before.

Washing the purple membrane in water for several days did not remove the purple color nor change the membrane's weight, indicating the purple compound was too large to exit the membrane or was trapped by surface bonded CE s, not unlike a portcullis in the entrance to a castle. These membranes remained purple for several months, even when exposed to the atmosphere. The fact that the neat membrane remained clear indicated that the purple compound could not enter the membrane, either because it was too large or because the membrane's channels were again blocked by CE s at their entrances. The nature of this purple compound is currently under investigation, as are similar highly colored compounds found to form between CE and either BF_3 or $FeCl_3$. Both $FeCl_3$ and BF_3 are Lewis acids and Friedel-Crafts catalysts.

The CE saturated carboxylic acid membranes were complexed with LiCl as described above and dried under vacuum. The ionic conductivity was found to be exceedingly high (Table 1). Because this material exhibited such high conductivity, samples of the original membrane were hydrolyzed in concentrated LiOH and then saturated with CE. These membranes were then complexed with LiCl, dried under vacuum and their conductivities measured. The ionic conductivity was even greater than that of the LiCl-CE complexes in Flemion carboxylic acid and well within the fast ion conductor range. A plausible reason for the higher ionic conductivity is that there are at least two energetically nearly equivalent sites for the Li⁺ ion: on the carboxylate and in the crown. This means there is a constant ion exchange occurring. In the carboxylic acid membrane, a similar exchange between H⁺ and Li⁺ probably produces some HCl, thereby removing charge carriers from the electric field.

The Li⁺ and Cl⁻ transference numbers in the membrane were measured using the Tubandt cell described above. The data obtained is given in Table 2. The average of two separate experiments gave $t^+ = 0.6$ and $t^- = 0.4$ indicating the membrane is a solid electrolyte with mobile anions and cations.

CONCLUSION

The structure of Flemion has been altered so as to produce a material bonded to CE s which are **probably** oriented around entrances to channels through the membrane. A second material has been produced that is a fast ion conductor with mobile anions and mobile cations. A series of highly colored compounds formed between CE and Lewis acids such as BF_3 , $C_5H_6NAl_2Cl_7$ and FeCl₃ have been found.

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Table I : The Specific Conductance of Various Materials

#	Material	k (Ω cm) ⁻¹
1	Unmodified Flemion Membrane	0
2	Hydrolyzed Flemion Membrane	4.23 x 10-5
3	Complex of LiCI with CE-Flemion	1.30 x 10-5
4	Crown Ether-LiCl	1.59 x 10 ⁻⁴
5	Flemion(H+) Containing LiCl	6.57 x 10-5
6	Flemion(H+) Containing CE-LiCI	1.18 x 10 ⁻⁴
7	Flemion(Li+) Containing CE-LiCI	1.15 x 10 ⁻³
8	Complex of LiCl with CE-Nafion	2.73 x 10-3

 Table II.
 Weight Changes of the Anodic and Cathodic Membranes

 in the Tubandt Cell

#	∆Wt o <u>f</u> Cathodic	∆Wt of Anodic	t+	t-
1	4.5mg	1.0mg	0.53	0.47
2	3.1mg	1.4mg	0.69	0.31



Cl⁻ Fig. 1: Li Cl Crown Ether Complex







Fig. 3: CE Dissolved in Flemion







MOLTEN SALT REGULAR MIXTURE THEORY APPLIED TO ION EXCHANGE MEMBRANES

by

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Exchange equilibria between a cation exchange membrane and an aqueous solution were studied experimentally and theoretically. By using thermodynamic components in terms of the Gibbs phase rule, and a suitable reference state a convenient method for data treatment was obtained. Thermodynamic mixture properties were derived for four systems having a pair of monovalent cations. The results show that when the difference in cation size is small, the membrane behaves nearly ideal. For larger differences, the membrane may be described as a regular mixture. Activity coefficients for membrane mixtures can be easily obtained for regular mixtures.

INTRODUCTION

The theory of regular mixtures (1-3) has proven very useful for treating mixtures of molten salts. Molten salts can be described as consisting of a cation lattice interlocking with an anion lattice with no interchange between the two, the Temkin model (4). For mixtures where the energy of interaction between salt components is small, the configurational entropy of the mixture can be calculated on the basis of a random distribution of the cations over all cation positions, and a random distribution of the anions over all anion position (5). Such a mixture is called a regular mixture.

The Temkin model for molten salts mixtures transfers the ideas for a solid solution to the liquid. Ion exchange membranes consist of a rigid lattice of ionogenic groups carrying a positive or negative excess charge which is compensated by exchangeable ions of the opposite sign, counter ions. The ion selective membranes ought to be equally well – or even better eligible for the treatment by the regular mixture theory than mixtures of molten salts, because the lattice of ionogenic groups is fixed.

Similarly as for molten salts one may expect that the regular mixture model is no longer valid if the interaction energy between two components is very large, or if the counter ions are of very different size. If the counter ions are of different valence, one may have to take into account vacant sites in the lattice.

Because of its importance in separation processes, the ion exchange equilibrium has been the subject of numerous studies. Equilibrium data are needed to understand transport coefficients. Descriptions based on irreversible thermodynamics using an operational approach have been given (6,7). Gaines and Thomas (8) have given a general thermodynamic procedure for treating ion exchange equilibria. They included in their treatment the effects of changes in water content, and of co-ion absorption. Henry's law standard state was chosen for the solution. For the solid phase they chose as standard state, the mono-ionic membrane in equilibrium with an infinitely dilute solution of that ion. Quite complicated expressions resulted. The equilibrium constant expression contained several correction terms. Meares and Thain (9) tested the theory on experimental results from the highly swollen phenolsulphonic acid exchanger, Zeo-Karb 315. They found that correction terms were insignificant when both cations were monovalent, and the solution was dilute. More recently, Høgfeldt (10,11), Holt et al.(12), and Skrede and Ratkje (13) have treated ion exchange equilibria as regular mixtures.

One aim of the present investigation is to obtain activity coefficients for ion exchange membranes. Such data are scarce. If regular mixture theory applies, they can be readily obtained. We shall develop equations for this mixture theory for a cation selective membrane in contact with a dilute aqueous solution. The treatment will be simplified compared to other treatments, through a suitable choice of reference state. The equations have a simple form. One can easily test if regular mixture theory applies.

PRINCIPLES

The treatment will be limited to a cation selective membrane in contact with a dilute aqueous solution. The solution contains a mixture of two salts of monovalent ions. The ionic strength of the solution will be kept constant. The membrane absorbs water, but there is no solubility of negative ions in the membrane. These conditions are fulfilled with our membrane (CR 61 AZL 386 from Ionics) for an aqueous solution of 0.03 m. Temperature and pressure are kept constant. In the development we shall use thermodynamic components in terms of the Gibbs' phase rule, and we shall avoid unmeasurable quantities such as chemical potentials of single ions in agreement with refs. (6,7).

Two equilibria are established simultaneously between the membrane and the aqueous solution of the chlorides ACl and BCl:

$$H_2O(aq) = H_2O(mem)$$
[1]

$$ACl(aq) + BM = BCl(aq) + AM$$
 [2]

where $H_2O(\text{mem})$ is water dissolved in the membrane, and M^- is a cationic site in the membrane for A^+ and B^+ , AM and BM are pure mono-ionic membranes. The number of variables in equations [1,2] is six. There are two equilibrium relations between the variables, hence there are four components, C. There are two phases, Ph, and the number of degrees of freedom, F = C - Ph + 2 = 4. We perform the experiments at constant temperature and pressure, and the ionic strength of the aqueous solution is kept constant. Under these conditions, the composition of the membrane is determined unequivocally by the composition of the solution, i.e. one variable.

At equilibrium for reactions [1,2], we have:

$$\mu_{\text{HzO,mem}} - \mu_{\text{HzO,ag}} = 0$$
[3]

$$\mu_{AM} - \mu_{BM} - (\mu_{ACI} - \mu_{BCI}) = \Delta_{T}G = 0$$
[4]

The thermodynamic equilibrium constant for the reaction is:

$$K_{\rm th} = (a_{\rm BCI}a_{\rm AM}/a_{\rm ACI}a_{\rm BM}) = K'(f_{\rm AM}/f_{\rm BM})$$
^[5]

The reference state for the solutes in the aqueous solution is chosen as 0.03 *m* solution. Raoult's law standard state is used for AM and BM in the membrane. With these reference states we have the activity coefficient ratio $\gamma_{m,BCl}/\gamma_{m,ACl} \approx 1$, and thus the selectivity coefficient $K' = (m_{BCl}/m_{ACl}) \times (x_{AM}/x_{BM})$. The mole fractions in the membrane are denoted x_{AM} and x_{BM} , and m_{ACl} and m_{BCl} are molalities. At 25 °C the Henry's law ratio $\gamma_{m,BCl}/\gamma_{m,ACl} = 0.992$ for KCl and NaCl in 0.03 *m* solution (14). For the membrane, the activity coefficient $f_{AM} = 1$ for pure AM, while $f_{BM} = 1$ for pure BM, in equilibrium with 0.03 *m* solution of ACl and BCl respectively. For reaction [2] we have for the standard states:

$$\mu^{o}_{AM} - \mu^{o}_{BM} - (\mu^{o}_{ACI} - \mu^{o}_{BCI}) = \Delta_{r}G^{o} = -RT\ln K_{th}$$
[6]

From eq.[5] we have:

$$\ln K_{\rm th} = \ln K' + \ln f_{\rm AM} - \ln f_{\rm BM}$$
^[7]

This equation may be multiplied by $dx_{AM} (= -dx_{BM})$ and integrated over the range from pure AM to pure BM. Since K_{th} is a constant we obtain:

$$\ln K_{th} = \int_{0}^{1} \ln K' dx_{AM} + \int_{x_{AW}=0}^{x_{AW}=1} [\ln f_{AM} dx_{AM} + \ln f_{BM} dx_{BM}]$$
[8]

The last integral is equal to:

$$\sum_{x_{AM}=0}^{x_{AM}=1} [x_{AM} lnf_{AM} + x_{BM} lnf_{BM}] - \int_{x_{AM}=0}^{x_{AM}=1} [x_{AM} dlnf_{AM} + x_{BM} dlnf_{BM}]$$

$$I \qquad II$$
[9]

Term I of equation [9] is equal to zero. By the Gibbs-Duhem relation we have:

$$x_{AM}d\mu_{AM} + x_{BM}d\mu_{BM} + n(H_2O,mem)d\mu_{HeO,mem} = 0$$
 [10]

Since $d\mu_{H_{HO,mem}} = d\mu_{H_{HO,aq}} = 0$, also term II of equation [9] is equal to zero, and we obtain from eq.[8]:

$$\ln K_{\rm th} = \int_0^1 \ln K' dx_{AM}$$
 [11]

The $\Delta_i G^\circ$ and $\ln K_{th}$ are valid for the reaction [2] where AM and BM are pure membrane phases. When these and the water present in the membrane are mixed, the Gibbs energy of mixing is:

$$\Delta_{\text{mix}}G = x_{\text{AM}}\Delta\mu_{\text{AM}} + x_{\text{BM}}\Delta\mu_{\text{BM}} + n(\text{H}_2\text{O},\text{mem})\Delta\mu_{\text{HzO,mem}}$$
[12]

According to Helfferich (15) the water in the membrane is present as water of hydration and as free water. The mixing may lead to take-up or shedding of water from the hydration shell. The water of hydration is in equilibrium with the free water, and $\Delta \mu_{\text{HiO,mem}} = 0$ in eq.[12]. There are only two independent equilibria, those given by eqs [1,2].

The change in $\Delta_{\min}G$ with composition is:

$$d\Delta_{mix}G/dx_{AM} = (\Delta\mu_{AM} - \Delta\mu_{BM}) + (x_{AM}d\mu_{AM}/dx_{AM} + x_{BM}d\mu_{BM}/dx_{AM})$$
[13]

Here $\Delta \mu_{AM} = \mu_{AM} - \mu_{AM}^{\circ}$, and similarly for $\Delta \mu_{BM}$. The first term on the right hand side of the equation combined with eqs [4,6] gives:

$$(\Delta \mu_{AM} - \Delta \mu_{BM}) = (\Delta \mu_{ACI} - \Delta \mu_{BCI}) + RT \ln K_{th}$$
[14]

The second term on the right hand side of eq.[13] is equal to zero according to the Gibbs-Duhem relation, compare eq. [10]. Since $\Delta \mu_{ACI} = RT \ln a_{ACI}$ and similarly for $\Delta \mu_{BCI}$, we have:

$$(\Delta \mu_{\rm ACl} - \Delta \mu_{\rm BCl}) = -RT \ln K' - RT \ln(x_{\rm BM}/x_{\rm AM})$$
[15]

Hence:

$$\Delta_{\min}G = RT(x_{AM}|nx_{AM}+x_{BM}|nx_{BM}) + RT(lnK_{th}x_{AM} - \int_{0}^{x_{AM}} lnK'dx_{AM})$$
[16]

If the membrane behaves as an ideal or regular mixture we have:

$$\Delta_{\min} S = -R(x_{AM} \ln x_{AM} + x_{BM} \ln x_{BM})$$
[17]

and thus:

$$\Delta_{\min} H = RT(\ln K_{th} x_{AM} - \int_{0}^{x_{AM}} \ln K' dx_{AM})$$
[18]

For an ideal mixture $\Delta_{mix}H = 0$ and $\ln K' = \ln K_{tb}$, a constant, while for a regular mixture $\Delta_{mix}H = bx_{AM}x_{BM}$ where b is a constant independent of composition and temperature. From eq.[18] we obtain for a regular mixture:

$$d\Delta_{\rm mix} H/dx_{\rm AM} = b(1 - 2x_{\rm AM}) = RT(\ln K_{\rm th} - \ln K')$$
^[19]

This means that if the membrane behaves as a regular mixture, $\ln K'$ is a linear function of x_{AM} . The value of b can be found from the slope of the line. The value of $\ln K_{th}$ is found from the mean value of $\ln K'$, and hence $\Delta_r G^o$ for the temperature of the experiment. If experiments are carried out at different temperatures one can also obtain $\Delta_r S^o$ and $\Delta_r H^o$ for the reaction. The activity coefficients in the membrane are found from the equations for regular mixtures:

$$\ln f_{AM} = b x_{BM}^2 / RT$$
 and $\ln f_{BM} = b x_{AM}^2 / RT$ [20]

In this development the membrane activity coefficients were based on equilibrium with 0.03 *m* solution. Application of the approximation $\gamma_{m,BCI}/\gamma_{m,ACI} = 1$ is equivalent to this choice. The change to the commonly used Henry's law standard state, leads to a slight difference in the value for $\Delta_r G^{\circ}$. For the exchange reaction [2] with A⁺=K⁺ and B⁺=Na⁺ it can be shown that there will be a subtraction of 20 J mol⁻¹ when going from a 0.03 *m* solution reference state to Henry's law standard state at 25°C.

EXPERIMENTAL PROCEDURE

The experimental procedure was described in detail elsewhere (12). Only the main points are given here.

The membrane was CR 61 AZL 386 from Ionics, a cation selective membrane containing cross-linked sulfonated copolymers of vinyl compounds. Electrolyte absorption

was not detected at experimental conditions. The variation in water content of the membrane with the cations present is small (5% difference between K^* -form and Sr^{2*} -form (12)). All solutions were made from analytical grade chemicals from Merck, and ion-exchanged and distilled water. Calibrated equipment was used.

Prior to the experiments the membrane discs were kept in solutions of LiCl, NaCl, KCl or RbCl to secure the pure LiM, NaM, KM or RbM form respectively.

From stock 0.0300 *m* aqueous solutions of the above mentioned salts, nine mixtures of each pair of salt solutions, ACl-BCl, were prepared with mole fractions of BCl, x_{BCl} , equal to 0, 1/8, 2/8, ...7/8, 1. The membrane discs were equilibrated in the mixed solutions at temperatures 10°C, 25°C, and 40°C. The solution was replaced by fresh solution several times in the course of equilibration. After the equilibration the cations were eluted from the discs by means of 0.1 *m* HCl. The amount of the alkali ions was determined by flame-emission on a Perkin-Elmer spectrophotometer, type 503. Parallel experiments were carried out, using membranes of two different sizes.

RESULTS

The experimental values for large and small membranes showed no significant differences and average values were taken. From experimental values of m_{ACI} , m_{BCI} , x_{AM} , and x_{BM} the corresponding values of $\ln K'$ were calculated. These were plotted as functions of x_{AM} for each temperature, see Figs 1.a and b. In the figures were drawn theoretical lines consistent with the regular mixture theory. The slope of the line gives the value of b from:

$$b = RT(\ln K'_1 - \ln K'_0)/2$$
[21]

where $\ln K'_0$ is found by extrapolation of $\ln K'$ to $x_{AM} = 0$, and $\ln K'_1$ is found by extrapolation of $\ln K'$ to $x_{AM} = 1$. Each line is given a constant slope, consistent with the same value for b at all temperatures. The standard Gibbs energy of the reaction is:

$$\Delta_{\rm r} G^{\rm o} = -RT (\ln K_1' + \ln K_0')/2$$
[22]

The lines are given a distance that will give a constant value for $\Delta_r S^\circ = -d\Delta_r G^\circ/dT$ and $\Delta_r H^\circ = \Delta_r G^\circ + T\Delta_r S^\circ$.

It can be seen from Figs 1. a and b that the systems KM-LiM and RbM-NaM can be treated as regular mixtures. These results are correct within a small uncertainty.

The systems NaM-LiM and KM-NaM, however, seem to be near ideal mixtures, and the results are thus treated in a different manner. For an ideal mixture, $\ln K_{\rm h} = \ln K'$ and thus $\Delta_{\rm c}G^{\circ}$ was obtained from the average of experimental values for $\ln K'$ for each temperature, assuming deviations from a horizontal line for $\ln K'$ as a function of $x_{\rm AM}$ to be experimental errors. Practically constant values of $\Delta_{\rm c}S^{\circ}$ and $\Delta_{\rm c}H^{\circ}$ were obtained in the same manner as above.

Table I.Thermodynamic values for the ion exchange reactionACl + BM = BCl + AM

The aqueous solution contains 0.03 *m*. The membrane is CR 61 AZL 386. Uncertainties given are calculated from standard deviations for $\Delta_i G^{\circ}$.

А	В	Δ _r H°/kJ mol ⁻¹	$\Delta_r S^{\circ}/J \text{ mol}^{-1} \text{ K}^{-1}$	b
Na	Li	-5.3 ± 0.2	-15 ± 1	_
К	Na	-5.2 ± 0.7	-13 ± 2	-
К	Li	-9.9	-25	-1.6×10^{3}
Rb	Na	-4.5	-10	-1.0×10^{3}

The results are given in Figs 1.a and b, and Table I. It can be seen from Table I that the uncertainties are larger for the system KM–NaM than for the system NaM–LiM. The reason for this was probably lack of experimental experience, as the system KM–NaM was first studied. From the results for $\Delta_i G^\circ$ reported by Skrede and Ratkje (13), we calculate $\Delta_i S^\circ = -9 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta_i H^\circ = -4.1 \text{ kJ mol}^{-1}$. Uncertainties are not given for the systems KM–LiM and RbM–NaM, as these were obtained by a forced fit. As can be seen from Figs 1.a and b, the uncertainties are rather small.

DISCUSSION

By two examples it has been shown that the theory of regular mixtures gives a good fit with experimental data, when the system does not behave ideally. Near ideal behaviour was found for the systems NaM-LiM and KM-NaM, where there is a relatively small difference in ionic size, while a regular behaviour was found when the difference in ionic size is larger, the systems KM-LiM and RbM-NaM. (The size of the hydrated ions varies in the opposite direction to the size of the unhydrated ions).

Other examples are found in the literature, as can be shown by the linear relations between $\ln K'$ and x_{AM} (10,11). The measurements at different temperatures give a good test on the theory since the slopes of the lines as well as their separation or intercepts with the ordinate must agree with the theory.

The values of the constant b given in Table I can be used with eqs [20] to find activity coefficients of the membrane.

If the two cations are of different valence, e.g. A^+ and B^{2+} , there are more M^- sites than there are cations. We may consider two extreme cases of random distribution of the cations:

- (i) a random distribution of A $^+$ and B²⁺ over all M⁻ sites leaving some sites empty, cation vacancies CV⁻,
- (ii) a random distribution limited by the requirement that the B^{2+} ions have two M⁻ sites as neighbours.

Holt et al. (12) studied the system $KM-SrM_2$ in the membrane CR 61 386. Their results indicate presence of separate cation vacancies at low concentrations of Sr^{2+} . Høgfeldt (11) reports on a system of NaM and CaM₂ on bleached kraft pulp. The results do not indicate presence of vacancies.

The validity of the regular mixture model approach depends on the composition of the ion exchange material. Høgfeldt (11) reports many cases where $\ln K'$ is not a linear function of x_{AM} . According to our treatment the water content of the membrane should not influence the application of the regular mixture model, since the two equilibria [1,2] are independent. Any other equilibrium involving water would not be independent.

CONCLUSION

The choice of a convenient standard state leads to a simplification in the development of the theory for the equilibrium between a dilute aqueous solution and an ion exchanger. With known values for the activity coefficients in the aqueous solutions, the small correction for the change from the chosen reference state to Henry's law standard state can be calculated. Many systems fit the regular mixture model. This may prove useful when activity coefficients for the membranes are needed.

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In both figures experimental points are average values for large and small membranes, except where marked with an asterisk. These points are only based on one value. Solid lines are drawn from the regular mixture theory, and $\ln K_{th}$ are mean values of $\ln K'$.

THEORY OF THERMOCELLS; TRANSPORTED ENTROPIES AND HEAT OF TRANSFER IN SULPHATE MIXTURES

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A practical method for determination of thermoelectric powers is developed. The method includes contributions from heat capacities and Thomson effects. We have applied the method to the cell $Ag(T_1) | Ag_2SO_4-Li_2SO_4 | Ag(T_2)$, and calculated the transported entropy, S_{Agt}^* , and the heat of transfer Q^* , from thermopotential measurements. Results shows that the Thomson coefficient, τ_{Agt}^* , is significant and that S_{Agt}^* is relatively constant with structure and composition variations (0.1< $x_{Ag_2SO_4}$ < 0.175). With electrolytes containing less than 10 mole% Ag_2SO_4 , S_{Agt}^* increases strongly with decreasing composition. For solid mixtures containing 10–17.5 mole% Ag_2SO_4 , Q^* is negative and varies with composition. The negative sign indicates that Ag_2SO_4 is enriched at the hot side. For solid mixtures containing less than 10 mole% Ag_2SO_4 , Q^* is approximately zero.

INTRODUCTION

Knowledge about transported entropies is important in calculating local heat effects in electrochemical cells, fuel cells and thermoelectric generators. Few values of transported entropies have been published, and there exist no good models. Data are mainly reported for single salts. The main purpose of this work is to contribute to the understanding of transported entropies and the phenomena causing heat transport in electrochemical systems. An additional purpose is to present results for salt mixtures. We shall present data of transported entropies and heats of transfer of the cell :

$$Ag(T_1) \mid Ag_2SO_4 - Li_2SO_4 \mid Ag(T_2)$$
 [a]

There are three high temperature phases with different structures in mixtures of Ag_2SO_4 -Li₂SO₄ (1). We shall consider the Li-rich phase in the solid state, and molten and solid Ag_2SO_4 . Our theoretical derivations follow Førland et al. (2).

PRINCIPLES

The temperature difference across cell [a] causes an electromotive force (Seebeck effect), and a flux of matter (Soret effect). A current through the cell will cause Peltier effects. In the following derivation we denote Li_2SO_4 as component 1 and Ag_2SO_4 as component 2. The symbol x_i is used for the molefraction, s_i for the partial molar entropy, and S_i for the molar entropy.

Five forces exist, $-\nabla \ln T$, $-\nabla \mu_{1,T}$, $-\nabla \mu_{2,T}$, $-\nabla \mu_{Ag,T}$ and $-\nabla \varphi$. Here T is the temperature, $\mu_{i,T}$ is the chemical potential, and $\Delta \varphi$ is the electric potential. The fluxes are J_q (heat flux), J_{1} , J_2 , J_{Ag} (mass fluxes), and j, electric current density. The dissipated energy per unit time, $T\Theta$, can be expressed by:

$$T\Theta - J_{q} \nabla \ln T - J_{1} \nabla \mu_{1,T} - J_{2} \nabla \mu_{2,T} - J_{Ag} \nabla \mu_{Ag,T} - j \nabla \varphi$$
^[1]

Since there is no pressure gradient in the system, $\nabla \mu_{Ag,T} = 0$. The sulfate ion is chosen as the frame of references, i.e.

$$J_{SO_{2}^{2-}} = 0$$
 and $t_{SO_{2}^{2-}} = 0$ [2]

The condition of electro-neutrality must be fulfilled, hence :

$$J_{\text{Li}+} + J_{\text{Ag}+} - \frac{1}{2}(J_1 + J_2) - 0$$
 [3]

The chemical potentials of Li₂SO₄ and Ag₂SO₄ are dependent through the Gibbs-Duhem equation, $x_1 \nabla \mu_{1,T} + x_2 \nabla \mu_{2,T} = 0$. With the use of eq.[3] and Gibbs-Duhem eq., J_1 and $\nabla \mu_1$ can be eliminated from eq.[1]. Since the sum of the mole fractions is equal to unity, the term $(1 + x_2/x_1)$ can be reduced to $1/x_1$. This gives :

$$T\Theta - -J_q \nabla \ln T - J_2 \frac{\nabla \mu_{2,T}}{x_1} - j \nabla \varphi$$
[4]

Eq.[4] contains the three *independent* forces $-\nabla \ln T$, $-\nabla \mu_{2T}$ and $\nabla \varphi$, with the conjugate fluxes J_q , J_2 , and j. The flux equations are then :

$$J_{q} - -L_{11} \nabla \ln T - L_{12} \frac{\nabla \mu_{2,T}}{x_{1}} - L_{13} \nabla \varphi$$
 [5a]

$$J_{2} - -L_{21}\nabla \ln T - L_{22}\frac{\nabla \mu_{2,T}}{x_{1}} - L_{23}\nabla \varphi$$
 [5b]

$$j - -L_{31} \nabla \ln T - L_{32} \frac{\nabla \mu_{2,T}}{x_1} - L_{33} \nabla \varphi$$
 [5c]

The coefficients L_{ij} are the phenomenological coefficients. Positive direction of transport is from left to right, and one dimensional cases are considered. Eq.[5c] is solved with respect to $\nabla \varphi$, and introduced into eqs.[5a] and [5b]. This gives :

$$J_{q} = -l_{11} \nabla \ln T - l_{12} \frac{\nabla \mu_{2,T}}{x_{1}} + \left(\frac{L_{13}}{L_{33}}\right) j$$
 [6a]

$$J_{2} - -l_{21} \nabla \ln T - l_{22} \frac{\nabla \mu_{2,T}}{x_{1}} + \left(\frac{L_{23}}{L_{33}}\right) j$$
 [6b]

where $l_{ij} = (L_{ij} - L_{3j}/L_{33})$.

From eqs. [5a] and [5c] the Peltier heat, π , can be expressed as :

$$\left(\frac{J_{q}}{j}\right)_{\Delta T=0,\Delta \mu_{2}=0} - \frac{L_{13}}{L_{33}} - \pi$$
^[7]
There is only one *independent* transference coefficient. We choose t_2 :

$$\left(\frac{J_2}{j}\right)_{\Delta T = 0, \Delta \mu_2 = 0} - \frac{L_{23}}{L_{33}} - t_2$$
[8]

According to Onsager, the cross coefficients are related :

$$L_{ij} - L_{ji}$$
 (i.e. $l_{12} - l_{21}$) [9]

By introducing the relations given in eqs.[7], [8] and [9], into eqs.[6a] and [6b] we find:

$$J_{q} = -l_{11} \nabla \ln T - l_{12} \frac{\nabla \mu_{2,T}}{x_{1}} + \pi j \qquad [10a]$$

$$J_2 - -l_{21} \nabla \ln T - l_{22} \frac{\nabla \mu_{2,T}}{x_1} + t_2 j$$
 [10b]

Expressions for transported entropies, using well defined, measurable quantities, shall be derived. A reversible entropy balance and mass balances will be used. Consider first the local mass changes when one faraday of positive charges are transferred from left to right. The mass changes are listed in Table I. Table I shows that the transference coefficient of Ag_2SO_4 , t_2 , is equal to $-\frac{1}{2}t_{Li+}$.

The Peltier heat is obtained from a reversible entropy balance at the electrodeelectrolyte interface. We define the Peltier heat as positive if the left-hand side electrodeelectrolyte interface receives heat. Each of the contributions to the heat balance are illustrated in Figure 1, and they are listed in Table II.

From Table II we have :

$$\frac{\pi}{T} + S_{Ag} + \frac{1}{2}t_{Li+}S_1 + S_{Ag}^* - t_{Li+}S_{Li+}^* + t_{Ag+}S_{Ag+}^* + \frac{1}{2}t_{Li+}S_2$$
[11]

Left-hand side electrode (T_1)		Right-hand side electrode (T_2)	
Ag:	-1 mole	1 mole	
Ag ⁺ :	$(1-t_{Ag+}) = t_{Li+}$ mole	$-(1-t_{Ag+}) = t_{Li+} \text{ mole}$	
Li⁺ :	$-t_{\text{Li+}}$ mole	t _{Li+} mole	
Ag_2SO_4 :	$\frac{1}{2} t_{\text{Li+}}$ mole	$-\frac{1}{2} t_{\text{Li+}}$ mole	
Li ₂ SO ₄ :	$-\frac{1}{2} t_{\text{Li+}}$ mole	$\frac{1}{2} t_{\text{Li+}}$ mole	
	Junction		
Ag_2SO_4 :	$\frac{1}{2} \int dt_{\text{Li+}}$ mole		
Li ₂ SO ₄ :	$-\frac{1}{2} \int_{1}^{2} dt_{Li+}$ mole		

Table I. Local mass changes in the cell $Ag(T_1) | Ag_2SO_4-Li_2SO_4 | Ag(T_2)$. One faraday positive charges are transferred.

Table II. Reversible entropy balance at the left-hand side electrode-electrolyte interface.

The entropy consumed and received is given for the transfer of one faraday of positive charges.

ENTROPY RECEIVED				
π/T :	the interface receives entropy from the heat reservoir.			
S _{Ag} :	the disappearance of one mole Ag, liberates entropy.			
$\frac{1}{2}t_{\text{Li}+}s_1$:	the disappearance of $\frac{1}{2}t_{Li+}$ mole Li_2SO_4 , liberates entropy.			
S^*_{Ag} :	entropy transported through the electrode to the interface.			
ENTROPY CONSUMED				
$t_{\text{Li+}}S^*_{\text{Li+}}$:	entropy transported through the electrolyte away from the interface.			
$t_{Ag+}S^*_{Ag+}$:	entropy transported through the electrolyte away from the interface.			
$\frac{1}{2t_{Li+}s_2}$:	the formation of $\frac{1}{2}t_{Li+}$ mole Ag ₂ SO ₄ , consumes entropy.			

We return to eq.[5c], solve the equation with respect to $\nabla \varphi$, and introduce the relations

given in eqs.[7], [8] and [9]. This yields :

$$\nabla \varphi - -\left(\frac{\pi}{T}\right) \nabla T - t_2 \frac{\nabla \mu_{2,T}}{x_1} - \left(\frac{1}{L_{33}}\right) j \qquad [12]$$

We start with a mixture of uniform composition. The expression for the initial thermoelectric power, ε_0 , is then, from eq.[12]:

$$F\varepsilon_{0} - \left(\frac{\nabla\varphi}{\nabla T}\right)_{j=0,t=0} - \lim_{\Delta T \to 0} \left(\frac{\Delta\varphi}{\Delta T}\right)_{j=0,t=0} - \frac{\pi}{T}$$
[13]

where F is the Faraday's constant.

When eqs.[11] and [13] are combined, and remembering that $t_{Ag+} = (1-t_{Li+})$, the following expression for the initial thermoelectric power is obtained :

$$F\varepsilon_{0} - S_{Ag} + S_{Ag}^{*} - S_{Ag+}^{*} + \frac{1}{2}t_{Li+} \left[(s_{1} - s_{2}) - 2(S_{Li+}^{*} - S_{Ag+}^{*}) \right]$$
[14]

At stationary state the flux J_2 is zero. Then the net entropy change in the electrolyte at the interface is the same as that caused by the transport of one mole of Ag⁺ away from the interface. This gives (3) :

$$S_{Ag+}^{*} - t_{Ag+}S_{Ag+}^{*} + t_{Li+}S_{Li+}^{*} - \frac{1}{2}t_{Li+}S_{1} + \frac{1}{2}t_{Li+}S_{2} + \frac{1}{2}t_{Li+}\frac{Q}{T}^{*}$$
[15a]

Rearranging this equation and remembering that $t_{Ag+} = (1-t_{Li+})$ we obtain :

$$\frac{Q}{T}^* - s_1 - s_2 - 2(S_{\text{Li}*}^* - S_{\text{Ag}*}^*)$$
[15b]

All the terms in eq.[15b] are independent of forces, and the equation is valid whether we have stationary state or not. We can then combine eqs.[14] and [15b].

$$F\varepsilon_0 - S_{Ag} + S_{Ag}^* - S_{Ag+}^* + \frac{1}{2}t_{Li+}\frac{Q}{T}$$
[16]

There is only one observable heat of transfer in our system. This heat of transfer, Q', is defined as :

$$\left(\frac{J_{q}}{J_{2}}\right)_{\Delta T=0,j=0} - \frac{l_{12}}{l_{22}} - Q^{*}$$
[17]

Eq.[10b] is solved with respect to $\nabla \mu_{2,T}/x_1$ when $J_2 = 0$ (i.e. stationary state). This gives:

$$\left(\frac{\nabla \mu_{2,T}}{x_1}\right)_{t=\infty} - \left(\frac{Q}{T}\right) \nabla T + \left(\frac{t_2}{t_{22}}\right) j$$
[18]

Remembering that $t_2 = -\frac{1}{2}t_{\text{Li+}}$, a combination of eqs.[12] and [18] yields :

$$\mathbf{F}\boldsymbol{\varepsilon}_{\infty} - \left(\frac{\nabla\varphi}{\nabla T}\right)_{\mathbf{j}=0,\mathbf{t}=\infty} - \lim_{\Delta T \to 0} \left(\frac{\Delta\varphi}{\Delta T}\right)_{\mathbf{j}=0,\mathbf{t}=\infty} - \frac{\pi}{T} - \frac{1}{2}t_{\mathbf{L}\mathbf{i}} + \frac{Q}{T}^{*}$$
[19]

By introducing eqs.[11] and [15b] into eq.[19] we obtain the transported entropy of Ag^+ , the ion to which the electrode is reversible:

$$S_{Ag+}^* = S_{Ag} + S_{Ag}^* - F\varepsilon_{\infty}$$
 [20]

The expression for the heat of transfer is obtained from a combination of eqs.[13] and [19].

$$\frac{Q^*}{T} - \frac{F(\varepsilon_0 - \varepsilon_{\infty})}{\frac{1}{2}t_{\text{Li}*}}$$
[21]

Thermoelectric powers are usually determined from plot of $\Delta \varphi$ versus ΔT . The entropy is generally a function of temperature. For large values of ΔT , the variation with T must be taken into account. We return to eq.[20], and assume that $S_{Ag}^* \approx 0$ (9). This gives:

$$\Delta \varphi_{t-\infty} - \int_{T_1}^{T_2} (S_{Ag} - S_{Ag+}^*) dT$$
 [22]

For constant $C_{P,i}$, the molar entropy, S_i , is :

$$S_{i}(T) - S_{i}(T_{1}) + C_{p,i} \int_{T_{1}}^{T} \frac{dT}{T} - [S_{i}(T_{1}) - C_{p,i} \ln T_{1}] + C_{p,i} \ln T$$
 [23a]

We can then carry out the integration of $S_i dT$ from T_1 to T_2 .

$$\int_{T_{1}}^{T_{2}} S_{i} dT - S_{i}(T_{1}) \Delta T + C_{P,i} \left[\ln \left(\frac{T_{2}}{T_{1}} \right)^{\frac{T_{2}}{\Delta T}} - 1 \right] \Delta T$$
[23b]

In the same way, we can find S_i^{\bullet} as a function of the temperature, when the Thomson coefficient, τ_i , is constant. We are now able to express $\Delta \varphi_{t=\infty}$ as a function of ΔT when T_1 is fixed. When all expressions are introduced into eq.[22], we get :

$$\Delta \varphi_{t-\infty} - [S_{Ag}(T_1) - S_{Ag+}^*(T_1)] \Delta T + [C_{P,Ag} - \tau_{Ag+}] \left[\ln \left(\frac{T_2}{T_1}\right)^{\frac{T_2}{\Delta T}} - 1 \right] \Delta T$$
[24]

The term $[\ln(T_2/T_1)^{T2/AT_1} - 1]$ in eq.[24] has the limit value 0, when $\Delta T \rightarrow 0$. Similar expressions can be derived for other thermocells like e.g. $X_2 \mid AX \mid X_2$ and $A \mid AX \mid A$ (3). If $\Delta T/T_1 \ll 1$ we can introduce the approximation $\ln(T_2/T_1) \sim \Delta T/T_1$. By introducing this approximation into eq.[24], we obtain :

$$\Delta \varphi_{t-\infty} = \left[S_{Ag}(T_1) - S_{Ag+}^*(T_1) \right] \Delta T + \left[\frac{\left(C_{p,Ag} - \tau_{Ag+} \right)}{T_1} \right] \Delta T^2$$
[25]

This equation shall be used for evaluation of measurements.

EXPERIMENTAL

All experiment were performed in a "standard laboratory furnace". Details of its construction have been given by Motzfeldt (4). The cell inside the furnace is shown in Figure 2. An extra heating element (C in Figure 2), made from Kanthal wires embedded in aluminum cement, was used to produce temperature differences over the electrolyte. The furnace and the inner heating element were controlled separately by two temperature regulators. To reduce temperature variations, the thermocouples for control (D in Figure 2) of the extra heating element and the heating element were placed as close as possible to the Kanthal windings. The temperatures were measured with two Pt/Pt10Rh thermocouples. The silver electrodes were connected to a Hewlett Packard digital multimeter (HP 3457A). The *emf* was determined to an accuracy of $\pm 2 \cdot 10^{-6}$ V. N₂(g) was used as a protection gas in all experiments.

The solid mixtures were made by melting dried Li_2SO_4 (Merck, Darmstad, Germany) at about 900°C. A Ag_2SO_4 crystal was then dropped into the melt. The Ag_2SO_4 melted and dissolved quickly. After some stirring, the mixture was rapidly cooled by placing the cell into ice. The mixture was then grounded to a fine powder, filled into a quartz cell and pressed together with a silver electrode at each end. For sintering, and to smooth out concentration gradients, the cell was placed in the furnace, at the actual temperature, for at least a day before starting the measurements.

To determine the initial thermoelectric power, the emf was measured at various

temperature differences in the range -10° C to 30° C. The length of the sample was about 7 cm. The temperatures at the top and the bottom of the sample were measured with two thermocouples, F in Figure 2, placed close to the electrodes. At the start of each measurement, the temperature difference, between the top and the bottom of the cell, was zero. The temperature on the top was increased. After about 15 minutes the temperatures became stable, and the *emf* and both temperatures were recorded. After each measurement the temperature difference was reset to zero, and maintained at zero for at least 30 minutes before changing the temperature again. This procedure was repeated for several temperature differences.

The same arrangement was used for determination of the thermoelectric power at stationary state. However, in this case the length of the sample was smaller. The distance between the electrodes was 1.5 cm. The procedure was as follows: First the temperature difference was set to a few degrees. The *emf* and temperatures were recorded after 3 days. Then the temperature difference was increased by a few degrees by increasing the temperature on the top, and the *emf* and temperatures were recorded after 2 days. This procedure was repeated for several temperature differences. Tyrrel (5) has derived the time dependency of the thermoelectric power :

$$\varepsilon_t - \varepsilon_{\infty} - \frac{8(\varepsilon_{\infty} - \varepsilon_0)}{\pi^2} \exp(-t/\theta)$$
 [26]

$$\theta - \frac{h^2}{D\pi^2}$$
[27]

Here θ is the characteristic time and governs the rate at which the steady state equilibrium is established, *h* is distance between the electrodes, and *D* is the diffusion coefficient. If we assume that *D* is of the magnitude $1 \cdot 10^{-5}$ cm² s⁻¹, an electrode distance of 1.5 cm will correspond to $\theta \approx 6.5$ hrs. A running time of 48 hrs will be equal to 7.5 θ .

RESULTS

Typical experimental observations for the *emf*, $\Delta \phi$ of the cell [a] as a function of ΔT at stationary state, are shown in Figure 3. Eq.[25] contains a second order term in ΔT . Therefore "general regression significance tests" (6) were performed. In this case this means a check of the significance of adding a second order term to a linear model. For all compositions the adding of a second order term were found to be significant (95% confidence level). As a consequence, second order terms were included in the regression model for fitting the data (i.e. $\Delta \phi_{\infty} = A + B\Delta T + C\Delta T^2$). The thermoelectric powers at

stationary state, ε_{∞} , are summarized in Table III.

Table III. Thermoelectric power, \in_{∞} , at stationary state in the cell Ag | Ag₂SO₄-Li₂SO₄ | Ag.

The quoted errors are standard deviations. The number of experimental points, n, in the determination is given in parenthesis.

mole% Ag ₂ SO ₄	$\epsilon_{\infty} (mV K^{-1})$	T ₁ (°C)
5.0	-0.659 ± 0.004 (n=16)	590
7.5	-0.558 ± 0.004 (n=70)	590
10.0	$-0.279 \pm 0.005 $ (n=32)	555
12.5	$-0.326 \pm 0.011 $ (n=29)	543
15.0	$-0.289 \pm 0.004 $ (n=28)	540
17.5	-0.355 ± 0.002 (n=33)	540

Table IV. Thermoelectric power, \in_0 , at initial state in the cell Ag | Ag₂SO₄-Li₂SO₄ | Ag.

The quoted errors are standard deviations. The number of experimental points, n, in the determination is given in parenthesis.

mole% Ag ₂ SO ₄	$\epsilon_0 (mV K^{-1})$	T ₁ (°C)
5.0	$-0.652 \pm 0.001 $ (n=44)	590
7.5	-0.550 ± 0.001 (n=43)	590
10.0	-0.541 ± 0.002 (n=15)	555
12.5	$-0.546 \pm 0.005 $ (n=15)	543
15.0	-0.485 ± 0.005 (n=14)	540
17.5	-0.472 ± 0.005 (n=7)	540

In a similar way, as for the stationary state data, the significance of adding a second order term for the fitting of the initial state data was tested. For this case, however, the addition of a second order term was not found to be significant (95% confidence level). Hence the results were fitted to linear regression models. A typical plot of $\Delta \varphi$ versus ΔT for experimental observations at initial state are shown in Figure 4. The thermoelectric powers at initial state, ε_{0} , are given in Table IV.

From the plot of $\Delta \varphi$ versus ΔT for the thermocell Ag | Ag₂SO₄ | Ag, the addition of a second order term was found to be significant in the solid state, but not in the molten state. The thermoelectric power in pure silver sulphate, ε , is given in Table V.

SOLID Ag ₂ SO ₄			
T ₁ = 500°C $\epsilon = -0.438 \pm 0.008 \text{ (mV K}^{-1} \text{)} \text{ (n=34)}$			
MOLTEN Ag_2SO_4			
$T_1 = 680^{\circ}C$	$\varepsilon = -0.316 \pm 0.003 (\text{ mV } \text{K}^{-1}) (n=7)$		

Table V. Thermoelectric power, \in , in the cell Ag | Ag₂SO₄ | Ag. The quoted errors are standard deviations. The number of experimental points, n, in the determination is given in parenthesis.

Table VI. Transported entropies of the silver ion, S_{Ag+}^* , in the cell Ag | Ag₂SO₄-Li₂SO₄ | Ag.

The quoted errors are standard deviations. All values are for solids except the one with pure Ag_2SO_4 at $T=680^{\circ}C$.

mole% Ag ₂ SO ₄	S^{\bullet}_{Ag+} (J K ⁻¹ faraday ⁻¹)	<i>T</i> (°C)
5.0	134.5 ± 0.4	590
7.5	124.8 ± 0.4	590
10.0	96.6 ± 0.4	555
12.5	101 ± 1	543
15.0	97.1 ± 0.4	540
17.5	103.5 ± 0.2	540
100	110.1 ± 0.7	500
100	104.3 ± 0.3 (molten)	680

Transported entropies of the silver ion, S_{Ag+}^{*} , calculated from eq.[20] are listed in Table VI. The values of S_{Ag} used in the calculations, were taken from Barin (7). The heat of transfer, Q^{*} , calculated from eq.[21] is listed in table VII. The transference number of silver ion, t_{Ag+} , was taken from Øye (8).

mole% Ag ₂ SO ₄	$-Q^*$ (kJ mole ⁻¹)	T (°C)
5.0	-1 ± 1	590
7.5	-2 ± 1	590
10.0	49 ± 2	555
12.5	42 ± 3	543
15.0	39 ± 2	540
17.5	24 ± 1	540

Table VII. Heat of transfer, Q^* , in solid mixtures of Ag₂SO₄-Li₂SO₄. The quoted errors are standard deviations.

DISCUSSION

Thermoelectric power and Thomson coefficient of Ag⁺, τ_{Ag+} .

The thermoelectric powers obtained in this work are all negative. This means that heat is transported from low to high temperature.

Our method for determination of thermoelectric power include a second order term, see eq.[25]. With pure Ag_2SO_4 as electrolyte, we find that the second order term is significant in the solid state, but not in the molten state (data not shown). This is in agreement with observations by Kvist and Randsalu (9). They found that the temperature dependency of the thermoelectric power, of the cell with solid Ag_2SO_4 , could be described by a linear relation. With molten Ag_2SO_4 as electrolyte, no temperature dependency of ε was observed. The temperature dependency reported by these authors cannot be directly compared with our result for the second order term, because they used a different calculation technique.

The second order term is significant for ε of all *mixtures* at stationary state. The magnitude of the second order terms varies somewhat with composition, but it is mainly of the same magnitude as $C_{\text{P,Ag}}/T_1$. The standard deviation of the calculated second order terms were rather high, about 25% of the estimated value. The second order term was not significant for ε_{0} .

The experimental results for the thermoelectric power of a cell with pure Ag_2SO_4 can be compared with results reported in the literature (9,10). With molten Ag_2SO_4 as

electrolyte we obtain the thermoelectric power $-0.316 \pm 0.003 \text{ mV K}^{-1}$. This result agrees well with the values -0.31 mV K^{-1} (9) and -0.33 mV K^{-1} (10). With solid Ag₂SO₄ as electrolyte (T= 500°C), we obtain $\varepsilon = -0.438 \pm 0.008 \text{ mV K}^{-1}$. This agrees reasonably well with the value -0.45 mV K^{-1} reported by Kvist and Randsalu (9). The result reported by Glagoleva and Markov (10), -0.47 mV K^{-1} , is somewhat higher than our result. Glagoleva and Markov determine the thermoelectric power by fitting the plot of *emf* versus ΔT to a straight line, ΔT being in the range -66° C to 65° C. Thus, the difference between theirs and our result is due to different measuring and calculation techniques.

We conclude that entropy variations with temperature may be significant for thermoelectric powers. This has a bearing on the practical method used for its determination. We have developed a procedure which takes second order terms into account. The procedure should be applicable in other contexts. For solid mixtures of Ag₂SO₄-Li₂SO₄, and for Ag₂SO₄(s) we have confirmed by statistical methods that τ_{Ag+} is smaller than $C_{P,Ag}$. For Ag₂SO₄(l) we conclude that $\tau_{Ag+} \approx C_{P,Ag}(680^{\circ}\text{C}) = 30 \text{ J K}^{-1}$ faraday⁻¹.

The transported entropy of Ag⁺

Values presented in Table VI for the transported entropy of the silver ion, $S'_{\Delta g+}$, vary relatively little with composition, when $0.1 < x_{Ag,SO_4} < 0.175$. The change from solid to molten state also has a small bearing on S'_{Ag+} (Table VI).

The structure of the high temperature modification of pure Ag_2SO_4 is hexagonal, while the structure of Ag_2SO_4 -Li₂SO₄ in the Li-rich phase is cubic face centered (1). The transported entropy does not seem to depend on these structure variations. A similar result for $S_{0^{2-}}^*$ was obtained by Tomii and Ratkje (11) for solid mixtures of ZrO_2 and Y_2O_3 .

Kvist (12) measured the specific conductance, κ, in Ag₂SO₄-Li₂SO₄ mixtures. The activation energy of conductivity, E_a , was calculated from a plot of ln(*T*κ) versus 1/T. Results are $E_a=20$ kJ mol⁻¹ for molten Ag₂SO₄, $E_a=117$ kJ mole⁻¹ for solid Ag₂SO₄, and $E_a=42$ kJ mol⁻¹ for solid Ag₂SO₄-Li₂SO₄ containing 17.5 mole % Ag₂SO₄. No correlation between E_a and ε_o or S_{Age}^+ can be predicted from these results, as expected from a theory of Rice and Roth (13). Similar tendencies were observed by Tomii and Ratkje (11).

The transported entropy is calculated for the ion in the electrolyte which is reversible to the electrode. Results reported in the literature were used to analyze possible variations in S_{Ag+}^{*} with the remaining ions in the electrolyte. Data are mostly available for pure salts. For the thermocell $Cl_2(g) \mid MCl \mid Cl_2(g)$, with M = Li, Na, K, Rb, Cs; we find that S_{Cl}^{*} varies between 81 and 92 J K⁻¹ faraday⁻¹ (14,15). For the thermocell Ag | AgX | Ag, with X= Cl, Br, I; S_{Ag+}^{*} varies between 104 and 119 J K⁻¹ faraday⁻¹ (16–18). Vreuls (19) has calculated S_{Ag+}^{*} for the thermocell Ag | AgNO₃–MNO₃(l) | Ag, with M= Li,Na,K,Rb,

and Cs. For all compositions with more than 20 mole% AgNO₃ at T=633, except for M=Cs, the results were between 88 and 110 J K⁻¹ faraday⁻¹. In mixtures containing less than 10 mole% Ag₂SO₄, the transported entropy increases strongly with decreasing composition. This tendency was also reported by Vreuls (19) for cells with AgNO₃-MNO₃, M=Li,Na,K,Rb and Cs. We may also note that the value of S_{Agt}^{*} is almost the same in sulphate and nitrate mixtures. Furthermore it is clear that the model of Ødegård et al.(21), using $S_{M+}^{*}=S_{M}$ in fluoride melts, is not valid. The molar entropy of Ag differs by 40–50 J K⁻¹ mol⁻¹ from S_{Agt}^{*} . We conclude that the transported entropy is little affected by the presence of other ions in the electrolyte, provided there is a minimum amount of the ion reversible to the electrode. For mixtures containing small amounts (< 0.1) of the silver ion, the transported entropy seem to be strongly affected by concentration changes. We have no explanation for this at present.

The heat of transport in Ag₂SO₄-Li₂SO₄

The values obtained for the heat of transfer are all negative for mixtures containing 10 mole%-17.5 mole% Ag₂SO₄. The negative sign means that Ag₂SO₄ is enriched at the hot side, see eq.[18]. In this concentration range the absolute value of the heat of transfer increases with decreasing mole fraction of Ag₂SO₄, see also Table VII. In mixtures containing less than 10 mole% of Ag₂SO₄ the heat of transfer is approximately zero. This is in agreement with earlier observations by Lunden and Olsson (20). They have studied thermal diffusion in Ag₂SO₄-Li₂SO₄ containing 4–5 mole% Ag₂SO₄. Their reported Soret coefficient corresponds to $Q^* = -2 \pm 2$ kJ mole⁻¹. Vreuls (19) also reports that the heat of transfer becomes zero in systems of the type AgNO₃-MeNO₃, Me=Li,Na,K,Rb, and Cs, when the mole fraction of AgNO₃ becomes small (less than 0.1). Since we found that the second order term is not significant for ε_0 , we expect that the "heat capacity" of Q'/T in the solid mixtures, is of the same magnitude as $-2C_{P,A_2}/t_{Li+}$, see eq.[16].

Haase (22) and Kempers (23) have proposed that the heat of transfer is a function of the partial molar enthalpy of the components in the mixture. We shall show in a future work that this model is unlikely from a theoretical point of view.

At this point we emphasize the difference between the two quantities. S_{Ag+}^* is a property of the cell and the electrode-electrolyte interface, while Q^* is a property of the electrolyte only.

CONCLUSION

A new method for determination of thermoelectric powers is presented. We have applied the method to the cell $Ag(T_1) | Ag_2SO_4 - Li_2SO_4 | Ag(T_2)$, and calculated the transported entropy, $S_{Ag_4}^*$, and the heat of transfer Q^* .

The result extends and enhances information presented on thermocells by earlier investigators. The transported entropy of the ion reversible to the electrode is fairly independent of the other cation or anion present in the mixture, while the heat of transport show a larger relative variation at moderate concentrations. At low concentrations of Ag^+ this picture changes. There are no good models for the heat of transport as well as for the transported entropy. More work must be done, to get a better understanding of these important effects.

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Figure 1. Schematic illustration of the thermocell Ag | Ag₂SO₄-Li₂SO₄ | Ag.



Figure 2. Cell and furnace, cross section.



Figure 3. Plot of $\Delta \varphi_{\infty}$ versus ΔT for the cell $Ag(T_1) \mid Ag_2SO_4 - Li_2SO_4 \mid Ag(T_2)$.

The plot is shown for a electrolyte containing 15 mole% Ag_2SO_4 . $\Delta \phi_{\infty}$ is the emf at stationary state. T_1 is held constant at 540°C.



Figure 4. Plot of $\Delta \varphi_0$ versus ΔT for the cell $Ag(T_1) \mid Ag_2SO_4 - Li_2SO_4 \mid Ag(T_2)$.

The plot is shown for a electrolyte containing 5 mole% Ag_2SO_4 . $\Delta \phi_0$ is the emf at initial state. T_1 is held constant at 590°C.

The Nature of Proton in Ambient-Temperature Chloroaluminate Molten Salts

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ABSTRACT

Proton is a ubiquitous contaminate in ambient-temperature molten salts composed of mixtures of aluminum chloride and 1-ethyl-3-methylimidazolium chloride (ImCl). FT-IR, NMR, and electrochemistry have been used to study the nature of proton in these ionic liquids. In oxide free basic melts (excess ImCl) there exist two forms of proton, HCl and HCl_2^- , which are in an equilibrium that strongly favors the formation of the hydrogen dichloride ion. In oxide free acidic melts (excess AlCl₃) HCl is the only proton containing species present. The HCl vapor pressure in basic and acidic melts is sufficiently high such that evacuation effectively removes HCl and subsequently all proton from the melts.

INTRODUCTION

Chloroaluminate molten salts, composed of mixtures of aluminum chloride with either N-butylpyridinium chloride (BuPyĈl) or 1-ethyl-3-methylimidazolium chloride (ImCl), are liquid at or below ambient-temperature over a wide range of compositions. When the mole ratio of AlCl₃ to organic chloride is greater than, less than, or equal to unity, these liquids are characterized as acidic, basic, or neutral, respectively. These ambient-temperature ionic liquids were initially thought to be aprotic and totally anhydrous solvents (1-3). However, subsequent studies showed this not to be the case (4,5). The extremely hygroscopic organic chlorides (BuPyCl and ImCl) used in these melts, when prepared by normal methods, are invariably contaminated by small quantities of water. When these salts are mixed with AlCl₃, the resulting melts contain millimolar quantities of both oxide and proton impurities. The ubiquitous nature of these impurities and their reactivity towards solutes necessitates a clear understanding of their chemistry if the ambient-temperature chloroaluminates are to be routinely employed as solvents. As part of an ongoing effort in this laboratory investigating the chemistry of water in the chloroaluminate molten salts, we have employed FT-IR, NMR, and electrochemistry to investigate the various proton containing species in the melts. Furthermore, we have employed the information obtained on proton speciation to develop a clean and efficient method for removal of proton from the melts.

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EXPERIMENTAL

All melt preparation and electrochemical experiments were performed in a Vacuum Atmospheres drybox under a nitrogen atmosphere. The preparation of ImCl and AlCl₃ was performed as previously described (6,7). All basic melts were treated with phosgene and evacuated to remove oxide and proton impurities. A detailed description of the phosgene and vacuum procedure is given elsewhere (8). Acidic melts were prepared by adding AlCl₃ to a slightly basic melt (0.99:1.0) that had been treated with phosgene and vacuum. Slightly acidic and slightly basic melts (0.95:1.0 to 1.1:1.0) were prepared from an oxide and proton free neutral melt by addition of small amounts of either ImCl or AlCl₃ (7). 1– ethyl–3–methylimidazolium hydrogen dichloride (ImHCl₂) and its deuterated analogue 1– ethyl–3–methylimidazolium deuterium dichloride (Im²HCl₂) were used in the AlCl₃:ImCl melts as quantitative sources of proton and deuteron, respectively, and were prepared by reacting liquid hydrogen chloride with ImCl (9). ²H₂O (99.98%) and H₂¹⁷O (20% isotopic enrichment) were obtained from Cambridge Isotope Laboratories.

NMR samples were prepared in the drybox, pipetted into 10–mm NMR tubes (Wilmad Glass Co.), and then capped and sealed with parafilm. The NMR samples of acidic melts saturated with ²HCl were placed in 9" long 10–mm tubes with a constriction at 8" (Wilmad Glass Co.). These NMR tubes were filled with melt in the drybox, attached to a vacuum line, saturated with ²HCl (98% D, Cambridge Isotope Laboratories), and then sealed. Natural abundance D_2O in water was the reference for the ²H NMR analyses, and natural abundance $H_2^{17}O$ in water was used as the reference for the ¹⁷O NMR analyses. Both references were assigned a value of 0 ppm with referencing performed by substitution. All ²H and ¹⁷O NMR spectra were acquired with the spectrometer unlocked. The ²H and ¹⁷O NMR experiments were performed using a Varian VXR–400 S, operating at 61.395 and 54.219 MHz, respectively.

The electrochemical experiments were performed using an EG&G PARC Model 273 Potentiostat/Galvanostat controlled by a PDP–8e computer (10). Normal Pulse Voltammograms (NPV) were recorded at 25 °C with a pulse time of 0.1 s and a waiting time of 7 s (the waiting time included 3 s of stirring). The working electrode was a platinum disk (area 0.02 cm^2) obtained from Bioanalytical Systems. The reference electrode was an Al wire (5N Alfa Inorganics) immersed in a 1.5:1.0 AlCl₃:ImCl melts in a separate fritted tube. The counter electrode was a platinum flag.

Infrared data were collected using a MIDAC High Resolution FT–IR Spectrometer. All spectra were acquired at 4 cm⁻¹ resolution with a total of 100 scans acquired per spectrum. The temperature of the sample compartment was 30 ± 1 °C. The sample cell and handling procedures used were the same as those employed by Tait and Osteryoung (11).

RESULTS AND DISCUSSION

NMR Studies of Deuteron in Oxide Free Melts

In an earlier study Zawodzinski and Osteryoung (9) presented data showing the effect of melt composition on the ²H NMR chemical shift of ²HCl. These data, after

changing the referencing to D_2O and correcting the melt composition for the addition of chloride from Im^2HCl_2 , are shown in Figure 1a. We repeated this experiment, and the data are shown in Figure 1b (12). Both sets of data in Figure 1 exhibit a strong dependence of the ²HCl chemical shift on melt composition. Zawodzinski and Osteryoung (9) explained this dependence by suggesting that deuteron speciation in the melts can be described by the equilibrium

2
HCl + Cl⁻ \Longrightarrow 2 HCl₂⁻ [1]

which is in fast exchange on the NMR time scale. The high chloride concentrations in the basic melts (excess ImCl) shift the equilibrium towards formation of the ${}^{2}HCl_{2}^{-}$ ion. In acidic melts (excess AlCl₃) the absence of chloride ion leaves ${}^{2}HCl$ as the sole deuteron containing species.

The chemical shifts for the data of Zawodzinski and Osteryoung in the basic melts are consistently less than our data. This may be due to differences in experimental temperature (90 vs. 30 °C) and the presence of small amounts of oxide impurities in the melts of Zawodzinski and Osteryoung. Our melts were treated with phosgene prior to use to remove all oxide impurities (8). Still, the behavior of both sets of data in the basic melts (Figure 1) are consistent with an equilibrium between ${}^{2}\text{HCl}_{2}^{-}$ and ${}^{2}\text{HCl}$ (Equation 1).

In the acidic melts, Zawodzinski and Osteryoung (9) gave the chemical shift of ²HCl as 2.4 ppm. Our initial ²H NMR studies of ²HCl in acidic melts appeared to agree with this assignment with the exception of the neutral melt where we found the chemical shift of ²HCl to be -2.9 ppm. This inconsistency lead us to conduct more detailed experiments which eventually showed that the peak assigned to ²HCl at 2.4 ppm was, in fact, deuterium at the 4,5 position on the imidazolium cation ring. Further experiments with time resolved FT–IR spectroscopy demonstrated that deuterium from ²HCl was exchanging with protium at the 4,5 position of the imidazolium ring. The details of this hydrogen–deuterium (H–D) exchange on Im⁺ will be described in a separate article in these proceedings (13).

During the experiments of Zawodzinski and Osteryoung (9) enough time apparently elapsed between sample preparation and spectral acquisition for all the ²HCl to be converted to HCl. Also the NMR experiments of Zawodzinski and Osteryoung were perfored at 90 °C where the rate of H–D exchange is significantly greater that at 30 °C (see below). Thus, they only observed the deuterium signal from the ²H–4,5 on the imidazolium ring. In our experiments we were able to obtain chemical shift data for ²HCl in the actual dependence of the ²HCl chemical shift does not remain constant through the actual dependence of the ²HCl chemical shift does not remain constant through the acidic melt region, but shifts from –2.9 to –3.6 ppm going from a 1.0:1.0 to a 1.976:1.0 melt, respectively. The upfield shift in the ²HCl menter is toward the gas phase value (14). This indicates an increase in charge density on the deuterium and a corresponding increase in covalent character of the ²H–Cl bond. From this one may infer that ²HCl becomes less solvated as the melt acidity increases.

Although there were some errors in their data the conclusions drawn by Zawodzinski and Osteryoung (9) about the deuteron (and proton) equilibrium are essentially correct. In the absence of oxides the deuteron equilibrium is described by Equation 1. In the basic melts ${}^{2}\text{HCl}_{2}{}^{-}$ and ${}^{2}\text{HCl}$ are in fast exchange under equilibrium control, and in acidic melts ${}^{2}\text{HCl}$ is the only deuteron containing species.

FT-IR Studies of Proton and Deuteron in Oxide Free Melts

FT-IR spectroscopy was used to confirm the conclusions made from the above ²H NMR studies. Figure 2a shows the spectrum of a 0.394:1.0 melt containing 98.6 mM ²HCl after the melt background has been subtracted. The spectrum of the same melt containing instead 122.4 mM HCl is displayed in Figure 2b. The absorption features and isotopic shift of the spectra in Figure 2a and b are essentially the same as those of ²HCl₂⁻ and HCl₂⁻, respectively, in nonaqueous solvents (15). The absorbance features of HCl₂⁻ and ²HCl₂⁻ in the basic melts are compared in Table I with the features found for these molecules in acetonitrile. The work of Evans and Lo (15) showed that the dichloride ion in acetonitrile leads us to conclude that the HCl₂⁻ and ²HCl₂⁻ bands in the basic melts also exists as a linear symmetrical species.

The background subtracted spectra of 98.9 mM ²HCl in a 0.9973:1.0 melt (12.5 mM Cl⁻) and 125.6 mM HCl in a 0.9971:1.0 melt (13.2 mM Cl⁻) are shown in Figures 3a and b, respectively. The shape, position, and isotopic shift of the bands in Figure 3 are characteristic of hydrogen chloride (16,17). Hydrogen chloride was the only proton containing species observed in oxide free acidic melts; this is in agreement with the ²H NMR data presented above and with the conclusions made by Smith et al. (18). The HCl and ²HCl fundamental vibration bands from Figure 3 and two other acidic melts are given in Table II. For comparison the vibration bands of hydrogen chloride in several solvents are also given in Table II. The shape and isotopic shift of the hydrogen chloride band remained relatively constant throughout the acidic melts. However, the position of the band shifted towards higher wavenumbers as the melts were made more acidic. The shift in HCl vibration frequency to higher wavenumbers for the solvents in Table II has been attributed to a decrease in the association of the solvent with the HCl dipole (19). Consequently, the increase in the HCl vibration frequency with increasing melt acidity seems to indicate a significant decrease in the interaction of the solvent with HCl. A similar conclusion was reached from the upfield shift in the ²HCl resonance at higher Al₂Cl₇⁻⁻ concentrations (see above). Interestingly, this decrease in solvent interaction occurs in conjunction with an increase in the Brønsted superacidity of HCl (18,20). However, the relationship between these two phenomena is still not clear.

The above data confirm the presence of HCl and HCl_2^- in the AlCl₃:ImCl melts. To demonstrate the equilibrium between these two species infrared spectra were obtained for 124 mM HCl in basic melts containing 210, 78, 31, and 13 mM Cl⁻. Figure 4 shows this family of spectra. The presence of two isosbestic points at 2820 and 2350 cm⁻¹ is indicative of an equilibrium between HCl and HCl₂⁻ (21). Figure 4 also demonstrates that in basic melts the proton equilibrium (Equation 1) strongly favors the formation of HCl₂⁻, and only under conditions of very low chloride concentrations are significant amounts of

HCl present; these observations are in complete agreement with the ²H NMR data presented above.

Proton Removal from Basic and Acidic Melts

As has been demonstrated above, hydrogen chloride exists in both acidic and basic melts. In addition to the equilibrium with hydrogen dichloride ion (Equation 1), HCl in the melts is also in equilibrium with HCl in the gas phase. We have found that HCl may be removed from the melts by evacuation to a pressure significantly less than the HCl vapor pressure; this, in turn, displaces the melt proton equilibrium towards formation of HCl and after several hours of evacuation results in the complete removal of proton from the melts. Figure 5a shows the ${}^{2}H$ NMR spectrum and Figure 6a shows the normal pulse voltammogram (NPV) of an oxide free 0.8:1.0 melt containing 19.8 mM ²HCl. The large ²H peak in Figure 5a at 7.9 \pm 0.1 ppm corresponds to the population weighted average of the ${}^{2}HCl$ and ${}^{2}HCl_{2}^{-}$ resonances under fast exchange conditions, and the smaller peaks are the natural abundance deuterium resonances for Im⁺. The wave at ca. -0.35 V in Figure 6a is due to the reduction of proton. This melt was then evacuated for 5 hours at ca. 5×10^{-6} torr and then a ²H NMR spectrum and NPV taken giving Figures 5b and 6b, respectively. In Figure 5b the ²H resonance for ²HCl/²HCl₂⁻ is clearly absent. From the signal to noise ratio of the natural abundance Im⁺ peaks we estimate the ²HCl/²HCl₂⁻ concentration to be less than 0.2 mM. In Figure 6b a very small wave due to proton reduction, $i_1 = 150 \,\mu$ A, is present. This corresponds to a proton concentration of ca. 74 μ M. After a longer evacuation of this solution, ca. 16 h, the small proton reduction wave was no longer observed. Similar results were also obtained for proton removal by evacuation from basic melts containing oxides (8).

In studying the removal of proton from acidic melts by evacuation we were limited to using ¹⁷O NMR because the H–D exchange between ²HCl and Im⁺ in acidic melts and the poor reproducibility of proton electrochemistry in acidic melts prohibited the quantitative use of ²H NMR and NPV. Consequently, the following experiment was performed. A 1.2:1 acidic melt was made 13.1 mM in 20% ¹⁷O enriched water. The ¹⁷O NMR of this solution shows three resonances at 87, 69, and 44 ppm (Figure 7a). The peaks at 87 and 69 ppm have been assigned to the aluminum oxychloro species, $Al_3O_2Cl_6^-$ and $Al_3OCl_8^-$ respectively, and the peak at 44 ppm has been assigned to the aluminum hydroxychloride species, $Al_2Cl_6OH^-$ (22). This melt was then evacuated overnight and the ¹⁷O NMR repeated (Figure 7b). While the total integrated intensity remained the same, the NMR exhibited only the two peaks due to the aluminum oxychlorides (Figure 7b). The aluminum hydroxychloride concentration was estimated from the signal to noise ratio to be less than 0.1 mM. In acidic melts it has been proposed that HCl and $Al_2Cl_6OH^-$ are involved in the following equilibrium (22)

$$Al_3OCl_8^- + HCl + AlCl_4^- \Longrightarrow Al_2Cl_6OH^- + Al_2Cl_7^-$$
 [2]

Assuming this equilibrium is valid the absence of detectable $Al_2Cl_6OH^-$ indicates that HCl is also absent. Thus, it appears evacuation also removes proton from acidic melts.

SUMMARY

Proton in oxide free basic melts exists as either HCl₂⁻ or HCl. The equilibrium between these two species strongly favors HCl2⁻ except in those basic melts with very low chloride concentrations. In oxide free acidic melts, HCl is the only proton containing species. NMR and NPV results demonstrate that protons can effectively be removed from basic melts by evacuation, and ¹⁷O NMR results indicate that evacuation also removes proton from acidic melts.

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Ba	Basic AlCl ₃ :ImCl ^b		Acetonitrile ^{b,c}			Assignment
HCl ₂	$^{2}\text{HCl}_{2}^{-}$	H/ ² H	HCl_2^-	² HCl ₂	H/2H	
2014 vw, vb	_	-	2040 vw, b	_		$2v_2$
1562 w,b	1192 vw, vb	1.31	1600 w, b	1170 w	1.37	2v ₃
~1140 s, b ~984 s, b	~750 s, b	_	~1150 s, b ~950 s, b	~780 s, b	_	ν2
~802 s, b	~563 s, b	1.42	800 s, b	560 s, b	1.43	v ₃

Table I. The HCl_2^- and $^2HCl_2^-$ absorption features in basic AlCl_3:ImCl melts and acetonitrile^a

^a Abbreviations: vw = very weak; w = weak; s = strong; b = broad; vb = very broad; $2v_2 =$ first overtone bending mode; $2v_3 =$ first overtone asymmetric stretch; $v_2 =$ doubly degenerate bending mode; $v_3 =$ asymmetric stretch.^b All absorbances in cm⁻¹. ^c Data obtained from Ref. 15.

Solvent	HCl ν , cm ⁻¹	² HCl v, cm ⁻¹	H/2H	Reference
CCl ₄	2834	2054	1.380	а
CCl ₂ CCl ₂	2830	2051	1.380	a
1.887:1.0° AlCl ₃ :ImCl	2762	2002	1.380	b
C ₆ H ₆	2758	2004	1.376	a
1.194:1.0° AlCl ₃ :ImCl	2721	-	_	b
0.997:1.0 ^d AlCl ₃ :ImCl	2709	1972	1.374	b
C ₆ H ₆ NO ₂	2693	-	_	e
CH ₃ CN	2542	1851	1.373	с

Table II. The HCl and ²HCl fundamental vibration bands in AlCl₃:ImCl melts and in various solvents

^a Ref. 16. ^b This work. ^c Melt with ca. 200 mM HCl (²HCl) added as ImHCl₂ (Im²HCl₂). ^d Melt with ca. 100 mM HCl (²HCl) added as ImHCl₂ (Im²HCl₂). ^e Ref. 17.



Figure 1: Plots of ²HCl chemical shift versus mole ratio; (a) data from Zawodzinski and Osteryoung (+); 200 mM ²HCl (added as Im^2HCl_2) at 90 °C. (b) data from the present work (O); spectra obtained at 30 °C, 98 mM ²HCl (added as Im^2HCl_2) for melts < 1.0:1.0, and ca. 200 mM ²HCl (added as 1 atm ²HCl_(g)) for melts $\ge 1.0:1.0$.



Figure 2: IR spectra of a 0.394:1.0 melt at $30 \,^{\circ}$ C containing; (a) 98.6 mM ²HCl (added as Im²HCl₂); (b) 122.4 mM HCl (added as ImHCl₂). Spectra are background subtracted and smoothed. Dashed lines represent regions of severe interference. Spectra obtained at 4 cm⁻¹ resolution.



Figure 3: IR spectra of slightly basic melts containing (a) 12.5 mM Cl⁻ and 98.9 mM ²HCl (added as Im^2HCl_2); (b) 13.2 mM Cl⁻ and 125.6 mM HCl (added as $ImHCl_2$). Spectra obtained at 30 °C. Data are background subtracted and smoothed. Spectra obtained at 4 cm⁻¹ resolution.



Figure 4: IR spectra 124 mM HCl in basic melts containing: (a) 210 mM Cl⁻; (b) 78 mM Cl⁻; (c) 31 mM Cl⁻; (d) 13 mM Cl⁻. Spectra were obtained at 30 °C. Data were background subtracted and smoothed. Dashed lines represent areas of severe interference.



Figure 5: ²H NMR spectra of an oxide free 0.8:1 melt (a) containing 19.8 mM protons; (b) the same melt after 5 hours of evacuation at 5×10^{-6} torr. Spectra were obtained at 90 °C.



Figure 6: Normal pulse voltammograms of an oxide free 0.8:1.0 melt (a) containing 19.8 mM protons (O). (b) The same melt after 5 h of evacuation (+).



Figure 7: ¹⁷O NMR spectra of a 1.2:1.0 melt (a) containing 13.1 mM of 20% ¹⁷O- enriched water. (b) The same melt after evacuation. Spectra were obtained at 90 °C.

The Chemistry of Proton in Ambient-Temperature Chloroaluminate Molten Salts

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ABSTRACT

In basic mixtures of the molten salt composed of aluminum chloride and 1ethyl-3-methylimidazolium chloride, proton is partitioned between HCl and HCl_2 . The equilibrium between these two species was studied using ¹H and ²H NMR. The values obtained for the equilibrium constants demonstrate that the equilibrium strongly favors the formation of the hydrogen dichloride ion. The magnitude of the enthalpy of reaction suggests that the chloride ion interacts more strongly with the melt than the hydrogen dichloride ion. The equilibrium isotope effect for the reaction of hydrogen chloride/hydrogen dichloride ion indicates that deuterium accumulates in the hydrogen chloride molecule. In acidic melts proton is a Brønsted superacid which exists primarily as HCl. ²H NMR and FT-IR spectroscopies were used to show that in acidic melts deuterium, from ²HCl, exchanges with the imidazolium cation ring hydrogens at the 4.5 position. The equilibrium isotope effect for the hydrogen-deuterium (H-D) exchange shows that deuterium accumulates in the imidazolium cation. The rate of H-D exchange increases with increasing melt acidity. The reaction is first order in hydrogen chloride and appears to be first order in Al_2Cl_7 .

INTRODUCTION

Ambient temperature molten salts, composed of mixtures of aluminum chloride $(AlCl_3)$ with 1–ethyl–3–methylimidazolium chloride (ImCl) have been employed in numerous chemical and electrochemical studies (1-3). These ionic liquids are referred to as acidic, basic, or neutral depending on whether the mole ratio of AlCl₃ to ImCl is greater than, less than, or equal to unity, respectively.

Proton is a ubiquitous contaminate in the AlCl₃:ImCl ambient-temperature chloroaluminate molten salts (4). Recent NMR and IR studies have demonstrated that proton in oxide free basic melts is partitioned between HCl and HCl_2^- (4,5). Proton rapidly exchanges between these two species in the following equilibrium.

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$$HCl + Cl^{-} = HCl_{2}^{-}$$
 [1]

In this work ²H NMR and, when possible, ¹H NMR have been used to obtain equilibrium constants and limiting chemical shifts for the basic melt hydrogen chloride/dichloride equilibrium (Equation 1) at various temperatures. The equilibrium constants from ²H and ¹H NMR were compared to determine the presence of an equilibrium isotope effect, and the temperature dependence of the equilibrium constants were used to determine the enthalpy and entropy of reaction.

In oxide free acidic AlCl₃:ImCl molten salts the absence of Cl leaves HCl as the only proton containing species. The initial ²H NMR studies of deuteron in acidic melts were complicated by incorrectly assigned resonances (4). These errors arose because, at that time, it was not known that deuteron, from ²HCl, reacts with the imidazolium cation ring hydrogens resulting in the exchange of deuterium for protium. In the present work FT–IR and ²H NMR spectroscopies have been employed to demonstrate this hydrogen–deuterium (H–D) exchange reaction, evaluate its equilibrium isotope effect, and investigate the effect of melt acidity on its rate.

EXPERIMENTAL

All melt preparation was performed in a Vacuum Atmospheres drybox under a nitrogen atmosphere. The synthesis and purification of the ImCl and AlCl₃ was performed as previously described (6,7). All basic melts were treated with phosgene and evacuated to remove oxide and proton impurities (8). Acidic melts were prepared by adding AlCl₃ to a slightly basic (0.99:1.0) oxide and proton free melt. Slightly acidic and slightly basic melts (0.95:1.0 to 1.1:1.0) were prepared from an oxide and proton free neutral melt by addition of small amounts of either ImCl or AlCl₃ (7). 1-ethyl-3-methylimidazolium hydrogen dichloride (ImHCl₂) and its deuterated analogue 1-ethyl-3-methylimidazolium deuterium dichloride (Im^2HCl_2) were prepared by reacting liquid hydrogen chloride with ImCl (5). ²HCl was the source of deuteron in the acidic melts used for ²H NMR (see below). For all other AlCl₃:ImCl melt samples, ImHCl₂ and Im²HCl₂ were used as the quantitative sources of proton and deuteron, respectively. 1–ethyl–3–methylimidazolium–2,4,5– d_3 chloride (ImCl- d_3) was prepared by a base catalyzed H–D exchange with D₂O (9). Following preparation, the crude $ImCl-d_3$ was dissolved in acetonitrile and filtered to remove residual KCl. 1-ethyl-3-methylimidazolium-2,4,5-d₃ hydrogen dichloride (ImCl- d_3 (HCl)) was prepared in the same manner as ImHCl₂ by substituting ImCl- d_3 for ImCl.

NMR samples were prepared in the drybox, pipetted into NMR tubes, and then capped and sealed with parafilm. Melt samples for ¹H NMR were placed into 5-mm tubes fitted with precision coaxial inserts (Wilmad Glass Co.), and melt samples for ²H NMR were placed into 10-mm tubes (Wilmad Glass Co.). The NMR samples of acidic melts saturated with ²HCl were placed in 9" long 10-mm tubes with a constriction at 8" (Wilmad Glass Co.). These NMR tubes were filled with melt in the drybox, attached to a vacuum line, saturated with ²HCl (98% D, Cambridge Isotope Laboratories), and then sealed. ¹H NMR chemical shifts were referenced to 0.1% TMS in CDCl₃ (MSD Isotopes) in the coaxial insert. Natural abundance D₂O in water was the reference for the ²H NMR

analyses and was assigned a value of 0 ppm. Referencing was performed by substitution, and all 2 H NMR spectra were acquired with the spectrometer unlocked. The 1 H and 2 H NMR experiments were performed using a Varian VXR–400 S, operating at 399.952 and 61.395 MHz, respectively.

Infrared data were collected using a MIDAC High Resolution FT–IR Spectrometer. The temperature of the sample compartment was 30 ± 1 °C. The sample cell and handling procedures used were the same as those employed by Tait and Osteryoung (10).

RESULTS AND DISCUSSION

The Proton Equilibrium in Basic AlCl₃:ImCl Melts

The NMR spectra of proton (deuteron) in oxide free basic melts, in most cases, exhibit a single line resulting from the fast exchange between hydrogen chloride and hydrogen dichloride ion (Equation 1). The observed chemical shift, δ_{obs} , is the population weighted average chemical shift of these two species. The strong dependence of the ²H NMR chemical shift on chloride ion concentration is shown in Figure 1. The equilibrium constant for Equation 1 was determined from the dependence of δ_{obs} on chloride concentration using the Benesi–Hildebrand–Scott (B–H–S) method (11–13). ²H NMR data at 30, 50, 70, and 90 °C were obtained and analyzed. However, for ¹H NMR, 90 °C proved to be the only temperature where a sufficient number of proton resonances were observed to perform a reasonable B–H–S analysis. Even at 90 °C, melts where [HCl] ≥ [HCl₂] (i.e. near neutral melts) the rate of chemical exchange slowed sufficiently such that the proton lines were broadened into the baseline noise. At lower temperatures exchange broadening and interference from the large Im⁺ peaks prevented observation of most of the proton resonances.

Table I lists the values of the chemical shift difference between hydrogen chloride and hydrogen dichloride ion (ΔHCl_2^-) for proton and $\Delta^2 HCl_2^-)$ for deuteron) and the equilibrium constants (K_{eq}) obtained from the B–H–S analysis of the ²H and ¹H NMR data. Also given in Table I are the measured chemical shifts of HCl (δ_{HCl}) and ²HCl (δ_{2HCl}), and the calculated chemical shifts of HCl₂⁻ ($\delta_{HCl_2^-}$) and ²HCl₂⁻ ($\delta_{2}^2 HCl_2^-$). The values of K_{eq} shown in Table I are significantly less than the ca. 600 L mole⁻¹ reported for the HCl₂⁻/HCl equilibrium in tetrachloroethane at 34 °C (11). Also $\delta_{HCl_2^-}$ is sifted upfield ca. 1 ppm and δ_{HCl} is shifted ca. 0.5 ppm downfield with respect to values reported in tetrachloroethane, methylene chloride and acetonitrile. The shift in $\delta_{HCl_2^-}$ may be due to an increase in charge density on the hydrogen atom (14). The result would be weakened hydrogen–bonds in HCl₂⁻ making the formation of dichloride ion less favorable in the melts, which is consistent with the smaller K_{eq}'s observed. The upfield shift in δ_{HCl} is indicative of a decrease in charge density on the hydrogen (14); this may result from an increase in the HCl dipole due to greater solvation in the melts.

The substitution of deuterium for protium effects the hydrogen chloride/dichloride ion equilibrium (15–18). This equilibrium isotope effect can be viewed as the following reversible reaction

$$HCl_2^- + {}^2HCl \Longrightarrow {}^2HCl_2^- + HCl$$
 [2]

The value of the equilibrium isotope effect, $K_{\mbox{\scriptsize EIE}}$ is simply the equilibrium constant for Equation 2

$$K_{EfE} = \frac{[{}^{2}HCl_{2}] [HCl]}{[HCl_{2}] [{}^{2}HCl]} = \frac{K_{eq}({}^{2}H)}{K_{eq}({}^{1}H)}$$
[3]

where $K_{eq}(^{2}H)$ is the equilibrium constant for the $^{2}HCl_{2}^{-/2}HCl$ system and $K_{eq}(^{1}H)$ is the equilibrium constant for the $HCl_{2}^{-/}HCl$ system.

For our data we are able to compare equilibrium constants at 90 °C. The ratio of these two values (Equation 3) gives $K_{EIE} = 0.67 \pm 0.26$. While the standard deviation is large the equilibrium isotope effect appears to be real, and the magnitude indicates that the equilibrium favors the left side of Equation 2. A value of 0.60 ± 0.01 has been found for the K_{EIE} of the dichloride ion in the gas phase (18). The surprisingly close agreement between ours and the published value may be coincidence considering the large differences between reactions in solution and the gas phase. However, the published value does confirm the overall direction of the KEIE toward accumulation of deuterium in the hydrogen chloride molecule. By employing standard statistical thermodynamic arguments the dichloride ion equilibrium isotope effect can be calculated from the fundamental vibrational frequencies of the species in Equation 2 (19). Using the vibrational frequencies given in reference 4 we obtained a K_{EIE} of 0.712 at 90 °C (20). This value is in surprisingly good agreement with the experimentally determined value. Interestingly, the calculated dichloride ion K_{EEE} arises primarily from rotational and translational partition function ratios and not from zero-point energy differences. This most likely results from the large differences in the moments of inertia for HCl and ²HCl and the fact that these two molecules do not have bending vibrations to contribute to zero-point energy differences (18).

From a plot of ln K_{eq} versus 1/T one can obtain the values of ΔH_{RXN} and ΔS_{RXN} (21). This plot was made for the ${}^{2}HCl_{2}{}^{-}/{}^{2}HCl$ equilibrium constant data in Table I giving Figure 2. From the slope of the line through the data in Figure 2 we obtain $\Delta H_{RXN} = -9.79 \pm 0.84$ and $\Delta S_{RXN} = 4.79 \pm 2.42$. While isotopic substitution does not alter the potential energy surface of a system it does effect the thermodynamic properties. Consequently the values we obtained for ΔH_{RXN} and ΔS_{RXN} differ somewhat from the values for the $HCl_{2}{}^{-}$ /HCl equilibrium. However, these differences should be small (estimated to be larger by ca. 0.05 kJ mol⁻¹) (22). The value of ΔH_{RXN} for the dichloride ion equilibrium in sulfolane and propylene carbonate have been reported as -33.9 and -10.5 kJ mol⁻¹, respectively (23). The difference in ΔH_{RXN} between sulfolane and propylene carbonate appears to result from differences in the heats of solvation of the anions. Propylene carbonate solvates HCl₂⁻ significantly less than Cl⁻ while in sulfolane the differences in solvation of the two anions are not as large. This same rational may also explain the relatively small ΔH_{RXN} for the dichloride equilibrium in the basic AlCl₃:ImCl melts. It is well know that Cl⁻ in basic melts strongly interacts with the imidazolium cation forming hydrogen-bonds with the ring hydrogens (9,24,25). On the other hand HCl₂⁻ shows no evidence of hydrogen-bonding to Im⁺ (7). Thus, one would expect the heat of solvation for Cl⁻ to be larger than for HCl_2^- .

The value obtained for ΔS_{RXN} in Table I has a large error associated with it, so any conclusions from it must be regarded as tentative. However, assuming no change in the number of solvent (Im⁺) molecules associated with the negative ions, a positive value is consistent with Equation 1.

Interaction of Hydrogen Chloride with the Imidazolium Cation in Acidic Melts

Infrared spectroscopy was used to investigate the reaction of hydrogen chloride with the imidazolium cation in acidic melts. Im^2HCl_2 was added to an acidic $AlCl_3$:ImCl melt, which, after correcting for the chloride added by the Im^2HCl_2 , resulted in a 1.887:1.0 melt with 185 mM ²HCl. This melt was immediately loaded into an IR cell. The cell was capped, transferred out of the drybox, and then placed in the spectrometer. Spectral acquisition was begun after the sample chamber was purged with N₂ for 5 min. To obtain reasonable signal to noise at 4 cm⁻¹ resolution a total of 10 interferograms were collected per spectrum. The time between the start of each spectral acquisition was 10 min. The spectra were background subtracted, using the spectrum of the original melt before addition of Im^2HCl_2 , and then smoothed by applying an 11–point second–order Savitsky–Golay algorithm. The resulting family of spectra are shown in Figure 3. The same procedure was followed for a 1.904:1.0 melt containing 197 mM HCl and the spectra shown in Figure 4.

The acidic melt containing ²HCl (Figure 3) shows three peaks the intensity of which change with time; the peak at 2002 cm⁻¹ decays and the peaks at 2361 and 2762 cm⁻¹ grow in. In comparison, the melt with HCl (Figure 4) exhibits a single band at 2762 cm⁻¹ which does not change. The vibronic bands at 2762 and 2002 cm⁻¹ have been assigned to HCl and ²HCl, respectively (4). From previous work with deuterated melts, the band at 2361 cm⁻¹ appears to be the imidazolium ion ²H–4,5 stretch (9). The 'differences in the spectra for the acidic AlCl₃:ImCl melts containing ²HCl (Figure 3) versus HCl (Figure 4) are indicative of protonation/deprotonation at the 4,5 position on the imidazolium ring. When the reaction involves HCl there is no net change in the system. However, when the reaction is carried out with ²HCl, deuterium is exchanged for protum on the imidazolium ring resulting in the loss of ²HCl and the formation of HCl (i.e. an H–D exchange).

The conclusions made above were tested by studying the reaction of HCl with an acidic melt made from 1–ethyl–3–methylimidazolium–2,4,5– d_3 chloride (ImCl– d_3). A 1.925:1.0 AlCl₃:ImCl– d_3 melt with 164 mM HCl (added as ImCl– d_3 (HCl)) was treated in the same manner as the previous two melts. The resulting family of spectra for this melt are shown in Figure 5. As expected the changes in the spectra in Figure 5 are opposite of those observed for the AlCl₃:ImCl melt containing ²HCl (Figure 3); the HCl absorbance decays and the ²HCl band grows in with time. These results demonstrate conclusively the presence of the H–D exchange reaction.

The H–D exchange reaction of 1,3–dimethylimidazolium ion in strong aqueous acid has been shown to proceed by an electrophilic aromatic substitution mechanism (26). The

relative rates of deuteration of the 2, 4, and 5 positions on the imidazolium ring were 1:39:39, respectively. The lesser rate of substitution at the 2 position results from a greater charge repulsion of the electrophile in the transition state due to the closer proximity of the two positive nitrogens. The data presented above for the H–D exchange reaction in the chloroaluminate melts follow these results indicating the reaction also proceeds by an acid catalyzed electrophilic substitution mechanism. Interestingly, ²H NMR data show no evidence of exchange at the 2 position even after heating ²HCl in the most acidic melts at 90 °C for several hours (22); this indicates a very large rate difference between the H–D exchange reaction at the 2 position versus the 4 and 5 positions.

The H–D exchange reaction in the chloroaluminate melts may be described by the following reversible reaction

$$Im-H^{+} + {}^{2}HCl \xleftarrow{k_{f}} Im-{}^{2}H^{+} + HCl \qquad [5]$$

where k_f is the forward rate constant, k_r is the reverse rate constant, and Im–H⁺ and Im– ²H⁺ are the protonated and deuterated imidazolium cations, respectively. The data shown in Figure 3 represents the forward reaction of Equation 5, and the data shown in Figure 5 represents the reverse reaction of Equation 5. Both experiments were performed under pseudo–first–order conditions where the concentrations of all species except hydrogen chloride were large and constant. Thus, we were able to fit the changes in HCl and ²HCl absorbance maxima with time for the spectra in Figures 3 and 5 to a pseudo–first–order rate expression (19,22). The resulting values for k_f^* , the pseudo–first–order forward rate constant, and k_r^* , the pseudo–first–order reverse rate constant, are listed in Table II. The Im–H⁺/²HCl and Im–²H⁺/HCl exchange reactions were repeated and the resulting rate constants are also listed in Table II.

The overall the fit of the absorbance data was reasonably good ($R \ge 0.99$). Because the data follow pseudo-first-order kinetics we may conclude that the forward reaction (Equation 5) is first order in ²HCl, and the reverse reaction (Equation 5) is first order in HCl. Inspection of the rate constant data in Table II reveals some interesting features. The values obtained for both k_f^* and k_r^* from the growth curves are slightly larger than the values obtained from the decay curves. In addition, the reproducibility of the rate constants obtained from changes in the ²HCl absorbance is much better than for those obtained from changes in HCl absorbance. A possible explanation for these observations may be the slow contamination of the melt by water. The infrared cells employed in these experiments were reasonably well sealed. However, because of the long duration of these experiments (4 - 5 hr) outside the drybox some contamination by water undoubtedly took place. Since water reacts with acidic melts to produce HCl, the result of water contamination would be to increase the concentration of HCl. For the forward reaction this would increase the rate of growth of the HCl absorbance and result in larger values of k_{f}^{*} . In the case of the reverse reaction, the rate of decay of the HCl absorbance would decrease resulting in smaller values of k_r^* . Contamination with water does not introduce deuterium into the system, so the rate constants obtained from changes in the ²HCl absorbance should be relatively unaffected. Regardless of the complications of water contamination the rate constants obtained from the changes in absorbance of HCl versus ²HCl for the forward and reverse reactions are reasonably close. Thus, we can conclude that the H–D exchange reaction does not generate significant amounts of an intermediate species.

The effect of the location of the isotopic atom on the rate of the forward and reverse exchange reactions can be seen by inspecting the rate constant data in Table II. The clear and significant difference in reaction rates is evidence of the equilibrium isotope effect in the H–D exchange reaction (K_{EIE}). The value of K_{EIE} , which is simply the equilibrium constant for Equation 5, may be obtained by using

$$K_{EIE} = \frac{k_f}{k_r}$$
[6]

Because $[Im-H^+] \approx [Im-2H^+]$ for the data in Table II we may use k_f^* and k_r^* in Equation 6 to determine K_{EIE} . Using the mean values of the forward and reverse rate constants in Table II, a K_{EIE} of 1.52 ± 0.28 was obtained. Because of the possible systematic deviation of the HCl generated rate constant data due to water contamination, this may be an over estimation of K_{EIE} . Assuming the samples were contaminated with water, a more accurate estimate of K_{EIE} would be calculated using only the rate constants determined from the ²HCl data. If this is done a value of K_{EIE} of 1.12 ± 0.04 is obtained. Nevertheless, both values of K_{EIE} are greater than one indicating that for Equation 5 deuterium will accumulate on the imidazolium cation ring.

The order of the H–D exchange reaction with respect to each of the three melt components (Im⁺, AlCl₄⁻, Al₂Cl₇⁻) could not be rigorously determined because the concentration of a single component cannot be varied without changing the concentration of the other two. However, the effect of the melt acidity on the rate of reaction can be evaluated allowing some conclusions to be drawn as to the relative influence of each component. ²H NMR was used to study the rate of the H–D exchange in three acidic melts: 1.105:1.0, and 1.976:1.0. To minimize the amount of H–D exchange prior to analysis the three melts were saturated with 1 atm of ²HCl_(g) at 0 °C. The NMR tubes were sealed and then stored at –20 °C until use. The resulting ²HCl concentration for the three melts was ca. 100 mM at the experimental temperature of 50 °C (27).

The samples were placed in the spectrometer heated to 50 °C and allowed to equilibrate for 10 min before data acquisition. A total of 16 fids were acquired per spectrum with a 10 s delay between each fid. The total acquisition time per spectrum was 80 s. The observed integrated intensities, therefore, are the averages for this 80 s period. For each spectrum the integrated intensities (areas) of the ²H–4,5 and ²HCl peaks were determined. The area of the ²H–4,5 peak was then corrected for the contribution of the natural abundance deuterium. (The contribution of natural abundance ²H–4,5 was calculated using the integrated intensities of the natural abundance deuterium peaks for NC²H₂ and NC²H₃.) The corrected ²H–4,5 integrated intensity was then normalized by dividing by the total integrated intensity (²H–4,5 + ²HCl) to give a value which represented the exchange reaction. These data for all three melts are displayed in Figure 6.

The H–D exchange reactions in each of the three melts were carried out under pseudo–first–order conditions (i.e. all concentrations were large and constant except the concentration of ²HCl). The fit of the NMR data to pseudo–first–order kinetics is shown by the solid line through the data points in Figure 6 (19,22). The resulting rate constants

along with the melt component concentrations are given in Table III. The fit of the data from the 1.105:1.0 and 1.506:1.0 melts was excellent (R > 0.9995). Because the reaction was almost complete before data acquisition began there was more scatter in the 1.976:1.0 data; however, the fit was still very good (R = 0.9945). The NMR data clearly follows pseudo-first-order kinetics. Therefore, in agreement with the FT-IR results above, we may conclude that the forward reaction for Equation 5 is first order in ²HCl.

The data for the three melts in Figure 6 and the corresponding rate constants given in Table III clearly show a strong dependence of the rate of H–D exchange on melt composition. As stated earlier and demonstrated in Table III, the concentrations of the three major melt species change with each of the three melts. Thus, any change in k_f^* could result from one or a combination of the changes in concentrations of the three melt species. Still, from inspection of the data some insight into nature of the H–D exchange may be gained.

The concentration of Im^+ changes relatively little between the three melts. Although, it is possible that the reaction is first order in Im^+ this cannot be determined from our data. The concentration of AlCl₄⁻, on the other hand, decreases almost 15 fold going from the 1.105:1.0 to 1.976:1.0 melt. At the same time k_f^* increases by greater than a factor of six. It is, therefore, unlikely that the rate of the H–D exchange reaction is dependent on the concentration of AlCl₄⁻. From the 1.105:1.0 melt to the 1.976:1.0 melt the concentration of Al₂Cl₇⁻ and k_f^* increase by factors of 6.22 and 6.13, respectively, which would seem to indicate a 1:1 relationship. Qualitatively, the data suggests that the forward reaction (Equation 5), and by analogy the reverse reaction, are first order in Al₂Cl₇⁻. (We did not take into account the effect of Al₃Cl₁₀⁻ on the rate of exchange because the concentration of Al₃Cl₁₀⁻ is significant only in the 1.976:1.0 melt.(28).)

The fact that the exchange reaction appears to be first order in $Al_2Cl_7^-$ implies that the slow step in the reaction mechanism involves $Al_2Cl_7^-$. This taken with the fact that the exchange reaction is clearly first order in hydrogen chloride suggests that the rate limiting step involves the protonation of the imidazolium ring where $Al_2Cl_7^-$ acts as a chloride acceptor (Equation 7).



In Equation 7 the $Al_2Cl_7^-$ is in essence acting as a Friedel–Crafts catalyst for the protonation reaction (29). Alternatively, the $Al_2Cl_7^-$ may not necessarily participate directly in the rate limiting process. Instead the effect of $Al_2Cl_7^-$ on the H–D exchange reaction may simply result from its enhancement of the acidity of hydrogen chloride (30,31). These two possibilities are in fact not distinct, but differ only in the degree of involvement of $Al_2Cl_7^-$. However, at this time the data does not allow us to clarify this issue.

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Table I. The equilibrium constants and chemical shift data for proton and deuteron in basic $AlCl_3$:ImCl melts.

		² HCl ₂ ^{-/2} HCl Eq	uilibrium	
T, °C ^a	$\delta_{^{2}HCl}$, ppm ^{b,c}	$\delta_{^{2}HCl_{2}^{-}}$, ppm ^{c,d}	$\Delta_{2}_{\text{HCl}_2}$, ppm ^e	K_{eq} , L mole ^{-1 e}
30.0	-2.80	8.70	11.51 ± 0.04	82 ± 23
50.0	-2.85	8.57	11.42 ± 0.04	70 ± 19
70.0	-2.87	8.50	11.37 ± 0.05	56 ± 14
90.0	-2.90	8.44	11.33 ± 0.05	45 ± 10
		HCl ₂ ⁻ /HCl Equ	ilibrium	9994 (J.). BUITERS - 19995 (BUITERS - 1999) (BUITERS - 1999)
T, °C ^a	δ_{HCl} , ppm ^{f,g}	δ_{HCl_2} , ppm ^{g,h}	Δ_{HCl_2} -, ppm ^e	K_{eq} , L mole ^{-1 e}
90.0	1.610	12.997	11.387 ± 0.032	67 ± 18

^a Temperatures are to \pm 0.5 °C. ^b Data for ²HCl in 1.0:1.0 melt. ^c Chemical shifts versus D₂O at 30 °C. ^d Calculated from $\delta_{^2HCl}$ and $\Delta^{^2}HCl_{^2}$. ^e Values are \pm one standard deviation. ^f Data for HCl in a 1.01:1.0 melt. ^g Chemical shifts versus TMS. ^h Calculated from δ_{HCl} and $\Delta_{HCl_2}^{-}$.

		AlCl ₃ :ImCl	with ² HCl		
$[Al_2Cl_7^-],^{b,c}$	[Im–H+], ^b	[² HCl], ^b	$k_{f}^{*} \times 10^{4}$, s ⁻¹		
mole L ⁻¹	mole L ⁻¹	mole L ⁻¹	(² HCl decay)	(HCl growth)	
2.8591	3.4568	0.1854	2.836	3.301	
2.8540	3.4506	0.1829	2.965	4.175	
			$\overline{k}_{\rm f}^*$ = (3.32 ± 0.60) × 10 ⁻⁴		
		AlCl ₃ :ImCl-	d ₃ with HCl		
$[Al_2Cl_7^-],^{b,c}$	$[Im-^{2}H^{+}],^{b}$	[HCl], ^b	$k_r^* imes 10^4$, s ⁻¹		
mole L ⁻¹	mole L ⁻¹	mole L ⁻¹	(² HCl growth)	(HCl decay)	
2.8922	3.4166	0.1636	2.772	2.256	
2.8919	3.4163	0.1586	2.432	1.268	
			$\overline{k}_{r}^{*} = (2.18 \pm 0.65) \times 10^{-4}$		

Table II. FT–IR rate constant data for the H–D exchange between proton and the imidazolium cation at 30 $^{\rm o}C.^a$

 $K_{\text{EIE}} = \left(\frac{k_{\text{f}}}{\bar{k}_{\text{r}}^*}\right) = 1.52 \pm 0.28$

^a Reported errors are \pm one standard deviation. ^b Initial concentrations. ^c These concentrations take into account the formation of Al₃Cl₁₀⁻ (28).

Melt	$[Al_2Cl_7^-],^b$ mole L ⁻¹	[Im ⁺], mole L ⁻¹	[AlCl ₄], ^b mole L ⁻¹	$k_{\rm f}^* \times 10^4,$
1.105:1.0	0.4608	4.3759	3.9151	3.158
	(4.20)	(0.87)	(0.48)	(3.11)
1.506:1.0	1.9101	3.8223	1.9002	9.822
	(1.50)	(0.87)	(0.14)	(1.97)
1.976:1.0	2.8663	3.3268	0.2702	19.36

Table III. ²H NMR rate constant data for the H–D exchange between proton and the imidazolium cation at 50 $^{\circ}$ C.^a

^a Values in parenthesis are the factors by which the following number changes from the proceeding number. ^b Concentrations take into account the formation of $Al_3Cl_{10}^{-}$ (28).



Figure 1: The effect of chloride ion concentration on the ²H NMR chemical shift of 98 mM ²HCl in basic AlCl₃:ImCl melts. Data obtained at 30 °C.



Figure 2: Plot of $\ln K_{eq}$ versus 1/T for the ${}^{2}HCl_{2}$ -/ ${}^{2}HCl$ equilibrium.



Figure 3: The time dependence of the FT–IR spectrum of a 1.887:1.0 AlCl₃:ImCl melt with 185 mM ²HCl. Spectral resolution is 4 cm⁻¹. The data are background subtracted and smoothed. Spectra were acquired at 30 °C.



Figure 4: The time dependence of the FT–IR spectrum of a 1.904:1.0 AlCl₃:ImCl melt with 197 mM HCl. Spectral resolution is 4 cm⁻¹. The data are background subtracted and smoothed. Spectra were acquired at 30 °C.



Figure 5: The time dependence of the FT–IR spectrum of a 1.925:1.0 AlCl₃:ImCl– d_3 melt with 164 mM HCl. Spectral resolution is 4 cm⁻¹. The data are background subtracted and smoothed. Spectra were acquired at 30 °C.



Figure 6: The extent of H–D exchange (²H–4,5 integrated intensity/total integrated intensity) versus time for (a) 1.105:1.0 melt; (b) 1.506:1.0 melt; (c) 1.976:1.0 melt. Melts saturated with 1 atm 2 HCl_(g) at 0 °C. Experiments performed at 50 °C. Time t = 0 was arbitrarily set at the time of the first spectrum.

IONIC EQUILIBRIA IN AMBIENT TEMPERATURE MOLTEN SALTS

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Ionic equilibria associated with acidic protons present in $ImHCl_2$ ($Im^* \equiv 1$ -ethyl-3-methyl-1*H*-imidazolium) ionic liquids (0.38 < X_{HCl} < 0.67) have been investigated by 200 MHz ¹H-NMR Spectroscopy. We conclude that proton speciation in $ImHCl_2$ is governed largely by the equilibrium

$$H_2Cl_3^- + Cl^- \rightleftharpoons 2HCl_2^-$$

for which the equilibrium constant has been evaluated as 174 +/- 20; the concentration of molecular HCl is virtually negligible relative to the anionic species. Our results suggest that at high HCl mole fractions (X_{HCl} > 0.5), and when molecular HCl is provided in the gas phase, species of the general form H_nCl_{n+1} (n>2) may be generated in significant concentrations. Though kinetically favoured, the latter are unstable, and equilibrate to the mono and diprotic anions. Virtually identical behavior is observed in basic ImAlCl₄ ionic liquids. We conclude that in order to be taken up in appreciable quantity, HCl must be solvated so as to give rise to an ionic species. In keeping with this general principle, we propose that in acidic melts, HCl is likely solvated to some degree; possible routes of solvation are explored.

Introduction

Ambient temperature molten salts generated by the reaction of 1-ethyl-3-methyl-1*H*-imidazolium chloride (ImCl) with aluminum chloride have been widely investigated in a number of laboratories (for reviews see references 1-4). Though a variety of organic base/Lewis acid systems have been investigated, 1-ethyl-3-methyl-1*H*-imidazolium chloroaluminates (ImAlCl₄) have been found to combine high conductivity and low viscosity with a wide electrochemical window (1). Hence a

great deal of work conducted with these liquids involves electrochemical investigations; notably, a variety of transition metal halide complexes which are unstable in other media may be studied in ambient-temperature ionic liquids (5,6,7). The Lewis acidity of the melt can be controlled by varying the proportions of organic base and Lewis acid used to prepare the melt; AlCl₃ mole fractions less than 0.5 afford a basic melt, while those greater than 0.5 afford an acidic medium. The acid/base behaviour of the melts is controlled largely by the following reaction, which is believed to adequately describe the speciation of chloroaluminate melts over a wide range of compositions (1):

$$Al_2Cl_7 + Cl^- \rightleftharpoons 2AlCl_4$$
 [1]

The equilibrium constant for the above is of the order of 10^{17} to 10^{18} near ambient temperature (8,9). In basic melts, the predominant anionic species are AlCl₄ and Cl⁻ while in very acidic melts, Al₂Cl₇ predominates and provides a high Lewis acidity. In highly acidic melts, larger adducts must be considered, *e.g.* Al₃Cl₁₀.

Smith *et.al.* report that in the acidic chloroaluminates, protons added as HCl are Bronsted superacids, and will protonate a variety of arenes (10,11). Protons may be conveniently added to the chloroaluminate melts as $ImHCl_2$, another ambient-temperature molten salt which results from reaction of ImCl with anhydrous HCl (12). Protons present in $ImHCl_2$ liquids, as well as those added to the chloro-aluminate melts, are believed to exist as molecular HCl and the hydrogen dichloride anion HCl_2^- , in accord with the following equilibrium:

$$HCl + Cl^{-} \rightleftharpoons HCl_{2}^{-}$$
 [2]

For a review of the hydrogen dihalides, and strong hydrogen bonding, see Tuck (13) and Emsley (14), respectively. The equilibrium constant for reaction [2] in nitrobenzene has been reported (18) as 500 at 298K, and hence in the presence of excess chloride (basic ImHCl₂ or ImAlCl₄), the predominant species is the hydrogen dichloride anion. In acidic chloroaluminates, the proton is believed to exist as molecular HCl (12,15,16,17). Although ImHCl, has been used as a reagent by several investigators, no detailed investigations of the liquid itself, previous to the current work, have appeared in the literature. Details and results of an NMR investigation concerning the identity of protic species in this liquid are reported in the current paper. It is demonstrated that molecular HCl does not contribute significantly to proton speciation, *i.e.* species other than hydrogen dichloride exist. Further, the chemistry of protons in the basic chloroaluminate ionic liquids is virtually identical to that in ImHCl₂. The state of the proton in acidic ImAlCl₄ appears less certain; we suggest that species other than molecular HCl may contribute to proton speciation in these melts.

Experimental

Materials. 1-ethyl-3-methyl-1*H*-imidazolium chloride (ImCl) was prepared by the method of Smith *et.al.* (10) affording a 70% yield of ImCl, m.p. 94°C. Aluminum chloride (Fluka, puriss) was further purified by two successive vacuum sublimations from reagent grade Al and NaCl (Fisher, ACS Reagent) which had been prepared by heating at 400 °C for 4 days under an atmosphere of dry HCl. The synthesis of ImCl and the purification of AlCl₃ were conducted under an atmosphere of dry argon and the resulting products were immediately stored in sealed Pyrex ampoules under same. All further manipulations were conducted in a glovebox under an atmosphere of dry argon or nitrogen, or in "airless" glassware. The glovebox atmosphere was circulated continuously through a Cu furnace and equilibrated over P_2O_5 . Anhydrous HCl was prepared by the addition of conc. HCl to conc. H_2SO_4 , followed by passage through a dry ice/acetone cold trap, and finally, a column of anhydrous MgClO₄.

Preparation of Melts. The preparation of $ImHCl_2$ was accomplished by the addition of dry HCl to weighed samples of ImCl. In some instances, excess HCl was pumped off so as to afford the desired HCl mole fraction (X_{HCl}). The HCl content of these samples was determined by a titrimetric procedure described below. ImAlCl₄ ionic liquids were prepared by the gradual addition of AlCl₃ to a known mass of ImCl; following preparation of the melt, the total AlCl₃ was determined gravimetrically. Solutions of HCl in a basic ImAlCl₄ (35.0 m/o AlCl₃) ionic liquid were prepared by the direct addition of dry HCl to freshly prepared chloroaluminate liquids. For these samples, the total HCl content was determined gravimetrically and by integration of NMR signal intensities.

¹H-NMR Spectroscopy. ¹H-NMR spectra (200 MHz) were aquired at 297 K with a Bruker AM 200 NMR Spectrometer. NMR samples were prepared in the glovebox in standard 5 mm NMR tubes; each of these contained a coaxial capillary filled with DMSO-d₆. All spectra are referenced to TMS at 0 ppm. In the case of ImHCl₂, approximately 1 g of ImHCl₂ was added to a previously weighed NMR tube. Following aquisition of NMR spectra, the samples (in NMR tube) were weighed and analyzed for HCl content by reacting with an excess of aqueous Na₂CO₃ (BDH, AnalR). In carrying out this reaction, the NMR tube was opened under the surface of the basic solution so as to ensure complete reaction of HCl contained in the sample; no odour of HCl was detectable during this procedure. The HCl content of the sample, and hence X_{HCl} , was then determined by back-titration of the reaction mixture with HCl.

Results and Discussion

ImHCl₂ liquids were found to exist as such (298K) for HCl mole fractions in the range *ca.* 0.38 to 0.67, the latter composition having a HCl:ImCl stoichiometry of 2:1. A typical proton NMR spectrum of ImHCl₂ is illustrated for a $X_{HCl} = 0.47$ melt in Figure 1. The downfield resonance near 13 ppm is ascribed in the literature, to the HCl₂⁻ ion (12,19). For $X_{HCl} < 0.5$, a sharp singlet is observed. For X_{HCl} greater than about 0.55 however, a complex signal is observed immediately after preparation of the sample. Such a spectrum is illustrated in Figure 2 for a melt of composition $X_{HCl} = 0.57$. This spectrum was aquired approximately 1 hr after preparation (same sample) revealed a single sharp singlet (Figure 3) which appears to be one of the component signals of the original spectrum. The decay of the complex signal is illustrated as a function of a melt of composition $X_{HCl} = 0.62$ in Figure 4. Application of a vacuum to the melt causes rapid decay of the signal to a sharp singlet.

The dependence of the chemical shift of the acidic proton on X_{HCI} is illustrated in Figure 5. In all cases, the shifts refer to melts in which any complex signal was first allowed to relax to a single signal. As the chemical shift varies over a range of *ca*. 5 ppm, it is clear that the proton is engaged in rapid exchange amongst several environments, with that predominating on the basic, chloride-rich side (X_{HCI} < 0.50) being deshielded relative to to that on the acidic, chloride-deficient side. For X_{HCI} < 0.50, the shift is relatively independent of composition. These results suggest that as the HCl mole fraction increases from its minimum value near 0.38, HCl reacts with chloride forming HCl₂⁻⁻ in accord with reaction [2]. In light of the reported equilibrium constant, this reaction is virtually quantitative, and hence the chemical shift is relatively invariant. On the acidic side, however, the shift is observed to migrate strongly upfield with increasing X_{HCI} , suggesting a rapid increase in the concentration of the corresponding environment(s).

Initially, it was supposed in accord with the literature, that as X_{HCI} increases from 0.50, molecular HCl accumulates in the melt resulting in an upfield shift of the signal. Unfortunately, this model offers no explanation for generation of the decaying complex signal. It appears that the formation of species contributing to this signal is kinetically facile, but the process yields a state of disequilibrium. The existence of molecular HCl in the "acidic" melt ($X_{HCI} > 0.5$) would seem to imply the spontaneous generation and subsequent decay of a transient species without any net change in the composition of the system, and is therefore contrary to the Second Law of Thermodynamics. In order to explain the generation of the complex signal, and to quantify the curve in Figure 5, the following hypothesis was put forth:

i) For all compositions, the concentration of molecular HCl is small compared to that of other species harbouring the acidic proton.

- ii) For $X_{HCl} < 0.5$ the equilibrium reaction [2] is dominant.
- iii) For $X_{HCl} > 0.5$ an additional equilibrium must be considered:

$$HCl + HCl_2^- \rightleftharpoons H_2Cl_3^-$$
 [3]

The species involved in this equilibrium undergo rapid exchange (relative to the timescale of the NMR experiment) such that a single, sharp signal is observed.

iv) When the concentration of $H_2Cl_3^-$ becomes sufficiently high, and when molecular HCl is provided in the atmosphere over the melt, further HCl adducts may be generated:

$$HCl + H_n Cl_{n+1} \longrightarrow H_{n+1} Cl_{n+2}$$
[4]

Though favoured kinetically, the larger hydrogen chloride aggregates (n>2) are unstable relative to HCl_2^- and $H_2Cl_3^-$, and after equilibration yield, ultimately, a predominance of the latter species. The existence of such aggregates was postulated by Shuppert and Angell in a study of the pyridinium chloride:HCl system (19), and by Kaufler and Kunz in 1909 (20). In 1914, Ephraim established that the formation and dissociation process is reversible (21). This is consistent with the observation that the complex signal may be induced to relax through the reduction of pressure. The statement iv) is therefore not without precedent. It is presumed here that proton exchange of some or all of the transient species with other species in the melt is sufficiently slow that the corresponding resonance(s) are partially resolved from that of the more rapidly exchanging environments.

In testing the above hypothesis, it was found that after allowing an acidic melt to equilibrate so that a sharp singlet is observed, the complex resonance can be regenerated by re-exposing the melt to an atmosphere of HCl. This confirms i) above, and suggests that in order to be taken up by the melt in appreciable quantity, HCl must react. In doing so, it must therefore exist as some species other than HCl₂⁻. It is notable that the upper limit (298K) for X_{HCl} lies somewhere near 0.67, which corresponds closely to the stoichiometry of H₂Cl₃⁻. Additionally, it is somewhat pleasing that reactions [2] and [3] exhibit a distinct parallel with the corresponding reactions in the chloroaluminate melt:

$$AlCl_3 + Cl^- \rightleftharpoons AlCl_4^-$$
 [5]

$$AlCl_3 + AlCl_4 \implies Al_2Cl_7$$
 [6]

This parallelism suggests that under certain conditions, HCl, and presumably the other hydrogen halides, will mimic Lewis acid behavior through formation of a hydrogen bond to an additional halide ion, and lends support to the view that hydrogen may sometimes be regarded as the simplest metal. Tuck, for example, suggested that the dihydrogen halide ion should be named dihalohydrogen(I) in recognition of the fact that, here, hydrogen is the more electropositive element (13).

For a nucleus engaged in rapid exchange amongst several environments, the observed chemical shift is given by the population-weighted average of the shifts in each discrete environment. Specifically, for a proton undergoing rapid exchange amongst HCl, HCl_2^- and $H_2Cl_3^-$, the shift is given by:

$$\delta_{\rm H} = (1/X_{\rm HCl}) \{ X(\rm HCl)\delta(\rm HCl) + X(\rm HCl_2)\delta(\rm HCl_2) + 2X(\rm H_2Cl_3)\delta(\rm H_2Cl_3) \}$$
[7]

where X_{HCl} is the total HCl mole fraction here defined by:

$$X_{HC1} = X(HC1) + X(HC1_2) + 2X(H_2C1_3)$$
[8]

X(HCl), X(HCl₂), and X(H₂Cl₃) are the relative mole fractions of the proposed environments, and the δ 's are their respective chemical shifts; ionic charges have been omitted for convenience. The mole fraction of ImCl, $X_{Im} = 1 - X_{HCl}$, is given by:

$$X_{im} = X(Cl) + X(HCl_2) + X(H_2Cl_3)$$
 [9]

The concentrations of the various species are here related to one another by the stoichiometric equilibrium constants corresponding to reactions [2] and [3]:

$$k_{2} = \frac{X(HCl_{2})}{X(HCl)X(Cl)} \qquad k_{3} = \frac{X(H_{2}Cl_{3})}{X(HCl)X(HCl_{2})}$$
[10]

Initially, an attempt was made to fit the model encompassed by equations [7] through [10] to the experimental curve (Figure 5) by non-linear regression in terms of the variable parameters k_2 , k_3 , δ (HCl) and δ (H₂Cl₃). The chemical shift of the proton in the HCl₂⁻ environment was extrapolated from Figure 5 as approximately 13.5 ppm. This seems reasonable considering the reported value ($k_2 = 500$ in nitrobenzene) for the formation constant of the hydrogen dichloride ion. Unfor-

tunately, regression analysis was unsuccessful in reaching convergence. This appears to have been related to the fact that some of the derivatives contained denominators capable of assuming exceedingly small values during the course of regression; specifically, these terms contained X(HCl) and higher powers thereof. In deference to this obstacle, an abductive network (22) program (AIMTM, 23) was employed in an effort to determine the general requirements for a good fit of the model to the data, and so extract the unknown parameters.

Several abductive networks were synthesized on the basis of training databases each consisting of 300-600 sets of data. The training sets were generated via equations [7] through [10] and involved parameters spanning the following ranges: k_2 , $10^2 - 10^9$; k_3 , $10^1 - 10^8$ (note that k_2 must be greater than k_3); δ , 0-13.5 ppm. Only those parameter sets which generated calculated curves within 0.1 ppm of the experimental curve (Figure 5) were included in the training database. Each training set consisted of the parameter values and 10 $\delta_{\rm H}$ vs. $X_{\rm HCI}$ data points calculated from the specified parameters. The parameter values were specified as output variables, and the resulting data were defined as input variables, so that following its synthesis, the network could be queried for the parameter set corresponding to 10 selected experimental data points. Though the treatment did not yield unique values for k_2 , k_3 or δ (HCl), parameter sets generated upon feeding of the experimental data into the resulting networks, were consistently characterized by the shift $\delta(H_2Cl_3)$ being near 8.5 ppm, by the ratio k_2/k_3 being close to 2 x 10², and by the individual equilibrium constants being much greater than unity. This suggests that for X_{HCI} approaching 0.67, H₂Cl₃⁻ is the predominant species, and hence the concentration of molecular HCl must be correspondingly low. This was corroborated by the subsequent use of direct search techniques in which it was found that the difference between calculated and experimental curves was minimized for k_2 and k_3 greater than ca. 10^5 . Qualitatively, these results indicate that the concentration of molecular HCl, must indeed be very small, so small as to be neglected in equilibrium calculations. Inspection of equations [2] and [3] reveals that the ratio k_2/k_3 is the equilibrium constant for the reaction

$$H_2Cl_3^+ + Cl^- \rightleftharpoons 2HCl_2^-$$
 [11]

which one immediately recognizes as being analogous to reaction [1], the autosolvolysis reaction in chloroaluminate melts. The difference in magnitudes of the equilibrium constants for reactions [1] and [11] is a reflection of the fact that the Lewis acid behavior [*sic*] of HCl is limited to the formation of strong hydrogen bonds. More importantly, the existence of the equilibrium [11] suggests that in acidic chloroaluminate melts, Al_2Cl_7 should shift it to the left. Taken alone, this identifies H_2Cl_3 as a potential candidate for the proton-bearing species present in the acidic chloroaluminate liquids. It is acknowledged here, however, that there may exist additional equilibria which serve to further satisfy the Lewis acidity of the heptachloroaluminate species. This possibility is explored further in a later section. A simpler model for proton equilibria in ImHCl₂ liquids was generated by allowing X(HCl) in equations [7] through [10] to vanish; that is, to assume that the equilibrium [11] is sufficient to reasonably define the composition of the melts. Non-linear regression of this model was successful and for 30 data points yielded K = 174 +/- 20, $\delta(\text{HCl}_2) = 13.59$ +/- 0.02 ppm, and $\delta(\text{H}_2\text{Cl}_3) = 8.56$ +/- 0.02 ppm. In retrospect, difficulties in regression of the first model probably arose in its incorrectness, *i.e.* reaction [11] is sufficient to describe the disposition of the *major* fraction of acidic protons in ImHCl₂ ionic liquids.

Pople et.al. reported the chemical shift of liquid and gas phase HCl as 1.41 and 0.78 (corrected to the standard TMS reference) respectively (24). In addition, solutions of HCl in CCl₄ may be prepared at concentrations approaching 0.02 m/o (25). The chemical shift of HCl in rigorously dried CCl_4 has been determined as ca. 0.2 ppm in this laboratory. Though the value obtained in CCl_4 is probably the best estimate for the shift of unassociated molecular HCl, it is possible that weak interactions (26) with Im⁺ might cause some variation. However, owing to its low concentration, and small chemical shift, molecular HCl makes a negligible contribution to equation [7] and hence has little effect in minimizing the difference between experimental and calculated δ_H vs. X_{HCI} curves. In order to obtain an estimate of the magnitude of k₂ and k₃, an attempt was made to allow for the existence of molecular HCl according to equations [7] through [10]. This was accomplished by use of a direct search in which k_2 was varied through the range $10^1 - 10^9$. The values of k_{2}/k_{3} , $\delta(HCl_{2})$, and $\delta(H_{2}Cl_{3})$ were varied through the ranges indicated by the regression results for the simple model. For the purposes of performing the minimization, the chemical shift of molecular HCl was held constant at 0.2 ppm. For 2 x 10^6 permutations within the above ranges (2000 values of k₂, 40 values of k_2/k_3 , and 5 values of each chemical shift) 1458 sets were found which minimized the total difference between experimental and calculated curves to within 0.68 ppm (0.023 ppm per datum). For these sets k_2 and k_3 spanned the ranges: 2.5×10^5 to 4.3×10^7 and 1.3×10^3 to 2.4×10^5 , respectively. That set which provided the best agreement (k_2 ca. 2×10^7 , k_3 ca. 10^5) with the experimental curve was used to calculate the solid curve in Figure 1. Though these results demonstrate that the concentration of molecular HCl is indeed small, they may be misleading. It appears quite likely, for example, that reaction [3] should, in fact, be treated in conjunction with reactions [4], i.e. HCl is more likely to be solvated as larger, albeit unstable (relatively), anionic aggregates, than to exist in its molecular form, and hence the concentration of molecular HCl may be lower than would be calculated from the above estimates of k₂ and k₃. Hence, these estimates should probably be regarded It is notable in this respect that deviations of the calculated and as minima. experimental curve are maximal for $X_{HCI} > 0.5$ (see Figure 6). Attempts to fit such a model (*i.e.* including H_3Cl_4) to the data by non-linear regression are difficult as it is not possible to calculate the necessary derivatives analytically without introducing terms containing X(HCl) (Inclusion of such terms leads to failure of regression). Other curve-fitting techniques are currently being explored in an effort to evaluate the significance of reactions [4].

Based on the equilibrium constants obtained in this study (k_2 is estimated as $2x10^7$), alpha values have been calculated as a function of X_{HCl} ; a plot of these values for Cl⁻, HCl₂⁻, and H₂Cl₃⁻, appear in Figure 7. It is apparent that for "stoichiometric" ImHCl₂, *i.e.* $X_{HCl} = 0.50$, *ca.* 12 % of the total HCl exists as the H₂Cl₃⁻ ion. Calculated values of X(HCl) vary from *ca.* $8x10^{-8}$ to 10^{-4} over the entire composition range; as per the above discussion, these values probably represent maxima. The odour of HCl is readily observed above ImHCl₂ melts of all compositions in the range studied. Given the apparent low concentration of molecular HCl, the equilibrium constant for the expression

$$HCl_{(g)} \rightleftharpoons HCl_{(l)}$$
 [12]

is much smaller than might have been assumed previous to this work. We have neglected this equilibrium in our model, with no justification other than the fact that the amount of HCl above the melt in the NMR tube was insignificant relative to the total HCl contained in the tube, and in the NMR probe.

Proton Equilibria in Basic ImAlCl₄ Ionic Liquids

The behavior of protons was studied in a highly basic ImAlCl₄ ionic liquid $(X(AlCl_3) = 0.350)$ by means of an analogous series of NMR experiments. The chemical shift of the acidic proton in this melt is plotted as a function of HCl content in Figure 8. The HCl concentration is expressed relative to the "free" chloride present in the basic melt without added HCl, *i.e.* that over and above chloride required for reaction with AlCl₃. Inspection of this figure reveals close resemblance to the curve aquired for ImHCl₂ ionic liquids (Figure 8a). In addition, the same transient species as observed in ImHCl₂, are observed in basic ImAlCl₄ liquids. HCl concentrations determined by the relative intensities of NMR signals (Figure 8b) of the acidic proton and those of Im⁺, are in reasonable agreement with the gravimetric results (Figure 8c). Non-linear regression of the curves derived by gravimetry and NMR yield k₂/k₃ values of 129 +/- 34 and 200 +/- 67 respectively, and hence it is not possible to discern any difference from the value obtained in ImHCl₂ liquids. Admittedly, a larger data set would provide more definite results. Qualitatively, the behavior of HCl in both liquids appears to be very similar as reflected in the $\delta_{\rm H}$ vs. $X_{\rm H}$ curves. Notably, however, the chemical shift of HCl₂⁻ appears to be somewhat lower in the chloroaluminate melts.

Modelling discussed in the current paper assumes that the shifts of the various species are invariant with respect to the overall ionic environment of the melt. Considering the apparent change in the chemical shift of the hydrogen dichloride species in going from $ImHCl_2$ to $ImAlCl_4$ liquids, one might anticipate that this assumption is not strictly valid, and we must therefore allow for the possibility that

the chemical shift of each discrete species may vary slightly through weak interactions with the medium, ie. solvent effects. The variation of the chemical shift of the $Im-H_2$ proton with X_{HC1} is illustrated in Figure 9 (this work, ImHCl, liquids). This behavior is also observed for H_4 and H_5 to a lesser extent. Similar behavior was observed by Seddon et.al. for ImAlCl₄ liquids (26). For both of these molten salts, the variation in the chemical shift of the Im⁺ ring protons is greatest in the composition range where the rate of change of the chloride concentration is maximal, i.e. for acidic component mole fractions less than 0.5. This indicates that the chemical shift of the ring protons is strongly dependent on the chloride ion con-Seddon and coworkers conclude that a hydrogen bonding interaction centration. between the Im⁺ ring protons and anions in the melt is reponsible. This raises the question of whether the protic anions themselves interact with the ring protons, leading to variation of the chemical shifts of all species involved. Figure 10 illustrates the variation of the chemical shift of Im-H₂ with the alpha values of the various anions present in ImHCl₂. Examination of the region in which the chloride ion fraction is negligible reveals that the interaction of $\text{Im}-\text{H}_2$ with HCl_2^- and $\text{H}_2\text{Cl}_3^$ is much weaker, and hence should not lead to excessive variation in the chemical shifts of these anions. This suggests that the assumption of invariant chemical shifts of the protic anions is reasonable to a first approximation.

Protic Species in Acidic ImAlCl₄ Ionic Liquids

Speciation of the proton in acidic ImAlCl₄ is much less certain than in basic Though other workers have concluded that the proton exists as molecular melts. HCl in the these melts, our results with ImHCl₂ and basic ImAlCl₄ have led us to entertain several other possibilities. It was found that for neutral and acidic chloroaluminates, one cannot introduce sufficient HCl so as to generate a detectable ¹H-NMR signal (this work). Indeed, this cannot be achieved by the addition of ImHCl₂; in the case of the acidic melts most of the protons added in this fashion are visibly driven out as HCl owing to the extreme Lewis acidity endowed by the heptachloroaluminate species. We have come to the suspicion that unless HCl can form an ionic species, *i.e.* unless HCl can be solvated, it simply won't dissolve appreciably in the melt. Hence, in these liquids, the concentration(s) of protic Osteryoung et.al. report that the electrochemistry of protons in species is(are) low. acidic BuPyAlCl₄ (BuPy \equiv butylpyridinium) is not reproducible; peak and limiting currents for CV and NPV were observed to decrease with time (16). This may be caused by diffusion of HCl from the melt, i.e. HCl may be added (via the addition of water) in quantities which exceed its solubility in the melt. Though undetectable by ¹H-NMR, the acidic proton is manifested by its protonation of arenes (10,11). Additionally, when melts are prepared with DCl, the signal of the acidic species may be detected through ²H-NMR (12); presumeably, this is owing to the low overall ²H concentration, and hence a greater signal to noise ratio. For ImHCl, and basic chloroaluminates, the concentration of the acidic proton is limited only by the availability of chloride, and by the potential to form stable species. Owing to the lack of chloride available for anion formation, and the small equilibrium constant for reaction [12], the total solubility of HCl in acidic chloroaluminates is correspondingly low.

As the melt is made more acidic by the addition of aluminum chloride, the equilibrium [11] is shifted to the left, and hence we expect the shift of the acidic proton to move upfield. This has been observed in this laboratory in ¹H-NMR spectra of basic ImAlCl₄ melts, and in ²H-NMR studies of basic and acidic melts reported by Osteryoung *et.al.*, who observed the shift to decrease to *ca.* 6.9 ppm near X(AlCl₃) = 0.5, and remain essentially constant as X(AlCl₃) increases (12). It must be noted however, that the deliberate addition of water to acidic ImAlCl₄ gives rise to several additional ¹H resonances, one of which has been observed very close to 7 ppm; none of these resonances are observed upon treament of the melt with HCl (29). Though it is clear that the shift of the acidic proton decreases as a basic melt approaches neutrality, it appears possible that the deuterium resonance (12), but a hydroxychloroaluminate species which arises due to the presence of impurities in the melt, *i.e.* adventitious water (16,27,28). In any event, the shift of 6.9 ppm is more consistent with H₂Cl₃⁻ than with molecular HCl.

It appears, at least at the outset, that $H_2Cl_3^-$ may contribute to proton speciation in acidic chloroaluminates. However, we must acknowledge that reactions [2] and [3] may also be drawn to the left producing HCl (as is observed to leave solution upon addition of ImHCl₂ to acidic ImAlCl₄), and simultaneously satisfying the melts capacity to take up chloride ion. The equilibria defined by reactions [2] through [4] may be re-written in the form:

 $HCl_{(g)} \rightleftharpoons HCl_{(1)}$ $k \ll 1$ [12]

 $HCl_{0} + Cl^{-} \rightleftharpoons HCl_{2}^{-}$ $k \gg 1$ [13]

 $H_2Cl_3^- + Cl^- \rightleftharpoons 2HCl_2^-$ k ca. $2x10^2$ [14]

 $H_{3}Cl_{4}^{-} + Cl^{-} \rightleftharpoons H_{2}Cl_{3}^{-} + HCl_{2}^{-} \qquad k > 2x10^{2} \qquad [15]$

 $H_4Cl_5^- + Cl^- \rightleftharpoons 2H_2Cl_3^- \qquad k > 2x10^2 \qquad [16]$

etc.

The form of these reactions suggest that as the melt acidity increases, *ie*. as the chloride ion concentration decreases, the larger anionic aggregates should accumulate. Indeed, if an equilibrated (single Lorentzian NMR signal) solution of $ImHCl_2$ in basic $ImAlCl_4$ ([HCl] > 100 % available Cl⁻) is reacted with acidic $ImAlCl_4$ (ca.

67 m/o AlCl₃), the complex signal is generated (this work), suggesting that solvation as above is not unreasonable. If the proton were to exist solely as molecular HCl, its solubility should be governed by a Henry's Law constant, and hence for a constant HCl pressure, should be relatively invariant with respect to X(AlCl₃). If HCl is solvated however, its solubility should vary with the Lewis acidity of the melt. Specifically, if solvation occurs as per reactions [13] through [16], HCl solubility should decrease with increasing Lewis acidity. Preliminary measurements of the solubility of HCl (1 atm HCl) as a function of melt acidity indicate that the proton concentration decreases with increasing X(AlCl₃), suggesting that solvation does indeed play a role in the acidic melts (29). When $ImHCl_2$ is added to an acidic chloroaluminate melt, the fraction of added proton driven off as HCl, and the fraction solvated as per reactions [13] through [16] will depend on the magnitudes of the associated equilibrium constants, *i.e.* the solubility of HCl will depend on the relative values of these constants.

In considering the appetite of $Al_2Cl_7^-$ for chloride, we propose that under certain conditions, the proton might also exist as the hydrochloronium ion, H_2Cl^+ , which is believed to exist in liquid HCl and in HCl/AlCl₃, as well as in some solid compounds (30). A cationic form for the proton allows electrostatic stablization in the presence of relatively large anionic chloroaluminate species. More importantly, the existence of the proton as H_2Cl^+ maximizes the amount of chloride available to the heptachloroaluminate species. The florine analogues, H_2F^+ and $H_3F_2^+$, are known to exist in HF:SbF₅ superacids (31). Driven by reaction [1], formation of the hydrochloronium ion may be written:

$$Al_2Cl_7^- + 2HCl_0 \rightleftharpoons 2AlCl_4^- + H_2Cl^+$$
 [17]

Presumeably, further solvation of HCl is conceivable, as in the case of HF. Reaction [17] is the sum of reaction [1] and the self-ionization reaction of HCl

$$2\text{HCl} \implies \text{Cl}^- + \text{H}_2\text{Cl}^+ \qquad [18]$$

and hence the extent of reaction [17] will depend on the relative magnitudes of the equilibrium constants for reactions [1] and [18]. At very high Lewis acidities, and perhaps at low temperatures, solvation as per reaction [17] may indeed become significant. In this case, solvation is consistent with HCl solubility being proportional to melt acidity.

Conclusions

Our results indicate that in order to be taken up by $ImHCl_2$ and $ImAlCl_4$ ionic liquids, HCl must be solvated. It has been demonstrated that in addition to hydrogen dichloride, solvation may encompass the formation of $H_2Cl_3^-$ and larger aggregate ions. Molecular HCl does not contribute significantly to proton speciation in $ImHCl_2$ and basic $ImAlCl_4$ melts. In accord with the apparent requirement of solvation, we have proposed two general routes of solvation in acidic melts, one of which is suggested by observations in the latter liquids. Evaluation of these possibilities necessitates accurate measurement of HCl solubility as a function of melt acidity, and perhaps temperature and HCl pressure. Several methods of aquiring such data are evident:

1) Electrochemical measurements might be employed. However, since all protic species might not be electroactive, and will certainly exhibit variation in their diffusion coefficients, analysis would be difficult, if not impossible. Nonetheless, such experiments may be qualitatively useful.

2) Measurement of solubility by means of the protonation of arenes (12,13). Reaction of HCl-equilibrated melt samples with arenes, *e.g.* mesitylene or pentamethylbenzene, followed by aquisition of UV-Vis spectra might prove a useful method. However, owing to the large extinction coefficients associated with the protonated forms of these hydrocarbons, small path length cells are necessary. In addition, dilution of the melts may also be required.

3) ²H-NMR Measurements. Unfortunately, this may be precluded by the report that protons undergo exchange with the H-4 and H-5 ring protons of the Im^+ cation (15).

4) Gravimetric determination of HCl solubility using large samples of melt.

Of the first three methods, arene protonation is probably the best choice, though difficulties have been encountered in preparing acidic melts sufficiently devoid of proton to serve as diluent. The proton-removal techniques reported by Osteryoung (15) may prove useful in this regard. It would also be necessary to employ oxide-free melts (15,32) so as to avoid HCl solvation by oxychloroaluminate species (*e.g.* $Al_2OCl_5^-$, 15). Of all the above methods, the last will probably yield the most accurate results. Unfortunately this method is also the most material intensive. Several methods are currently being employed in the measurement of HCl solvation in these liquids.

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FIGURE 1 ¹H-NMR Spectrum of a chloride-rich ImHCl₂ ionic liquid.



FIGURE 2 1 H-NMR Spectrum of a chloride-deficient ImHCl₂ ionic liquid.



FIGURE 3 Loss of signal complexity in melt of Figure 2 (top left).

- FIGURE 4 Decay of complex NMR signal as a function of time (top right).
- FIGURE 5 Chemical shift of acidic proton as a function of HCl mole fraction; ImHCl₂ ionic liquids; points are experimental; solid curve calculated on basis of model (bottom left).
- FIGURE 6 Residues after curve fitting (bottom right).



FIGURE 7 Anion fractions (α) as a function of X_{HCI}, ImHCl₂ ionic liquids (top left).

- FIGURE 8 Chemical shift of acidic proton in 35.0 m/o ImAlCl₄ as a function of HCl content: a) + ,ImHCl₁ data; b) __, ImAlCl₄, proton content determined from NMR signal intensity; c) _>, ImAlCl₄, proton content determined gravimetrically (top right).
- FIGURE 9 Chemical shift of $Im-H_2$ proton as a function of X_{HCI} , $ImHCl_2$ ionic liquids (bottom left).
- FIGURE 10 Anion fractions (α) as a function of Im-H₂ chemical shift; ImHCl₂ ionic liquids (bottom right).

DUAL SPIN PROBE NMR RELAXATION STUDIES OF MICRODYNAMICS IN CHLOROALUMINATE MELTS

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The microdynamics of EtAlCl₂ containing melts are examined by 13 C and 27 Al NMR relaxation methods as a function of melt composition and temperature. Application of the Dual Spin Probe (DSP) method to these systems reveals interaction between the MEI⁺ methyl group and various EtAlCl₂ containing species. Unlike MEICl-AlCl₃ room temperature melts, there is no indication of interaction between the MEI⁺ ring CH's and EtAlCl₂.

INTRODUCTION

It is important to understand the microdynamics of molten salt solutions if they are to be developed as electrochemical and solvent systems in the future. The use of ¹³C NMR relaxation studies provides useful information about the dynamics and structure of various chemical systems and chloroaluminate systems in particular(1). In a previous work(1), ¹³C NMR relaxation measurements were used to investigate the motion and interactions of the MEI cation as a function of temperature and magnetic field. The results indicate that $AlCl_4^-$ in a NaCl buffered (N=0.55) melt ($AlCl_3 > MEICl$) forms a complex by interacting with the C-2, C-4 and C-5 hydrogens on the MEI⁺ ring shown below.



This work was followed by studies (2,3) in which the Dual Spin Probe (DSP) method(4) was used to verify the existence of $MEI(AlCl_4)_n^{-(n-1)}$ complexes in basic(N=0.33), neutral(N=0.50) and NaCl-buffered neutral melts. ²⁷Al, ²³Na and ¹³C NMR relaxation results confirmed the existence of the chloroaluminate-MEI⁺ complexes and yielded ²⁷Al and ²³Na liquid state quadrupole coupling constants(1-3).

Application of the DSP relaxation method requires knowledge of ${}^{13}C$ dipolar relaxation rates which are defined by [1], the basic equation in which the ${}^{13}C$ nucleus is relaxed by ${}^{1}H(5)$:

$$R_1^{dd} = N_H (\hbar \gamma_C \gamma_H)^2 r_{CH}^{-6} \tau_{eff}$$
^[1]

where $R_1^{dd} (= 1/T_1^{dd})$ is the dipolar relaxation rate, N_H is the number of hydrogens attached directly to the carbon atom, γ_C and γ_H are gyro-magnetic ratios and $r_{CH} = 1.09$ Å. τ_{eff} is the effective correlation time and varies exponentially with temperature.

Equation [1] is operative under the "extreme narrowing condition" ($\omega \tau_{eff} < <1$) which is usually applicable for small molecules including the chloroaluminate melts(1). R_1^{dd} is obtained by measuring T_1 , the Nuclear Overhauser Enhancement factor, η ($\eta_{max} = \gamma_H/2\gamma_C$) and using eqn [2](6):

$$R_1^{dd} = \eta R_1 / 1.988$$
 [2]

The other part of the DSP method involves determination of quadrupolar relaxation rates for nuclei such as 27 Al and 23 Na. If there is a distortion from tetrahedral or cubic symmetry, nuclei such as 27 Al and 23 Na will be under the influence of an electric field gradient which produces the quadrupole interaction. The quadrupole interaction is affected by the reorientation motion of the 27 Al or 23 Na containing molecule(complex) and the quadrupolar relaxation rate in the "extreme narrowing region" is given by[3](5,7):

$$R_{1} = [3\pi^{2}(2I+3)/10I^{2}(2I-1)][1+(z^{2}/3)][e^{2}Qq/h]^{2}\tau_{c}$$
[3]

where I = 3/2 for ²³Na and 5/2 for ²⁷Al, eQ is the nuclear quadrupole moment, eq is the maximum component of the electric field gradient tensor, and z is the asymmetry parameter of the electric field gradient tensor(z = 0 for AlCl₃).

The quadrupole coupling constant, QCC, is given by:

$$QCC = [e^2 Qq/h]$$
^[4]

If there are two spin probes within the same molecule(or complex) and the motion of the molecule(complex) is isotropic within the "extreme narrowing region", it is possible to equate τ_{eff} from [1] with τ_c from [3]. This results in a linear plot of R_1^{dd} vs R_1 (quadrupolar)(see eqn [5]) which must pass through or near the origin(2,3). Furthermore, values for the QCC in the liquid state are easily obtained from the slope of the linear plot(2,3).

The Dual Spin Probe (DSP) NMR relaxation method has been successfully applied to chloroaluminate melts buffered to neutrality with NaCl(8). Use of ¹³C, ²⁷Al and ²³Na NMR has produced evidence[1-3] that MEI⁺, AlCl₄⁻ and Na⁺ form complexes in the melt(1,2) with the ring hydrogens of MEI⁺ interacting with the tetrachloroaluminate anion. The existence of such complexes has been verified by linear plots of ¹³C dipolar relaxation rates(R₁^{dd}) vs. quadrupolar ²⁷Al relaxation rates(R₁) that pass through the origin as predicted by equation [5]:

$$R_1^{dd}({}^{13}C)/N_H(\hbar\gamma_C\gamma_H)^2 r_{CH}^{-6} = R_1({}^{27}Al)/\alpha\chi^2$$
 [5]

where $\alpha = [3\pi^2/10][(2I + 3)/I^2(2I - 1)][1 + (z^2/3)],$

In this study, the DSP method is applied to melts containing MEICl, $AlCl_3$ and $EtAlCl_2$. The inclusion of $EtAlCl_2$ provides a "baseline" as there is a covalent bond between the ethyl group and aluminum in $EtAlCl_2$. The existence of covalent bonding(or complex formation) between quadrupolar and dipolar nuclei in a molecule results in a linear plot of eqn. [1] that passes through the origin. In the MEICl-EtAlCl₂ melts reported herein, we observe a linear plot of eqn [1] that passes through the origin when applied to the terminal CH₃ carbon in EtAlCl₂.

EXPERIMENTAL

Materials

The 1-methyl-3-ethylimidazolium chloride(MEICl) and chloroaluminate molten salts were prepared as described previously(9). Ethylaluminum dichloride(EtAlCl₂) was obtained from Aldrich. All materials were stored under anhydrous helium gas atmosphere in a dry box. All molten salt preparations and manipulations were performed in the dry box. Samples were loaded into 5 mm sample tubes, capped in the dry box, removed, and sealed immediately with a torch.

NMR Measurements

¹³C and ²⁷Al NMR spectra were recorded on a Varian XL-300 spectrometer operating at 75.43 or 78.15 MHz. Temperature measurements were calibrated against methanol or ethylene glycol and are accurate to within 0.5° C. Pulse widths(90°) were typically 8.6(75.43 MHz) and 7.6(78.15 MHz) μ s. Longitudinal(spin-lattice) relaxation times were measured by the the inversion-recovery method ($180^{\circ}-\tau$ -90°-T) with T>10T₁. At least 12 delay times(τ) were used and the results fitted to a three parameter exponential. NOE (η) measurements were made using the gated decoupler method(10) in which the fully decoupled spectrum is compared with one in which decoupling is present only during the acquisition time. It is likely that the error in the NOE measurements is in the 5-10% range(10).

RESULTS AND DISCUSSION

Theoretical

In an attempt to determine the relative stability of the various neutral and anionic Alcontaining species and gain an indication of their relative concentrations, we have used semi-empirical methods(MNDO-PM3) to determine the heats of formation of the various species that might be present in these melts. The semi-empirical methods tend to overestimate the heats of formation by a factor of two for the various aluminum containing species when compared with ab initio results. The semi-empirical methods indicate that the order of stability is $AlCl_4^- \approx EtAlCl_3^- > Et_2Al_4 \approx EtAl_2Cl_5 \approx$ $Al_2Cl_6 >$ mixed anionic dimers. The differences in heats of formation between each group of compounds is approximately 6 kcal, using the semi-empirical results to extrapolate the ab initio calculations.

NMR Peak Assignments

The ability of both AlCl₃ and EtAlCl₂ to form C_{2h} dimers(11,12) led us to examine the ²⁷Al spectra of neat EtAlCl₂ and 50/50 mixtures of MEICl-EtAlCl₂. The EtAlCl₂(neat) ²⁷Al NMR spectrum shown in Fig. 1 contains two peaks. Peak 1 is a broad downfield peak that dominates the spectrum. The second peak(upfield) overlaps peak 1 and is only a fraction of peak 1 in peak area. Peak 2 collapses into peak 1 as the temperature is lowered from 60 to 25°C. These two aluminum sites would account for the monomer-dimer formation in liquid EtAlCl₂. The relaxation time of peak 1 is in the μ s range(Table I) with its relative concentration preventing the accurate determination of peak 2's relaxation time.

The MEICl-EtAlCl₂ (N = 0/0.5/0.5) melt ²⁷Al NMR spectrum shown in Fig. 2 contains two peaks. In this case, peak 1(downfield) is very broad and has a relaxation time of 211 μ s while peak 2 is very sharp, has a low peak area and a relaxation time of 88 ms. Peak 2 increases slightly in area and peak 1 broadens as the temperature is lowered from 70 to 0°C.

We shall make the tentative assignments of the two species $EtAlCl_3^-$ and $Et_2Al_2Cl_4$ for peak 1(downfield) and a mixture of $AlCl_4^-$ and various dimers for peak 2. The differences in line widths between peaks 1 and 2 may be attributible to differences in symmetry and volume between the two species. On the average, the mixture of species responsible for peak 1($Et_2Al_2Cl_4 - C_{2H}$; $EtAlCl_3^- - C_{3v}$) exist in a higher symmetry state and occupy more volume than those responsible for peak 2. This would account for the variations in relaxation time between the two peaks. A similar interpretation has been made for $AlCl_4^-$ and $Al_2Cl_7^-(13)$ for ²⁷Al relaxation times assuming that the liquid state structure of $Al_2Cl_7^-$ has similar symmetry(C₂) in both the liquid and solid state(14).

Results of the DSP method(eqn. [5]) applied to this 0/50/50 melt(Fig. 3) indicate interactions between the Al-containing species and the NCH₃ group of MEI⁺. There is no evidence for interaction between the ring hydrogens on MEI⁺ and any Al-containing species.

The 78.15 MHz ²⁷Al NMR spectrum of a AlCl₃-MEICl-EtAlCl₂ melt(N = 0.25/0.4/0.35) contains three peaks as shown in Fig. 4. Peak 1 is the broad downfield peak, peak 2 is the major peak and peak 3 is a small but sharp upfield peak. The ²⁷Al relaxation times of peaks 2 and 3 are in the ms range while the relaxation time of the peak 1 is in the μ s range (Table I). In similar melts(Fig. 5,6) where the mole fractions of AlCl₃ and EtAlCl₂ are changed(N = 0.3/0.4/0.3 and 0.35/0.4/0.25), both the downfield and upfield peaks rapidly decrease, with peak 3 barely visible as a shoulder

in the 0.35/0.4/0.25 melt at 60°C. In the case of all three melts, the ²⁷Al relaxation time of the downfield peak(peak 1) is in the μ s range while the other peaks(2 and 3) are in the ms range(Table I). Our assignments for these melts are the same as for the others with peak 1 representing a mixture of EtAlCl₃⁻ and the dimer of EtAlCl₂. Peak 2 contains AlCl₄⁻ and mixed dimers, while peak 3 represents residual EtAlCl₂ monomer, as in the neat EtAlCl₂ sample.

Melt Composition	1		2	2		3	
(AlCl ₃ /MEICl/EtAlCl ₂)	Τ ₁ (μ	s) δ	T ₁ (ms	ς) δ	T ₁ (m	s) δ	
EtAlCl ₂ (neat)	115	128.2		96			
0/40/60	80	131.0	16.4	103.0			
0/45/55	85	130.0	37.0	103.0			
0/50/50	201	128.5	87.7	103.0			
25/40/35	68	130.8	6.1	102.6	3.8	95	
30/40/30	68	130.2	5.7	102.6	3.3	95	
35/40/25	59	127.0	1.7	102.5	1.8	95	
15/50/35	206	129.2	100	103.5		102.5	
20/50/30	205	129.2	80	103.4		102.4	

Table I: Spin-lattice Relaxation Times(T₁) and Chemical Shifts $(\delta \text{ in ppm})^*$ of EtAlCl₂ Melts at 60°C and 78.15 MHz

Peak Number

* - Chemical shifts relative to $Al(H_2O)_6^{3+}$

Application of the DSP method to the 25/40/35 and 35/40/25 melts yield results similar to those obtained for the 0/50/50 melt(Fig. 3). The only correlation that exists other than the EtAlCl₂ baseline is the one between the EtAlCl₂ ²⁷Al relaxation and the NCH₃ ¹³C dipolar relaxation. Table II contains the QCC values obtained from the slopes of the various relaxation plots(eqn. 3). If a value of N_H = 9(3 methyl groups) is used for the QCC calculations, similar values are obtained for both NCH₃ and EtAlCl₂ as expected. This suggests that the Al-containing species is interacting with more than one MEI⁺ cation in the melts.

Table II: Quadrupolar Coupling Constants (MHz) for EtAlCl₂ Melts[N_H = 3(9)]

Peak Number

Melt Composition (AlCl ₃ /MEICl/EtAlCl ₂)	$\frac{1}{\text{NCH}_3 \text{ EtAlCl}_2}$	NCH ₃ EtAlCl ₂	$\frac{3}{\text{NCH}_3 \text{ EtAlCl}_2}$
(0/50/50)	58(100) 103	23(4.0) 4.2	
(25/40/35)	159(275) 285	9.9(17.9) 18.6	10.9(18.9) 22.2
(35/40/25)	164(285) 284	24.7(42.8) 51.0	

CONCLUSIONS

Application of the DSP probe method to these mixed melt systems indicates a lack of complexation between the ring hydrogens of MEI^+ and any of these aluminum containing species. These results suggest that the formation of various neutral dimers containing $EtAlCl_2$ takes precedence over the formation of complexes between $EtAlCl_3^-$ and the MEI^+ ring hydrogens. However, there is evidence of interaction between the various Al-containing species and the methyl group of MEI^+ in these melts.

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Fig. 6. ²⁷Al NMR spectrum of 35/40/25 (AlCl₃/MEICl/EtAlCl₂) melt at 60°.

NMR MEASUREMENTS IN SOLUTIONS OF DIALKYLIMIDAZOLIUM HALOALUMINATES

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Abstract

Nuclear magnetic resonance (NMR) spectra using ²⁷Al and ³⁵Cl were measured for AlCl₃-1-ethyl-3-methylimidazolium chloride (EMIC) melts with initial compositions ranging from 50 to 67 mol% AlCl₃ at room temperature. It was shown by changing the preaquisition delay time (DE value) that the dominant aluminum species are AlCl₄⁻ in the melt formed by mixing 50 mol% AlCl₃ with EMIC and Al₂Cl₇⁻ in the 67 mol% AlCl₃ melt. In the equimolar mixture, the chemical shift of the ²⁷Al NMR resonance is 103.28 ppm, and the line width is 22.83 Hz. In the 67 mol% AlCl₃ mixture, the chemical shift is 103.41 ppm, and the line width is 2624 Hz. A third species observed at 97 ppm in the ²⁷Al spectra for the 55 and 60 mol% AlCl₃ mixtures is identified to be a product of the reaction with residual water. The relaxation rates were determined for each species in the melts.

Introduction

Dialkylimidazolium chloroaluminates are promising new room-temperature molten salts.¹ In addition to their importance for fundamental electrochemical studies, these chloroaluminates have potential applications for high-energy batteries² and for use in carrying out chemical reactions. Recently, AlCl₃ - 1-ethyl-3-methylimidazolium chloride (AlCl₃-EMIC) has been used successfully for the electroplating of Al on iron steels.³

The major equilibrium describing the acid-base properties of the tetrachloroaluminate ionic liquids is given in eqs (1) and (2).

Cl ⁻ + AlCl ₃ ≓AlCl ₄ ⁻	(1)
AlCl₄ + AlCl3,⇔Al2Cl7	(2)

In basic solutions, i.e., when the AlCl₃ composition is less than 50 mol%, the major aluminum-containing species is AlCl₄⁻. At more acidic compositions, when the AlCl₃ composition is approximately 67 mol%, Al₂Cl₇⁻ becomes the predominant species. The structure of the Al₂Cl₇⁻ ion consists of two AlCl₄⁻ tetrahedra sharing a corner chloride moiety. These species have been identified from electrochemical,⁴ NMR (¹H, ¹³C, ²⁷Al),^{5,6} and IR techniques.

To understand the detailed structure and dynamics of AlCl₃ - EMIC melts, we have initiated a series of measurements involving X-ray and neutron diffraction, Raman spectroscopy, and NMR of both ²⁷Al and ³⁵Cl. In this paper, we report results obtained by the latter technique.

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Experimental

The ²⁷Al and ³⁵Cl NMR spectra were recorded using a General Electric GN-300 spectrometer and 10-mm probe that could be tuned for ²⁷Al or ³⁵Cl. The receiver coil was tuned to optimize the detection of ²⁷Al resonances at 78.3 MHz or ³⁵Cl resonances at 29.5 MHz. The ²⁷Al NMR chemical shifts were referenced to an external Al(H₂O)₆³⁺ standard. The ³⁵Cl NMR chemical shifts were referenced to an external Cl⁻ standard. The molten salts were obtained by mixing highly anhydrous AlCl₃ with EMIC at 60°C. The mixtures were prepared by weighing corresponding amounts of AlCl₃ and EMIC in a glovebox, where the levels of H₂O and O₂ were maintained at less than 2 ppm. The water content of the mixture was measured by IR and found to be less than 100 ppm.

Results

The ²⁷Al and ³⁵Cl NMR spectra were recorded for five nominal compositions of the AlCl₃-EMIC molten salt system, covering the neutral melt to the acidic region. In what follows we present results obtained for these mixtures and highlight the effect of compositional changes and time resolution.

A- Effect of composition changes The dependence of the ²⁷Al NMR spectra on the initial AlCl₃ mol% was measured at room temperature. The ²⁷Al NMR spectrum of the 60 mol% AlCl₃ mixture is shown in Fig. 1. In the neutral melt, the chemical shift is 103.28 ppm, and the line width, i.e., the full peak width at half height ($\Delta v_{1/2}$), is 22.83 Hz. With increasing AlCl₃ content, the chemical shifts become slightly larger and the line width markedly broader. At 67 mol% AlCl₃ mixture, the chemical shift is 103.41 ppm and the line width is 2624 Hz. The ³⁵Cl NMR spectrum of the melt with 60 mol% AlCl₃ is shown in Fig. 2. At the equimolar mixture, only one ³⁵Cl resonance was observed. An additional ³⁵Cl resonance appears in more acidic melts.

B- Effect of time resolution It is possible to resolve species with substantially different line widths by varying the preaquisition delay time (DE), because the free induction decay falls off more rapidly for species with large line widths than for species with sharp NMR resonances. This technique is particularly useful to resolve species at trace concentrations, provided that the species in question have a sharper line width than the line width(s) of the major component(s) of the molten salt. The ²⁷Al NMR spectra obtained with a 300 µs DE for molten salts with two AlCl₃ contents are shown in Fig. 3. The $\Delta v_{1/2}$ for the 50 and 67 mol% AlCl₃ mixtures were independent of the preaquisition delay time. In contrast, two partially resolved peaks were seen by varying the DE value for the metts with 55 to 64 mol% AlCl₃ mixture at preaquisition delay times longer than 2.25 ms. Similarly, for the 60 mol% AlCl₃ mixture, the sharp peak at approximately 97 ppm was observed at preaquisition delay times longer than 0.7 ms. The $\Delta v_{1/2}$ was constant for the peak at 97 ppm as the delay time was varied.

Discussion

The tetrahedral symmetry of the AlCl₄⁻ species minimizes line broadening due to the quadrupole moment of the ²⁷Al nucleus. In contrast, the lower symmetry of the Al₂Cl₇⁻ ion, which is composed of two corner-sharing AlCl₄⁻ tetrahedron, results in efficient nuclear quadrupolar induced spin relaxation. The results shown in Fig. 1 demonstrate the

substantial line broadening due to the presence of $Al_2Cl_7^-$, at $AlCl_3$ compositions greater than 50 mol%. In addition, the ³⁵Cl spectra (Fig. 2) support the formation of $Al_2Cl_7^-$, because the additional peak at 1800 ppm may be associated with the bridging chloride moiety in the $Al_2Cl_7^-$ ion.

At room temperature, the spectra for the 50 and 67 mol% AlCl₃ mixtures were unaffected by increasing the DE value, t_1 . This implies that only one aluminum species exists for these melt compositions. If it is assumed that only one species is formed, then the value of the relaxation rate $(1/T_2^*)$ is obtained from eq.(3),

$$M_{\Lambda} = M^{0} exp(-t_{1}/T_{2\Lambda}^{*})$$

 $M_{B} = M^{0} exp(-t_{1}/T_{2B}^{*})$ (3)

where A refers to AlCl₄⁻ and B to Al₂Cl₇⁻. Furthermore, M_A, M_B are the total magnetic moments for species A and B, respectively. Plots of ln M_A and ln M_B vs. DE were found to be linear. A relaxation rate, $1/T_{2A}^*$, of 65.7 s⁻¹ is obtained for the AlCl₄⁻ species from the slope for the 50 mol% AlCl₃ mixture. The corresponding $1/T_{2B}$ * is 8500 s⁻¹ for the Al₂Cl₇ species from the slope for the 67 mol% AlCl₃ mixture. For the 55-64 mol% AlCl₃ mixtures, the $\Delta v_{1/2}$ values changed with the DE values, indicating that more than one aluminum-containing species is present in these solutions. However, using a DE value greater than 2.25 ms for the 55 mol% AlCl₃ mixtures produced no further reduction in the $\Delta v_{1/2}$. This indicates that the delay time resolution is adequate at a DE value of 2.25 ms. For DE values greater than 2.25 ms, the ln M vs. DE plot shows a single exponential decay. The value of 1/T₂* for the third component at 97 ppm is 503 s⁻¹. Gray and Maciel⁷ concluded that this narrow peak corresponded to AlCl₄ in the AlCl₃-butylpyridinium chloride system. However, we believe that this peak is due to another species, because the chemical shift is low, 97 ppm, and the concentration of this species is quite small, 0.3%. This third aluminum-containing species at 97 ppm is considered to be the result of the minute quantity of water in the initial mixtures. As mentioned earlier, IR measurement of these mixtures revealed less than 100 ppm of H₂O. For the 60 mol% AlCl₃ mixture, the ln M vs. DE plot shows a single exponential decay for delay times greater than 0.7 ms and vields a value of 854 s⁻¹ for $1/T_2^*$.

Conclusion

In this ²⁷Al and ³⁵Cl NMR study, we have shown that the dominant aluminum species in AlCl₃-EMIC melts are AlCl₄⁻ in the equimolar mixture and Al₂Cl₇⁻ in the 67 mol% AlCl₃ mixture. In the acidic melts (>50 mol% AlCl₃), very small amounts of a third species exist. This third species is a product of the reaction with residual water contained in the initial mixtures. The concentration of the Al₂Cl₇⁻ ion increases, as expected, with the degree of acidity. The relaxation rate $1/T_2^*$ is ~70 s⁻¹ for AlCl₄⁻ and ~8500 s⁻¹ for Al₂Cl₇⁻, consistent with the symmetry of these two ionic species and a nuclear quadrupole-electric dipole relaxation mechanism.
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Chemical shift δ / ppm

Fig. 1 ²⁷Al NMR spectra of 60 mol% AlCl₃ mixture at room temperature.



Fig. 2 ³⁵Cl NMR spectra of 60 mol% AlCl₃ mixture at room temperature.



Fig. 3 ²⁷Al NMR spectra with 300 μs DE value for AlCl₃ - EMIC mixtures at room temperature.
(a) 60 mol% AlCl₃ mixture; (b) 67 mol% AlCl₃ mixture

THE ELECTROCHEMISTRY OF ALUMINUM AND PROTONS IN ROOM TEMPERATURE CHLOROALUMINATE MOLTEN SALTS BUFFERED WITH SODIUM CHLORIDE

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ABSTRACT

As an electrolyte the Lewis neutral, room temperature, chloroaluminate molten salt, MEICl/AlCl₃ (MEICl = 1-methyl-3ethylimidazolium chloride) provides a voltage window of greater than 4V. To maintain this voltage window, the electrolyte must be buffered by a chloride salt such as NaCl. In the present work the electrochemistry of a NaCl buffered melt was studied using Pt, W, and glassy carbon electrodes. When excess NaCl is added to an N=0.55 melt a "neutral" melt results, saturated with NaCl. On Pt and W electrodes, the cyclic voltammetry shows several small overlapping reduction peaks which lead to a small, but distinct oxidation peak at about -0.1V (vs an Al/Al³⁺ N=0.6 melt reference). Comparison to the voltammogram of an N=0.5002 melt (no NaCl) suggests that the oxidation process is aluminum stripping. Voltammograms of the neutral melt and N=0.5002 melt after prolonged reductions both display very The potential of the stripping peaks large, sharp stripping peaks. does not match that of a very acidic N=0.55 melt. This is because the stripping peak shifts from about -0.1V to 0.3V as the Lewis acidity increases from neutrality to N=0.55. The presence of the Al stripping peak in the voltammogram of the buffered melt means that this melt is still slightly Lewis acidic even when saturated with NaCl.

Although treated with ethylaluminum dichloride, residual protons are still present in the buffered melts. Overlapping reduction peaks in the voltammograms lead to a sharp, intense oxidation at 0.8V on a Pt electrode. Using a W electrode the peak is less pronounced, and it is absent from voltammograms obtained using a glassy carbon electrode. On the metal electrodes protons are believed to be reduced leading to adsorbed H₂, which then is oxidized near 0.8V.

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INTRODUCTION

Lewis neutral room temperature chloroaluminate molten salts made by mixing 1-methyl-3-ethylimidazolium chloride (MEICl) and aluminum chloride are being investigated as possible battery electrolytes because of their wide potential windows (1,2). It has been shown that such Lewis neutral (N=0.5) MEICl/AlCl₃ melts can provide a voltage window of 4.4V(2). To maintain this voltage window, the electrolyte must be Lewis buffered, which can be achieved by the addition of alkali chloride salts such as NaCl(3). If the Lewis acid AlCl₃ is added to a buffered melt, reaction with NaCl produces the neutral species, AlCl₄⁻. If the Lewis base MEICl is added, the chloride ion is removed by precipitation with sodium ion. Thus, such a melt is buffered against the addition of both Lewis acids and bases and a wide voltage window can be maintained in the presence of other species.

Although a few studies of alkali metal reductions in neutral and/or buffered melts have appeared (4-7), no detailed examinations of the melts themselves have been made. We present here a detailed investigation of the electrochemistry of NaCl buffered MEICI/AlCl₃ melts at Pt, W and glassy carbon electrodes. Within the voltage window established by the buffered melt, the cyclic voltammograms show several small reduction and oxidation peaks which correspond to low concentrations of aluminum species and residual protons.

EXPERIMENTAL

Instrumentation

Cyclic voltammetry and chronoamperometry were performed using a Princeton Applied Research (PAR) Model 273 Potentiostat/Galvanostat interfaced to a personal computer using PAR 270 software. A three-electrode system was used. The working electrode was either a Bioanalytical Systems (BAS) model MF-2013 Pt electrode, a BAS model MF-2012 glassy carbon electrode, or a homemade W electrode consisting of a W wire, 0.5 mm dia., 99.98% (Alfa), sealed in a Pyrex tube and polished smooth. The auxiliary electrode was a Pt flag and the reference electrode was an aluminum wire, 0.58 mm dia., 99.999%, (Alfa), inserted into an N=0.60 MEICl/AlCl₃ melt in a Pyrex tube with an asbestos tip for the junction. All electrochemical experiments were carried out in a Vacuum Atmospheres dry box under a helium atmosphere estimated to contain combined oxygen and water of less than 10 ppm.

Scanning electron microscopy was carried out using an Amray Model 1830 scanning electron microscope. The SEM was fitted with an ECON IV EDAX detector from which energy dispersive spectra of electrode surfaces were obtained.

The data was processed with PV9900 software and ZAF corrections were made when possible.

Reagents and Melt Synthesis

Sodium chloride (Aldrich, 99.999%) was dried in an oven before use. Acetonitrile (Fisher, HPLC grade) was refluxed over P₂O₅ before use.

The melt components, MEICl and AlCl₃ were made and purified as described earlier (1,3). The melts were made in the glove box by the slow addition of AlCl₃ to MEICl. Protons were removed from Lewis neutral melts by the dropwise addition of ethylaluminum dichloride (Aldrich, 97%) (8). Neutral buffered melts were made by first slowly adding enough AlCl₃ to MEICl to form an N=0.55 (acidic) melt. Based on the calculated concentration of Al₂Cl₇⁻, a 20% excess of NaCl was added and the melt was stirred overnight before use. Cyclic voltammetry indicated that the melt was neutral by the absence of both the reduction peak for Al₂Cl₇⁻ and the oxidation peak for Cl⁻. For plating experiments followed by SEM examination, the buffered melts were filtered before use to remove the excess NaCl.

RESULTS AND DISCUSSION

Several steps are involved in preparing a NaCl buffered neutral melt (3). A neutral melt is first made by adding AlCl₃ to MEICl to reach a 1:1 stoichiometry, (N (mole fraction AlCl₃) = 0.5). Since such melts always contain some protonic impurities, EtAlCl₂ is added to reduce the protons to a residual level (8). The cyclic voltammogram of the resulting melt is flat and has a voltage limit of greater than 4V. At a Pt electrode the window is 2.4V to -2.2V (7). Because of their activity on Pt, the residual protons still show up as two low current, broad, overlapping reduction peaks between 0.0 and -1.0V. Less pronounced oxidation peaks sometimes are evident at positive potentials.

The next step in preparing a buffered melt is to make the melt Lewis acidic by adding AlCl₃. More acidic melts will give higher buffer capacities since more chloride salt is required to neutralize the Al_2Cl_7 . Typically an N=0.55 melt is used. The cyclic voltammogram of such a melt is given in Fig. 1. The Al_2Cl_7 is reduced to Al° at -0.38V. The plated aluminum is stripped from the electrode at 0.30V. The crossing of the two scan segments at -0.2V is indicative of a plating/stripping couple. Integration of the peaks indicates that 97.6% of the Al is stripped off. (Note that integration of the reduction peak includes the area under part of the reverse scan segment.) To buffer the melt, NaCl is added to neutralize the Lewis acid:

$$NaCl + Al_2Cl_7 \rightarrow Na^+ + 2AlCl_4^-$$

Based on a 1:1 stoichiometry, NaCl is added in a 20% molar excess over Al₂Cl₇⁻. The melt is stirred >12 hours to ensure equilibration. (The melt may also be heated up to 90°C to promote more rapid reaction.)

For the present work, buffered melts were prepared as described above and the resulting cathodic scan cyclic voltammogram using a Pt electrode is shown in Fig 2. Besides small proton reduction peaks in the 0.0 to -1.0V region, two new reduction peaks and two new oxidation peaks appear. The reduction peak at -1.2V is present on all cathodic scans, while the -1.6V reduction peak is not present on voltammograms using a freshly polished electrode. The anodic scan segment shows a small but distinct oxidation peak at about -0.1V and a large oxidation spike at 0.8V. (See also Fig. 1, ref. 7.) The rest potential of the system is about 1.0V, which is positive of both oxidation peaks. Thus, an initial anodic scan shows no oxidations (Fig. 3). This means that the oxidation peaks must be a result of the reduction processes rather than due to species originally present in the melt.

To determine which reduction peaks lead to the oxidations, a negative scan limit study was done. Several cathodic scan voltammograms were recorded, reversing the scans just after each reduction peak, proceeding more negatively with each experiment. The 0.8V oxidation first appeared when reversing the scan at -0.54V, while the -0.1V oxidation only appeared on scans going to -1.40V or more negative. The oxidation peaks get larger with more negative scans, but scanning beyond -2.0V leads to a black passivating film on the electrode. The reduction process at -0.3V and other small peaks may be proton reductions and seem to lead to the 0.8V oxidation. (This will be discussed later, in comparison to the results on W and glassy carbon electrodes.)

The reduction peak at -1.2V or a process buried under the broad reduction envelope, gives rise to the oxidation peak at -0.1V. The potential and shape of this peak suggest that it may be an Al stripping peak. To pursue this, a variety of chronoamperometry experiments were carried out at -1.4V. In most cases the electrodes were rinsed in acetonitrile after plating, to remove the melt. The plated electrodes were then examined with a scanning electron microscope and deposits on the surface were analyzed by collecting energy dispersive spectra. Although some spectra indicated excess aluminum (compared to that expected for residual AlCl₃) the results did not conclusively show Al plating. Further electrochemical experiments were done to identify the -0.1V oxidation peak. Chronoamperometry was again carried out at -1.4V. Immediately after this reduction process, a two-cycle anodic voltammogram was recorded (Fig. 4). On the first cycle there is a very sharp, intense, oxidation peak near the potential of the -0.1V oxidation of the original voltammogram. On the second cycle this peak is gone. This data suggests that Al is plated during the chronoamperometry step and stripped completely by one voltammetric scan.

Although the shape of the -0.1V oxidation peak is indicative of a stripping process, it does not match the shape or potential of Al stripping in an N=0.55 melt (Fig. 1). To investigate these differences, incremental additions of AlCl₃ were made to a neutral, unbuffered (no NaCl) melt. The first addition of AlCl₃ resulted in an N=0.5002 melt, whose voltammogram is given in Fig. 5. The reduction and oxidation peaks are quite similar to those seen in Fig. 2 for a buffered melt. Anodic scans produced no oxidations until a few complete cycles had been completed. Cathodic scans to -0.7V led to the 0.8V oxidation, while scanning to -1.6V was required before the -0.1V oxidation appeared.

Chronoamperometry at -1.6V was carried out in an experiment analgous to that for the buffered melt. The resulting voltammogram recorded immediately after the reduction step is shown in Fig. 6. Clearly, a stripping process occurred just as in the buffered melt experiment (Fig. 4). (A chronoamperometry experiment was also carried out at -1.3V on a neutral, unbuffered melt as a blank. No stripping peak was observed on the subsequent voltammogram.) These data indicate that a buffered melt is slightly Lewis acidic and permits the plating and stripping of Al.

Further additions of AlCl₃ were made to the neutral, unbuffered melt to investigate the shape and potential of the stripping peak as the concentration of $Al_2Cl_7^{-1}$ is increased. Melts with compositions of N=0.501, 0.510, and 0.530 were investigated. As the Lewis acidity increased, the Al plating and stripping peaks began to resemble those of the N=0.55 melt (Fig. 1). (The small reduction peaks and the oxidation at 0.8V disappeared due to the compressed current scale.) Specifically, the stripping peak became broader and shifted to more positive potentials, verifying its assignment to Al.

Nearly all of the experiments described above were also carried out on W with similar results. Figure 7 is a cathodic scan cyclic voltammogram of the NaCl buffered melt. It is quite similar to the Pt voltammogram (Fig. 2) except that the 0.8V oxidation peak is much less pronounced. An anodic scan shows no oxidations until after the scan proceeds through the reduction waves. The results of a negative scan limit study were similar to those on Pt, indicating that the reduction process at -1.4V is responsible for the -0.1V oxidation. The results of a plating

experiment at -1.4V are shown in Fig. 8. This anodic scan voltammogram was recorded immediately after plating and shows the -0.1V stripping peak as seen on Pt (Fig. 4). A similar plating experiment was done at -1.6V on W in the N=0.5002 melt. The resulting voltammogram again showed the sharp stripping peak at -0.1V. (The blank experiment on a neutral, unbuffered melt showed no peak).

The potential of the -0.1V oxidation peak was also monitored as a function of melt composition. As on Pt, the peak shifted positively as more AlCl₃ was added to the N=0.5002 melt.

Table I compares the Al stripping potentials for buffered, slightly Lewis acidic, and neutral unbuffered melts at Pt and W electrodes. In Lewis acidic melts Al_2Cl_7 is reduced via the reaction:

$$4\mathrm{Al}_{2}\mathrm{Cl}_{7}^{-} + 3\mathrm{e}^{-} \rightarrow \mathrm{Al} + 7\mathrm{Al}\mathrm{Cl}_{4}^{-}$$

$$\tag{9}$$

For an N=0.5002 melt, $[Al_2Cl_7] = 3.70 \times 10^{-3} M$. The data indicate that for the buffered melt Al_2Cl_7 is near this concentration and hence the melt is slightly Lewis acidic.

Table II shows that in unbuffered melts the Al stripping peak potential shifts positively with increasing Lewis acidity, thus explaining the difference in potential between the N=0.55 melt and the buffered melt. Considering the data from both tables, it is clear that the buffered melt is acidic, but its composition is probably somewhat less acidic than N=0.5002 and thus $[Al_2Cl_7]$ is less than 3.70 x 10^{-3} M.

To help identify the oxidation peak seen at 0.8V on Pt (and much less pronounced on W) the buffered melt was also examined using a glassy carbon electrode. Glassy carbon is very insensitive to protons as verified by the voltammogram for a neutral, unbuffered melt on which the residual protons were not seen. An N=0.55 melt showed the Al plating and stripping peaks at very high currents, but no smaller peaks. Also, the voltammogram of the buffered melt on glassy carbon was featureless. This means that low concentrations of Al_2Cl_7 and protons are inactive on glassy carbon.

In summary, the residual proton reduction peaks and the 0.8V oxidation peak are pronounced on Pt, weak on W, and not observed on glassy carbon. Thus, it is proposed that on Pt, protons are reduced to $H_2(g)$ which is adsorbed on the electrode. The sharpness of the 0.8V oxidation peak suggests that it is a "stripping" peak for the oxidation of adsorbed H_2 back to a protonic species.

Table I

A1 Stripping Potentials*

Melt	Working Electrode		
Composition	<u>Pt</u>	W	
Buffered	-0.1582V	-0.1212V	
N=0.5002	-0.0642	-0.0872	
Neutral unbuffered (blank)	No peak	No peak	

*From anodic cyclic voltammograms recorded immediately after chronoamperometry.

Table II

Al Stripping Potentials of Unbuffered Melts*

Melt Composition	Working Electrode		
N	<u>Pt</u>	$\underline{\mathbf{W}}$	
0.5002	-0.1122V	-0.0872V	
0.5010	-0.0872	-0.0232	
0.5100	0.0508	0.0018	
0.5300	0.1988	0.0998	
0.5500	0.3088	0.1238	

*From cathodic cyclic voltammograms.

CONCLUSIONS

It has been shown that NaCl buffered MEICl/AlCl₃ melts remain slightly Lewis acidic when equilibrated. The buffering of an acidic melt with NaCl is analogous to buffering a basic melt with a metal chloride (10). In both cases true Lewis neutrality is probably not reached. Nonetheless, NaCl buffered melts have been shown to resist change upon the addition of a Lewis acid or base (3) and the currents resulting from low concentrations of Al_2Cl_7 do not appear to limit the useful voltage window of the electrolyte.

The effect of residual protons appears to depend on the working electrode material. As with the small concentration of Al_2Cl_7 , the residual protons do not appear to affect the useful voltage window of the electrolyte. On the other hand, these species may result in unwanted side reactions or short lifetimes for operating batteries.

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Fig. 1 Cathodic scan cyclic voltammogram of an N=0.55 MEICI/AlCl₃ melt at a Pt electrode. Scan rate: 100 mV/sec.



Fig. 2 Cathodic scan cyclic voltammogram of a NaCl buffered MEICI/AlCl₃ melt at a Pt electrode. Scan rate: 100 mV/sec.



Fig. 3 Anodic scan cyclic voltammogram of a NaCl buffered MEICl/AlCl₃ melt at a Pt electrode. Scan rate: 100 mV/sec.



Fig. 4 Two continuous anodic scan cyclic voltammograms of a NaCl buffered MEICI/AICl₃ melt at a Pt electrode. Scan rate: 100 mV/sec. Recorded immediately after chronoamperometry at -1.40V for 600 sec. with stirring.



Fig. 5 Cathodic scan cyclic voltammogram of an N=0.5002 MEICl/AICl₃ melt at a Pt electrode. Scan rate: 100 mV/sec.



Fig. 6 Two continuous anodic scan cyclic voltammograms of an N=0.5002 MEICI/AICl₃ melt at a Pt electrode. Scan rate: 100 mV/sec. Recorded immediately after chronoamperometry at -1.60V for 600 sec. with stirring.



Fig. 7 Cathodic scan cyclic voltammogram of a NaCl buffered MEICI/AICl₃ melt at a W electrode. Scan rate: 100 mV/sec.



Fig. 8 Two continuous anodic scan cyclic voltammograms of a NaCl buffered MEICI/AICl₃ melt at a W electrode. Scan rate: 100 mV/sec. Recorded immediately after chronoamperometry at -1.40V for 3600 sec. with stirring.

STANDARD REDUCTION POTENTIALS FOR LITHIUM AND SODIUM IN AMBIENT-TEMPERATURE CHLOROALUMINATE MOLTEN SALTS

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ABSTRACT

By adding protons to LiCl buffered neutral AlCl₃:1-methyl-3-ethylimidazolium chloride

(MEIC) melts, it is possible to measure directly the Li⁺/Li(s) couple. From potential measurements performed in a large number of melts, the standard reduction potential for the Li⁺/Li(s) couple is found to be -2.166 V (std. dev. = 0.005 V) versus Al(III)/Al in a 1.5:1.0 AlCl₃:MEIC reference melt. A Na⁺/Na(s) standard reduction potential of -2.101 V is determined directly in NaCl buffered neutral chloroaluminate melts based on 1,2-dimethyl-3-propylimidazolium chloride (DMPIC) and containing added protons. Using an iridium mercury film electrode (Ir-MFE), the standard reduction potential for Na⁺/Na(s) is found to be -2.144 V in MEIC based melts.

INTRODUCTION

The alkali metals are promising anodes for use in high-energy density batteries which employ ambient-temperature chloroaluminate molten salts as electrolytes (1). Of particular interest are the recently described alkali metal chloride buffered neutral melts AlCl₃:MEIC:MCl where MEIC = 1-methyl-3-ethylimidazolium chloride and MCl is an alkali metal chloride (2-5). Our group has recently determined the formal reduction potentials for the alkali metals in buffered neutral AlCl₃:MEIC:MCl melts by measuring the reduction potentials of the alkali metal mercury amalgams using normal pulse voltammetry (4). From this analysis, we determined that only lithium and sodium are thermodynamically stable towards reduction of the organic cation.

By adding protons to an AlCl₃:MEIC:NaCl buffered neutral melt, Riechel and Wilkes have demonstrated that elemental sodium can be deposited near the negative end of the melt electrochemical window (2). This discovery has opened the way for direct measurement of alkali metal standard reduction potentials in these melts. We report here the extension of this proton addition method to AlCl₃:MEIC:LiCl and AlCl₃:DMPIC:NaCl (DMPIC = 1,2-dimethyl-3-propylimidazolium chloride) buffered neutral melts for the purpose of measuring the standard reduction potentials for lithium and sodium. We are also presenting more detailed studies of the reduction of Li⁺ and Na⁺ at iridium mercury mercury film (Ir-MFE) electrodes. Finally, we will describe *in situ* optical observation

made during the deposition of Li and Na from melts with and without added protons.

EXPERIMENTAL

MEIC and DMPIC were synthesized as previously reported (6,7). Melts were prepared by addition of sublimed AlCl₃ to the organic chloride until the desired mole ratio was obtained. The alkali metal chloride buffered melts were prepared by addition of an excess of the alkali metal chloride to an acidic melt having an initial Al₂Cl₇⁻ concentration equal to the desired alkali metal ion concentration. The mixture was allowed to stir overnight at ambient temperature. The resulting melt was a buffered neutral melt with an alkali metal ion concentration taken to be equal to the original Al₂Cl₇⁻ concentration. MEIHCl₂ was prepared by bubbling HCl gas into MEIC (8). Excess HCl was removed by vacuum. DMPIHCl₂ was prepared in a similar manner starting from DMPIC.

Electrochemical studies not requiring *in situ* optical observations were performed in a Vacuum Atmosphere glove box using a glass vessel fitted with a drilled Teflon cap for the electrochemical cell. For microscopic observations, a specially designed electrochemically cell with an optical glass bottom was employed. A Nikon Epiphot inverted stage microscope was used to make the *in situ* microscopic observations. For all electrochemical experiments, the working electrode was either a a 250-mm diameter disk tungsten electrode or a 127- μ m diameter disk iridium electrode. The reference electrode consisted of an Al wire immersed in a 1.5:1.0 AlCl₃:MEIC (N=0.6) melt contained in a separate glass capillary. The counter electrode was an Al wire dipped directly into the analyte solution. All voltammetric experiments were performed using an EG&G PARC model 273 Potentiostat/Galvanostat controlled with an EG&G PARC 270 software package.

RESULTS AND DISCUSSION

Elemental lithium deposition from AlCl3:MEIC:LiCl.

Figure 1a shows a staircase cyclic voltammogram (scan rate = 500 mV/s) for the reduction of Li⁺ from AlCl₃:MEIC:LiCl (1.1:1.0:0.1; [Li⁺] = 0.445 M) at tungsten before addition of HCl₂⁻. No significant stripping peak is observed upon scan reversal indicating rapid reaction of Li with the melt cation. Optical observations reveal that at -2.2 V (chronoamperometry), the lithium deposits as gray granules; however, this deposit rapidly decomposes to a brown film which slowly fades to a cream color. For long deposition times, an orange film is formed which passivates the electrode surface. The surface of the electrode can be electrochemically cleaned by sweeping the potential to +3.0 V to generate Cl₂ gas by oxidation of AlCl₄⁻.

Figure 1b shows the deposition/stripping behavior for the

Li⁺/Li(s) couple following addition of approximately 0.06 M HCl₂⁻. Gray-blue deposits are formed at -2.1 V (chronoamperometry) which are stable under open-circuit conditions for times up to 15 min. This deposition behavior was reproducible. No passivating film remains on the electrode surface after each run, and no electrode cleaning is required.

Because the addition of protons permits elemental Li to be deposited onto an electrode surface, it is now possible to measure directly the potential of the half-reaction

$$Li^{+} + e^{-} \iff Li(s)$$
 [1]

The standard reduction potential for Eq. [1] is given by

$$E^{O} = E - RT/nF\{\ln(a_{I,i}+)\} = E - RT/nF\{\ln(m_{I,i}+)(\gamma_{I,i}+)\}$$
[2]

where a, γ , and m are the activity, activity coefficient, and molality, respectively, for Li⁺ in the melt. The standard reduction potential can also be expressed in terms of the formal reduction potential, E⁰', using

$$E^{O} = E^{O'} - RT/nF\{\ln(\gamma_{I,i}+)\}$$
 [3]

where

$$E^{O'} = E - RT/nF\{\ln(m_{T};+)\}$$
 [4]

To determine E^{O} , it is necessary to plot the formal potential of the Li⁺/Li(s) couple as a function of m_{T_i} and extrapolate the data to m_{T_i} = 0 where γ_{T_i} = 1 and E^{O} = $E^{O'}$.

We have prepared a number of AlCl₃:MEIC:LiCl melts and deposited elemental Li onto the electrode surface using chronopotentiometry. By releasing the manual "cell enable" switch on the Model 273 Potentiostat/Galvanostat while still recording the potential, we obtain a trace of the open-circuit potential for the Li⁺/Li couple. A typical experiment is shown in Figure 2. We have found that the major error in measuring the Li⁺/Li(s) potential is the variation in the potential of the 1.5:1.0 Al(III)/Al reference potential from day to day; however, the reference potential remains constant during the course of one day's experimentation. Although the Ag⁺/Ag(s) couple in AlCl₃:MEIC has been reported to be a more stable reference electrode (9), we chose to stay with the more commonly used 1.5: 1.0 Al(III)/Al reference electrode for all our studies. To overcome some of the drift in the reference electrode potential and to obtain more Li⁺ concentration data, some of our experiments were performed by adding aliquots of

MEIHCl₂ to the LiCl buffered melt, thus, incrementally lowering the Li⁺ concentration by the buffering action

$$HCl_{2}^{-} + Li^{+} ---> HCl + LiCl(s)$$
[5]

Protons have been shown to exist as HCl in these melts (see the work of Trulove and Osteryoung in these Proceedings). By depositing a fresh film of Li following each HCl₂⁻ addition and monitoring the open-circuit potential as in Figure 2, a series of potential measurements is obtained for melts with decreasing Li⁺ and increasing HCl concentrations. The reference electrode potential is assumed to remain constant for each series of measurements; however, each series may contain a constant shift from another series.

The Li⁺/Li(s) potential measurements for a number of randomly varied Li⁺ concentrations and for two series experiments are plotted as a function of ln[Li⁺] and of ln[H⁺] in Figure 3. Clearly there is a strong linear correlation between E and ln[Li⁺] as expected; however, no correlation exists between E and ln[H+] indicating the measured potentials are independent of the HCl concentration. The slope of the E vs. ln[Li+] plot is larger than the theoretical slope of 0.026 V due to a variation in the activity coefficient for Li⁺ in the melts. To obtain the standard reduction potential for Li⁺/Li(s), it is necessary to calculate the formal potential for each Li+ concentration from Eq. [4] and extrapolate this data to m_{Li}+ = 0. Figure 4 shows a plot of E^O vs. m_{Li}+ for the data in Figure 3 where data sets Li2 and Li4 are series experiments, while Li1 is a random collection of different melt compositions. To avoid the introduction of a systematic potential error in the E^O determination, the random data set, Li1, with m_{Li}+ < 1 is used to extrapolate to zero molal.

This plot is shown in Figure 5 where the standard reduction potential for the Li⁺/Li(s) couple is found to be -2.066 V (s.d. = 0.005 V) versus Al(III)/Al (1.5:1.0 reference melt).

Lithium deposition at an Iridium Mercury Film Electrode (Ir-MFE) from AlCl3:MEIC:LiCl.

In our early work with alkali metal depositions at Ir-MFEs, we utilized cyclic voltammetry and normal pulse voltammetry to determine formal reduction potentials (4). To avoid errors resulting from amalgam saturation and quasi-reversible electron transfer kinetics, we have perform open-circuit measurements at Li(Hg) amalgams employing the same Ir-MFEs. This is done by first depositing a known quantity of Hg onto the 127-µm Ir disk electrode. Next, using chronopotentiometry, a known quantity of Li is deposited into the Ir-MFE, and the "cell enable" switch is released to provide an open-circuit potential trace for that particular Li(Hg) concentration. The Li is then stripped from the mercury, and a different quantity of Li is introduced into the same Ir-MFE for another open-circuit measurement. By randomly varying the quantity of Li introduced into the mercury, systematic errors are avoided. A plot of the measured potential versus $X_{Li(Hg)}$ (mole

fraction Li in the mercury) is shown in Figure 6 for a typical experiment which was duplicated for two Ir-MFEs using the same AlCl₃:MEIC:LiCl melt. With increasing $X_{\text{Li(Hg)}}$, the potential shifts negative and reaches a constant value at approximately $X_{\text{Li(Hg)}} = 0.013$, the saturation value for Li(Hg) (10).

The potential measured in the these experiments is for the electrochemical process

$$Li^{+} + e^{-} + Hg \iff Li(Hg)$$
 [6]

and is given by

$$E = E^{O} - RT/nF\{\ln(a_{Li(Hg)}/(a_{Li}+))\}$$

= E^O - RT/nF{\ln(X_{Li(Hg)})(\(\gamma_{Li}(Hg))/(m_{Li}+)(\(\gamma_{Li}+))\)} [7]

The standard reduction potential for the Li⁺/Li(Hg) couple is calculated from

$$E^{O}_{Li(Hg)} = E + RT/nF\{ln(X_{Li(Hg)})\} - RT/nF\{ln(m_{Li}+)\} + RT/nF\{ln(\gamma_{Li(Hg)})/(\gamma_{Li}+)\}$$
[8]

Therefore, it is necessary to account for two activity coefficients in calculating $E^{O}_{Li(Hg)}$. This is done by first correcting E for $X_{Li(Hg)}$ by adding the second term in Eq. [8] to the data and extrapolating to $X_{Li(Hg)} = 0$ where $\gamma_{Li(Hg)} = 1$ as shown in Figure 7. This is repeated for a number of different melts. The zero extrapolated values for several melts are given in Table I as $E^{O'}1$. The $E^{O'}1$'s are then corrected for m_{Li} + using the second term in Eq. [8]; these values are listed as $E^{O'}2$ in Table I. By plotting $E^{O'}2$ versus m_{Li} + and extrapolating to zero, E^{O} is obtained. Due to the lack of change in $E^{O'}2$ for m_{Li} + > 0.5, only the three lowest $E^{O'}2$ values are used in the extrapolation. The standard reduction potential for the Li⁺/Li(Hg) couple is found to be **-1.237 V** versus Al(III)/Al (1.5:1.0 reference melt). Using the value of 0.8438 ± 0.0002 V for the standard potential of the cell Li(s)ILi⁺, X⁻ILi(Hg) which is independent of solvent (11), this value for the Li⁺/Li(Hg) couple gives a standard reduction potential for Li⁺/Li(S) of **-2.081 V**. This value agrees with the value of -2.066 V calculated above; however, we believe the value of -2.066 V is more accurate since it is determined for a larger number of melt compositions.

Finally, by adding MEIHCl₂ to melts used for the amalgam measurements, we are able to measure both the Li⁺/Li(Hg) and Li⁺/Li(s) couples in the same melt. After making a small correction for the change in melt composition resulting from the reaction in Eq. [5], we can calculate the standard potential for the cell Li(s)lmeltILi(Hg) which should have a value of 0.8438 \pm 0.0002 V as determined by Cogley and Butler in DMSO (11). For AlCl₃:MEIC:LiCl melts having compositions of 1.091:1.0:0.091 (m_{Li}+ = 0.313) and 1.066:1.0:0.061 (m_{Li}+ = 0.229), we measure Li⁺/Li(s) values of -2.091 and -2.070 V, respectively, after adding HCl₂⁻. Combining these Li⁺/Li(s) values with the appropriate E^{0'}1 values in Table I, we calculate a Li(s)lmeltILi(Hg) cell potential of 0.848 V for both melts, in agreement with the literature value (11). The internal consistency of the data, and its agreement with literature results is good evidence that our methodology for measuring alkali metal potentials is valid.

Elemental sodium deposition from AlCl3:MEIC:NaCl and AlCl3:DMPIC:NaCl.

Figure 8a shows a staircase cyclic voltammogram (scan rate = 500 mV/s) for the reduction of Na⁺ from AlCl₃:MEIC:NaCl (1.1:1.05:0.05; $[Na^+] = 0.227$ M) at tungsten before addition of HCl₂⁻. No stripping peak is observed upon scan reversal indicating rapid reaction of Na with the melt components. Optical observations reveal that at -2.2 V (chronoamperometry), the sodium deposits as a gray-greenish granular material. During stripping it turns brown and disappears. Cleaning was not required except after long depositions (more than 15 s). If the scan is stopped at -2.1 V, the deposit does not show any signs of decomposition. A passivating layer may form fast enough to protect the remaining deposit, or by maintaining a negative potential, cathodic protection of Na is achieved. A fast scan rate of 1V/s was required to produce a dark gray deposit (no brown was observed until after the potential was stepped back).

Figure 8b shows the sodium deposition/stripping behavior following addition of ca. 0.06 M HCl_2^- . Because the sodium reduction is so near the negative limit of the MEIC melt, these results are ambiguous. It was difficult to determine if Na or MEI⁺ reduction is occurring. A gray-brown deposit was formed at -2.4 as accrtained from *in situ* optical observations.

The extended negative window of the DMPIC salt allows better quantitation of the Na⁺/Na(s) couple (7). Figure 9a shows the reduction behavior (scan rate = 500 mV/s) of Na⁺ in 1.1:1.0:0.1 AlCl₃:DMPIC:NaCl at tungsten prior to proton addition. After adding DMPIHCl₂, well-defined deposition/stripping behavior is observed for sodium as seen in Figure 9b. Using chronopotentiometry to deposit sodium on the tungsten electrode, an open-circuit potential of -2.107 V was measured for this AlCl₃:DMPIC:NaCl melt. Employing the sodium analogue of Eq. [2] and using m_{Na} + = 0.34 and γ_{Na} + = 2.3 (calculated from the lithium data for which $ln(\gamma_{Li}+) = (2.33)(m_{I,i}+) + 0.53)$, the standard

reduction potential for the Na⁺/Na(s) couple is calculated to be **-2.101 V** versus Al(III)/Al (1.5:1.0 reference melt).

The potential for the Na⁺/Na(s) couple in the AlCl₃:MEIC:NaCl melt in Figure 8 was determined from its cyclic voltammogram to be -2.371 V. The more negative value results from co-reduction of MEI⁺.

Sodium deposition at an Iridium Mercury Film Electrode (Ir-MFE) from AlCl3:MEIC:LiCl and AlCl3:DMPIC:LiCl.

To determine the standard reduction potential for the Na⁺/Na(s) couple in MEIC based melts, we performed experiments at an Ir-MFE which were similar to those performed for lithium.; however, fewer melts were examined. One experiment was also performed in a DMPIC based melt. Figure 11 shows the data for the sodium analogue of Figure 7; Na(Hg) saturates at $X_{Na(Hg)} = 0.053$. Table II is the sodium analogue of Table I. The data in Table II is not ideal, and we can only estimate an E⁰ for the Na⁺/Na(Hg) couple of -1.412 V by averaging together the three E⁰ 2's for the MEIC melts (i.e., γ_{Na} + is taken to be 1.0).

To calculate E^o for the Na⁺/Na(s) couple we need a value for the standard potential of the cell Na(s)INa⁺, X⁻INa(Hg). Unfortunately, the only values we could find in the literature were 0.8548 V and 0.8456 V for Na(Hg) mole fractions of 0.0056 (12) and 0.018 (13), respectively; these values are for a_{Na} = 1, but not for $a_{Na}(Hg)$ = 1. Using the second term in Eq. [8] to correct the potentials to $X_{Na}(Hg)$ = 1 and assuming $\gamma_{Na}(Hg)$ = 1 (reasonable based on $\gamma_{Li}(Hg)$ data), we calculate standard potentials for the Na(s)INa⁺, X⁻INa(Hg) cell of 0.7219 and 0.7426 V from the two literature values. These literature values are averaged to give a standard cell potential of 0.7323 V which is used with our value of -1.412 V for the Na⁺/Na(Hg) couple to calculate a standard reduction potential for the Na⁺/Na(s) couple in AlCl₃:MEIC:NaCl of **-2.144 V**. In a similar fashion the single DMPIC value of -1.390 V is used to calculate a standard reduction potential for the Na⁺/Na(s) couple in AlCl₃:DMPIC:NaCl of **-2.122 V**. These values agree with the E^O value of -2.101 V determined directly in DMPIC. We estimate an error of ca. ± 50 mV in these values.

CONCLUSIONS

The standard reduction potential for the Li⁺/Li(s) couple in AlCl₃:MEIC:LiCl is found to be -2.066 V (std. dev. = 0.005 V) at ambient temperature. The standard reduction potential for the Na⁺/Na(s) couple at ambient temperature is estimated to be -2.144 V (\pm

0.050 V) in AlCl₃:MEIC:NaCl and -2.101 V (\pm 0.050 V) in AlCl₃:DMPIC:NaCl. Potentials are referenced to Al(III)/Al in a 1.5:1.0 AlCl₃:MEIC reference melt.

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molal Li ⁺	E ^{0'} 1 (V)	E ^{0'} 2 (V)	
0.143	-1.266	-1.216	
0.229	-1.243	-1.205	
0.313	-1.222	-1.192	
0.560	-1.193	-1.178	
1.080	-1.177	-1.179	
1.25	-1.175	-1.181	

Table I. Potential data for Li⁺/Li(Hg) in AlCl₃:MEIC:LiCl.

 $\label{eq:constraint} Table \ II. \ Potential \ data \ for \ Na^+/Na(Hg) \ in \ AlCl_3: MEIC: NaCl^a \ and \ AlCl_3: DMPIC: NaCl^b.$

molal Na ⁺	E ^{o'} 1 (V)	E ⁰ '2(V)	
0.373 ^a	-1.342	-1.317	
0.720 ^a	-1.345	-1.337	
1.080 ^a	-1.330	-1.332	
0.932 ^b	-1.306	-1.304	



Figure 1. Lithium reduction in 1.1:1.0:0.1 AlCl₃:MEIC:LiCl (a) without protons and (b) with protons.



Figure 2. Typical chronopotentiogram for measuring the $Li^+/Li(s)$ couple in AlCl₃:MEIC:LiCl melts containing added protons.





Figure 3. Plots of E for $Li^+/Li(s)$ in AlCl₃:MEIC:LiCl melts versus $ln[Li^+]$ and $ln[H^+]$.



Figure 4. Li⁺/Li(s) formal potentials versus molal Li⁺ in AlCl₃:MEIC:LiCl melts.



Figure 5. $Li^+/Li(s)$ formal potentials versus molal Li^+ for AlCl₃:MEIC:LiCl melts using Li1 data set with molal $Li^+ < 1$.



Figure 6. $Li^+/Li(Hg)$ potentials versus $X_{Li(Hg)}$ in 1.091:1.0:0.091 AlCl₃:MEIC:LiCl measured at an Ir-MFE.



Figure 7. Li⁺/Li(Hg) potentials versus $X_{Li(Hg)}$ in 1.091:1.0:0.091 AlCl₃:MEIC:LiCl measured at an Ir-MFE showing data before and after correcting for potential for $X_{Li(Hg)}$.



Figure 8. Sodium reduction in 1.05:1.0:0.05 AlCl₃:MEIC:NaCl (a) without protons and (b) with protons.



Figure 9. Sodium reduction in 1.1:1.0:0.1 AlCl₃:DMPIC:NaCl (a) without protons and (b) with protons.



Figure 10. Na⁺/Na(Hg) potentials versus $X_{Na(Hg)}$ in 1.04:1.0:0.04 AlCl₃:MEIC:NaCl measured at an Ir-MFE.

LOW TEMPERATURE MOLTEN SALT ELECTROLYTES BASED ON QUATERNARY ALKYL PHOSPHONIUM SALTS

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Abstract

A new room temperature molten salt comprised of a 1:2 mixture of quaternary alkylphosphonium chloride and aluminum chloride has been discovered. Formation of a room temperature melt was unexpected due to the high melting point of tetramethylphosphonium chloride and the absence of an inversion vibration. The melt has good conductivity and also has higher stability toward electrochemical reduction than any previously studied room temperature melt. Aluminum metal can be reversibly plated and stripped from the melt.

Introduction

In this bicentennial year of the birth of Michael Faraday, it is most appropriate to have an international symposium on molten salts. Faraday studied the electrolysis of about fifty molten salts [1]. The study of molten salts was crucial for two reasons, first for the determination that the many types of electricity were identical and second for the formulation of the laws of electrolysis (Faraday's Laws). The experiments were critical because the results from the electrolysis of aqueous solutions were quite complicated in general and required much additional knowledge to show that the quantities of products were proportional to the quantity of electricity passed and that the quantities of elements deposited were in relation to the ratio of their equivalent weights. Electrolysis of molten salts on the other hand often led to simple products of known or easily determined equivalent weights. The products could be separated from the molten state by segregation of a solid or liquid metal phase because of a density difference or by capture of a gas such as one of the halogens in the case of a halide melt. The exceptional difficulty of carrying out these studies even with these simplifications should not be minimized, however. Complex glass and ceramic apparatus had to be constructed to withstand the temperature of

the coal fires and the corrosiveness of the molten salts, product collection equipment had to be constructed and accurate chemical analysis had to be performed. Another important result was the establishment of an electrochemical series of the elements. This body of work alone would have been sufficient to cement the reputation of Faraday as one of the great scientists of all time. As electrical power sources became economical, the pioneering work of Faraday made clear the advantages of molten salt electrolysis for the preparation of pure metals, especially the active ones, and processes were developed which are used to this day.

Our program has focussed on room temperature molten salts to attempt to realize some of the same advantages alluded to above in a temperature range which can be used more conveniently, especially for consumer battery applications. The fairly narrow electrochemical window provided by the room temperature melts has been a major deficiency which has inhibited the development of these applications. Organic cations normally used to reduce the melting points have been too readily reduced so that the range of negative electrode materials has been severely limited. In an ongoing program to investigate these limitations, a new family of room temperature molten salts with interesting properties has been discovered. The salt is comprised of a 1:2 mole ratio of tetraalkylphosphonium chloride with AlCl₂. The main organic compound studied was tetramethylphosphonium chloride (TMPC). The melt was originally discovered while trying to determine if molecular entropy was part of the reason that trimethylsulfonium chloride (TMSC) formed a room temperature melt when combined with AlCl₃ [2]. TMSC is a pyramidal compound and can undergo an inversion vibration. This additional degree of freedom increases the internal entropy of TMSC. It was thought that this additional entropy could be an important contribution to lowering the melting point for this material in combination with AlCl₂. TMPC is the tetrahedral analog of TMSC and cannot have an inversion vibration.

Experimental

The phosphonium salts (Aldrich) were dried under vacuum. The AlCl₃ (Fluka-Puris.) was used as received. Conductivities were measured using an ESI 253 impedance meter and YSI 3403 conductivity cells. Cannon-Fenske viscometers were used to measure viscosity, while densities were determined by weighing 5 ml graduated cylinders. All properties were measured in the dry box at approximately 27°C. Cyclic voltammetry measurements were made on a PAR 173 computer controlled potentiostat. The working and counter electrodes were glassy carbon. The reference electrode for the molten salts was an Al wire in a 0.6 mole fraction AlCl₃:MEIC melt separated from the test solution by a fine glass frit. For the acetonitrile solutions, the reference electrode was a Ag wire in 0.1 M tetramethylammonium perchlorate/acetonitrile solution separated from the sample by a fine glass frit.

Results and Discussion

Phosphorus is a second row element with compounds of relatively high polarizability compared to similar nitrogen compounds. The freezing point of the 1:2 TMPC:AlCl₃ melt has not been determined accurately at this time, but is believed to be between 0°C and -10°C. A 1:2 mixture of tetraethylphosphonium chloride:AlCl₃ had a freezing point of about 70°C while a 1:2 mixture of tetrabutylphosphonium chloride formed a room temperature melt with a conductivity of 1.3 mS/cm. That a 1:2 mixture of TMPC:AlCl₃ would form a room temperature melt was surprising in view of the high melting point of TMPC (396°C) compared to the other organic compounds that also form room temperature melts with AlCl₃. The melting points of N-(n-butyl)pyridinium chloride (BPC) (131.5°C), 1-methyl-3-ethylimidazolium chloride (MEIC) (78°C), trimethylphenylammonium chloride (TMPAC) (237°C, sub.), TMSC (192°C) are all substantially lower. However, the only combinations of TMPC:AlCl₃ that are liquid at room temperature are very close to the 1:2 ratio. Melts with other organic cations have a broader range of room temperature liquid compositions, often from 2:1 to 1:2. We believe that the high melting point of TMPC is the main reason for the narrow room temperature liquid range of TMPC:AlCl₃. From these results, we have concluded that the polarizability of the organic cation is the main factor leading to room temperature melts with aluminum chloride, with the melting point of the chloride a secondary factor. Molecular entropy probably plays an important role in determining the melting point of the pure salt, which then effects the breadth of the melting region in the phase diagram, but does not play a decisive role in the depth of the eutectic region near the 1:2 mole ratio. Molecular size also plays a role in determining the melting point of the pure chloride, since the lattice energy of the solid crystal is very sensitive to the separation of ions.

The 1:2 TMPC:AlCl₃ melt has a room temperature conductivity of 5.0 mS/cm, a density of 1.33 g/cm³, and a viscosity of 37.3 cP. Table 1 shows that these values are all relatively close to those of the 1:2 ratio melts made from BPC, MEIC, TMPAC, and TMSC [2, 3 and references therein]. It is of some interest to compare equivalent conductances and the Walden products of these various solutions to see if any structural effects are suggested. The Walden product, the product of the

viscosity and the equivalent conductance, was originally formulated using the equivalent conductance at infinite dilution and the solvent viscosity. Its formulation was justified on the basis of Stoke's law [4]. The use of the product in molten salts cannot be rationalized on theoretical grounds, except that at a zeroth level approximation the product can be viewed as a rough measure of the degree of association or other strong short range interaction in ionic media. The equivalent conductance was determined on the basis that the stoichiometry of a 1:2 melt is equivalent to the composition RAl_2Cl_2 , where R is the organic cation. The true composition could vary depending on the formation constants of the various monoand polynuclear complexes of aluminum chloride. Strong differences in these formation constants should be reflected in widely different Walden products. Table 1 summarizes the values of the equivalent conductances and the Walden products for the various solutions discussed. The high value of the equivalent conductance for MEIC is quite notable. The Walden products for MEIC, TMSC and TMPC are comparable, however, indicating the importance of viscosity in determining mobilities of the ions in these melts. The lower Walden products for TMPAC and BPC indicates some structural differences for these melts compared to the other three. All of the values are quite high compared to moderate concentration solutions in organic solvents. This is consistent with the very high degree of dissociation in molten salts in contrast with organic solvent solutions.

Figure 1 shows that the cyclic voltammetry (CV) of the 1:2 melt behaves very similarly to the previously investigated melts [2,3]. It can be seen from the cathodic and anodic peaks near 0 volts in the CV that aluminum can be plated and stripped from the melt. The CV also shows the reversal or loop in the cathodic peak which is typical for this type of melt and indicates the presence of a nucleation step in the aluminum deposition. Further confirmation of aluminum plating and stripping was obtained by cycling two aluminum electrodes in the 1:2 TMPC:AlCl₃ melt at a current density of 0.5 mA/cm^2 for 80 2-hour cycles. The anodic current in the 2.7 V region is also typical for this type of solution. The details of this highly irreversible reaction have not been worked out, but the initial step is most likely the oxidation of chloride ion to chlorine atoms, followed by further irreversible steps which remove chlorine from solution.

The other important characterization of the melt containing TMPC is by cyclic voltammetry of a solution of the organic chloride in acetonitrile. Figure 2 shows the CV curve in comparison with BPC and MEIC. Oxidation at about 1100 mV occurs with all of the chlorides and is due to oxidation of chloride to chlorine, followed by reduction back to chloride on the return sweep. Reduction of the phosphonium ion occurs at least 500 mV cathodic to the other organic compounds that make room

temperature molten salts, bringing the reduction potential close to the value of the blank, tetramethylammonium perchlorate (TMAP). Thus, TMPC is the first organic compound to form a room temperature melt that has a larger window of electrochemical stability than MEIC. This increased stability will allow a greater range of electrochemistry to be done in melts containing TMPC.

We believe that the reason for the increased stability of TMPC is the following. Surrounding the central phosphorus atom with the four alkyl groups raises the energy of the lowest unoccupied molecular orbital (LUMO) compared to phosphonium ions with aromatic substituents, or any ions with resonance stabilization such as those in TMPAC, MEIC or BPC. Thus, in the first step of a 1 electron reduction, the electron must first go into the LUMO as in (1)

$$\mathbf{R}_{4}\mathbf{P}^{+} + \mathbf{e} \rightarrow \mathbf{R}_{4}\mathbf{P} \boldsymbol{\cdot} \tag{1}$$

where R_4P is a free radical species. The higher energy of the LUMO compared to resonance stabilized ions would cause the potential to shift to more positive potentials. Subsequent steps (2) and (3), leading to the final reduction products, would be expected to occur without a reaction barrier and not effect the potential of the process.

$$\mathbf{R}_{4}\mathbf{P}\boldsymbol{\cdot} \rightarrow \mathbf{R}_{3}\mathbf{P} + \mathbf{R}\boldsymbol{\cdot}$$
(2)

$$2\mathbf{R} \cdot \rightarrow \mathbf{R}_2 \tag{3}$$

The smaller electrochemical window observed for TMSC is at first somewhat puzzling. The geometry of the sulfonium ion is known to be trigonal pyramidal [5], which indicates sp³ hybridized orbitals exactly as for TMPC. The same restriction may not apply for the excited state however and the availability of the 3d orbitals for hybridized excited state orbitals very likely lowers the energy of the LUMO compared to that for TMPC which is restricted to tetrahedral shape by the four space filling methyl groups. The bond angles of the trimethylsulfonium cation in the solid state are 103° rather than tetrahedral [5], which indicates some d orbital hybridization even in the ground state.

In summary, the wide electrochemical window and reasonably good conductivity make the 1:2 melt of tetramethylphosphonium chloride with aluminum chloride an interesting melt for further electrochemical studies.
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Table 1. Physical properties of 1:2 mole ratio of organic chlorides with $AlCl_3$ at ambient temperature.

	BPC	MEIC	TMPAC	TMSC	TMPC
Specific Conductance (mS/cm)	4.13	13.73	3.40	5.5	5.0
Density (g/cm ³)	1.35	1.394	1.35	1.40	1.33
Viscosity (cP)	36.5	16.0	36.2	39.3	37.3
Equivalent Conductance (S·cm ² /mole)	1.34	4.07	1.104	1.49	1.48
Walden Product (S·g/cm·mole)	0.489	0.652	0.400	0.586	0.552







Figure 2. Cyclic voltammetry comparison of the stabilities of various organic chlorides. The organic chloride was 20 mM in a solution of 0.1 M TMAP in acetonitrile.

NEW, STABLE, AMBIENT-TEMPERATURE MOLTEN SALTS

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New ambient-temperature organic molten salts are described. They are easily prepared (usually in one step) and consist of alkylsubstituted aromatic heterocyclic cations and trifluoromethanesulfonate (triflate) or methanesulfonate (mesylate) anions. For example, 1-ethyl-3-methylimidazolium triflate has $m.p.\simeq -10^{\circ}C$, σ =9.3 mS/cm and η =43 cP at 25°, an electrochemical stability window of >4V, and a weight loss rate of <0.03%/min at 350°C in N₂ Interesting differences between triflates and mesylates are discussed. The thermal and chemical stability. wide electrochemical window and high conductivity of some of the new salts make them promising electrolytes and antistats.

INTRODUCTION

Many ambient temperature molten salts are now known, and a few of them have been extensively studied. Wider recognition and commercial use have been slow to develop, however, largely because of preparation and/or stability difficulties; the more stable and accessible compounds tend to also have lower conductivities, therefore generating less interest. Following is a summary of the main existing types of ambient temperature molten salts and their limitations.

- Tetrachloroaluminates of some alkylated nitrogen cations, especially Nbutylpyridinium (1), 1-ethyl-3-methylimidazolium (2) and related compounds. Anions can also be Al₂Cl₇, GaCl₄ (3), BCl₄ (4), AlBr₄ (5), or HCl₂ (6); cations can also be trialkylsulfonium (7) or tetraalkyl/aryl ammonium/phosphonium (8, 9). Widely studied due to their high conductivities, wide electrochemical windows and interesting acid/base properties, they all are also very easily and irreversibly hydrolyzed.
- 2. Ethylammonium nitrate, CH₃CH₂NH³NO³ (10); has limited thermal and electrochemical stability.
- Trialkylammonium/phosphonium chlorocuprate(I) salts, e.g. Et₃NH⁺CuCl₂ (11). They are easily oxidized/reduced (narrow electrochemical window).

- 4. Some tetraalkylammonium (TAA) tetraalkylborides of low cation and/or anion symmetry, e.g. triethyl-n-hexylammonium triethyl-n-hexylboride (12). They are hard to prepare and not very stable.
- 5. Some higher molecular weight (MW) organic salts, usually with low cation and/or anion symmetry, e.g. many TAA-type C₂₀H₄₄N⁺ isomers with Br⁻ or ClO₄ as anions (13), also some C₁₈H₄₀N⁺ and C₁₆H₃₆N⁺ bromides (14). Because of their high viscosity and low carrier concentration, they have low conductivities and rather little "salt character".
- 6. Some lower-MW salts of an ether-containing TAA cation e.g. 2-methoxyethylethyldimethylammonium and a poor nucleophile for an anion $BF_{\overline{4}}$ or $ClO_{\overline{4}}$ (14, 15) (a AlCl₄ variant is also known (16)). More stable than other salts above, but not as conductive as most haloaluminates.
- 7. Many ambient-temperature molten salts hidden under the term "oil" i.e. compound that could not be crystallized in the organic chemistry literature. A very recent pertinent example is N-(2,2,2-trifluoroethyl)pyridinium trifluoromethanesulfonate (17).

The purpose of this study was to find new compounds that offer a combination of easy preparation, low melting, high conductivity and high stability. To this end, the well-known dialkylimidazolium tetrachloroaluminates and similar compounds (2, etc.) were chosen as a model, but the hydrolysis-sensitive anions were replaced halometallate with much more stable weak triflate (trifluoromethanesulfonate) or mesylate bases/nucleophiles, i.e. (methanesulfonate). The weak anion basicity contributes to thermal stability and minimizes the potential for ion pairing. As for low melting, although there is no known way to ensure it in new compounds it has often been found that lower molecular symmetry is helpful. Therefore the successful pattern shown in (2, 18) – different substituents on the two heteroatoms in the cyclic cation – has been followed here. The sulfonate ions also have lower symmetry than tetrahalometallates; they are shaped more like Al_2Cl_7 , which generally forms compounds that melt lower than the respective tetrachloroaluminates (18).

The new salts can be prepared from commercially available compounds in several ways. A general method (which however may leave ionic impurities in the product) is to make a halide salt in the usual way, then to ion-exchange it with the sulfonate, either by reaction with the appropriate silver or lead salt or on an ion-exchange column. The most direct method, and the one used in this study, is the reaction, previously used for the preparation of stable TAA triflate electrolytes (19), between the heterocycle and an alkyl ester of the sulfonic acid (20). This is a nucleophilic substitution at the alkyl carbon of the ester linkage, in which the sulfonate leaving group becomes the product's anion.

EXPERIMENTAL

Preparation

Ethyl triflate and ethyl mesylate (Aldrich) were used as received from freshly opened bottles. (Caution: alkyl sulfonates are reactive and hygroscopic and - as strong alkylating agents - probably highly toxic.) N-methylimidazole (Aldrich) and N-n-butylimidazole (Lancaster Synthesis) were fractionally vacuum-distilled before use: N-n-dodecylimidazole (Toronto Research Chemicals) and thiazole (Aldrich) were used as received. The reactions were performed under nitrogen. The triflate ester was added dropwise to a small excess of the heterocyclic compound, in a volume of toluene about twice that of the reagents. Reaction was instantaneous, requiring cooling and vigorous stirring. Ethyl mesylate reaction with N-methylimidazole was much slower (72 h at 23° + 4 h at 55°C, toluene/reagents=2/3 v/v). Under similar conditions, ethyl trifluoroacetate – another potentially interesting reagent – did not react significantly. For 1-butyl-3-ethylimidazole mesylate, vacuum-distilled ethyl mesylate was used and the room-temperature reaction was speeded up by using acetonitrile instead of toluene. In all cases the solvent was then evaporated and was the liquid residue extracted with toluene. cyclohexane. 2,2,4-trimethylpentane, or a mixture thereof (depending on salt-solvent miscibility), for at least 16 h, in a scaled-up version of Kontes' continuous liquid-liquid extractor (cat. # 291600). The salt was then subjected to vacuumevaporation at 60-70°C/0.05 torr and, where possible, to several freeze/thaw cycles under 0.05 torr. Typical batch size was 20-40 g.

Physical Properties

Specific conductivity (σ) was measured under N₂ in a YSI conductivity cell model 3403 (const.=1.0781 cm⁻¹, calibrated with 0.01 demal KCl solution (21)), by an HP 4275A multifrequency (10³-10⁷) Hz LCR meter. Kinematic viscosity (κ) was measured in calibrated, semi-micro, Cannon-Ubbelohde viscometers (Technical Glass Products) filled under N₂. Temperature was controlled to $\pm < 0.1^{\circ}$ C for both σ and κ . Thermogravimetry was performed in a Cahn TGA-131 balance, on ~80 mg samples, in open pans exposed to 50 cm³/min gas flow. Density (d) was measured to $\pm 0.5\%$ by weighing a filled 2 ml calibrated pipet. Melting points (m.p.) were determined visually to $\pm 2^{\circ}$ C.

Electrochemistry

For the electrochemical characterization of the molten salts, a twocompartment Pyrex cell was employed which utilized about 5 ml of solution. The working and counter electrodes were constructed from Pt wire, which was sealed into Pyrex tubing. The reference electrode was based on the following redox couple:

$$3I^{-} \rightleftharpoons I_{3}^{-} + 2e^{-}$$

In this electrode system, the same molten salt solvent being investigated in the working electrode compartment was employed in conjunction with a Pt electrode. The $Pt/(I_3 + I^-)$ reference electrode has been shown to be very stable and reversible in other non-aqueous media (22, 23). A solution of 0.06 M tetramethylammonium iodide and 0.012 M iodine was made up using the molten salt under study; this resulted in a 4:1 ratio of I⁻ : I_3. A fine glass frit connected the reference electrode solution to the main body of the cell. Solutions were maintained under N₂. Standard electrochemical equipment was employed, viz. PAR 173 potentiostat, PAR 175 signal generator and a Yokogawa 3033 X-Y recorder.

RESULTS AND DISCUSSION

The compounds prepared and values of some of their properties are listed in Table I. Following are some additional observations.

$Et - N = CH_2 - X = R$ $\downarrow + / Y^-$ $CH = CH$		At 25°C:			
X-R =	Y =	m.p., °C	d, g/cm ³	σ, mS/cm	η, Poise
N-methyl	triflate	-10	1.38(3)	9.2(9)	0.427
N-methyl	mesylate	39	1.24(7)	2.67	1.60
N-butyl	triflate	none	1.27(1)	2.7	
N-butyl	mesylate	none	1.14(1)	0.55	
S:	triflate	26	1.50(9)	4.2(8)	
N-dodecyl	triflate	32	1.10(9)		

1 able 1. Properties of the New Compo	ounds
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The liquid triflates and mesylates are nearly colorless; a yellowish tint appears to be carried over from the ester. An unidentified $\sim 1\%$ anionic impurity,

also present in commercial "pure" triflic acid samples, was found in 1-ethyl-3-methylimidazolium ("e.m.i.") triflate by ion chromatography. (Fractional vacuum-distillation of the esters before use is therefore desirable). The compounds have varying viscosities and are easily supercooled; the two 1-butyl-3-ethyl compounds could not be crystallized at all, despite repeated slow cycling and annealing between -79 and 0°C. All compounds are miscible with moderately polar organic solvents and, except for 1-dodecyl-3-ethyl triflate (which has a ~0.05% solubility in water), with water. Mixing with an equal volume of water results in a temperature drop of several degrees for the triflates, while for the mesylates a similar temperature increase is produced. The salts absorb water when exposed to the ambient, but can be redried by repeating the vacuum treatment outlined above. Thermogravimetry on e.m.i. triflate shows it to be very stable thermally and of very low volatility, losing <1% weight in 30 min at 350°C in N₂ and only 1.3% (with degradation into a sooty suspension) under the same conditions in air.

Fig. 1 shows a cyclic voltammogram for a stationary Pt electrode in 1-ethyl-3-methylimidazolium triflate at 25°C. This voltammogram reveals that an electrochemical window of solvent stability exists from ca. -2.2 V to 1.9 V (vs. $I_{\overline{3}}/I^{-}$), or a little greater than 4.0 V. It is probable that a larger window exists for less active electrode materials, e.g. glassy carbon or tungsten (24, 25). However, it was noted that excessive excursions into the potential regions of solvent decomposition lead to generation of decomposition products which underwent further reaction in the otherwise reaction-free window region. The oxidation currents observed at -0.5 V and ca. 1.4 V are related to impurities in the electrolyte, which have not been identified. The reduction current observed in the potential region -1.2 V to -2.2 V prior to the onset of solvent decomposition appears to include contributions due to reduction of dissolved O₂ impurity, and at potentials more negative than -1.9 V, the reduction of H₂O impurity. Analysis of the current - potential curves recorded on addition of various amounts of H₂O indicated that the original concentration of water present was $< 10^{-2}$ M.

In fig. 2 is displayed a cyclic voltammogram of a Pt electrode in 1-ethyl-3-methylimidazolium mesylate which was recorded at 40°C to prevent electrolyte solidification. The solvent window is somewhat narrower than in the triflate case; in the anodic scan, electrolyte decomposition commences at ca. 1.75 V, while in the cathodic scan, decomposition begins at ca. -1.8 V. The intermediate potential region is relatively free of extraneous reactions.

At or near room temperature, e.m.i. triflate is slightly more conductive than the widely used N-butylpyridinium tetrachloroaluminate (26) but significantly less so than e.m.i. tetrachloroaluminate (18). From data in Table I, triflates are 3-5 times more conductive (and more fluid) at room temperature than their mesylate counterparts. Ethylthiazolium triflate, despite its smaller cation, is less than half as conductive as e.m.i. triflate. For an attempt to understand the causes of these differences we now turn to Table II, which contains comparative data of two sulfonates and two chloroaluminates of the same widely studied e.m.i. cation. (Data for the chloroaluminates are calculated from the equations in (18); for the heptachlorodialuminate, data given there for 66 mol% AlCl₃ in the e.m.i. chloride - AlCl₃ system have been extrapolated to 66.67 mol% AlCl₃).

Anion Property	Al ₂ Cl ₇	AICI₄	Triflate	Mesylate
d, g/cm ³	1.389	1.294	1.383	1.247
MW, g/mol	413.22	279.96	260.23	206.26
V _{mol} , cm ³ /mol	297.54	216.4	188.2	165.4
σ, mS/cm	14.5	22.6	9.29	2.67
Λ , S cm ² /mol	4.308	4.898	1.748	0.4416
κ , cm ² /s	0.100	0.138	0.309	1.28
η , g/(cm·s)	0.139	0.178	0.427	1.60
Λη	0.598	0.872	0.747	0.707

Table II. Properties of Four E.m.i. Salts at 25°C

As shown in Table II, e.m.i. triflate is ~2.5 times less conductive and more viscous than the respective tetrachloroaluminate, and the mesylate is ~3.5 times less conductive still. The molar volumes (V_{mol}) of the three salts are too similar to justify such large differences in transport properties; note that the much larger heptachlorodialuminate does not differ from the tetrachloroaluminate as much as the triflate does. Stable "complex" formation (or weakly dissociated ion pairs) cannot be important, since the Walden product ($\Lambda\eta$, equivalent conductivity x dynamic viscosity) values are similar. The explanation probably lies rather in differences in the strength of the cohesive forces in these liquids, most likely in a more important role played by hydrogen bonding in the sulfonate liquids, the mesylate in particular. Given the less extensive charge delocalization in the sulfonates – over 3 (smaller) oxygens rather than 4 (larger) chlorines – the direction of the effect is as expected. Furthermore, the charge is more delocalized in the triflate than in the mesylate ion due to the inductive effect of the CF₃ group; thus the basicity order, like the observed viscosity, is

AlCl_{$\bar{4}$} < triflate < mesylate. The significant triflate basicity implied by this analysis correlates well with triflate behavior elsewhere, e.g. ion-pairing in organic solvents (27) and in salt-polyether conductors (28, 29).

The different sign of the heat of mixing with water for mesylates and triflates attests to the much higher capability of mesylate anions to contribute to hydrogen bonding. Note also that V_{mol} of the mesylate salt is 12% smaller than the triflate's; this can be explained only partly by the modest size difference between the respective methyl and trifluoromethyl groups, and the rest must be due to stronger inter-ionic forces in the mesylate. As for the participation of dialkylimidazolium hydrogens in hydrogen bonding, extensive supporting evidence now exists (30, 31).

The case of ethylthiazolium triflate is worth mentioning. It was prepared mainly in order to find out whether a cation smaller than e.m.i. (since S in thiazolium does not carry a methyl group) would exhibit higher conductivity. The opposite actually occurs. The removal of the methyl group reduces steric hindrance around C-2 (the carbon between the heteroatoms), perhaps making the hydrogen attached to it much more accessible for hydrogen bonding. If this is so, then ethylthiazolium tetrachloroaluminate may still turn out to be highly conductive, since hydrogen bonding to $AlCl_{4}$ should be less important.

The temperature dependence of σ (specific conductivity) was investigated for three compounds; the kinematic viscosity, κ , was measured at different temperatures only for e.m.i. triflate. In fig. 3 the data are presented in logarithmic form as f(1/T); to facilitate comparison between the two transport properties, "kinematic fluidity", $1/\kappa$, rather than κ , is shown. (Comparing σ to the same compound's $1/\kappa$ is equivalent to comparing Λ to $1/\eta$, since $\Lambda = \sigma V_{mol} = MW\sigma/d$ and $\eta = \kappa d$, so $\Lambda \eta/\sigma \kappa = MW$, independent of T; the advantage is that unavailable d=f(T) data are not needed). Because of the short temperature range and few experimental points, far-reaching conclusions are not warranted. Still, it is worth noting the following: (a) the plots are non-Arrhenius (they can be roughly fitted to a Vogel-Tammann-Fulcher (VTF) (32) type of equation); (b) for e.m.i. triflate the ratio of the activation energies E_{κ}/E_{σ} is not far from 1; (c) the e.m.i. mesylate's conductivity is significantly more temperature-dependent than the two triflates', and its imminent cross-over near 75°C with the ethyl thiazolium triflate plot suggests that more than just different VTF-defined T₀ values are involved. The first two observations resemble what was found in the AlCl_{$\overline{4}$} analogues (18).

CONCLUSIONS

The combination of high thermal and environmental stability, low volatility, high conductivity and wide electrochemical windows gives the new liquid salts a clear advantage over previously known low-temperature molten salts and makes them promising candidates for various uses, such as:

- Battery non-aqueous electrolytes, especially where volatility of an organic solvent might be a problem (e.g. when both use at ambient temperature and excursions to much higher temperatures can be expected);
- Electrodeposition of electropositive metals, e.g. under vacuum, or from salts (oxoanion etc.) that may react with haloaluminates;
- Antistatic uses, especially under vacuum or in very dry environments where
 regular antistats are inefficient, e.g. for SEM examination of insulators
 without the need to deposit a permanent metal or carbon conductive layer
 (33); also, where high temperature stability is needed, e.g. for blending with
 engineering thermoplastics.

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Fig. 1. Cyclic voltammogram for a stationary Pt electrode in e.m.i. triflate at 25° C. Sweep rate = 50 mV/s.



Fig. 2. Cyclic voltammogram for a stationary Pt electrode in e.m.i. mesylate at 40° C. Sweep rate = 50 mV/s.



Fig. 3. Transport properties (σ = specific conductivity; $1/\kappa$ = kinematic fluidity) of some sulfonate salts as a function of the reciprocal absolute temperature (1/T). Curves connecting the experimental points are a guide to the eye.

MIXED CHLOROBORATE AND CHLOROALUMINATE ROOM TEMPERATURE MELTS

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ABSTRACT

Room temperature chloroborate and mixed chloroborate/chloroaluminate melts of n-butylpyridinium chloride were prepared. It was found that BCl₃ was displaced from BCl₄⁻ by AlCl₃. Cyclic voltammetric studies indicated that boron species other than BCl₄⁻ were electroactive in acidic chloroborate and mixed chloroborate/chloroaluminate melts.

INTRODUCTION

Room temperature acidic chloroaluminate molten salts of organic chlorides like n-butylpyridinium chloride(BPC) are prospective electrolytes for high density batteries since room temperature melts containing the Al_2Cl_7 ion permit the reversible electrodeposition of Al metal. Japanese scientists have reported such systems as a battery electrolyte (1). Tetrachloroborate salts with n-butylpyridinium or methyl-3-ethylimidazolium cations are known to be room temperature melts; Raman spectral studies have indicated, however, that an excess of BCl₃ over the BCl₃:RCl mole ratio 1:1 did not lead to the presence of $B_2Cl_7^-$ ions, even when the melts were cooled to 77K (2). It would be of interest for battery electrolyte development to see if mixed chloroaluminate/chloroborate systems are useful for reversible Al deposition and if mixed complex species of type [BAlCl₇]⁻ form, since boron compounds would decrease electrolyte density. Therefore, mixed chloroborate and chloroaluminate melts have been prepareed and some preliminary electrochemical studies on the mixed chloroborate/chloroaluminate melts have been made at room temperature.

EXPERIMENTAL

Chemicals

Fluka A.G. brand aluminum chloride was purified by sublimation and nbutylpyridinium chloride was prepared by following the methods of Gale and Osteryoung (3). Boron trichloride was used as supplied (Matheson).

Procedures for Making Melts

Chloroaluminate melts were prepared by mixing accurately weighed quantities of aluminum chloride and BPC in the glove box. Chloroborate melts were prepared by the following procedure: 1. quantities of BPC were weighed accurately in a flask in the glove box; 2. the flask was closed in the glove box, then brought out into a fume hood; 3. before BCl₃ was released into the flask, the teflon connecting tubing and the other parts exposed to air were flushed fully with dry nitrogen; ice water was used to cool the flask and BCl₃ was released to react with the BPC under stirring; 4. the melt prepared was taken into the glove box and the extra pressure was released. By the weight increase, the compositions of the melts could be calculated. The experimental setup for making chloroborate melts is shown in figure 1. Mixed chloroaluminate/chloroborate melts were prepared by dissolving aluminum chloride or adding acidic chloroaluminate melts into chloroborate melts.

Electrochemical cell

The electrochemical cell was a conventional three-electrode system, with a coiled aluminum wire immersed in 2:1 AlCl₃:BPC melt as reference electrode, platinum foil as counter electrode, vitreous carbon disk (area: 0.10 cm²) as working electrode. The potentiostat was a model RDE 3, Pine Instrument Company.

RESULTS AND DISCUSSION

Chloroborate Melts

By following the procedures described above, clear viscous chloroborate melts were obtained at room temperature and normal pressure. Table 1 contains the results for final stoichiometries of chloroborate melts in four separate experiments. The results show that at room temperature, the compositions of the melts are almost constant. The mole ratio of boron chloride and BPC is approximately equal to 52:48. Mamantov (2) and coworkers studied the Raman spectra of neutral and acidic chloroborate melts and found evidence for BCl₄⁻ and BCl₃ species. However, even in the very acidic melts, unlike chloroaluminate melts, evidence for polyborochloride species such as $B_2Cl_7^-$ was not found. If we suppose only the following reaction happened quantitatively:

$$BPCl + BCl_3 = BP^+ + BCl_4^-$$

- - -

excess boron chloride dissolved in the melt would be primarily in the form BCl_3 . Thus, at room temperature and normal pressure, BCl_3 will have a fixed solubility in the melt of about 0.25 M.

Mixed Chloroborate/Chloroaluminate Melts

Mixed chloroborate/chloroaluminate melts were prepared in three ways; namely adding either slightly basic chloroaluminate, acidic chloroaluminate melts, or aluminum chloride into the 51.50:48.50 BCl₃-BPC melt. 1. When 0.95:1 mole ratio AlCl₃-BPC melt was added into the chloroborate melt, no visible experimental phenomena happened and no weight was lost. 2. When 2:1 AlCl₃-BPC melt was added into 51.50:48.50 BCl₃-BPC melt, bubbling was observed and weight was lost. The moles of BCl₃ lost were approximately equal to the moles of excess AlCl₃ in the 2:1 AlCl₃-BPC melt, bubbling was observed and weights were lost again. Weights lost are shown in Table 2. From Table 2, it can be seen that one mole of aluminum chloride displaced approximately one mole of boron chloride. The following displacement reactions might occur:

$$BCl_4^- + AlCl_3 \rightleftharpoons AlCl_4^- + BCl_3$$
[2]

$$BCl_4^- + Al_2Cl_7^- \rightleftharpoons 2AlCl_4^- + BCl_3$$
[3]

Possible mechanisms may involve unstable intermediates,

for reaction [2]:

$$BCl_{4}^{-} + AlCl_{3} \rightleftharpoons [AlBCl_{7}]^{-}$$
$$[AlBCl_{7}]^{-} + BCl_{4}^{-} \rightleftharpoons [B_{2}Cl_{7}]^{-} + AlCl_{4}^{-}$$
$$[B_{2}Cl_{7}]^{-} \rightleftharpoons BCl_{4}^{-} + BCl_{3}$$

for reaction [3]:

$$BCl_4^- + Al_2Cl_7^- \rightleftharpoons [AlBCl_7]^- + AlCl_4^-$$

These two net reactions are not surprising because the Gibbs free energies of formation of BCl₃ and AlCl₃ are -389 KJ mol⁻¹ and -570 KJ mol⁻¹ respectively (4). This indicates that chlorine bonds to aluminum more strongly than to boron. By the total weight of BCl₃ lost, the weight of BCl₃ in the original chloroborate melt, the weight of BCl₃ remaining in the melt and the final weight of the melt, the solubility of BCl₃ in the mixed melt can be estimated to be 0.19 M, lower than that in the chloroborate melts.

Cyclic Voltammetry of Chloroborate and Mixed Chloroborate/Chloroaluminate Melts

Chloroborate Melt Figure 2 is the CV of a room temperature chloroborate melt (51.50:48.50 BCl₃-BPC) at vitreous C electrode at room temperature. At -0.88 V, an irreversible reduction wave was found before solvent reduction. However, in the second scan, this wave almost disappeared. After cleaning the electrode or scanning to positive limit, this irreversible reduction wave appeared

again. This would happen if the reduction product was nonconducting and passivated the carbon electrode surface. The behavior of this irreversible reduction wave is very similar to that of oxygen in the basic chloroaluminate melts, reported by Hussey and Osteryoung (5). Therefore, oxygen or other impurities in our system might be responsible for this reduction wave. However, addition of BPC to neutralize the excess boron chloride in the melt to a slightly basic melt, removed this irreversible reduction wave. When AlCl₃ was added, bubbling occurred and the reduction wave appeared again. This suggested that the reduction wave was caused by a boron species, likely, BCl₃, or an acidic species. It is known that boron powders can be prepared electrochemically from fused metal fluoroborates at carbon electrodes, but the mechanism is thought to involve the indirect reduction of the boron species with reduced alkali metal (6). An attempt to reduce BCl₃ with the metal earlier did not provide a route to pure B and the possibility of aluminum boride formation has been suggested (7). It is possible, therefore,that the reduction mechanism involves the participation of a reduced aluminum intermediate.

Mixed Melts When AlCl₃ was added into slightly acidic chloroborate melts, an irreversible reduction wave similar to that in the chloroborate melt was observed. However, after the AlCl₃:BCl₃ ratio was over 1:1, another irreversible reduction wave just before the above irreversible reduction wave was observed. Figure 3 is the CV of a mixed melt when AlCl₃ was added into 51.50:48.50 BCl₃-BPC melt such that the mole ratio AlCl₃:BPC=1.23:1. Alternatively, when acidic chloroborate melt was added to acidic chloroaluminate melt, two similar irreversible reduction waves were observed. Figure 4 is a CV of a mixed melt when 0.96 g 51.80:48.50 BCl₃-BPC melt was added into 15.97g 1.2:1 AlCl₃-BPC melt. It can be seen from the second scan that the first reduction wave was passivated far less than the more negative reduction wave.

When AlCl₃ was added into a chloroborate melt and before the mole ratio of AlCl₃ added and BPC was over 1:1, only the displacement reaction [1] happened, perhaps caused by boron species BCl₃. After the mole ratio was over 1:1,that is the displacement reaction was completed, AlCl₃ may be a sufficiently strong Lewis acid to remove a chloride ion from BCl₃ to form an electroactive BCl₂⁺:

$$BCl_3 + AlCl_3 \rightleftharpoons BCl_2^+ + AlCl_4^-$$
[4]

Therefore, the first irreversible reduction wave might be caused by the species BCl_2^+ . In acidic chloroaluminate melts, it is known that the following equilibrium exists:

$$2\text{AlCl}_4^- \rightleftharpoons \text{Al}_2\text{Cl}_7^- + \text{Cl}^-$$
[5]

When a small amount of the chloroborate melt was added into an acidic chloroaluminate melt, Al_2Cl_7 species would first react with BCl_4 and produce BCl_3 which dissolves in the mixed melt. After this reaction is complete, Al_2Cl_7 might react with BCl_3 and produce BCl_2^+ . The overall reactions can be expressed as follows:

$$Al_2Cl_7^- + BCl_4^- \rightleftharpoons BCl_3 + 2AlCl_4^-$$
[3]

$$BCl_3 + Al_2Cl_7 \rightleftharpoons BCl_2^+ + 2AlCl_4^-$$
[6]

Therefore, in the cyclic voltammetry of mixed BCl₃-AlCl₃-BPC melt, the two irreversible reduction waves might respond to two electroactive species BCl_2^+ and BCl₃ respectively. However, more study is necessary to confirm the responsible species and unravel the reductive pathways.

SUMMARY

- 1. BCl₃ is displaced from BCl_4^- by Al_2Cl_6 or $Al_2Cl_7^-$.
- 2. Boron species are electroactive in acidic chloroborate melts and mixed chloroborate/chloroaluminate melts. There is evidence in the boron literature that boron species can be reduced by aluminum metal.
- 3. Boron does not form B₂Cl₆ readily like Al₂Cl₆. It does form stable subvalent species like B₂Cl₄ and B₄Cl₄ [8].
- 4. If B_2Cl_7 exists, it readily dissociates into BCl_4 + BCl_3 (volatile).

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Table 1. Compositions of BCl ₃ -BPC Melt
(1 atm and room temperature)

#	BPC(g)	BCl ₃ (g)	Mole Ratio BCl3-BPC
1	20.09	14.87	52.05:47.95
2	20.56	15.41	52.33:47.66
3	21.04	15.19	51.40:48.60
4	21.00	15.22	51.50:48.50
	Average		51.82:48.18

Table 2. Evolved Weights of BCl3 When Adding AlCl3into 11.08 g 51.50:48.50 BCl3-BPC Melt

AlCl ₃	Weight	Mole Ratio	Mole Ratio
Added(g)	Lost(g)	AlCl3:BCl3	AlCl3:BPC
0.32	0.32	1:1.14	0.06:1
1.69	1.40	1:0.92	0.40:1
2.25	1.97	1:1.00	0.85:1
1.04	0.66	1:0.72	1.06:1
0.68	0.03	1:0.05	1.20:1



Fig. 1. Schematic view of the experimental setup for making BCl₃-BPC melt.



Fig. 2. Cyclic voltammetry of 51.50:48.50 BCl₃-BPC melt at room temperature, vitreous C electrode (0.10cm²), 150 mV/s (top), 100 mV/s (middle), 50 mV/s (bottom).



Fig. 3. Cyclic voltammetry of mixed BCl₃-AlCl₃-BPC melt at room temperature, C electrode(0.10 cm²), 100 mV/s (adding AlCl₃ into 51.50:48.50 BCl₃-BPC such that AlCl₃:BPC = 1.23:1).



Fig. 4. Cyclic voltammetry of mixed BCl₃-AlCl₃-BPC melt at room temperature, C electrode (0.10 cm^2) , 150 mV/s (adding 0.96 g 51.80:48.50 BCl₃-BPC melt into 15.97 g 1.2:1 AlCl₃-BPC melt, saturated, about 0.20 M, in BCl₃).

ELECTROCHEMISTRY OF 9,10-ANTHRAQUINONE IN THE PRESENCE OF PROTON AND TETRACHLOROALUMINATE IN AMBIENT TEMPERATURE MOLTEN SALTS

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ABSTRACT

The electrochemistry of 9,10-anthraquinone (AQ) in a basic room-temperature molten salt composed of AlCl₃ mixed with 1ethyl-3-methylimidazolium chloride (ImCl) is described. AQ is reduced in a quasireversible two electron transfer to $AQ(AlCl_3)_2^{2-}$ in the absence of a proton source. Addition of proton as imidazolium hydrogen dichloride (ImHCl₂) causes the reactions coupled to electron transfer to shift from solvent leveling of AQ^{2-} by $AlCl_4^-$ to the more facile protonation of the reduced quinone. The hydroquinone formed, AQH_2 , is unstable in the $AlCl_3$:ImCl melt, but is stable in neat ImHCl₂ on the voltammetric time scale. The AQ/AQH_2 redox couple is quasireversible under these conditions. Experiments in molten ImCl, at 90 °C, show that AQ^{-} and AQ^{2-} are stable only under conditions where no Lewis acid is available for adduct formation.

INTRODUCTION

In this paper, we describe investigations of the Brønsted acid-base properties of basic room-temperature melts using AQ as the probe molecule. Quinones exhibit well-understood electrochemical and acid-base behavior and are well-suited for studies of the acid-base properties of ionic liquids. Their electrochemistry has been reviewed (1,2).

Room-temperature ionic liquids composed of mixtures of $AlCl_3$ and an organic chloride, RCl, (R = Im⁺ or 1-n-butylpyridinium, BP⁺) are useful solvents in which to study a wide variety of inorganic and organic redox and

other reactions (3-5). These media are basic, neutral or acidic, depending on whether the mole ratio $AlCl_3$:RCl is less than, equal to or greater than one, respectively (6).

An interesting feature of room-temperature melts is that, while the Lewis acidity is trivially adjustable by varying the amounts of the two solids (AlCl₃ and RCl) mixed together to yield the ionic liquid,

$$AlCl_3 + RCl \longrightarrow R^+ + AlCl_4^-$$
 [1]

the Brønsted acidity of proton donors deliberately added to the melt is a function of the underlying Lewis acidity (7-11). The Lewis acidity is controlled via the solvolysis reaction

$$2 \operatorname{AlCl}_4^- \longrightarrow \operatorname{Cl}^- + \operatorname{Al}_2\operatorname{Cl}_7^- \operatorname{K} = 10^{-17}$$
 [2]

In basic melts protons exist in the equilibrium

$$HCl_2^- \longrightarrow HCl + Cl^- K_{eq} = 0.016 M$$
 [3]

with eq. [3] shifting to the right as the melt composition approaches the neutral point (11). Here proton behaves as a typical strong acid in aqueous solution. In acidic melts protons behave as superacids (7-10), i.e., they display acidity greater than that of 100 % H_2SO_4 . Thus, a wide range of both Lewis and Brønsted acidities are accessible without resort to extreme experimental conditions; a fine degree of experimental control is possible over both the Lewis and Brønsted acid-base characteristics of the solvent.

This work is a continuation of our investigations into the behavior of quinones in these molten salt media (12-16).

EXPERIMENTAL

Preparation and Purification of Melt Components and Other Chemicals.

Aluminum chloride (Fluka) was purified by sublimation as described previously (17). ImCl was prepared by a modification (11) of a previously reported procedure (18). 9,10-Anthraquinone (AQ) was obtained from Fluka and sublimed once under vacuum before use. FeCl₂ (Alpha Products) was used as received.

Chloroaluminate melts were prepared by mixing together aluminum chloride and the organic chloride in the proper mole ratio. Experiments in AlCl₃:ImCl melts were performed at 35 ± 1 °C. Experiments in molten ImCl were performed at 90 ± 1 °C, slightly above the melting point of the organic chloride.

Imidazolium hydrogen dichloride (ImHCl₂) was used as the proton source and as a solvent for electrochemical studies. Its preparation has been described previously (19). This compound is a room temperature molten salt and offers the advantage over other proton sources (e.g., water) of introducing no chemical species into the melt, other than protons, that are not native melt components. ImHCl₂ was added to chloroaluminate melts volumetrically (density = 1.151 g/cm³). Voltammetric experiments using ImHCl₂ as a solvent were performed at 35 ± 1 °C.

Protonic impurities were removed from basic chloroaluminate melts by heating at 75 $^{\circ}$ C, with vigorous stirring, at a static pressure of 5 X 10⁻⁶ torr (20). In this way, melts containing protonic impurities at less than 10⁻⁴ M can be obtained easily. Absence of protons was confirmed by performing normal pulse voltammetry in the region of proton reduction in the melt, at a Pt disk electrode.

Instrumentation.

All voltammetric experiments were performed under purified He atmosphere in a Vacuum Atmospheres Co. drybox. Oxygen and water levels were maintained below 2 ppm.

Electrochemical measurements were performed in glass cells with a Teflon[™] cap fitted for introduction of electrodes and solutes and maintained

at constant temperature, as indicated in the text, to ± 1 °C using an aluminum heating block with a receptacle for jacketing of the entire cell.

Working electrodes were glassy carbon disks (geometric area, 0.071 cm²) and Pt disks (geometric area, 0.025 cm²) from Bioanalytical Systems. Counter electrodes were Pt coils. For work in chloroaluminate and ImHCl₂ melts, the reference electrode was an aluminum wire immersed in 1.5:1 melt and separated from the bulk melt by a VycorTM frit. This electrode is denoted Al/Al(III). For molten ImCl work, a Pt flag was used as quasireference electrode (QRE). The potential of this reference electrode at 90 °C was +0.344 V vs. Al/Al(III) at 35 °C. These potentials were compared using FeCl₄²⁻ (FeCl₂ added to a basic melt or to molten ImCl) oxidation at a Pt disk electrode in the respective media.

All experiments were performed using a Princeton Applied Research model 273 potentiostat controlled with custom software by a Digital Equipment Corp. PDP-8/e minicomputer (21).

Electronic absorption spectra were obtained on a Hewlett-Packard model 8452A spectrometer. Quartz cells of 100 μ m pathlength (Wilmad Glass Co.) were used. Absorption spectroscopy was performed directly on the melt samples used in voltammetric measurements, without dilution.

RESULTS

Cyclic Staircase Voltammetry in Chloroaluminate Melts.

A typical cyclic staircase voltammogram (CSV) of 5.2 mM AQ at a glassy carbon electrode, in proton-free 0.8:1 melt ($35 \,^{\circ}$ C) is shown in Fig. 1a (dashed curve). AQ is reduced at -0.432 V vs. Al/Al(III). A second, much smaller wave is observed at ca. -0.6 V. The origin of this wave is believed to be from an adsorption process and is discussed in the subsequent section. A single, somewhat more reversibly shaped oxidation wave is found at 0.312 V upon scan reversal. The general characteristics for currents and potentials in CSV experiments are summarized in Table I.

Values of $|E_{px} - E_{px/2}|$, where E_{px} is the peak potential and $E_{px/2}$ the halfpeak potential (x = c, a for the cathodic and anodic portions of the experiment, respectively) varied from 127 mV to 140 mV for the cathodic wave and from 59 mV to 75 mV for the anodic wave, as v was increased (Table 1). The value of $|E_{px} - E_{px/2}|$ for the reversible case at 35 °C is 58.4/n mV, where n is the number of electrons transfered in the redox reaction. Separation of the cathodic and anodic peak potentials, ΔE_p , was 616 mV $\leq \Delta E_p \leq$ 810 mV and increased with increasing v. This value is much larger than that for a reversible n-electron transfer at 35 °C, where $\Delta E_p = 61.1/n$ mV. We have previously shown that n=2 for the reduction of AQ in basic melts (12). Thus, ΔE_p would be 30.6 mV in this system, for a simple, two electron reduction.

In the absence of protons, i_{pa}/i_{pc} , the ratio of anodic to cathodic peak currents, was close to 1 at all v (see Table I), indicating that no reduction product was lost on the time scale of the CSV measurement due to homogeneous coupled chemistry. The values of i_{pc} and i_{pa} were linear functions of v^{1/2}, but with slightly negative intercepts on the current axis, also suggesting kinetic complications to the voltammetry.

Addition of proton (ImHCl₂) to the melt caused large changes in the CSV response. A typical example (385 mM ImHCl₂ added to an initially proton-free 0.8:1 melt) is shown in Fig. 1b (solid curve) for 5.0 mM AQ. Results are summarized in Table I. The value of E_{pc} shifted to more positive potentials in the presence of ImHCl₂. In Fig. 1, E_{pc} shifted from -0.43 V vs. Al/Al(III) in proton-free melt to -0.164 V in the presence of 385 mM ImHCl₂. Values of ΔE_p narrowed significantly compared to the proton-free case, but remained larger than the reversible value. For example, $\Delta E_p = 744$ mV in proton-free melt *vs.* 443 mV when 385 mM ImHCl₂ was present, at 200 mV/s.

The reduction wave narrowed considerably (Table I), with addition of ImHCl₂. Thus electron transfer to AQ becomes more facile and approaches the 2 electron, reversible limit $(|E_{pc}-E_{pc/2}| = 29.2 \text{ mV at } 35 \text{ }^{\circ}\text{C})$ as excess proton is added. For example, at 5 mV/s, $|E_{pc}-E_{pc/2}|$ narrows from 127 mV in proton-free melt to 44 mV in melt containing 385 mM proton. Values of $|E_{pa}-E_{pa/2}|$ were comparable to those found in proton-free melt, but E_{pa} shifted to more negative potentials by about 32 to 40 mV.

The normalized peak current, $i_{pc}/AD^{1/2}v^{1/2}C$, where A is the area of the glassy carbon electrode, D is the diffusion coefficient of AQ (see below) and C is the concentration of AQ, increased by a factor of 2.1 to 2.5, depending on v, on going from a proton-free melt to one containing 385 mM proton. The value of i_{pa} also was enhanced in the presence of ImHCl₂, by a factor of 1.4 to 1.8 (Table I).

The increase in peak current for AQ reduction upon addition of $ImHCl_2$ to the melt is not due to a change in viscosity of the melt. Experiments were performed on a 0.8:1 melt at 35 °C containing 24.8 mM $FeCl_4^{2-}$. The limiting

current for oxidation of FeCl_4^{2-} was monitored by normal pulse voltammetry in the absence and presence of ImHCl₂. After correction of the limiting currents for dilution of FeCl_4^{2-} , a 5% increase in current for FeCl_4^{2-} oxidation can be attributed to decrease in the viscosity of the medium.

The large values of ΔE_p observed are not merely due to effects of heterogeneous charge transfer. Using nonlinear curve fitting routines (22, 23), the CSV curve in Fig. 1a was fitted to the Butler-Volmer kinetic case for a 2 e⁻ quasireversible redox couple. The kinetic parameter is

$$\kappa = k^{0} / D_{0}^{(1-\alpha)/2} D_{r}^{\alpha/2} t_{c}^{1/2}$$
[4]

where k^o is the heterogeneous rate constant (cm/s), D_o and D_r are the respective diffusion coefficients of the oxidized and reduced forms of AQ (taken here to be equal), α is the transfer coefficient and t_c is the characteristic time of the CSV experiment, i.e., the duration of a staircase increment. The value of D_o at 35 °C in the melt was estimated using the Stokes-Einstein equation , the viscosity of the 0.8:1 melt (24), $\eta = 24.7$ cP (35 °C) and the value of the diffusion coefficient of AQ in DMF/ 0.3 M TEAP at 21 °C (9.0 X 10⁻⁶ cm²/s) reported by Rosanske and Evans(25). Equal hydrodynamic radii of AQ in the two systems were assumed. Using this method, we estimate the value of D_{AQ} = 3.0 X 10⁻⁷ cm²/s (0.8:1 chloroaluminate melt, 35 °C). The value of k^o obtained (2.3 ± 0.3 X 10⁻⁷ cm/s) was several orders of magnitude smaller than previously reported for electron transfer reactions of AQ in aprotic solvents (25,26). Such a small rate constant would make the reduction wave insensitive to following chemistry. This is not the case based on the voltammetry of Figure 1.

Pulse Voltammetry in Chloroaluminate Melts.

Normal pulse voltammetry (NPV) in AlCl₃:ImCl melts containing 4.9 mM AQ at 35 °C are shown in Fig. 2a (proton-free melt, 5.2 mM AQ) and Fig. 2b (385 mM proton-containing melt, 4.9 mM AQ). In NPV experiments, the potential of the working electrode was stepped from +0.8 V vs. Al/Al(III) to the initial potential of the experiment (+0.2 V). Table II summarizes the results of NPV experiments, performed at pulse times $0.05 \text{ s} \le \text{tp} \le 1.0 \text{ s}$. In the absence of added ImHCl₂, AQ is reduced in single wave as shown in Fig. 2a. Its position on the potential axis is pulse time (t_p) dependent . We also observe a smaller wave at ca. -0.6 V vs. Al/Al(III) which is not reproducible

in magnitude and can be observed as a postwave on the main reduction wave in CSV (Fig. 1a). It may be due to adsorption of AQ onto the GC electrode.

Slopes of log plots of the rising portion of the NPV wave varied from 200 mV/decade to 95.2 mV/decade, as t_p was increased, showing that the overall reduction process is kinetically hindered on this time scale (2.303 RT/nF = 61.1/n mV at 35 °C). Upon addition of ImHCl₂, Fig. 2b, the reduction wave became much more reversible, with a log plot slope of 56.1 mV/decade at $t_p = 1$ s and [ImHCl₂] = 385 mM. $E_{1/2}$ was a linear function of log [ImHCl₂], the line obtained having a slope of 136 mV/decade increase in proton concentration. Introduction of ImHCl₂ resulted in weak adsorption of AQ at the GC surface as shown by the slight maximum prior to the limiting current plateau of the reduction wave in Fig. 2b. Maxima in pulse voltammetry produced by adsorption processes have been described previously (27).

The enhancement of the limiting current, i_{lim} , upon addition of protons is not as pronounced here as in CSV experiments. This is likely to be due to kinetic limitations of the electron transfer reactions on the time scale of the NPV measurement. In both proton-free and proton-containing melts, i_{lim} was a linear function of $t_p^{-1/2}$, but these plots had negative intercepts on the current axis. Thus, these reactions are not diffusion controlled on the NPV time scale. At the longer t_p studied, i_{lim} is ca. 20-33% larger for the protoncontaining melt than for the proton-free case, but at shorter pulse times, e.g., $t_p \leq 0.1$ s, values of i_{lim} are closer to each other under the two different conditions (only 7-10% enhancement in the presence of protons).

Reverse pulse voltammetry(RPV) for the reoxidation of reduced AQ are shown for the proton-free case in Fig. 3a and the 385 mM proton case in Fig. 3b. The concentration of AQ in each experiment is the same as that in Fig. 2. In these experiments, the potential of the GC electrode was stepped from +0.8 vs. Al/Al(III) to -1.0 V, where reduction of AQ occurs at its rate-limited velocity. The working electrode potential was maintained here for 12 s, after which the analysis pulse was applied to more positive potentials for various tp. Following the pulse, the potential of the working electrode was stepped back to +0.8 V for 12 s (with stirring and establishment of quiescence as above in NPV experiments). RPV $E_{1/2}$ values were essentially constant at all [ImHCl₂] investigated. The potentials were within ± 5 mV of each other for these experiments.

The value of i_{lim} for the reoxidation process was slightly enhanced by the presence of proton, as in CSV measurements, since the concentration of AQ in Fig. 3b is 94% of that in Fig. 3a. There is no trend in the dependence of the slopes of log plots of the rising portion of the RPV wave on [ImHCl₂], as shown in Table II. The degree of reversibility of the overall oxidation process

does not depend on the presence of protons. These reactions are not diffusion controlled, by examination of the pulse time dependences of $E_{1/2}$ and i_{lim} , shown in Table II.

The ratio, i_{rp}/i_{np} , of the limiting currents obtained in RPV and NPV under identical experimental conditions is close to 1 at [ImHCl₂] = 0 and all t_p investigated. This is also the case for $t_p \ge 0.1$ s and [ImHCl₂] > 0. However, at longer t_p and high [ImHCl₂], this ratio become much less than 1. For a reversible redox reaction where the oxidized and reduced forms of the couple are stable on the time scale of the experiment, the limiting currents obtained in NPV and RPV should be equal, at all t_p and t_p .

Pulse voltammetric experiments are consistent with participation of proton in facile chemical steps coupled to the electron transfer reactions of AQ which compete with much slower chemical steps that can only predominate if no proton source is present, perhaps due to reaction of the reduction product with AlCl₄⁻. In contrast, the reoxidation of reduced AQ is much less sensitive to proton, implying that the reduced form of AQ which is ultimately formed at the electrode surface is not the hydroquinone, AQH₂, even when a large molar excess of ImHCl₂ is present.

Voltammetry in Molten ImCl.

A typical CSV at GC of 7.1 mM AQ in molten ImCl, at 90 °C, is shown in Fig. 4 (v = 100 mV/s). In the absence of AlCl₃ (Fig. 4a), AQ is reduced in two successive electron transfer steps with $E^{0'}$ = -0.540 V and -0.915 V vs. Pt QRE. The QRE was used in order to avoid introducing AlCl₄⁻ and Al₂Cl₇⁻ into the melt from a conventional chloroaluminate reference electrode. The values of ΔE_p for each couple were 88 ± 40 mV for the first reduction and 88 ± 24 mV for the second reduction. Measurements of AQ reduction in molten ImCl were subject to some irreproducibility and are therefore highly qualitative. Similar measurements on the FeCl₄^{2-/-} system, used to calibrate the Pt QRE potential vs. chloroaluminate systems, were quite reproducible, however. The value of $\Delta E_{\rm p}$ for the reversible case at 90 °C is 73.1/n mV. Thus, these redox couples are 1 e⁻ reactions, in the absence of AlCl₄⁻. Observation of the working electrode after removal from the melt following a long potential step to a value negative of the second reduction wave revealed that a red species was produced, indicative of the dianion, AQ²⁻ (28). The qualitative characteristics of the voltammetry in molten ImCl are very similar to those observed in nonaqueous systems where no Lewis acid is available to react with the quinone anion radical and dianion (25,26).

When AlCl₃ was added to molten ImCl containing AQ (see Fig.4b) the voltammetric behavior changed to a single reduction wave of slightly less than twice the height of the original two waves. Upon addition of AlCl₃, AQ electrochemistry becomes equivalent to that observed in basic chloroaluminate melts.

Voltammetry in 1-ethyl-3-methylimidazolium Hydrogen Dichloride.

A typical CSV of 4.5 mM AQ in neat ImHCl₂ at 35 °C is shown in Fig. 5. Experiments performed in neat ImHCl₂ provide conditions where no chloroaluminate species are present, but the native proton concentration is quite large (ca. 6.5 M HCl_2^{-}). Results are summarized in Table III. AQ is reduced in a single wave and reoxidized at potentials comparable to the reduction process, in contrast to the results in chloroaluminate melts. Epc is shifted to more positive potentials than the corresponding reduction process in the chloroaluminate media (either with or without added proton) and E_{pa} occurs at a somewhat more negative potential than the corresponding process in the other melts. At $v \le 20$ mV/s, the peak potentials were essentially independent of $\nu,$ with the onset of a shift in E_{pa} and E_{pc} to more positive and more negative potentials, respectively, occuring at $v \ge 50 \text{ mV/s}$. $|E_{pc}-E_{pc/2}|$ and $|E_{pa}-E_{pa/2}|$ tend toward that of a reversible 2e⁻ process (29.2 mV at 35 °C) at slow sweep rate. Shifts in peak potentials were symmetrical about $E^{o'}$ = 0.168 ± 0.003 V vs. Al/Al(III), suggesting that they are due solely to electron transfer kinetic effects. No other redox processes were observed within the electrochemical window of the melt.

The cathodic peak current was a linear function of $v^{1/2}$ over the range of n investigated ($5 \le v \le 500 \text{ mV/s}$) with zero intercept on the current axis. Ratios i_{pa}/i_{pc} were close to 1 at all v (Table III), indicating stability of the reduced form of AQ on the CSV timescale.

CSV experiments were fitted to theory for quasireversible 2 e⁻ transfer (*vide supra*). Using $D_{AQ} = 1.2 \times 10^{-6} \text{ cm}^2/\text{s}$, obtained from the essentially diffusion controlled dependence of NPV limiting current on $t_p^{-1/2}$ (Table III) we obtained $k^0 = 7.8 \pm 0.6 \times 10^{-4} \text{ cm/s}$, $\alpha = 0.51 \pm 0.02$ and $E^{0'} = 0.172 \pm 0.002 \text{ V}$ vs. Al/Al(III). In neat ImHCl₂, the redox process cannot be distinguished from a simple 2e⁻ quasireversible case, i.e., any chemical steps occurring between electron transfers are not rate determining.

Electronic Absorption Spectroscopy of 9,10-Anthraquinone.

Visible absorption spectra of AQ in the various media described above were obtained to determine whether the facilitation of the reduction process observed in the presence of proton donor was due to prior protonation of AQ (forming, e.g., AQH^+ or AQH_2^{2+}) or to a homogeneous reaction of the proton donor with reduced AQ (e.g., AQ^- and AQ^2 -).

In 0.8:1 melt, with and without proton, spectra displayed a single absorption band centered at $\lambda_{max} = 328$ nm. A typical spectrum of 4.9 mM AQ in 0.8:1 melt containing ImHCl₂ is shown in Fig. 6. This is consistent with previously reported spectra of neutral AQ in DMF (28) and in AlCl₃:BPC melt (12). Protonation of AQ at the carbonyl oxygens would be expected to yield an absorbance band at shorter wavelengths (311 nm) than that observed here (29).

Voltammetry in Acidic Chloroaluminate Melts.

Experiments were attempted in 1.5:1 melt with added ImHCl₂. Under these conditions HCl is superacidic and our interest was in finding whether the proton could displace AlCl₃ from the AQ(AlCl₃)₂ adduct found in acidic melts (12). Unfortunately, there are no changes in the CSV of AQ observed after addition of proton (in excess over AQ) to 1.5:1 melt containing 5 mM AQ to suggest that AlCl₃ is displaced by proton.

DISCUSSION

The redox chemistry of AQ in AlCl₃:ImCl melts and related media is of two types, depending on the availability of a Lewis acid for formation of an adduct with the reduced forms of AQ.

$$AQ + e^{-} \longrightarrow AQ^{-}$$
 [5]

$$AQ^{-} + e^{-} \implies AQ^{2-}$$
 [6]

In molten ImCl, only Im⁺ and Cl⁻ are available in the melt and the reduced forms of AQ in eqs. [5] and [6] are stable on the time scale of the voltammetric measurement. Voltammetry in molten ImCl closely resembles that observed for quinone reduction in nonaqueous systems where no Lewis acid is present (1, 2, 26).

In neat ImHCl₂, AQ redox chemistry proceeds at potentials considerably positive of those observed in the other media. This can be understood in terms of equation [5] followed by

$$AQ^{-} + HCl_2^{-} \longrightarrow AQH^{-} + 2Cl^{-}$$
 [7]

$$AQH + e^{-} \implies AQH^{-}$$
 [8]

$$AQH^{-} + HCl_2^{-} \longrightarrow AQH_2$$
 [9]

Here, only a single quasireversible 2 e⁻ transfer is observed. In this case, fast protonation of AQ^{-} in eq. [7] would yield AQH[.] which is expected to be reduced at potentials positive of the first 1 e⁻ reduction, eq. [5] giving an overall apparent 2e⁻ process. Thus, AQ exhibits electrochemical behavior (ECEC) here which is analogous to previous studies in nonaqueous media to which proton donors have been added deliberately (30).

Voltammetry in AlCl₃:ImCl melts (with or without added proton donor) shows that the overall redox behavior of AQ in this system is more complex than in the other cases discussed above. The results are consistent with the following scheme (in proton-free 0.8:1 melt): equation [5] followed by

$$AQ^{-} + AlCl_4^{-} \longrightarrow AQ(AlCl_3)^{-} + Cl^{-}$$
 [10]

$$AQ(AlCl_3)^{-} + e^{-} \implies AQ(AlCl_3)^{2-}$$
 [11]

$$AQ(AlCl_3)^{2-} + AlCl_4 \longrightarrow AQ(AlCl_3)_2^{2-} + Cl^{-}$$

The relatively irreversible nature of the reduction process in proton-free melt suggests that the solvent leveling reaction, eq. [10] is kinetically hindered on the time scale of the voltammetric measurement. However, if sufficient time is allowed, e.g., in bulk electrolysis experiments (12), the overall reduction will involve 2e⁻ per molecule of AQ.

Reoxidation of AQ(AlCl₃)₂²⁻ in proton-free chloroaluminate melt proceeds at potentials far positive of that expected for a reversible process. Furthermore, no value of α and k⁰ for CSV experiments in this medium could satisfy the shape, wave height and peak separation of the reduction and oxidation waves. It is likely that complexation of AQ²⁻ by two AlCl₃ molecules shifts the oxidation potential to much more positive values than can be explained by heterogeneous electron transfer kinetics (12). It is possible in such a scheme that the kinetics of reoxidation are different from those of the reduction step. The oxidation of hydroquinones is known to be complex (31,32) and we have not studied the oxidation reaction in detail. However, it is reasonable that the reduction of AQ proceeds at potentials characteristic of neutral AQ in the chloroaluminate melt and reoxidation at potentials characteristic of the adduct AQ(AlCl₃)₂²⁻. This type of behavior is analogous to a "square reaction scheme" described for redox chemistry accompanied by large structural changes (33).

Addition of ImHCl₂ to the 0.8:1 melt results in an increase of the peak current for reduction and facilitation of the overall process compared to the proton-free melt. This behavior is consistent with replacement of the sluggish reactions [10] and [12] by more facile steps involving protonation of AQ² and AQ² by HCl₂⁻.

The reoxidation of AQH₂ in 0.8:1 melt containing a proton donor appears to be the same process as occurs in proton-free melt. This process may involve the reaction of AQH₂ with $AlCl_4^-$, on the time scale of the voltammetric experiment.

$$AQH_2 + 2 AlCl_4^{-} \longrightarrow AQ(AlCl_3)_2^{2-} + 2 HCl$$
[13]

Therefore, the ultimately reoxidizable species in chloroaluminate melt is the same regardless of the availability of proton. This means that proton is essentially catalyzing the reduction of the quinone. Reaction of hydroquinones with the components of basic chloroaluminate melts has been previously described by our laboratory (16) and is consistent with the behavior observed.

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v/mV-s ⁻¹	[ImHCl ₂] /mM	Epc/V	Epa/V	$\Delta E_p/mV$	lE _{px} - x=c	·E _{px/2} 1/mV x=a	ipa/ipc	Ic
2	0	-0.357	0.259	616	127	59	0.89	3.84
	385	-0.084	0.219	303	44	49	0.68	9.65
10	0	-0.359	0.260	619	119	50	1.06	3.68
	385	-0.094	0.228	322	49	48	0.70	9.24
20	0 385	-0.360 -0.109	$0.274 \\ 0.240$	634 349	120 49	5 4 50	0.96 0.67	3.96 9.52
50	0	-0.378	0.285	663	113	60	1.04	3.71
	385	-0.120	0.252	381	49	52	0.66	9.34
100	0	-0.415	0.300	715	140	65	0.96	3.89
	385	-0.174	0.276	450	59	56	0.67	8.21
200	0	-0.432	0.312	744	137	72	0.97	3.96
	385	-0.164	0.279	443	59	64	0.64	8.88
500	0	-0.480	0.330	810	137	75	0.89	4.04
	385	-0.180	0.290	470	60	65	0.61	9.03
^a temperatu	tre, 35 °C. V	Working elect	rode, glassy c	arbon disk (A	= 0.071	cm ²).		

 $b \ [AQ] = 5.2 \text{ mM}$ in proton-free melt and 4.9 mM in melt containing 385 mM proton.

 $^{\rm C}$ 10- $^{\rm 5}{\rm i}_{\rm pc}/\rm AD^{1/2}v^{1/2}C$ with units of (A $^{\rm s3/2}\rm cm/V^{1/2}\rm -mol)$

t _p /s	Experiment ^b	[ImHCl ₂] /mM	log plot slope ^c /mV-decade ⁻¹	10 ⁻⁴ it _p ^{1/2} /D ^{1/2} C (A·s/mol·cm ²⁾	i _{rp} /i _{np}
0.05	NPV	0	200	1.18	1.01
	NPV	385	64	1.30	1.05
	RPV	0	85.5		
	RPV	385	107.5		
0.10	NPV	0	166	1.13	0.97
	NPV	385	59.7	1.21	0.96
	RPV	0	55.9		
	RPV	385	67.4		
1.0	NPV	0	95.2	0.93	0.88
	NPV	385	56.1	1.12	0.68
	RPV	0	69.8		
	RPV	385	59.5		

Table II. Pulse Voltammetry of AQ in 0.8:1 chloroaluminate melts.^a

^a [AQ] = 5.2 mM in proton-free melt and 4.9 in melt containing 385 mM proton. All other conditions as in Table 1.

^b NPV, Normal pulse voltammetry of AQ reduction. RPV, Reversed pulse voltammetry for oxidation of the reduced form of AQ.

^c slope of the rising portion of the wave in the form E vs. $log[(i_{lim}-i)/i]$.

$v/mV-s^{-1}$	E _{pc} /V	E _{pa} /V	$\Delta E_p/mV$	E _{px}	-E _{px/2} / /	mV i _{pa} /i _{pc}
				x=c	x=a	
5	0.133	0.190	57	37	40	0.98
10	0.140	0.190	50	35	30	0.95
20	0.140	0.200	60	35	35	0.98
50	0.130	0.210	80	45	45	0.97
100	0.120	0.220	100	50	50	1.1
200	0.110	0.230	120	55	55	0.97
500	0.095	0.240	145	55	55	0.97

Table III. Voltammetry of AQ in neat ImHCl₂.

A. Cyclic Staircase Voltammetry.

B. Normal Pulse Voltammetry.

t _p /s	E _{1/2} /V	log plot slope	it _p ^{1/2} /D ^{1/2} C
		/mV-decade ⁻¹	(Å·s/mol·cm ²)
0.02	0.103	65.51	0.84
0.05	0.110	62.74	0.76
0.10	0.119	59.1	0.76
0.20	0.126	58.26	0.74
0.50	0.140	55.13	0.74
1.00	0.145	47.2	0.72

C. Reverse Pulse Voltammetry.

t _p /s	E _{1/2} /V	log plot slope/mV-decade ⁻¹	it _p ^{1/2} (μA·s ^{1/2})	i _{rp} /i _{np}
0.05	0.212	61.9	36.3	0.97
0.20	0.193	54.5	35.1	0.96
0.50	0.178	63.6	34.9	0.95
1.00	0.167	55.4	34.3	0.97



Figure 1. Cyclic staircase voltammograms of (a) 5.2 mM AQ in proton-free 0.8:1 melt and (b) 5.0 mM AQ in 0.8:1 melt with 385 mM ImHCl₂. Sweep rate, 200 mV/s. Temperature, $35 \, {}^{\circ}$ C. Working electrode, glassy carbon.



Figure 2. Normal pulse voltammetry of (a) 5.2 mM AQ in proton-free 0.8:1 melt and (b) 4.9 mM AQ after addition of 385 mM ImHCl₂. Circles are currents measured on the analysis pulse and crosses are currents prior to the pulse. Pulse time, 500 ms. Other conditions are as in Figure 1.



Figure 3. Reverse pulse voltammetry for reoxidation of the reduced form of AQ in 0.8:1 melt (a) 5.2 mM AQ in the absence of protons and (b) 4.9 mM AQ in the presence of 385 mM proton. Other conditions are the same as in Figure 2.



Figure 4. Cyclic staircase voltammogram of 7.1 mM AQ in molten ImCl at 90 °C. Sweep rate, 100 mV/s. Working electrode, glassy carbon. (A) neat ImCl. (B) ImCl with added $AlCl_3$ (mole ratio $AlCl_3:AQ = 13.4$).



Figure 5. Cyclic staircase voltammetry of 4.5 mM AQ in neat ImHCl₂ at 35 °C. Sweep rate, 50 mV/s. Circles represent the experimental currents and the solid line the best fit for a 2e⁻ transfer with k^o = 7.93 X 10⁻⁴ cm/s, α = 0.53, and E^o = 0.173 V vs. Al/Al(III), D_{AO} = 1.2 X 10⁻⁶ cm²/s.



Figure 6. Uv-visible spectrum of 4.9 mM AQ in 0.8:1 melt with 385 mM ImHCl₂.

ELECTROCHEMICAL REDUCTION OF AROMATIC KETONES IN A ROOM-TEMPERATURE MOLTEN SALT

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ABSTRACT

The electrochemical behavior of fluorenone and benzophenone has been investigated in the aluminum chloride : 1-methyl-3-ethylimidazolium chloride molten salt system. Cyclic voltammetric studies have shown that melt acidity greatly influences the reduction potential of these ketones by complexation of the carbonyl oxygen in the acidic melt. The lifetime of the electrochemically generated ketyl also depends on melt acidity, becoming longer (more stable) as acidity increases. Preparative electrolyses have shown that reduction of fluorenone in the basic melt gives the pinacol (one-electron, dimeric) product, whereas benzophenone reduction forms the alcohol (two-electron, monomeric) product. In the neutral melt, buffered with sodium chloride, both ketones undergo reduction to form a pinacolone product, resulting from initial pinacol formation followed by rearrangement induced by oxide abstraction by the melt. Further evidence of oxide uptake by the melt is found in the reduction of fluorenone in the acidic melt, in which the pinacolone product and a small amount of bifluorenylidene (alkene, both oxygens removed) is formed.

INTRODUCTION

Previous studies of carbonyl compounds in this roomtemperature melt (1-4) have shown that the electrochemical properties are markedly affected by melt acidity, an increase of which causes the reduction potentials for these compounds to be shifted to more positive values. Complexation of the carbonyl groups by aluminum chloride in acidic melts is responsible for this phenomenon and seems to be rather general in these melts. In preliminary work, it has been found that the reduction process for ketones (4) is not as reversible as that for quinone systems (1,2), affording an opportunity to study the effect of melt acidity on the type and distribution of ketone reduction products. Of particular interest here is the possibility of oxide abstraction from the reduction products by aluminum species in the melt. This pathway has not been extensively investigated in this molten salt system, and provides an interesting insight into additional aspects of reactivity for oxygen-containing compounds.

EXPERIMENTAL

1-Methyl-3-ethylimidazolium chloride (MEIC) was prepared by reaction of 1-methylimidazole and a three-fold molar excess of ethyl chloride in a pressure bottle (5). Ethyl chloride (Aldrich Chemical Company) was used as received, and 1-methylimidazole (Aldrich Chemical Company) was vacuumdistilled over calcium hydride before use. Aluminum chloride was purified by distillation in a sealed tube (1). For removal of trace amounts of protonic impurities, either addition of ethyl aluminum dichloride or placement of the melt under vacuum was employed.

Voltammetric experiments were carried out at a PARC Model 174A Polarographic Analyzer, coupled with a Bioanalytical Systems CV-27 as potential scanner. A PARC Model 273 Electrochemistry System was used for preparative electrolysis and coulometric experiments. Cyclic voltammograms were recorded at 3 mm diameter vitreous carbon rod (Tokai GC-30 sealed in Pyrex) and are referenced against aluminum wire immersed in 2:1 aluminum chloride : MEIC melt.

Preparative electrolyses were run at reticulated vitreous carbon working electrodes using a PARC Model 273 Potentiostat. Following electrolysis, the melt was extracted with hexane or pentane while still in the drybox in order to separate neutral compounds from the melt. The melts were then taken outside the drybox, poured over ice, and then extracted with benzene to obtain the remainder of the electrolysis products.

RESULTS AND DISCUSSION

Electrochemistry of Fluorenone System.

The electrochemical behavior of fluorenone in the aluminum chloride : MEIC molten salt system has been described in a previous contribution (4) and will be summarized here. As is the case for other carbonyl compounds, the reduction potential for fluorenone is shifted to more positive values as the melt composition is changed from the basic region (-1.00 V) to the acidic domain (+0.10 V), this shift being due to complexation of the carbonyl oxygen by aluminum chloride. This complexation also has a profound effect on the spectroscopic properties of the solute, in this case causing a change from yellow (basic melt) to red (acidic melt). The voltammetric behavior of fluorenone has been rather well characterized, and subsequent work has involved determination of electrolysis products formed in fluorenone reduction in melts of various acidity levels.

In the basic melt, fluorenone undergoes a one-electron reduction, there being no anodic process on the return sweep at 100 mV/s. At 500 V/s, however, an anodic process appears approximately 500 mV positive of the reduction process and corresponds to the oxidation of the ketyl back to fluorenone. The ketyl anion, being negatively charged, apparently displaces chloride from tetrachloroaluminate, resulting in a ketyl species complexed by aluminum chloride. This interac-tion results in the separation in the observed potentials for the redox processes. At slower scan rates, the anodic process decreases in importance as the ketyl species couple to produce the pinacol, the oxidation of which is not observed in the basic melt. A preparative reduction of fluorenone in the basic melt resulted in the formation of fluorenone pinacol in 80% yield, there being also some pinacolone (10%) produced as well. As shown in Figure 1, the pinacolone results from rearrangement of the intially produced pinacol species in the melt.

From previous work on anthraquinone (1), chloranil (2), and fluorenone (4) in room-temperature molten salt systems, it has been observed that voltammetric studies in the neutral region typically involve the presence of many species and/or voltammetric responses, and that the relative amounts of these species depend critically on slight changes in melt acidity. For this reason, investigations in the neutral melt were carried out using the sodium chloride buffer system recently investigated by Wilkes et al. (6) Neutral conditions result from the addition of NaCl to a slightly acidic melt, the NaCl reacting with Al_2Cl_7 to produce $AlCl_4$. The effect on the voltammetry of fluorenone is shown in Figure 2, in which the behavior typical of the acidic melt (1) changes to that seen in the buffered neutral melt. In particular, it is seen that conditions are still acidic enough that fluorenone exists primarily in the complexed form, and that the oneelectron reduction process (Ic) in the acidic melt becomes more complex in the neutral melt. The presence of multiple processes in the neutral melt is probably due to depletion of the small amount of Al_2Cl_7 next to the electrode surface as complexation of the reduction product occurs, resulting in a slight shift in reduction potential as the local acidity changes. It can also be seen that the Ia process in the acidic melt, due to oxidation of the ketyl in the acidic melt, is absent in the neutral melt. Preparative electrolysis showed that fluorenone pinacolone was produced in 75% yield, with a trace of bifluorenylidene also being formed. This result implies that reduction results in initial formation of the pinacol product from rapid coupling of the ketyl, followed by rearrangement to the pinacolone. In the more acidic conditions of the neutral melt, this rearrangement is much more complete than it is in the basic melt, reflecting the greater ease of oxide abstraction from the reduction product as acidity increases.

The electrochemical behavior of fluorenone in the acidic melt is more complicated than in either the basic or neutral regions. As seen in Figure 2, the first reduction process, shown by coulometry to involve one electron, results in the formation of the ketyl which couples more slowly than in less acidic melts. Variation of scan rate showed that the products undergoing oxidation at IIa (two peaks) are formed at the expense of the ketyl, suggesting that the IIa peaks are due to oxidation of the pinacolate product. Verification of this premise was found from a preparative electrolysis, in which the product oxidizing at the more positive potential in IIa was found to be stable and could be oxidized back to fluorenone, as shown on the return sweep. By performing another electrolysis just positive of the pinacoloate oxidation wave, the amount of fluorenone regenerated served as a measure of the yield of the pinacol produced (25-35%). The presence of two waves in the IIa system suggests that the pinacolate exists in the acidic melt in two conformations, interconversion being difficult because of complexation of the oxygen anions by aluminum chloride. Even in more usual solvents such as DMSO and acetonitrile, some broadening of NMR resonances interconversion of fluorenone pinacol due to hindered conformers has been noted (7), giving support to this interpretation. As was stated earlier, only one form of the pinacolate is stable during the electrolysis, so that other products resulting from subsequent reactions should also be present. Product analysis showed that some of the pinacolone

product is also formed here. Bifluorenylidene (Figure 3) is also formed during the electrolysis (5-10% yield), giving a reversible couple at +1.20 V. Formation of this product evidently requires the abstraction of two oxide anions from the pinacolate and occurs only in the acidic melt.

Electrochemistry of Benzophenone System.

The series of cyclic voltammograms presented in Figure 4 illustrates the electrochemical behavior of benzophenone as the melt acidity is varied. As in the fluorenone system, complexation of the carbonyl group by aluminum chloride in the acidic melt results in a positive shift of the reduction potential; however, the benzophenone system as a whole is less easily reducible than is the fluorenone system. This is particularly evident in the acidic melt, in which reduction occurs immediately before the cathodic background process. Preparative electrolyses were attempted in the 1.2 : 1.0 acidic melt, but aluminum deposition eventually began and rendered the coulometric measurements meaningless.

As seen in Figure 4, reduction in the basic melt occurs in a rather broad process, there being no discernible reversibility at 100 mV/s. At higher scan rates, however, the ketyl oxidation process appeared, and at 10 V/s and higher the peak height ratios for the redox processes remained constant, indicating that further reaction of the ketyl occurs much more slowly than for the fluorenone system. Preparative electrolysis in the basic melt gave the alcohol (diphenylmethanol) as major product, with a smaller amount (10%) of tetraphenyloxirane also being produced. It was determined that the tetraphenyloxirane was formed in the electrolysis, and not during subsequent melt hydrolysis, by extraction of the melt with hexane immediately after the electrolysis, the epoxide product being found in the hexane extract. The more negative reduction potential of benzophenone apparently is responsible for the formation of a twoelectron product (alcohol), as opposed to the one-electron product (pinacol) seen in the fluorenone system. The formation of tetraphenyloxirane is an indication that the pinacol is formed in low yield and undergoes subsequent abstraction of oxide by the melt to produce an epoxide system. This pathway is not followed for the fluorenone system, presumably because the steric constraints would be too severe in the analogous epoxide system. The epoxide formation in the basic melt is very interesting because it shows that the tetrachloroaluminate ion has the ability to abstract oxide from

the products formed in the electrolysis.

In a weakly acidic melt (1.03 : 1.00), benzophenone reduction results in the formation of a relatively stable ketyl, as shown in Figure 5. Addition of sodium chloride to form the neutral buffered melt resulted in a situation much the same as that in the fluorenone system; that is, the reduction process shows evidence of multiple processes and following chemical reactions are now much faster than in the acidic melt. A preparative electrolysis produced pinacolone, so that the one-electron reduction mechanism (pinacol formation, followed by oxygen abstraction) is apparently followed here as well.

CONCLUSIONS

The products obtained in the electrolyses of fluorenone and benzophenone can be accounted for on the basis of both the structural aspects of the compounds themselves and on the melt acidity. In the basic melt, for instance, the structural differences between fluorenone and benzophenone cause the reduction of the latter compound to occur at rather more negative potentials, resulting in the production of the alcohol (two-electron) product as opposed to the formation of the pinacol (one-electron) product in the fluorenone system. The small amounts of epoxide formation in the benzophenone system and pinacolone formation in the fluorenone system show that the basic melt, in particular the tetrachloroaluminate ion, has the ability to abstract oxygen from the reduction products. The extent of this abstraction becomes greater, of course, as the melt acidity is increased, as is evident in the formation of pinacolone products from both systems in the neutral melt. Even further abstraction occurs in the acidic melt, at least in the fluorenone system, leading to the formation of bifluorenylidene. This uptake of oxide by the melt is undoubtedly driven by the large Al-O bond strength (8), coupled with the decrease in the carbon-oxygen bond order occurring upon ketone reduction. An interesting parallel between this work and recent synthetic methodology is found in the McMurry reaction, in which reaction of ketones with zero-valent titanium produces alkenes in very high yields (9).

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Fluorenone pinacolate



Fluorenone pinacolone

Figure 1. Reduction of fluorenone in the basic melt, showing formation of the pinacolate and pinacolone products.



Figure 2. Cyclic voltammetric behavior of fluorenone (31 mM).

(a) 1.04 : 1.00 acidic melt(b) NaCl - saturated melt (buffered neutral)

100 mV/s

Temperature = 40°C



Figure 3. Reduction of fluorenone in the acidic melt, showing formation of the pinacolate and bifluorenylidene.



Figure 4. Cyclic voltammetric behavior of benzophenone. Acidic melt: 24 mM Neutral melt: 35 mM Basic melt: 31 mM

100 mV/s

Temperature = 40°C



Figure 5. Cyclic voltammetric behavior of benzophenone (36 mM).

(a)	1.03	:	1.00 acidic melt	
(b)	NaCl	-	saturated melt (buffe	ered neutral)

100 mV/s

Temperature = 40°C

STUDIES ON CHARACTERISTICS OF THE ROOM TEMPERATURE MOLTEN SALT AICI3-1-BUTYLPYRIDINIUM CHLORIDE

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Abstract

The characteristics of ambient temperature molten salt, i.e., AlCl₃-BPC, was investigated by the conductivity, viscosity, EMF, and NMR measurements. The conductivity and viscosity of the melt changed with temperature and AlCl₃ content. The relationship between ion species and AlCl₃ content in the melt was obtained from the equilibrium constants for the ion species, K_M , K_0 , and K_2 which are simulated by using the EMF values. The changes of the conductivity and the viscosity were attributed to the change of the content of ion species, especially AlCl₄⁻, Al₂Cl₇⁻, and BP+, with the AlCl₃ content and temperature of the melt. These facts were also supported from ²⁷Al NMR and ¹H NMR measurements.

1.Introduction

The room temperature molten salt AlCl₃-1-butylpyridinium chloride(BPC) has slightly higher viscosity and lower conductivity than those of AlCl₃-1-ethyl-3-methylimidazolium chloride(EMIC) melt. However, the AlCl₃-BPC melt is widely used for an Al plating melt(1,2) and for an electrolyte of secondary battery with an Al electrode(3~5), because the handling of BPC is much easier than EMIC and the cost of BPC is much cheaper than EMIC. Characteristics of the AlCl₃-BPC melt have been investigated by several workers(6~8), but those changes with temperature are scarcely studied(9,10). The changes effect significantly on both the electroplated surface and the cell performance. We have investigated the changes of an Al plating surface, an Al / Polyaniline cell performance, and ion species in the melt with AlCl₃ concentration and with temperature. In this paper, characteristics of the melt and ion species in the melt were mainly studied as functions of AlCl₃ content and temperature.

2.Experimental

Measured AlCl₃ and BPC, which had been heated at 90°C for 24h in vacuo, were mixed, then purified by the Al wire immersion method(11). The characteristics were studied by the conductivity, viscosity, EMF, and NMR measurements. The temperature range was 30~80°C, and the AlCl₃ content range was 42.0~66.7mol%. The melts were treated under a dry N₂ atmosphere. The data at 30°C are shown unless the temperature is written.

The viscosity was determined by Vibroviscometer CJV2000 (Shisutemu Sogo Kaihatsu Co., Ltd.). The ²⁷Al and ¹HNMR spectra were measured by using JOEL FX-90Q spectrometer.

3.Results and Discussion

3.1 Characteristics of melt

Specific conductivity of the AlCl₃-BPC melt became high with temperature(Fig.1). On the other hand, in the acidic range, the conductivity became slightly low with increasing AlCl₃ content, while in the basic range, the conductivity became significantly high with AlCl₃ content.

The viscosity became low with increasing temperature and became low with increasing AlCl₃ content as shown in Fig.2. Especially, in the basic range at 30°C, the change was significant.

The potential of Al in the melts became noble with increasing temperature. In a low AlCl₃ content melts, the potential changed largely at 60°C. On the other hand, the value changed sharply at 50mol% AlCl₃ content.

3.2 Simulation for ion species in the melt

It was considered that the change of the melt characteristics are attributed to the change of ion species in the melt. Then, a simulation of the ion species(12~15) was done. Species in the melt were considered to be AlCl₄⁻, Al₂Cl₇⁻, Cl⁻, AlCl₃, Al₂Cl₆, and BP⁺. Equilibrium equations for these species are as follows.

$2AlCl_4 \rightleftharpoons Al_2Cl_7 + Cl_7$	• • •	KM
$2AICl_3 \rightleftharpoons Al_2Cl_6$	• • •	K0
$AlCl_3 + AlCl_4 \rightleftharpoons Al_2Cl_7$		K2

The electrode reaction for Al in the melt is as follows.

$$AlCl_4^{-}+3e \rightleftharpoons Al+4Cl^{-}$$

$$4Al_2Cl_7^{-}+3e \rightleftharpoons Al+7AlCl_4^{-}$$

The K₀ value was calculated by using the JANAF data(16). The K_M and K₂ values were simulated by fitting with a curve of AlCl₃ content in the melt vs. an equilibrium potential of Al in the melt(Fig.3). Here, the potentials for Al in the basic range are not sure, because BP⁺ is also reduced at these potentials. Then, the changes of the ion species in the melt with the AlCl₃ content were calculated by using these K_M, K₀, and K₂ values at various temperatures.

The typical results at 30°C are shown in Fig.4. The species are significantly changed at 50mol% AlCl₃. This fact is considered to be the cause why the conductivity and viscosity changed largely at 50mol% AlCl₃ content as mentioned above. Moreover, the numerical data are shown in Table 1 to study the change of ion species with temperature. It was considered that the conductivity increases with temperature because of increasing the mole fraction of AlCl₄⁻ ion. As the AlCl₄⁻ ion is small, it should effect mainly to the conductivity of the melt. Moreover, it was considered that viscosity

decreases with temperature because of decreasing the mole fraction of Al_2Cl_7 ion. As the Al_2Cl_7 ion is large, it should effect mainly to the viscosity. It was also known that the species contents change sharply at 50% AlCl₃ and change with temperature.

3.3 NMR measurements

The above facts were also investigated by 27 Al and 1 H NMR measurements. In the case of 27 Al NMR, one sharp peak was obtained for basic and neutral region melts and two peaks were obtained for acidic region melts except 66.7% AlCl₃ as shown in Fig.5. The former sharp peak suggests the presence of AlCl₄⁻ ion(17,18) and the latter two peaks suggest the presence of AlCl₄⁻ ions.

The ratio of AlCl₄⁻ / Al₂Cl₇⁻ was calculated from the ¹H NMR spectra by applying the method of J.S.Wilkes, et al.(10). One of ¹H NMR spectrum is shown in Fig.6. The calculated chemical shifts for H-4(proton on ring) at 30°C, 60°C, and 80°C are seen in Table 2. In the cases of 30°C and 60°C, the data from ¹H NMR spectra agreed well with the calculated values. However, at 80°C, both results disagreed. This reason is not clear now. The existence of Al₃Cl₁₀⁻ ion (13,19~22) in the melt may be considered.

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Fig.1 Effect of temperature on specific conductivity of $AlCl_3$ -BPC melts. \bigcirc :66.7mol%AlCl_3-33.3mol%BPC, \triangle :60.0mol%AlCl_3-40.0mol%BPC \bigcirc :50.0mol%AlCl_3-50.0mol%BPC, \bigcirc :46.0mol%AlCl_3-54.0mol%BPC



Fig.2 Dependence of AlCl₃ content on viscosity of AlCl₃-BPC melt at various temperatures. $\bigcirc:30^{\circ}$ C, $\triangle:60^{\circ}$ C, $\square:80^{\circ}$ C



Fig.3 Potential values for Al in AlCl₃-BPC melts at $60 \,\text{c}$.





 $-----: \operatorname{AlCl}_{4}^{-}, \qquad -----: \operatorname{Al}_{2}\operatorname{Cl}_{7}^{-}, \qquad -----: \operatorname{Cl}^{-}$ $-----: \operatorname{AlCl}_{3}, \qquad -----: \operatorname{Al}_{2}\operatorname{Cl}_{6}, \qquad ----: \operatorname{BP}^{+}$

		64m	iol%			67m	iol%	
	AICI4-	Al ₂ Cl ₇ -	BP ⁺	Al ₂ Cl ₆	AICI ₄ -	Al ₂ Cl ₇ ⁻	BP ⁺	Al ₂ Cl ₆
30°C	0.121	0.377	0.497	0.00529	0.0540	0.429	0.483	0.0343
40℃	0.125	0.372	0.496	0.00758	0.0617	0.419	0.480	0.0392
60℃	0.136	0.357	0.493	0.0133	0.0802	0.396	0.476	0.0473
70°C	0.149	0.341	0.489	0.0203	0.0981	0.374	0.472	0.0565

Table 1 Change of mole fraction for ion species with temperature







Fig.6 ¹H NMR spectrum of 66.7mol%AlCl₃-33.3mol%BPC melt at 60 c.

Me	lt (AlCl3mol%)	52.3	58.3	61.5	64.3
20.00	Observed(ppm)	8.6640	8.7096	8.7362	8.7627
30 C	Calculated(ppm)	8.6637	8.7096	8.7364	8.7625
(0)**	Observed(ppm)	8.7460	8.7845	8.8108	8.8303
000	Calculated(ppm)	8.7457	8.7846	8.8107	8.8302
0.0 %	Observed(ppm)	8.7685	8.8124	8.8539	8.8875
800	Calculated(ppm)	8.7724	8.8237	8.8503	8.8790

Table 2 Calculated and observed chemical shifts for H-4(proton at ring position)

Electrodeposition of Metals from Room-Temperature Chloroaluminate Molten Salts

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ABSTRACT

The electrodeposition of lead, silver and gold was studied in the aluminum chloride-1-methyl-3-ethylimidazolium chloride room-temperature molten salt. Evidence for the underpotential deposition of silver was found at polycrystalline gold in acidic melt. The electrodeposition of silver on tungsten and glassy carbon involves instantaneous and progressive three-dimensional nucleation, respectively, with hemispherical diffusion-controlled growth of the nuclei. The electrodeposition of lead at glassy carbon in acidic melt involves a progressive nucleation process with diffusion-controlled growth similar to that found for silver. The voltammetric reduction of gold(III) at glassy carbon in basic melt produces an intermediate gold(I) species. Although the Au(I)/Au formal potential is more positive than that of Au(III)/Au(I), this intermediate is observed because the electrodeposition of gold at glassy carbon is impeded by a large nucleation overpotential.

INTRODUCTION

Room-temperature chloroaluminate molten salts. Room-temperature chloroaluminate melts are mixtures of aluminum chloride with quaternary ammonium halide salts that possess "bulky" organic cations. There are two popular examples of this class of melts, the aluminum chloride-1-(1-butyl)pyridinium chloride (AlCl₃-BupyCl) (1) and the aluminum chloride-1-methyl-3-ethylimidazolium chloride (AlCl₃-MeEtimCl) (2) systems. The composition of these binary melts is typically described in terms of the mole fraction of aluminum chloride, X_{Al} .

These molten salts or ionic liquids have the very attractive feature of adjustable Lewis acidity. This means that the acidity can be varied by changing the molar ratio of the two components. An acidic melt ($X_{AI} > 0.5$) contains a molar excess of AlCl₃, because Al₂Cl₇⁻ ion, which is a chloride ion acceptor, is present. A basic melt ($X_{AI} < 0.5$) contains a molar excess of the organic salt and is basic because it contains chloride ion that is not covalently bound to aluminum. Those melts with X_{AI} equal to exactly 0.5 are termed neutral because only the organic cation and AlCl₄⁻ ion are present. The dissociation reaction describing the acid-base properties of room-temperature chloroaluminate melts is shown below:

$$2 \operatorname{AlCl}_{4}^{-} \rightleftharpoons \operatorname{Al}_{2}\operatorname{Cl}_{7}^{-} + \operatorname{Cl}^{-}$$
[1]

This reaction is analogous to the autosolvolysis of water:

$$2 H_2 O \rightleftharpoons H_3 O^+ + OH^-$$
 [2]

Room-temperature chloroaluminate melts are of interest for use as electrolytes for batteries and fluids for electroplating, electropolishing, and electrochemical etching. The development of these technological applications critically depends on information about the electrodissolution and electrodeposition of metals in these melts. But unfortunately, published studies of this nature are quite few (see (3) and references therein).

The AlCl₃-MeEtimCl system was chosen as the solvent for the work described herein. The reason for this is that this melt has a wider electrochemical window and a lower melting point than the AlCl₃-BupyCl system. The electrochemical window of the acidic AlCl₃-MeEtimCl melt is 2.2 V, whereas the basic melt has a window of nearly 2.4 V.

Although the electrodeposition of some metals, such as aluminum (4-8), copper (9), zinc (10), antimony (11), bismuth (12), cobalt (13), iron (14), lithium (15), and nickel (16), has been reported in <u>acidic</u> room-temperature chloroaluminate melts, only two metals, cadmium (17) and palladium (18), have been successfully deposited from <u>basic</u> melt for reasons that are not entirely clear. In order to search for other metals that can be electrodeposited from basic melt and to obtain insight into the reason that most metals can not be deposited from this melt, elements that are proximate to these two elements in the periodic chart, such as lead, silver and gold, have been studied. The electrodeposition of these metals on metallic and nonmetallic electrodes has been investigated in both acidic and basic melts. The results of these investigations indicate that both nucleation and UPD processes occur during the electrodeposition of metals.

EXPERIMENTAL

Apparatus. All experiments were carried out in a nitrogen-filled glove box system. This system as well as the method used for estimating the moisture and oxygen content of its atmosphere was described previously (3). The electrochemical instrumentation, X-Y-t recorder, electrochemical cell, furnace used to heat the cell, and electrode rotator were the same as those used before (3). The glassy carbon disk (0.196 cm²), polycrystalline gold disk (0.196 cm²), and polycrystalline platinum disk (0.196 cm²) working electrodes were purchased from Pine Instruments Co. The polycrystalline tungsten disk (0.070 cm²) working electrode is homemade, and its construction has been outlined (19). The working electrodes were polished with an aqueous slurry of 0.05 micron alumina on a Buehler Metaserv grinder-polisher, rinsed successively with distilled water, ethanol and dry acetonitrile and then dried in vacuo before use. The aluminum wire counter and reference electrodes have been described (20). Electronic resistance composition was employed during each experiment.

Chemicals. The purification of $AlCl_3$ by repeated vacuum sublimation, the synthesis and subsequent purification of MeEtimCl, and the preparation of the $AlCl_3$ -MeEtimCl molten salt have been discussed (21). Proton impurities were removed from the $AlCl_3$ -

MeEtimCl melt by evacuating the melt to $< 1 \times 10^{-3}$ torr for about 72 hours (22).

Lead(II) chloride, $PbCl_2$ (Johnson Matthey, ultrapure) and lead wire (Alfa Ventron, m2N) were used as received. Silver wire, 1.0 mm diameter, (Alfa, m3N) was lightly sanded and wiped with a tissue moistened with acetonitrile and then dried in vacuo before use. Gold(III) chloride (Johnson Matthey, Au 65%), gold(I) chloride (Pfaltz & Bauer, 99.9%), and 20 mesh gold powder (Aldrich, 99.999+ %) were used as received.

RESULTS AND DISCUSSION

Lead. The electrodeposition of lead was studied at a glassy carbon electrode in acidic melt containing various amounts of lead(II). The lead(II) was introduced either by the electrodissolution of a lead wire or by dissolving $PbCl_2$. The results were independent of the source of the lead(II). A cyclic voltammogram of lead(II) at a glassy carbon electrode is shown in Fig. 1. This voltammogram exhibits the presence of a current cross-over on the reverse scan indicating a nucleation rate controlled deposition process (23).

In order to gain greater insight into this nucleation process, potential-step experiments were conducted at a stationary glassy carbon electrode. These experiments were carried out by stepping the initial potential, E_i , from 1.80 V to a more negative value just sufficient to induce the onset of nucleation. The current-time transients resulting from one of these experiments are shown in Fig. 2, and they all exhibit the same essential characteristics: a time delay following the charging current spike, an ascending current due to the induction and subsequent growth of lead nuclei on the electrode surface, and a current maximum, i_M , whose position on the time axis, t_M , depends upon the potential applied during the step. The maxima in these transients are caused by the coalescence of the individual diffusion zones of the growing crystallites (24).

A variety of different models have been developed to explain the nucleation/growth processes that take place during the electrodeposition of metals on various substrates, and these models have been summarized (25). It has been suggested that because the charge-transfer rate of most metal deposition reactions is high and because very negative overpotentials are usually required to initiate the nucleation process the growth of the developing nuclei is likely to be a diffusion-controlled process (26). On this basis, two models were developed to describe the current growth as a function of time following the application of a potential step. These models are progressive and instantaneous three-dimensional nucleation with hemispherical diffusion-controlled growth of the nuclei, respectively. The current-time relationships for these models are given by Eqs. [3] and [4], respectively (27).

$$i(t) = [2zFAN_d \pi (2DC)^{3/2} M^{1/2} / (3\rho^{1/2})] t^{3/2}$$
[3]

$$i(t) = [zF\pi(2DC)^{3/2}M^{1/2}N/\rho^{1/2}] t^{1/2}$$
[4]

In these equations zF is the molar charge of the electrodepositing species, D is the diffusion coefficient, C is the bulk concentration, A is the steady state nucleation rate

constant per site, N_d is the number density of active sites, and M and ρ are the molecular weight and the density of the deposited material, respectively. Adherence to the first model is signaled by a linear plot of i versus $t^{3/2}$, whereas adherence to the latter is indicated when a plot of i versus $t^{1/2}$ is linear. For scaling proposes, it is more convenient to normalize each current by dividing by i_M and to then test the linearity of plots of $(i/i_M)^{2/3}$ and $(i/i_M)^2$ versus t, respectively. The rising portion of each current-time transient for lead deposition was analyzed, and the resulting plots of $(i/i_M)^2$ and $(i/i_M)^{2/3}$ versus t are shown in Figs. 3a and 3b,

The rising portion of each current-time transient for lead deposition was analyzed, and the resulting plots of $(i/i_M)^2$ and $(i/i_M)^{2/3}$ versus t are shown in Figs. 3a and 3b, respectively. Fig. 3b shows appreciable linearity during the initial current growth, but Fig. 3a does not, suggesting a progressive nucleation of lead on glassy carbon. A superior method for deciding between these models is to compare the entire current-time transients to the theoretical transients derived for both nucleation mechanisms. These theoretical transients are described by the following equations (27),

$$(i/i_M)^2 = 1.2254(t/t_M)^{-1} \{1 - \exp[-2.3367(t/t_M)^2]\}^2$$
[5]

$$(i/i_{\rm M})^2 = 1.9542(t/t_{\rm M})^{-1} \{1 - \exp[-1.2564(t/t_{\rm M})]\}^2$$
[6]

However, the data must first be corrected for the delay time, t_0 , preceding the start of the nucleation process by redefining the time axis as $t' = t - t_0$. Estimates of t_0 can be obtained from the intercepts of the linear plots of $(i/i_M)^{2/3}$ and $(i/i_M)^2$ versus t (28). It is clear from Fig. 4 that the experimental transients are in excellent agreement with the model derived for a progressive nucleation mechanism.

Silver. Cyclic voltammograms for the electrodeposition and stripping of silver at platinum, gold, tungsten, and glassy carbon working electrodes from solutions of silver(I) in acidic melt are shown in Figs. 5 and 6. The diversification of these voltammograms indicates that the silver electrodeposition process in this melt is highly dependent upon the electrode material.

The voltammograms recorded at platinum manifest a classical appearance, suggesting that the silver deposition-stripping process at this electrode is reasonably well-behaved. Cyclic voltammograms of the deposition and stripping of silver at the gold electrode are somewhat similar in appearance to those recorded at platinum except that two or more small "pre-waves" are embedded in the ascending portion of the bulk deposition wave. These reduction waves appear to have oxidation counterparts that are most apparent if the scan is reversed before the peak of the main reduction wave is traversed. They persisted despite repeated polishing of the electrode and/or prolonged immersion of the electrode in concentrated nitric acid.

In order to further probe the silver deposition-stripping process at this electrode, voltammograms were recorded at a gold RDE. These voltammograms are shown in Fig. 7. As was the case for the stationary electrode voltammogram in Fig. 5b, the silver(I) bulk reduction wave that begins at around 0.70 V in Fig. 7a is preceded by several small waves in the potential region between 0.75 and 0.70 V. Gold RDE cyclic voltammograms in which the potential was reversed before the large mass-transport-controlled wave was traversed are shown in Fig. 7b. These voltammograms reveal three peak-shaped surface

reduction waves each with an associated oxidation wave. All appear at potentials that are more positive than 0.70 V.

In order to deduce whether or not the small waves in Figs. 5b and 7 resulted from the underpotential deposition of silver, it is necessary to known the equilibrium potential, E_{eq} of the Ag(I)/Ag couple in this solution. An estimate of E_{eq} can be obtained from the zero current intercept of the reverse scan for the deposition of silver on platinum. Such a voltammogram was recorded, and it suggested that E_{eq} is about 0.70 V. On the basis of this observation, the small reduction waves in Figs. 5b and 7 must correspond to a silver underpotential deposition process. The cumulative charges corresponding to each of the surface waves in Fig. 7b are shown in Table I along with the charge needed to produce a close-packed monolayer of silver (193 μ C/cm²) on the gold electrode (29). It seems that the cumulative charges for these waves represent the deposition and subsequent stripping of more than one but less than two monolayers of silver atoms, respectively. In addition, the data in Table I suggest that not all of the UPD silver is removed from the electrode during the oxidation cycle of each voltammogram.

Many of the silver UPD characteristics found here, e.g., the deposition of more than one monolayer of silver prior to the bulk reduction process, the presence of multiple deposition and stripping waves, and the apparent retention of a small portion of the underpotential deposited silver during the stripping process, parallel those reported for the deposition of silver on gold and other noble metals in aqueous solvents (30-32). To date no universally accepted explanations appear to have been advanced for the first two characteristics. However, the latter effect may be related to alloy formation (33) where the stripping of silver atoms that have diffused into the platinum substrate occurs at a much slower rate than stripping of the adsorbed surface deposit. Although numerous papers have been published describing UPD in aqueous solutions, this phenomenon is rarely reported in molten salts. Some examples of UPD in molten salts include the deposition of silver, nickel, and other metals at platinum in molten LiCl-KCl (29, 34).

Cyclic voltammograms of silver(I) at tungsten and glassy carbon electrodes are shown in Fig. 6. These voltammograms exhibit nucleation loops similar to those seen for the deposition of lead on glassy carbon (vide supra). The nucleation/growth processes occurring at these electrodes were further studied by performing chronoamperometric experiments in quiescent solutions in which potential was stepped from 1.80 V in the case of tungsten and 1.50 V in the case of glassy carbon to potentials sufficiently negative to initiate the nucleation process. The resulting current-time transients were similar to those seen for the deposition of lead on glassy carbon.

In order to test the applicability of the models described by Eqs. [3] and [4], plots of $(i/i_M)^{2/3}$ and $(i/i_M)^2$ versus t were constructed from the rising portion of each of the current-time transients recorded at tungsten and glassy carbon electrodes. In the case of tungsten only the plot for instantaneous nucleation shows appreciable linearity during the initial stages of current growth, whereas for glassy carbon only the plot for progressive nucleation is linear. Dimensionless plots based on Eqs. [5] and [6] are shown in Fig. 8. It can be seen that the data for the deposition of silver on tungsten agree well with the model for instantaneous nucleation. On the other hand, the deposition of silver on glassy carbon clearly involves progressive nucleation.

Gold. Solutions of gold(III) were prepared by dissolving $AuCl_3$ in basic $AlCl_3$ -MeEtimCl melt. The resulting solutions were yellow-orange in color and appeared to be stable indefinitely if protected from moisture (35). Representative electronic absorption spectral data recorded in the 44.4-55.6 m/o melt and in the 49.0-51.0 m/o melt are collected in Table II along with literature data for the square-planar gold(III) chloride complex, $[AuCl_4]^-$. Although the 226.5 nm band in the spectrum of this complex can not be seen because it appears below the UV cutoff of this melt, the bands that are observed are in excellent agreement with the literature data for the $[AuCl_4]^-$ anion, indicating that gold(III) exits as this complex in basic melt.

Cyclic voltammograms involving the electrodeposition of gold at glassy carbon from a solution of [AuCl₄]⁻ in basic melt are shown in Fig. 9. These voltammograms exhibit two reduction waves with peak potentials of ca. 0.10 and -0.70 V and a single oxidation wave near 0.36 V. The latter wave possesses characteristics suggestive of the anodic dissolution of an electrode surface deposit. If the scan was reversed after the first reduction wave was traversed (Fig. 9a), then the large oxidation wave was not observed. The current for the first reduction wave was twice that for the second wave in protonfree melt. In order to produce a significant quantity of the electrode surface deposit, the glassy carbon working electrode was scanned to -1.00 V and was held at that potential for several minutes. The cell was disconnected from the potentiostat, and the working electrode was withdrawn from the solution. Visual inspection of the electrode surface revealed that it was covered with a poorly adherent, dull brown deposit of gold metal. No gold deposit was obtained if the glassy carbon electrode was held at 0 V for several minutes. Cyclic voltammograms of a solution of [AuCl₄]⁻ before and after the addition of AuCl are shown in Fig. 9b. From this figure, it is obvious that the reduction wave at -0.70 V arises from the reduction of gold(I).

A cyclic voltammogram of a basic melt solution containing only gold(I) (Fig. 10) shows the gold(I) reduction wave more clearly. Thus, it seems that the first reduction wave in Fig. 9 arises from the conversion of $[AuCl_4]^-$ to a gold(I) species, the second reduction wave is due to the reduction of this species to gold metal, and the oxidation wave corresponds to the dissolution of the gold metal deposit. It is obvious from the voltammogram for the reduction of gold(I) (Fig. 10) that the deposition of gold on glassy carbon requires a substantial nucleation overpotential.

In view of the apparent high stability of both gold(I) and gold(III) in basic melt, we attempted to estimate the formal potentials of the Au(I)/Au and Au(III)/Au(I) couples, $E^{0'}_{Au(I)/Au}$ and $E^{0'}_{Au(II)/Au(I)}$, respectively, by measuring E_{eq} for each couple in solutions containing different amounts of gold(I) or different ratios of gold(I) to gold(III). When combined with the Nernst equation, the experimental E_{eq} values and solution concentrations yielded $E^{0'}_{Au(I)/Au} = 0.374 \pm 0.002$ and $E^{0'}_{Au(III)/Au(I)} = 0.310 \pm 0.002$ V. Thus, it is clear that the formal potential of the Au(I)/Au couple is actually more positive than that of the Au(III)/Au(I) couple in basic melt as it is in molecular solvents.

Taken together, the foregoing results lead to the conclusion that the gold(I) species observed as an intermediate during the voltammetric reduction of $[AuCl_4]^-$ (Fig. 9) is actually a "kinetic artifact", i.e., gold(I) is only observed in this melt as an intermediate because a substantial nucleation overpotential is required to initiate the reduction of this

species to the metal at glassy carbon.

The E^{0} values for the Au(III)/Au(I) and Au(I)/Au couples suggest that gold(I) has a finite tendency toward disproportionation. Therefore, several attempts were made to directly measure the equilibrium constant for the disproportionation of gold(I) as described by Eq. [7]

$$3[\operatorname{AuCl}_2]^{-} \rightleftharpoons [\operatorname{AuCl}_4]^{-} + 2\operatorname{Au} + 2\operatorname{Cl}^{-}$$
 [7]

In these experiments, gold powder was added to stirred solutions of $[AuCl_4]^{-1}$ in melts that were incubated at 40.0 °C, and the concentration of $[AuCl_4]^{-1}$ was followed spectrophotometrically. Although the concentration of this gold(III) complex decreased during these experiments in accord with the reverse of Eq. [7], it failed to reach a constant value after many weeks had elapsed, indicating that the reaction between $[AuCl_4]^{-1}$ and gold metal is an extremely slow process in these melts. Hence, it was necessary to estimate the equilibrium constant, K, for the disproportionation of gold(I) from the experimental values of $E^{0}_{Au(I)/Au}$ and $E^{0}_{Au(III)/Au(I)}$; a value of $K = 1.3 \times 10^2$ resulted from these calculations. This equilibrium constant is approximately five orders of magnitude smaller than that found in aqueous solutions (36).

The voltammogram for gold deposition at glassy carbon (Fig. 10) also displays characteristics suggestive of a nucleation process. In order to further study this nucleation/growth process, potential-step experiments were performed in quiescent solutions of gold(I) prepared by electrolytic oxidation of a gold wire. Chronoamperometric experiments similar to those conducted for lead and silver were carried out by stepping the potential of the working electrode from 0.50 V, where the deposition of gold can not take place, to potentials just sufficient to start the nucleation/growth process. Current-time transients that resulted from these experiments were similar in shape to that recorded for lead. Plots of $(i_{\rm IM})^{2/3}$ and $(i_{\rm IM})^2$ versus t that resulted from the ascending portions of these transients were carried and it was found that only the former plot contains a linear component. The entire dimensionless current-time transients resulting from these experiments described by Eqs. [5] and [6], and the results are shown in Fig. 11. It is obvious that the model representing progressive nucleation best agrees with the data.

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E _s ^a	10 ⁵ ΣQ _d ^b	10 ⁵ ΣQ _s	
(V)	(C)	(C)	
0.736	1.6	1.1	
0.728	2.3	2.0	
0.710	6.0 ^c	4.8 ^c	

Table I. Cumulative charges for the underpotential deposition of silver on gold.

 ${}^{a}E_{eq} \sim 0.70 \text{ V}$ ${}^{b}Q_{monolayer} = 3.8 \times 10^{-5} \text{ C} \text{ (close-packed monolayer)}$ Contal charges corresponding to the three deposition waves and associated stripping waves shown in Fig. 7b.

Table II. Absorption spectroscopic data for gold (III).

Solute	Solvent	λ , nm(ϵ , L mol ⁻¹ cm ⁻¹)	Ref.
[AuCl ₄] ⁻	a	226.5 (3.4 x 10 ⁴),	c
		315 (5.1 x 10 ³), 385 ^b	
AuCl ₃	49.0-51.0 m/o	323 (4.6 x 10 ³), ~383 ^b	This work
	AlCl ₃ -MeEtimCl		
AuCl ₃	44.4-55.6 m/o	323 (4.7 x 10 ³), ~382 ^b	This work
	AlCl ₃ -MeEtimCl		

^aNot given.

^bShoulder.

^c C. K. Jørgensen, in "Advances in Chemical Physics," Vol. 5, I. Prigogine, Editor, P. 120, Wiley, New York (1963).



Fig. 1. Cyclic voltammogram of PbCl₂ at a glassy carbon electrode in 66.7-33.3 m/o AlCl₃-MeEtimCl melt at 40 ⁰C. The PbCl₂ concentration was 39.4 mM, the sweep rate was 50 mV s⁻¹, and the initial potential was 1.50 V.

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Fig. 2. Current-time transients for the deposition of lead on a glassy carbon electrode from a 21.5 mM solution of $PbCl_2$ in 66.7-33.3 m/o $AlCl_3$ -MeEtimCl melt at 40⁰C recorded at these potentials: (a) 0.280, (b) 0.270, (c) 0.260, (d) 0.250, and (e) 0.240 V.


Fig. 3. Plots of $(i/i_M)^2$ and $(i/i_M)^{2/3}$ versus t constructed from the current-time transients shown in Fig. 2: (a) (>) 0.240, (+) 0.260, and (\blacksquare) 0.280 V; (b) (>) 0.240, (>) 0.260, and (\blacksquare) 0.280 V.



Fig. 4. Comparison of the dimensionless experimental data derived from the current-time transients shown in Fig. 2 with the theoretical models for instantaneous and progressive nucleation (solid lines): ([]) 0.280, (+) 0.260, and (()) 0.240 V.



Fig. 5. Cyclic voltammograms of a 10.9 mM solution of silver(I) in the 66.7-33.3 m/o melt at different switching potentials: (a) platinum electrode; (b) gold electrode. The sweep rates were 0.050 V s^{-1} , and the temperatures were 40 $^{\text{0}}$ C.



Fig. 6. Cyclic voltammograms of a 10.9 mM solution of silver(I) in the 66.7-33.3 m/o melt at different switching potentials: (a) tungsten electrode; (b) glassy carbon electrode. The sweep rates were 0.050 V s⁻¹, and the temperatures were 40 $^{\circ}$ C.



Fig. 7. Voltammograms of a 10.9 mM solution of silver(I) in the 66.7-33.3 m/o melt at a gold rotating disk electrode: (a) potential sweep initiated at 1.20 V and terminated at 0.20 V; (b) scan initiated at 1.00 V and reversed at ca. 0.71 V. The electrode rotation rate was 78.5 rad s⁻¹, the sweep rates were 5 mV s⁻¹, and the temperature was 40 $^{\circ}$ C.



Fig. 8. Comparison of the dimensionless experimental data derived from the currenttime transients with the theoretical models for instantaneous and progressive nucleation (solid lines): (a) tungsten (\diamond) 0.590, (\times) 0.585, and (\blacksquare) 0.580 V; (b) glassy carbon (\diamond) 0.330, (\times) 0.320, and (\blacksquare) 0.310 V.



Fig. 9. Cyclic voltammograms of AuCl₃ and mixtures of AuCl₃ and AuCl at a glassy carbon electrode in the 44.4-55.6 m/o AlCl₃-MeEtimCl melt: (a) 34.7 mM Au(III) and (b) (--) 23.7 mM Au(III) and (--) 23.7 mM Au(III) + 15.6 mM Au(I). The scan rates were 50 mV s⁻¹, and the temperatures were 40.0 ⁰C.



Fig. 10. Cyclic voltammogram of a 30.74 mM solution of Au(I) at a glassy carbon electrode in the 44.4-55.6 m/o AlCl₃-MeEtimCl melt at 40.0 0 C. The Au(I) was produced by the electrolytic oxidation of a gold wire at 0.45 V.



Fig. 11. Comparison of the dimensionless experimental current-time data with the theoretical models for progressive and instantaneous nucleation (Eqs. [5] and [6]) (solid lines): (X) -0.710, (Q) -0.700, and (D) -0.680 V.

Electrodeposition of Palladium on Electrode Surfaces from Acidic, Neutral, Neutral-Buffered, and Basic AlCl₃-MEIC Molten Salts

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Abstract

The electrodeposition of palladium onto various electrode surfaces was examined in AlCl₃-MEIC molten salts at room temperature. The behavior of palladium electrodeposition was markedly dependent on the mole fraction of AlCl₃ in the molten salts. Shifting from basic to acidic melts, results in a 2.0 volt shift in the potential of palladium. Mole fractions from N=0.33 to N=0.67 AlCl₃ were examined. Nucleation overpotentials were evident in basic melts, and to a lesser extent in acidic and neutral melts.

Introduction

Room temperature molten salts are of interest due to their wide liquidus range and high conductivity. Of particular interest is aluminum chloride 1-methyl-3-ethylimidazolium chloride (AlCl₃-MEIC). Its wide liquidus range and its adjustable Lewis acidity make it a unique nonaqueous solvent. Variation of the Lewis acidity is accomplished by changing the mole ratio of AlCl₃ to MEIC. Therefore, basic melts contain excess Cl⁻ and acidic melts contain the Lewis acid Al₂Cl₇⁻ as the following equilibrium equation indicates.

$$2\text{AlCl}_4^- = \text{Al}_2\text{Cl}_7^- + \text{Cl}^-$$

This equation is similar to water, where, like the hydronium ion, Al_2Cl_7 is the acidic species and, like the hydroxide ion, Cl is the basic species.

Characterization of metals in this molten salt are important for its consideration as a possible battery electrolyte. Several different metals have already been examined (see reference 1 for list). The idea is to take advantage of the molten salt's wide electrochemical window. Various active metals have been studied as possible anodes with redox potentials close to the negative limit.²⁻³. This report is concerned with the study of metals useful at the positive melt limit. They must have a high theoretical energy density in relation to one of the active metals such as sodium. Several electrode combinations were looked at, but palladium coupled with sodium, which has a high energy density (>900 Watt-hours/Kg), looked the most promising.

The electrodeposition of palladium was originally examined in basic

 $AlCl_3-MEIC$ molten salts at 40°c by Hussey et al.⁴ In this study, an attempt was made to examine the deposition-stripping process of palladium throughout the entire room temperature composition range, N=0.33 to N=0.67 AlCl_3-MEIC.

Experimental

Synthesis and purification of melt components has been previously described⁵. $PdCl_2$ (Aldrich, 99.999%) and NaCl (Aldrich, 99.999%) were used without further purification. Polycrystalline palladium, platinum and tungsten metal electrodes were made by sealing the wire in glass tubes. The palladium and platinum electrodes are 1mm diameter disks. The tungsten electrode is a 0.5mm diameter disk. The glassy carbon (3mm diameter) and gold (1.65mm diameter) electrodes were purchased from BAS and Sargent Welch. Polishing was accomplished using a Struers DAP-V grinder-polisher producing a highly polished disk electrode. The rotating disk glassy carbon, palladium, and platinum electrodes were reported by the manufacturer to have a geometric surface area of 0.1964cm². The geometric areas of the rotating disk tungsten electrodes were 0.2815cm² and 0.2822cm². All rotating disk electrodes were purchased from Pine Instrument Co.

All experiments were performed in a UHP helium atmosphere using a Vacuum Atmosphere drybox at room temperature. The counter electrode was a platinum foil or tungsten wire and the reference electrode consisted of Al wire immersed in either a N=0.67 or N=0.60 AlCl₃-MEIC melt contained in separate fiber compartment. Cyclic voltammetry glass fritted or asbestos and EG&G were performed an PAR model 273chronocoulometry on potentiostat/galvanostat using the M270 Version 3 software environment with a Zenith 248 computer.

All melts were prepared by adding known amounts of AlCl₃ to weighed MEIC to achieve the desired mole fraction. All melts received approx. 70mg PdCl₂/30g AlCl₃-MEIC. Protonic impurities were removed by addition of EtAlCl₂. Care was taken to not use too much or the PdCl₂ would be reduced by the excess EtAlCl₂ to palladium metal. The melt compositions examined were N=0.33, N=0.444, N=0.49, N=0.50, N=0.55, N=0.67, and the neutral buffered melt of AlCl₃-MEIC-NaCl (1:0.78:0.22).

Results and Discussion

Addition of PdCl₂ (brick red) to a basic AlCl₃-MEIC melt results in an yellow-orange solution. Addition of PdCl₂ to an acidic melt results in a red solution. The basic melts have PdCl₂ at a concentration of 1.7×10^{-2} molar. PdCl₂ is not very soluble in acidic melts at room temperature, so the concentrations were at saturation. Heating the melts at 95 °C for one week helps dissolve more PdCl₂. The order of solubility is: all basic melts >> N=0.67 > N=0.55 > N=0.50.

Palladium deposition-stripping was unaffected by whether the electrode was platinum, tungsten, palladium, glassy carbon, or gold. The only exception is palladium in basic melts (see figure 1). The peaks are broader and the oxidation of chloride at the positive limit is shifted negative by 600mV. This gives some

indication of palladium's increased reactivity towards chloride. Figure 2 is an example of the palladium deposition-stripping in basic melts on a glassy carbon electrode. An obvious feature is the nucleation effect present, causing the negative overpotential in the reduction wave. The crossover in potential is from the overpotential of palladium reduction on a non-palladium surface. This is followed by a potential shift in the positive direction, since the electrode is now palladium coated, hence the crossover. Also present are the two oxidation waves instead of the expected one. Hussey et al⁴ calculated a Nernst plot of the reduction peak and found that the charge is representative of a two electron process. A plot of the peak current versus the scan rate indicates a diffusion dependence from the reduction wave and the more positive oxidation wave. The more negative oxidation wave does not fit for adsorption nor diffusion phenomena taking place, which may indicate some combination of the two. This phenomena of two oxidation peaks for a metal has been seen before (see reference 6 for Zn and reference 7 for Fe). There are a number of scenarios which may explain the two oxidation waves. 1) One may be bulk oxidation followed by a more strongly adsorbed underlayer. 2) The more positive oxidation peak may be the palladium complex and the more negative may be some protonic impurity. 3) Both peaks may be two complexes of palladium, and 4) Each may be one electron steps to complete oxidation.

In examining the above possibilities individually one may be able to, if not solve the problem, at least narrow the field. The first possibility should be eliminated, because the charge difference between the peaks is all wrong. The underlayer should be the smallest peak, since it represents a smaller charge than the initial bulk. Instead, the most positive peak is generally the largest of the two. The second possibility is negated in two ways. First, if the protonic impurity is present in the melt prior to PdCl₂ addition, it would show up in the blank melt. It doesn't. Secondly, addition of MEIC-HCl (shown in figure 3) is made to a N=0.444 melt using platinum as a working electrode. Platinum is used because of its sensitivity to hydrogen. As the figure indicates, addition of protons causes new peaks to form, but doesn't effect the original peaks

The third scenario Hussey et al⁴ tried to eliminate by doing a Nernst plot of different concentrations PdCl₂. The formal potentials from the intercepts shifted 124mV/pCl unit. This is what is expected for four chlorides present per palladium. UV-VIS spectroscopy (see table I) seems to indicate that in the basic melt PdCl₄⁻² is the only compound, which seems to contradict this scenario. If the fourth possibility was correct, I would have expected both oxidation peaks to be of equal charge, but the second or most positive peak is the largest.

This would seem to indicate that none of the possibilities presented are acceptable. Let's examine the neutral and acidic melt data. Figure 4 is of palladium deposition-stripping on a palladium electrode in neutral melt. Notice that there is only one oxidation peak instead of two. Also, the redox couple has shifted from -0.5 volts in basic melt to +1.5 volts in neutral melt. This is a tremendous shift in potential, which could be caused by a change in ligand on the palladium metal or due to a change in the chloride concentration of the melt. This shift in the redox potential of palladium is what makes it desirable as a cathode in the molten salt electrolyte.

Sometimes a second oxidative peak shows up as in the neutral buffered melt,

figure 5. The reason for it is explained below. Figure 6 shows the palladium redox in N=0.55 melt. Here is seen only one oxidation wave although two have been seen here as well. The oxidation is not as sharp as in the basic melt, because $PdCl_2$ is much more soluble in basic melt than any other. This means that when the palladium is reoxidized, it is forming a compound which is not very soluble and it shows a precipitation effect on the shape of the oxidation peak. The reduction peak is much sharper at the base than in the basic melt.

The final melt examined is the N=0.67 melt (see figure 7). It has only one oxidation peak and it has never shown two. The oxidation peak is broad as seen in other acidic melts for the same reason as before. Since this melt has shown only one oxidation peak, UV-VIS spectroscopy was done on it (see table I). The two dominate peaks and one shoulder are $\simeq 34$ nm further apart than the spectra in the basic melt. A spectra of PdAl₂Cl₈ has a longer wavelength d-d transition similiar to the acidic melt, but it does not have present the 350nm shoulder, which exists in all of this reports data. It is unclear whether this is indicative of a different compound, since other data presented earlier seems to indicate that the basic and acidic compounds are similar. The Bronsted acid source MEIC-HCl was added to this melt too. The protonic compound shows up right where the less positive oxidation peak in figure 5 shows it to be. This may indicate that, at least for acidic melts, the least positive oxidation peak is some protonic compound.

Let us go back to the previously defined scenarios. With the addition of the acidic melt data it would seem that the third possibility needs to be reexamined. If there is only one compound in acidic melt and its spectra is similar to $PdCl_4^{-2}$ not $PdAl_2Cl_8$, then the shift in potential must be due to the change in the activity of chloride in the different melts. This would also explain the precipitation effect experienced in the acidic melts on the oxidation peaks. $PdCl_4^{-2}$ is much less soluble than $PdAl_2Cl_8$. This still leaves the two peaks in basic melt. Neither should be a complex of $AlCl_4^{-}$ or it would form in acidic melt as well. The other oxidation peak could be some other chloro complex of palladium which is in equilibrium with the $PdCl_{4^{-2}}$ in solution. This would explain the reason the Nernst plot derived formal potential shifts an amount equating to 4 Cl⁻³ s per palladium. The other compound could have been consumed in the resulting change in equilibrium.

Conclusions

In summary, palladium deposition-stripping is possible in all examined mole fractions of MEIC-AlCl₃. There is a 2 volt shift in the couple when going from a free chloride source mole fraction (basic melt) to a chloride complexed mole fraction (all others). The Pd^{+2}/Pd^{0} couple is present near the positive limit of the melt, which is most desirable for use in a battery. Two oxidation peaks are present in basic melt, but only one is present in a neutral or acidic melt. This is, again, beneficial for the use of neutral melts as a battery electrolyte. Three dimensional nucleation is occurring in the reduction of palladium. Further nucleation studies are continuing to determine if progressive of instantaneous. Spectroelectrochemistry will be ongoing.

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Table I	Absorption	spectral	data	of	PdCI	-2

aq soln HCI⁰	Basic Melt⁵	Acidic Melt
223	°	^c
280	291	278
336 ^{sh}	345-	350-
	347 ^{⁵ʰ}	355 ^{sh}
474	480-	500-
	483	504
619"	620*	

a) see ref 8, b) both n=0.33 and ref 4 data, c) MEIC absorbance interference sh=shoulder, w=weak



Figure 1 Cyclic voltammogram of plating and stripping of palladium on palladium in basic melt with a scan rate of 1mV/sec. The reference electrode is an aluminum wire in 0.67 mole% AlCl₃ 0.33mole% MEIC.



Figure 2 Cyclic voltammogram of plating and stripping of palladium on glassy carbon in basic melt with a scan rate of 1mV/sec. The reference electrode is an aluminum wire in 0.67 mole% AlCl₃ 0.33mole% MEIC.



Figure 3 Cyclic voltammogram of plating and stripping of palladium on platinum in basic melt with a scan rate of 1 mV/sec. The reference electrode is an aluminum wire in 0.67 mole% AlCl₃ 0.33mole% MEIC. MEIC-HCL added, resulting in new peaks forming.



Figure 4 Cyclic voltammogram of plating and stripping of palladium on palladium in neutral melt (N=0.50) with a scan rate of 100mV/sec. the reference electrode is an aluminum wire in 0.60 mole% AlCl₃ 0.40 mole% MEIC.



Figure 5 Cyclic voltammogram of plating and stripping of palladium on palladium in neutral buffered melt with a scan rate of 100 mV/sec. the reference electrode is an aluminum wire in 0.60 mole% AlCl₃ 0.40 mole% MEIC.



Figure 6 Cyclic voltammogram of plating and stripping of palladium on palladium in N=0.55 acidic melt with a scan rate of 100mV/sec. The reference electrode is an aluminum wire in 0.60 mole% AlCl₃ 0.40 mole% MEIC



Figure 7 Cyclic voltammogram of plating and stripping of palladium on palladium in N=0.67 acidic melt with a scan rate of 100mV/sec. The reference electrode is an aluminum wire in 0.60 mole% AlCl₃ 0.40 mole% MEIC

NUCLEATION AND MORPHOLOGY STUDIES OF ALUMINUM DEPOSITED FROM AN AMBIENT-TEMPERATURE CHLOROALUMINATE MOLTEN SALT

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ABSTRACT

Thin, continuous aluminum coatings can be electrodeposited onto a tungsten substrate from a 1.1:1.0 AlCl₃:MEIC (1-methyl-3-ethylimidazolium chloride) ambient-temperature molten salt using controlled potential deposition. At deposition potentials negative of -0.2 V versus an Al(III)/Al reference electrode, the resulting coating consists of nuclei (or cluster) sizes below optical microscopic resolution (< 0.5 μ m). At less negative potentials, the microscopic structure consists of larger (> 0.5 μ m), optically observable nuclei. Chronoamperometric analyses performed at 250- μ m tungsten electrodes indicate that the deposition process involves progressive nucleation with diffusion-controlled growth of the three-dimensional nuclei. Calculated nuclear site densities and average nuclei sizes are in agreement with images obtained with optical microscopy (SEM), and scanning tunneling microscopy (STM).

INTRODUCTION

The ambient-temperature chloroaluminate molten salts derived from the combination of AlCl₃ with the organic salts N-butylpyridinium chloride (BuPyCl) or 1-methyl-3-ethylimidazolium chloride (MEIC) are promising electrolyte baths for industrial aluminum electroplating (1,2), and in fact, a continuous plating process has been recently reported (3,4). Aluminum deposition proceeds by reduction of the Al₂Cl₇⁻ ion which is present at high concentrations in melts with AlCl₃:MCl (MCl = organic chloride) molar ratios greater than one, termed acidic melts.

$$3e^{-} + 4 Al_2Cl_7^{-} <==> Al + 7 AlCl_4^{-}$$
 [1]

In melts with $AlCl_3$:MCl molar ratios less than one, termed basic melts, the $Al_2Cl_7^-$ concentration is extremely small, and the dominant chloroaluminate anion, $AlCl_4^-$, is not reducible within the electrochemical window of the melt (5).

The salient feature of the aluminum deposition process is a nucleation phenomenon with diffusion-controlled growth of the three-dimensional centers (6-9). At tungsten and platinum electrodes an underpotential deposition (UPD) of aluminum is also observed (6,7). The deposition/stripping efficiencies approach 100% indicating the production of stable, adherent aluminum deposits (6,10); however, in AlCl₃:BuPyCl melts, the N-butylpyridinium cation slowly reacts with the freshly deposited aluminum metal (6,7). The morphology of aluminum deposits produced using a 2:1 AlCl₃:MEIC molten salt is reported to be dense, smooth, and corrosion resistant (3,4). From published SEM images, the aluminum deposits appear to consist of crystallites or platelets ranging in size from 1 to 10 μ m (4,10).

To better understand the parameters influencing the aluminum deposition process, we have undertaken studies employing an inverted optical microscope to perform *in situ* observations of the coating morphology. A small (250- μ m diameter) tungsten disk electrode was chosen as the working electrode because tungsten is an excellent substrate for aluminum deposition (6-9). Also, the small size of the electrode has several benefits including 1) minimal errors resulting from IR-drop, 2) a uniform potential distribution over the electrode surface due to the negligible IR-drop, 3) reproducible current density distributions with somewhat higher current densities being observed at the electrode edge, and 4) easy observation of the entire electrode area at high magnification during the deposition process.

EXPERIMENTAL

The preparation of MEIC was performed as previously described (11). Melts were prepared by the addition of sublimed AlCl₃ to MEIC with stirring. All melt preparations and manipulations were performed under a purified N₂ atmosphere in a Vacuum Atmosphere glove box. All experiments were performed at ambient temperature, ca. 25 C.

Electrochemical experiments not requiring *in situ* optical observations were performed in the glove box using an electrochemical cell consisting of a glass vessel fitted with a Teflon cap in which holes were drilled for the electrodes. For the *in situ* optical observation of the deposition process, a sealed cell with an optically transparent bottom was employed. This cell was assembled in the glove box and transferred to the optical microscope stage where it was supported by a small Flexframe assembly. For all electrochemical experiments, the tungsten working electrodes were constructed by first sealing a length of 250- μ m diameter W wire (Alfa) in Pyrex capillary glass (25 mm O.D., 1 mm I.D.) under vacuum. The glass was cut at the seal to expose a circular W disk which was then polished consecutively with 1, 0.3, and 0.05 μ m alumina polishing compounds (Buehler). The reference and counter electrodes consisted of aluminum wires dipped directly into the analyte melt; therefore, measured potentials are true overpotentials. A Nikon Epiphot metallurgical inverted microscope equipped with brightfield/darkfield optics and with a 35mm Nikon N6006 camera was used for optical observations and photographs. Extra-long-working-distance objectives provided magnifications up to 400x. Using darkfield illumination, we estimate that this optical system allows us to discern structural features down to approximately 0.5 μ m in size, although resolution at these dimensions is poor. All electrochemical experiments were performed using an EG&G PARC Model 273 Potentiostat/Galvanostat controlled with a Dell System 310 computer using the EG&G PARC Model 270 software package.

The scanning tunneling microscopy was a Digital Instruments Nanoscope II STM fitted with the electrochemical option and so is termed an electrochemical scanning tunneling microscope (ECSTM). The electrochemical cell used in this investigation was supplied by Digital Instruments. The tungsten substrate was a tungsten foil (0.127 mm thick, Aldrich) which constituted the bottom of the electrochemical cell. The reference and counter electrodes were aluminum wire (0.25 mm diameter, Aldrich). The counter electrode was bent into a loop to provide more uniform current densities, while the reference electrode was a short length of wire. The imaging tip was 0.010" tungsten wire coated with glass to minimize background faradaic currents and was purchased from FHC, Brunswick, ME. An Eppendorf pipette was employed to introduce approximately 50 µl of the melt into the ECSTM electrochemical cell. Because the chloroaluminate molten salts are moisture sensitive, it was necessary to place the entire ECSTM microscope inside a glove bag filled with nitrogen. The glove bag provided only a marginally moisture-free environment, so some reaction with moisture was observed at the surface of the melt. Because relatively large imaging scans (not atomic level) were collected, it was not necessary to take extreme measures for vibration isolation; instead, the microscope assemble was positioned on a ca. 1' x 1' concrete slab placed in the glove bag which was in turn situated on a standard lab bench.

RESULTS AND DISCUSSION

Voltammetric studies and optical observations.

Staircase cyclic voltammetric studies indicated an overpotential for aluminum deposition which was dependent upon the electrochemical treatment of the tungsten electrode. By scanning to +3.0 V, the AlCl₄⁻ ion is oxidized to elemental chlorine, and an electrochemical cleaning occurs which lowers the overpotential for aluminum reduction. Therefore, prior to all chronopotentiometry and chronamperometry experiments, the tungsten electrochemical cleaning to voltammograms were obtained (see Figure 1). The electrochemical cleaning process also clearly revealed the Al underpotential deposition (UPD) at +0.22 V reported by other workers (see Figure 2). Integration of the current under the UPD wave gave a quantity of charge passed corresponding to 84% of a complete monolayer - higher than the values of 1/3 and 1/2 reported previously on tungsten (6,7).

Using the 1.1:1.0 AlCl₃:MEIC melt, efforts to produce smooth, continuous aluminum coatings using chronopotentiometry were unsuccessful as judged by *in situ*

optical observations. The deposits were not dendritic, but they consisted of nuclei with dimensions > 1 μ m. Application of an initial pulse to -1.0 V to initiate the nucleation process prior to constant current deposition failed to improve the morphology of the Al deposits. During all chronopotentiometric experiments, the deposition potential remained below -0.1 V. The non-dendritic, larger-nuclei (> 1 μ m) morphology is in agreement with previous studies (3,4,10).

Chronoamperometry and *in situ* optical observations were then employed to study the deposition of Al from 1.1:1.0 AlCl₃:MEIC. Under potentiostatic conditions, the resulting coatings consisted of smaller nuclei than seen for coatings obtained under galvanostatic conditions. Therefore, the potential of deposition is a critical parameter for determining the final coating morphology. At a deposition potential of -0.1 V, the coatings had optically resolved nuclei (> 0.5 μ m), while at potentials \leq -0.2 V, the nuclei could not be discerned when the electrode was viewed through the bottom of the electrochemical cell.

To view the deposits with improved resolution, the electrodes were plated with aluminum at a constant potential in the glove box, removed, and immediately washed with methanol. The chronoamperograms were recorded to permit determination of the thickness of the resulting aluminum coating. Deposition times were chosen so that a coating of ca. 0.1 μ m was achieved at all potentials; longer deposition times were required for lower overpotentials. Electrodes prepared in this manner were then examined on the inverted microscope employing darkfield illumination. As in the *in situ* studies, deposits made at - 0.1 V exhibited optically resolved nuclei; however, with the higher resolution, nuclei were seen for the -0.2 V deposits as well, albeit the nuclei were smaller than for -0.1 V deposits. A deposition potential of -0.3 V was required to produce an aluminum coating for which no nuclei could be discerned at a magnification of 400x.

Figures 3 and 4 show photographs (darkfield illumination, 400x) of 250- μ m tungsten disks having calculated aluminum coating thicknesses of 0.093 and 0.094 μ m produced at overpotentials of -0.1 and -0.4 V, respectively. It should be noted that darkfield photographs of an uncoated tungsten electrodes are almost completely black with only scratches in the tungsten surface showing as bright lines. The presence of discernable nuclei are indicated by the bright features seen in Figure 3 while few such features are observed in Figure 4. Therefore, based on our microscope resolution, the nuclei sizes for the -0.4 V coating are estimated to be < 0.5 μ m, while they are > 0.5 μ m for the -0.1 V coating. It is noteworthy that the scratches in the tungsten substrate are still visible in Figure 4 indicating that these coatings are able to conform to small structures on the substrate surface. The scratches are obscured by the coating in Figure 3.

To examine in more detail the electrocrystallization process, chronoamperograms were collected over a range of overpotentials, and the curves were analyzed following the method of Scharifker and Hills (12). In this analysis, the nucleation process may be instantaneous or progressive while the growth of the individual nuclei is limited by diffusion of the electroactive species to the growing nuclei. The diffusion layer profile at each nucleus is initially hemispherical; however, after sufficient time, the individual diffusion zones overlap forming a diffusion layer characteristic of semi-infinite linear diffusion.

In the method of Scharifker and Hills, an initial analysis of the chronoamperograms can be performed by plotting log(i) vs. log(t) for the rising portion of the curves; the slope of this log-log plot will be 1/2 for instantaneous nucleation and 3/2 for progressive nucleation (12). A more stringent analysis of the nucleation process is obtained by comparing the chronoamperometric curves to the theoretical curves for instantaneous, Eq. [2], and progressive, Eq. [3], nucleation processes

$$(i/i_m)^2 = 1.9542(t/t_m)^{-1} \{1 - \exp[-1.2564(t/t_m)]\}^2$$
 [2]

$$(i/i_m)^2 = 1.2254(t/t_m)^{-1} \{1 - \exp[-2.3367(t/t_m)^2]\}^2$$
 [3]

where i_m and t_m are the current density and time, respectively, at the peak in the chronoamperograms (12). The comparison of experimental curves to theoretical curves is done by plotting $(i/i_m)^2$ versus t/t_m , the dimensionless current and time parameters.

Chronoamperometric data collected for deposition potentials from -0.075 to -0.20 V are shown in Figure 5, and the comparisons of the -0.075 and -0.175 V experimental curves to theoretical curves are shown in Figure 6. Plots of log(i) vs. log(t) have slopes ranging from 1.5 to 2.0 reflecting a progressive nucleation process. Confirmation of this progressive nucleation process is provided by the similarity of the experimental curves to the theoretical progressive nucleation curve in Figure 6.

After determining that the nucleation process is progressive, Eq. [4] and [5] are employed to calculate the product AN_{∞} where A is the steady state nucleation rate constant

per site, N_{∞} is the number density of active sites on the electrode, and M and ρ are the atomic weight and density of aluminum (12).

$$i_m = 0.4615 n FD^{3/4} C(kAN_{\infty})$$
 [4]

$$k = 4/3(8\pi CM/\rho)^{1/2}$$
 [5]

Finally, the saturation number density sites, N_s (i.e., the nuclear site densities observed at long time) is calculated with Eq. [6]. The important parameters are summarized in Table I.

$$N_s = (AN_{\infty}/2kD)^{1/2}$$
 [6]

From the analysis of the nucleation process, some predictions can be made regarding the final morphology of the aluminum coating. If the completed coating is assumed to result from the eventual overlap of individual nucleation sites, then the average nucleus size will be inversely proportional to the number of nucleation sites. Also, for hemispherical growth, the individual nuclei of the completed surface can be approximated as have a two-dimensional circular geometry on the electrode surface with a radius given by Eq. [7].

$$r = (1/\pi N_s)^{1/2}$$
[7]

The average nucleus radius will decrease with increasing overpotential because the higher overpotential increases the number of nucleation sites per unit area. As seen in Table I, the calculated radius varies from 0.2 to 2.0 μ m for the deposition potentials studied. These calculated radii are consistent with the optical observations discussed above. At deposition overpotentials negative of -0.2 V, no nuclei were observed implying the average nucleus size is < 0.5 μ m, while in Table I, the radius is calculated to be < 0.5 μ m for depositions performed negative of -0.150 V. Clearly, this method of calculating the average nucleus size is only an approximation; however, it provides a qualitative picture of how the nucleation process can influence the morphology of the final deposit.

The density of bright features in Figure 3 were measured by projecting a slide of the figure onto a white screen and counting the number of features in a given area of the projected image; a value of 50×10^6 features cm⁻² was obtained. These bright features should represent the presence of individual nuclei in the coating and can be be taken as representative of the number of individual nucleation sites produced at -0.1 V. Therefore, this number corresponds to the nuclear site density and is close to the theoretical values of 18.4 x 10^6 sites cm⁻² and 42.1 x 10^6 sites cm⁻² predicted from the chronoamperograms obtained at overpotentials of -0.1 V and -0.125 V, respectively.

Electrochemical scanning tunneling microscope investigations.

For aluminum depositions performed at potentials negative of -0.2 V, the *in situ* optical images did not have sufficient resolution to estimate the size of the Al nuclei. To overcome this problem, we have recently begun investigating the aluminum deposition process using electrochemical scanning tunneling microscopy (ECSTM).

The application of standard scanning tunneling microscopy (STM) and ECSTM to the study of surfaces in a variety of environments is an exploding field (13,14). Of particular interest to us is the ability to image surfaces under solutions during surface corrosion (15), electrochemical deposition (16), and anodic dissolution (17)

Cyclic voltammetry at the tungsten foil substrate in the ECSTM cell showed an onset of aluminum deposition at -0.6 V; the Al/Al(III) equilibrium potential, E_{eq} , was estimated to be -0.52 V from the zero-current crossover following scan reversal. Initially, the uncoated tungsten substrate was imaged under the melt, then the tungsten potential was stepped to -1.1 V (overpotential = E - E_{eq} = -0.6 V) for increasing times to deposit increasing quantities of aluminum on the tungsten substrate. During Al deposition, the imaging tip was withdrawn several microns from the surface to prevent interference with

diffusion of Al₂Cl₇⁻ to the substrate. Images of aluminum coatings formed following total deposition times of 30 and 90 s are shown in Figures 7 and 8 (constant-current mode, bias voltage = +1.713 V, setpoint current = 0.5 nA). The two photographs have the same x, y, and z scalings to clearly show the changes in the morphology of the surface with longer aluminum deposition times. The aluminum coatings display features resembling ridges which may correspond to Al plates. These appear as parallel ridges in Figure 7. Importantly, the structural features in the two figures have dimensions in the 20-100 nm range (0.02-0.1 μ m). These sizes are below the optical resolution discussed above and are in reasonable agreement with the average nucleus size predicted in Table I for aluminum deposited at more negative potentials.

The surface roughness was quantitated with an option in the Digital Instrument software which provides a mean roughness (R_a), a ten-point mean roughness (R_z , calculated from the five highest and five lost points), and a maximum roughness (R_{max}). Theses values are presented in Table II for the uncoated tungsten, for Figures 7 and 8, and for a 390 s deposition. For short deposition times, the aluminum deposit remains smooth and regular indicating formation of a continuous, small-nuclei deposit. At longer deposition times, the thicker Al deposits exhibit an increasing roughness. Such increases in roughness may be due to the development of larger aluminum clusters on top of the smoother aluminum undercoating.

CONCLUSIONS

Thin, continuous aluminum coatings can be produced on a tungsten substrate from the 1.1:1.0 AlCl₃:MEIC molten salt at room-temperature using constant-potential deposition. The average nucleus size of the deposit is estimated to be < 0.5 μ m when the deposition potential is negative of -0.2 V versus Al(III)/Al. Analysis of the nucleation process gives calculated nuclear site densities and estimated nuclei sizes in agreement with optical microscopy and STM images. The growth process for thick Al coatings (> 0.1 μ m) may involve the formation of larger aluminum clusters on top of a smooth Al undercoating.

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Е	t _m	i _m x 10 ²	$AN_{\infty} \ge 10^{-6}$	N _s x 10 ⁻⁶	r
(V)	(ms)	(A cm ⁻²)	(sites cm ⁻² s ⁻¹)	(sites cm ⁻²)	(µm)
-0.075	378	2.27	32	8.94	1.89
-0.100	200	3.26	137	18.4	1.31
-0.125	83	4.93	719	42.1	0.87
-0.150	35	7.64	4149	101	0.56
-0.175	30	9.44	9640	154	0.45
-0.200	18	12.1	25768	252	0.36
-0.250	11	17.4	111068	523	0.25
-0.300	6	23.2	350620	929	0.19

Table I. Analysis of chronoamperometric data for aluminum deposition from 1.1:1.0 AlCl₃:MEIC at a 250- μ m diameter tungsten electrode.

Table II. Surface roughness for Al deposited on tungsten substrate at -0.6 V

Deposition Time (s)	R _a (nm)	R _z (nm)	R _{max} (nm)
0	0.53	2.5	4.2
30	1.0	4.2	8.6
90	1.3	6.0	12
390	3.0	15	38



Figure 1. Staircase cyclic voltammograms for aluminum deposition and stripping at a 250- μ m tungsten disk electrode in a 1.1:1.0 AlCl₃:MEIC molten salt following successive scans to +3.0 V.



Figure 2. Staircase cyclic voltammetry showing aluminum underpotential deposition at a 250-µm tungsten disk electrode in a 1.1:1.0 AlCl₃:MEIC molten salt: (a) following electrode pretreatment; (b) prior to electrode pretreatment. Integration of the charge under the peak at ca. 0.2 V indicates formation of a monolayer.



Figure 3. Darkfield illumination of 0.093-µm thick aluminum coating on a 250-µm diameter tungsten disk electrode. Deposition potential: -0.1 V. Magnification: 400x.



Figure 4. Darkfield illumination of 0.094- μ m thick aluminum coating on a 250- μ m diameter tungsten disk electrode. Deposition potential: -0.4 V. Magnification: 400x.



Figure 5. Chronoamperograms for aluminum deposition at a $250-\mu m$ tungsten disk electrode in a 1.1:1.0 AlCl₃:MEIC molten salt. Deposition potentials (V): (a) -0.075, (b) - 0.1, (c) -0.125, (d) -0.150, (e) -0.175, (f) -0.20.



Figure 6. Comparison of (a) experimental aluminum nucleation processes at overpotentials of -0.075 V and -0.175 V to theoretical (b) progressive and (c) instantaneous nucleation processes.



Figure 7. STM image of an aluminum deposit produced after 30 s at E - $E_{eq} = -0.6$ V.



Figure 8. STM image of an aluminum deposit produced after 90 s at E - $E_{eq} = -0.6$ V.

ELECTRODEPOSITION OF MOLYBDENUM AND MOLYBDENUM CARBIDE COATINGS FROM OXIDE BASED MOLTEN SALTS

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ABSTRACT

Dense, well-adherent molybdenum and molybdenum carbide coatings have been deposited on mild steel substrates by electrochemical deposition from a Na_2WO_4 - K_2WO_4 molten bath containing alkali molybdates and carbonates. Coatings with a thickness of up to 30 µm have been prepared at cathodic current densities between 30 and 50 mA.cm⁻² under air as ambient atmosphere. The coating morphology depends strongly on melt composition, temperature and moisture content. Addition of $Na_2B_4O_7$ to the basic non-lithium bath composition causes significant quality and morphology improvements.

INTRODUCTION

Recently, considerable attention has been focused on the development of coatings of molybdenum and molybdenum carbide by molten salt electrochemical deposition (MSECD). These coatings are considered candidate materials for coating the container and positive-electrode current collector of high-temperature power sources such as the sodium-sulfur and lithium-FeS₂ batteries.

MSECD is a powerful method which can be used to produce various compound-based coatings having improved properties compared with those of the pure single chemical elements. This method offers the ability to coat complex shapes and provides good process control by making use of current/potential variation.

Formation of refractory metal and metal carbide deposits by MSECD using several different bath composition (chloride, chloride-oxide, fluoride) has been demonstrated by many authors (1-11). However, all these methods have difficulties in practical use, especially: inert atmosphere is required; complicated treating steps, special purity requirements for the electrolyte baths etc., so the practical potential of these methods is insufficient. Recently, a different method was found, using a non-fluoride based electrochemical deposition from a melt consisting completely of oxides, with air as ambient atmosphere (12-16).

The method can be summarized as follows. Mo₂C coatings are deposited directly on mild steel from a Na₂WO₄-K₂WO₄-Li₂MoO₄-Li₂CO₃ melt at 900 °C. Dense coatings with a thickness of up to 50 μ m are obtained at cathodic current densities between 20 and 100 mA.cm⁻².

The authors attribute the deposition of Mo_2C from oxide melts to the instantaneous chemical reaction of carbon and molybdenum produced from the corresponding oxygenated anions. As a result of this reaction a compact pore-free deposit of molybdenum carbide is obtained with good adhesion to the low carbon steel substrate.

Preliminary results on the corrosion and electrochemical behavior of Mo_2C coatings deposited electrochemically on low carbon steel show good promise for corrosion protection of the cathode container in lithium/iron sulfide and sodium/sulfur batteries (17).

The objectives of this study are (a) to produce dense and adherent molybdenum and molybdenum carbide coatings from sodium tungstate-potassium tungstate based melts containing alkali molybdates and carbonates; (b) to determine correlations with process parameters such as temperature, current density, melt composition, moisture content etc.

EXPERIMENTAL

The electrochemical plating cell assembly is schematically presented in Figure 1. It consists of an α - Al₂O₃ crucible positioned on the bottom of an electroresistance furnace, a cover of thermo-insulating material with holes for the anode electrode, a low carbon steel cathode, a platinum flag as quasi-reference electrode, and a chromel-alumel thermocouple. The electrodes and thermocouple passed through the holes of the cover and were immersed in the electrolyte melt which occupied the bulk of the crucible. A small Hoskins (Model FD 101) electric furnace was used to fuse the electrolyte and ensure the necessary working temperature.

A molten bath consisting of an equimolar mixture of Na_2WO_4 and K_2WO_4 was used. The molybdenum and carbon species were introduced as alkali molybdate and carbonate, by

direct mixing with the base tungstates as a powder. Initially all individual components were dried at 200-300 °C for 2-3 hours in order to remove as much moisture as possible from the commercially available laboratory chemicals. Following this, the melt components were weighed and mixed to give the desired electrolyte composition. As a second step, in some cases an additional electrochemical purification was carried out. To remove the remaining moisture completely, the melt was electrolyzed at about 1.5-2.0 V at 650 °C between two carbon electrodes until the current dropped to a low constant value typically less than 1 mA.

After placing the crucible with the dried powder mixture in the furnace, the temperature was raised slowly to 600 °C at which point the electrolyte started to melt. One to two hours were necessary after melting to produce a clear melt. After melting, the temperature of the electrolyte was raised to 650 °C, the carbon electrodes for preelectrolysis were positioned above the crucible, and after thermal equilibration they were very slowly immersed. The pre-electrolysis electrodes were removed immediately after completion of pre-electrolysis. The plating electrodes were then positioned above the crucible, and after some additional equilibration, they were very slowly immersed in the molten electrolyte to avoid thermal shock. After reaching thermal equilibrium (usually in 1-1.5 hours), the temperature was raised again very slowly to the working temperature, 900 °C. Electrolysis was started within 1 hour after reaching this temperature.

Following electrolysis the temperature was decreased again very slowly, and at 600°C the electrode assembly was removed. After complete cool-down, the electrodes were ultrasonically stripped of adherent frozen melt.

Cylindrical cathodes of 3.1 or 6.3 mm dia and about 30 mm length were cut from a lowcarbon steel rod (AISI 1018). Each cathode substrate was screwed or compressed into a long low-carbon steel holder of 6.3 mm dia to ensure excellent electrical connection. The cathodes were initially etched with 10% hydrochloric acid followed by rapid rinsing by water and acetone. Later, they were cleaned mechanically using successively finer grades of silicon carbide paper (240, 320, 400, 600), and then rinsed again by alcohol and water. Next, in most cases, they were polished with Alfa Micropolish Alumina Solution - 1.0 μ m (Buehler), followed by a final ultrasonication in alcohol and acetone.

The anodes were pure metallic molybdenum or carbon rod of 6.3 mm dia. They were installed as the central electrode of the electrochemical cell assembly.

The measuring instrumentation consisted of an EG&G PAR Model 175 Universal Programmer, a Model 179 Potentiostat/Galvanostat provided with Model 179 Digital Coulometer plug-in option, a Hewlett-Packard ColorPro Plotter and a Nicolet 310 Explorer II Digital-Storage Oscilloscope.

RESULTS AND DISCUSSION

Electrolyte Bath Composition

The electrolyte bath composition was varied in order to study the influence of the kind and amount of alkali molybdate and carbonate on the resulting deposits and on this basis to choose the optimal composition. Later, the process parameters of molybdenum and Mo_2C deposition from a fixed bath composition were studied in order to generate satisfactory coatings with reproducible surface topology and thickness.

Several different bath composition have been utilized with approximately 8 - 10 mol% alkali molybdate and variable amounts of alkali carbonate. Table 1 lists the chemical composition of the electrolyte baths used, while Table 2 shows the different plating conditions performed. The experiments, which were performed without pre-electrolysis of the electrolyte, gave in most cases unreproducible results. After pre-electrolysis, coatings of a more reproducible quality were obtained. Using non-lithium alkali molybdates and carbonates, coatings of an even better quality were obtained. Adding 3-8 mol% Na₂B₄O₇ to the basic non-lithium bath composition was observed to cause significant morphology and quality improvements. These bath compositions produce a more uniform small-grain-size coating, moreover they do not require extensive purification because they are apparently not very sensitive to moisture in the atmosphere.

Significant information about the coating quality was obtained from examination of sample cross-sections. Typical microscope cross-section pictures for the samples plated under different conditions are shown in Figures 2, 3 and 4. Generally it indicates approximately uniform thickness over irregular substrate profiles and a virtually dense pore-free coating. The deposit seems to consists of two zones: a) a region near the iron interface containing both iron and molybdenum, which is probably a molybdenum interlayer and/or Fe-Mo diffusion zone; b) a zone further out, which constitutes the true carbide coating - Figure 4. A typical ED-Analysis for a good quality sample plated under the conditions described above is shown in Figure 5.

Inert Atmosphere

To determine the influence of the inert atmosphere on the coating quality, several plating experiments were carried out in an argon-filled glove box. The results show significant changes in coating quality and morphology in the case of lithium-based electrolyte baths and no significant changes in the case of non-lithium salt baths.

Temperature

The working temperature was varied from 900 to 1000 °C. Below 850 °C no deposit was observed. Non-lithium electrolytes in all cases required higher working temperatures.
Moreover, when adding borate the temperature must be increased by 50 - 80 °C. Increase of temperature causes significant changes. Larger grain sizes are found at higher temperatures.

Current Modulation

Both constant current and reverse current patterns were applied during plating. A reverse current electrolysis was preferred in order to achieve a certain grain structure and thickness. This procedure consisted in applying an initial cathodic current, followed by current reversal characterized by the cathodic current I_c and the anodic current I_a , by cathodic and anodic current flow times t_c and t_a respectively, where $t_c+t_a=T$ represent the full period of the reversing-current wave - Figure 6. It seems that a very important characteristic of a reversing current is the ratio t_c/t_a . This current modulation produces smaller-grain-size coatings than the constant-current plating at the same working temperature. It also makes higher current densities possible and appears to be most effective in generating good quality coatings.

Using the electrochemical deposition cell described above, good quality well-adherent coatings of Mo_2C were obtained under the following conditions:

$Na_2WO_4 - K_2WO_4$	80 - 90 wt%	
Na ₂ MoO ₄	5 - 10 wt%	
Na ₂ CO ₃	3 - 8 wt%	
$Na_2B_4O_7$	0.5 - 3 wt%	
	950 - 1000 °C	
rate	low-carbon steel	
anode material		
ent density	30 - 50 mA.cm ⁻²	
	$Na_2WO_4 - K_2WO_4$ Na_2MoO_4 Na_2CO_3 $Na_2B_4O_7$ rate al ent density	

Chronoamperometry

A comparative study of nucleation and growth of molybdenum layers was carried out, using a single potential step technique. When the potential of the electrode is pulsed to a potential range where deposition of molybdenum occurs, corresponding current transients follow the dependence $i \sim t^n$, where n is a constant depending on the geometry and type of nucleation. The current transients have the shape shown in Figure 7. The transients are characterized by (1) an initial current drop due mainly to double layer charging and to the formation of a supersaturated (metastable) solid solution of molybdenum in the surface layers of the substrate (iron); and, (2) a subsequent current rise to a steady state value associated with the formation and growth of the molybdenum deposit. These curves have the characteristic shape often observed for the deposition of metals on foreign metal surfaces.

A preliminary analysis of the initial rising parts of the experimental current transients for relatively high overpotentials shows that they follow very closely $i-t^{1/2}$ dependence as shown in Figure 8. The initial stages of electrochemical deposition of molybdenum can be explained in terms of a model involving instaneous nucleation and three-dimensional (3-D) mass-transfer controlled growth, similar to the models for conventional electrolytic metal deposition.

As seen from Figures 7 and 8, with the increase of the applied cathodic potential the slope of the i- $t^{1/2}$ dependence rises greatly and the time required for reaching the steady state current decreases.

CONCLUSIONS

Dense, well-adherent molybdenum and molybdenum carbide coatings can be deposited from oxide-based melts. The coating morphology depends strongly on melt composition, temperature and moisture content. Initial pre-electrolysis significantly changes the composition and morphology of the coatings. Non-lithium electrolyte baths do not require extensive purification. Addition of Na₂B₄O₇ to the basic non-lithium bath causes marked morphology and quality improvements. Significant changes appear to be caused also by variation of deposition temperature.

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Figure 1. Electrochemical Plating Cell Assembly.



Figure 2. Cross-Section of a Sample of Condition D. (Lithium-Based Electrolyte, Pre-Electrolysis Performed, Plating in Air, Working Temperature 950 °C).



Figure 3. Cross-Section of a Sample of Condition M. (Lithium-Based Electrolyte, Pre-Electrolysis Performed, Plating in Air, Working Temperature 1000 °C, using Na₂B₄O₇ addition).



 $\begin{array}{lll} \mbox{Figure 4.} & \mbox{Cross-Section of a Sample of Condition Q. (Non-Lithium Based} \\ & \mbox{Electrolyte, Pre-Electrolysis Performed, Plating in Air, Working} \\ & \mbox{Temperature 1080 °C, using Na}_2B_4O_7 \mbox{ addition }). \end{array}$



Figure 5. Typical ED-Analysis for a Sample Shown in Figure 4.



Figure 6. Current Pattern: Reverse Current Modulation.



Figure 7. Typical Current-Time Profiles for Chronoamperometric Experiments.



Figure 8. I vs. $t^{1/2}$ Plots of the Initial Rising Parts of the Transients Shown in Figure 7.

\sim	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Na2WO4	•	•	•	•	•	•	•	•	•	•	•	•	•	•
K2WO4	•	•	•	•	•	•	•	•	•	•	•	•	•	•
LI2MoO4	•	•	•											•
Na2MoO4				•	•	•					•			
K2MoO4							•	•	•			•		
MoO3										•			•	
Li2CO3	٠			٠			•			•				•
Na2CO3		•			•			٠			٠		•	
К2СО3			•			٠			٠			•		
Na2B4O7											•	•	•	٠

 Table 1.
 Chemical Composition of the Electrolyte Baths Used in the Plating Experiments.

		Without Pre-	electrolysis	Pre-electrolysis	
		Glove box	Outside	Glove box	Outside
Without additions	Lithium baths	A	В	С	D
	Non-lithium baths	E	F	G	Н
Borate	Lithium baths	I	К	L	М
additions	Non-lithium baths	N	0	P	Q

Table 2.DifferentPlating ConditionsPerformed for MSECD from Oxide
Baths.

A NOVEL PULSATING CURRENT TECHNIQUE USED IN THE STUDY OF PLATINUM AND MOLYBDENUM ELECTRODES IN MOLTEN SILICATES, BORATES AND PHOSPHATES

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The time to oxygen evolution at platinum electrodes in molten soda lime silicate glass and sodium disilicate, diborate and diphosphate has been measured using a pulsating current method originally introduced by Hickling. At 0.083A/cm² and 1200°C the times measured were 50, 20, 20 and 9msec, respectively, and these varied hardly at all with temperature, but decreased with increasing current density. The reason for the delay using the silicate compositions was shown to be the periodic formation and removal of a monomolecular layer of PtO₂ on the anode. This did not occur in the borate to the same extent, probably because of the alloying of platinum with boron. In the phosphate melts the platinum dissolved as phosphate, probably with the formation of thick salt films on the electrode. At a molybdenum anode in silicate glass the voltage rose almost immediately to oxygen evolution on the application of the current.

During an investigation into the ac electrolysis of molten soda lime silicate glass at 1350° C and $0.6A/\text{cm}^2$ using platinum electrodes it was found that the platinum corroded extensively at a frequency of 50Hz, but not at a frequency of 500Hz(1). This was tentatively ascribed to the formation of oxygen bubbles round the electrode during the longer, 10msec, positive half cycle time at 50Hz, but not during the shorter, Imsec, positive half cycle time at 50Hz. It was important to decide this question by a direct measurement of the time taken to oxygen evolution and this measurement was carried out using an adaptation of an oscillographic pulsating current method originally due to Hickling(2).

It was found that the time to oxygen evolution at 1350° C and $0.6A/\text{cm}^2$ was 2.6msec at a platinum anode and so the oxygen gas does not have time to form during the lmsec half cycle time of the 500Hz ac input, but it does have time to form during the l0msec half cycle time of the 50Hz ac input(3). Thus the corrosion results above receive a logical explanation.

*Present address: 8 Delph Top, Greetby Hill, Ormskirk L39 2DX, Lancs, England Key Words: polarisation, melts, silicates, platinum. Since the method had proved successful in settling this question, the measurements were extended to different temperatures in the range $900^{\circ}C$ to $1350^{\circ}C$ using current densities from 0.017 to $1.333A/cm^2$. In addition, similar measurements were made in other systems such as sodium disilicate, diborate and diphosphate melts, (4) and at molybdenum electrodes in soda lime silicate glass with, and without, added sulphate refiner (5).

The above measurements of time to oxygen evolution were made using the internal time base of the oscilloscope, but it was also possible to record oscillograms of voltage against quantity of electricity passed. Much further information on the reactions occurring before oxygen evolution in all these systems was obtained using this technique: measurements were made of the electrical double layer capacity in the initial stages of polarisation; of the thickness of any oxide layer formed prior to oxygen evolution; of the reproducible values of oxygen evolution potential.

Finally, these results were compared with those obtained in the same electrolytes using a conventional, single pulse method. In general, the pulsating current method gave much more information on the electrochemical reactions occurring than did the single pulse method. However, the single pulse method was useful in giving information on one particular aspect of the polarisation: its decay time. This was extremely short at the electrodes of molybdenum in silicate glass melts, but at platinum electrodes the decay was slower and varied with the nature of the electrolyte.

EXPERIMENTAL

Figure 1 is a diagram of the circuit embodying Hickling's method but using modern, solid state components. The main loop is the one on the left of the diagram and consists of a constant current unit, a capacitor and the cell itself. Across the capacitor-cell combination is placed a thyristor with its gate biassed so that it trips into conduction when a pre-determined voltage is applied to its collector.

In operation a constant, preset current is passed through the capacitor and cell in series, from the constant current unit and the voltage on the plates of the capacitor rises. Eventually, the voltage on the upper plate of the capacitor reaches that required to trigger the thyristor into conduction, and the thyristor thus acts as a short circuit for the capacitor and the cell. Then the capacitor discharges a quantity of electricity exactly equal to that originally passed, flowing rapidly through the cell in the reverse direction.

This process should repeat itself indefinitely and, using a thyratron valve as in Hickling's original circuit, it does. However, this cannot happen with the thyristor because once in conduction it cannot switch itself off while current is flowing from the constant current unit. It is the function of the monostable oscillator in the right hand loop to overcome this. This detects the large discharge through the thyristor when it occurs and then sends a pulse to the constant current unit stopping it for a pre-determined blanking period, and thus allowing the thyristor to switch off. At the end of the pulse the constant current unit switches on again and the whole cycle of charge and discharge repeats itself indefinitely.

The voltage between the electrode in the cell which is being studied and a suitable reference electrode is fed to the Y-plates of the oscilloscope and the voltage across the capacitor (which is exactly proportional to the quantity of electricity passed at any time) is applied to the X-plates. Under these conditions the trace on the oscilloscope screen represents the variation of the potential of the working electrode with the quantity of electricity passed through the cell (V/q oscillograms). Alternatively, the internal time base of the oscilloscope may be used to record the X-axis displacement and then gives the time for any electrochemical reaction to occur directly (V/t oscillograms).

In all the experiments, starting with fresh electrodes, in the present investigation the trace on the oscilloscope screen moved downwards initially when the pulsating current was first switched on indicating some change in the surface of the electrode. After a few seconds, however, the trace stabilised and then remained stationary for hours and days at a time, and could be photographed at leisure. This fact, that the oscilloscope tracks are stationary, means that the technique is isolating the true and reproducible part of the polarisation, and that exactly the same change of potential is brought about by charging the electrode as discharging it - that is, there is no irreversible loss of electro - chemically active material from the electrode. It means that the electrode is brought back to its original state with no accidental variation in its condition at the end of every cycle: and this is the unique feature of the method compared with conventional, single pulse methods where the initial state of the electrode is not usually clearly defined and measurements are made on transients.

In order to illustrate some of the general characteristics of the tracks observed with this circuit we give a V/t oscilloscope trace in Figure 4(a) using a 10Ω resistor in place of the cell in Figure 1. The upper track shows the charge and discharge of the 100μ F capacitor C with the oscilloscope probe placed at monitor point MP3; the lower track shows the current through the 10Ω resistor obtained by placing the oscilloscope probe at monitor point MP1, just above the small, 0.1 Ω resistor used for monitoring the current.

We consider the first pulse at the start of the linear rise in voltage across the capacitor at the point denoted by the letter "s" on both the horizontal and the vertical axes. The current is switched on and continues at a constant value as the voltage across the capacitor rises. Eventually the thyristor goes into conduction, the voltage across the capacitor drops and a large current - shown by the spike in the track - flows through the 10Ω resistor in the opposite direction. This is followed by the blanking period during which the current is switched off and the capacitor voltage is constant. Next the current is switched on again and the capacitor voltage starts to rise for the second pulse. The reader should note that the switch-on point of the current and the start of the capacitor voltage rise coincide and occur at the end of the blanking period in each case.

The constant current unit consisted of two Darlington pairs made up from two MJE 340 and two MJE 350 transistors, respectively, and capable of supplying a maximum current of 500mA; the thyristor was a BTY-79 type; the monostable oscillator was a COSMOS 4098 chip. Any of a bank of four electrolytic capacitors of value 50, 100, 250 or 500 μ F could be switched into the circuit, but the 50 and 100 μ F ones were the capacitors most used for the measurements. These could all be by-passed to allow a constant current to flow through a dummy 10Ω load, of approximately the same resistance as the cell, in order to preset the constant current unit; and in some cases also to pass dc through the cell itself. With certain settings of the thyristor triggering and the blanking period controls the equipment could cease to operate, but could be restarted by changing both these controls to a more suitable value and then pressing the reset button shown just beneath the constant current unit. This broke the circuit temporarily, allowing the thyristor to switch off and the pulse cycle to be re-established.

The circuit used in the second, conventional single pulse method is shown in Figure 2. The most important component is the relay and this controls those components in the left hand loop of the diagram: the constant current unit, the cell and the load. When the relay is at position 3 the preset current from the constant current unit flows through the cell; on the other hand, when the relay is at position 2 the cell discharges through the load. The action of the relay is itself controlled by the monostable oscillator on the right hand side of the diagram. When the start button, SI, is pressed, the monostable oscillator below it emits a pulse of preset length and moves the relay contact from position 2 to position 3. Current from the preset constant current unit flows through the cell and the 0.1Ω current monitoring resistor for the duration of the preset pulse. At the end of the set pulse the relay contact moves back from position 3 to position 2, and the cell is allowed to discharge through the load, which may be of any sized resistor or a short circuit.

The shape of the pulse and the voltage decay may be examined by placing an oscilloscope across any two of the cell electrodes and the current through the cell and load monitored by placing a probe just above the 0.1Ω resistor. The residual voltage on the cell electrodes may be measured over long periods, if required, by opening the switch, S3, and reading off the voltage on the digital voltmeter.

The constant current unit consisted of the usual two Darlington pairs made using MJE 340 and MJE 350 transistors, and the monostable oscillator was a COSMOS 4098 chip fed into a 4049 buffer amplifier chip. The relay was a mercury wetted type 97-1-C-12-7 with a fast switching speed of 250µsec. A Tektronix, type 564, storage oscilloscope was used throughout these experiments. To measure the ac resistance of the cell a Wayne Kerr bridge, type B221, driven by a type S121 AF signal generator was used.

A diagram of the electrolysis cell is shown in Figure 3. It consisted of a 100cm³ conical, recrystallised alumina crucible containing 100gm of ground electrolyte. The electrodes were 0.625mm diameter platinum wires fitted through small, 1mm diameter holes in the square, 2mm thick, pure alumina top plate. The wires were crimped and held in position in this plate by a heavier, square 1cm thick Mullite block placed over them.

The length of the wires dipping into the glass was 1.5cm, and this corresponded to an area of 0.3cm². Four wires were inserted into the the cell, three of them being at the apices of an equilateral triangle of side 3cm and the fourth at the mid-point of any one of the sides. This last wire and that at the opposite apex served as reference electrodes, but it was found that there was no measurable difference between the results obtained with the reference electrodes in these different positions, and for most of the experiments the wire at the opposite apex of the triangle was the one most used as reference electrode. The electrodes in the furnace were connected to the electrical equipment by double strands of the same platinum wire twisted round their tops and insulated by alumina beads. The most usual temperatures used were from 900°C to 1400°C, and between electrical experiments the crucible and its contents were kept at 900°C in the silicon carbide furnace in order to minimise corrosion problems.

The wt% composition of the glass used was 69.2 Si0_2 , 11.2 Na_20 , 9.3 CaO and 5.3 K₂O; the minor constituents were MgO, BaO, Al₂O₃ and B₂O₃.

The sodium disilicate was made by heating the appropriate amount of silica (Limonges quartz) and AR sodium carbonate in an alumina crucible to 1300°C for 2 hours and then casting on stainless steel. For the sodium diborate, finely ground, commercial borax glass(Fison's) which had the sodium borate composition was used directly in the alumina cell. The sodium diphosphate was made by heating AR sodium metaphosphate with orthophosphoric acid and casting on stainless steel. Further details of all these preparations are given in reference (4).

When experiments were conducted with molybdenum, precautions had to be taken to protect the metal from the air due to the high reactivity of heated molybdenum with oxygen. First an inert atmosphere of $N_2/5\%$ H₂ was provided above the glass in the cell by passing the gas mixture down both channels of a double bored, $\frac{1}{4}$ inch diameter alumina tube passing through holes in the centre of the Mullite block and the alumina plate. Then the actual molybdenum wires were protected from the air by joining them to platinum connecting wires below the the Mullite block and alumina plate and thus in the inert gas atmosphere.

The diameter of the molybdenum wire was 0.12cm, and the electrode area below the glass surface was 0.6cm². The molybdenum metal was 99.9% pure (Materials Research). For further details on the exact procedure used during an experiment the reader is referred to reference (5). The glass used had the composition shown in Table 1.

Table I Analysis of Glass with and without Sulphate Refiner (wt%)

so3 A1203 Si0, Na₂0 K, 0 Ca0 Mg0 Fe₂0₂ 72.6 13.0 8.3 4.1 1.0 0.6 0.117 0.24 With Sulphate 4.0 73.1 12.9 8.3 1.0 0.6 <0.02 Sulphate Free 0.06

Two samples of the glass were examined, one to which sodium sulphate had been added as a refining agent and one to which no sulphate had been added; the SO₃ compositions of the two glasses are given in column 8 of Table I above.

RESULTS

Platinum-Soda Lime Silicate Glass

In Figure 4(b) is shown a V/t oscillogram at a temperature of 1350° C and a current density of $0.6A/\text{cm}^2$. The upper trace gives the change of voltage across the cell with time (oscilloscope probe at monitor point MP4 in Figure 1), and the lower trace gives the value of the current during the time of the experiment (second oscilloscope probe at monitor point MP1 in Figure 1).

The first part of the tracks show the large negative currents flowing followed by the blanking periods; next the long horizontal region in the lower current trace illustrates that the current flowing through the cell is constant. When this is first switched on, the voltage shown in the upper track rises, initially, so rapidly that the oscilloscope trace disappears. This rapid rise is then followed by a slower rise until a break in the curve occurs; then there is a futher small, slower rise until a plateau is reached when oxygen evolution occurs. The horizontal distance from the start of the current to the point at which the oxygen evolution plateau starts is 1.3 divisions and, since the time base scale is 2msec per division, this represents a time of 2.6msec. It thus takes 2.6msec from the start of the electrolysis for oxygen evolution to be attained.

The initial, extremely rapid rise in voltage following the swithch-on is due to the resistance of the glass. From the height of the jump and the constant current density it is calculated to be 8.30, and this is in good agreement with the value of 70 measured at 1000Hz using the ac bridge. In measuring oxygen evolution voltages we ignore this rise due to the glass resistance and start measurements from the beginning of the next, slower voltage rise, visible on the oscillogram. This point is denoted on the photograph by the letter "s" on both the horizontal and vertical axes and this point, thus specified, will be used as the starting point for all future oscillograms. Under the particular conditions of electrolysis of the present oscillogram the oxygen evolution voltage measured from this starting point to the beginning of the oxygen evolution plateau is about 1.8V,while it is about 2.2V if the measurement is made between the point marked "s" and the end of the plateau when oxygen evolution is occurring freely (see reference(3) for a fuller discussion of this point).

The high temperature and current density were chosen for this experiment because these were the conditions under which the corrosion discussed in reference (1) was occurring. However, for the later, systematic experiments we usually worked at the lower temperature of $1200^{\circ}C$ and a current density of $0.083A/cm^2$, and Figure 4(c) shows a V/t oscillogram obtained under these conditions. The general features are similar to those in Figure 4(a), but the time to the start of oxygen evolution is longer - 50msec - and the oxygen evolution voltage is 1.5v, measured across the cell from the working anode to earth for this oscillogram.

It is instructive to compare the three tracks obtained simultaneously with the oscilloscope probes across the various components of the working, auxiliary and reference electrodes. The three tracks shown in Figure 4(d) were obtained with the Y-axis differential amplifiers connected across the working and auxiliary electrodes (upper trace), across the working and platinum reference electrodes (middle trace), and across the reference and auxiliary electrodes (lower trace). The positive oscilloscope probe was connected to the first mentioned electrode in each case. Measurements of the Y-coordinates of these tracks showed that the voltage across the working-auxiliary electrode combination is the sum of those across the working-reference and the reference-auxiliary combination - and this, of course, is to be expect It should be carefully noted, however, that the track of worked. ing against auxiliary electrode is linear after oxygen evolution has started, when the electrode is heavily polarised, and that there is no curvature in opposing senses - positive and negative - in the other two tracks, which there would be if the potential of the reference electrode were changing. Of course, a measurement between a working and a reference electrode is much to be preferred to one between a working and an auxiliary electrode because the track levels off to a steady oxygen evolution value in the former case, but increases continuously in the latter case, as can be seen from Figure 4(d).

A series of measurements of the time to oxygen evolution was carried out, using V/t oscillograms, at current densities ranging from $0.017A/cm^2$ to $1.333A/cm^2$ and temperatures from 900° to 1350° C. The effect of change in current density is shown in Table II; all the measurements were made on tracks with the working electrode coupled to the platinum reference electrode.

Current Density	Time to Oxygen	Current Density x Time
A/cm ²	msec	C/apparent cm ²
0.017	122	2.07×10^{-3}
0.025	120	3.00×10^{-3}
0.033	108	3.56×10^{-3}
0.083	50	4.15×10^{-3}
0.167	20	3.34×10^{-3}
0.250	14	3.50×10^{-3}
0.333	10	3.33×10^{-3}
0.500	8	4.03×10^{-3}
0.600	5	3.03×10^{-3}
0.667	7	4.67×10^{-3}
1.000	3	3.00×10^{-3}
1.333	1.4	1.87×10^{-3}

Table II Effect of Current Density on Time to Oxygen Evolution in Soda Lime Silicate Glass at 1200°C

The time to oxygen evolution decreases with increasing current density but, surprisingly, the product of the current density and the time remains fairly constant apart from the values at the highest and lowest current densities. A similar type of behaviour has been observed in connection with ac electrolysis in reference (1), and this subject will be examined in the discussion section.

The results obtained when the temperature was varied are shown in Table III. The low current density of $0.025 A/cm^2$ was chosen for these experiments because it was difficult to exceed this current density at the lower temperatures.

Table III Effect of Temperature on Time to Oxygen Evolution in SodaLime Silicate Glass at a Current Density of 0.025 A/cm²

Temperature °C	Time to Oxygen Evolution msec	Current Density x Time C/apparent cm ²
	· · ·	2
900	96	2.40×10^{-3}
1000	118	2.95×10^{-3}
1100	132	3.30×10^{-3}
1200	120	3.00×10^{-3}
1300	116	2.90×10^{-3}
1350	106	2.65×10^{-3}

Again the product of current density and time is remarkably constant, apart from the two extreme values at $900^{\circ}C$ and $1350^{\circ}C$ which are slightly lower. From column 2 it is seen that the time to oxygen evolution also remains fairly constant with change in temperature when the current density is fixed at $0.025A/cm^2$, in contrast to its behaviour with change in current density at constant temperature shown in Table II.

The growth of the voltage across the cell and its decay may also be studied using the second, conventional single pulse circuit of Figure 2. An oscillogram made using this circuit with the probes connected across the cell (upper trace) and also across the 0.10 resistor (lower trace) is shown in Figure 4(e); the current density was $0.083A/cm^2$ and a pulse width of 100msec was used. The zero voltage lines for the upper and lower traces are located two and three large divisions, respectively, below the central X-axis line in Figure 4(e), and these are marked out with a zero, "0".

Considering the upper trace, the voltage across the cell rises smoothly with time with none of the breaks in the curve found in the growth curve using the first, pulsating current circuit. The final voltage recorded is about 1.1V - or 0.9V allowing 0.2V off for the voltage drop due to the glass resistance, and this may be taken as a oxygen evolution voltage, although the trace appears not to have stopped rising at this point. It will be recalled from Figure 4(c), using the first circuit, that the start of oxygen evolution was clearly shown 50msec after the commencement of electrolysis. The oxygen evolution voltage of 1.5V recorded then may be compared with the 0.9V It seems that oxygen evolution found now with the second circuit. may not be attained with the 100msec pulse using the second circuit, and this is noteworthy in that it was attained in 50msec using the first, pulsating current circuit.

When the current is switched off the voltage across the cell decays in one of three ways depending on the load resistance into which the cell is discharged: into an open circuit or a $10M\Omega$ resistor (upper trace) the voltage decay is very slow; into a 10Ω resistor (middle trace) the rate of decay increases; finally, if the cell is discharged into a short circuit (lower trace) then the voltage decay is relatively rapid and occurs in about 20msec.

The behaviour of the current during the decay is interesting. Only the trace obtained with the cell short circuited is given, but this shows that the current actually reverses direction during the decay period and appears below the lower zero line before decaying to zero in about 20msec. The decay time of the current into a short circuit does not seem to depend on the current density: Figure 4(f) shows the tracks of growth and decay at four different current densities and the decay time for each is the same. Whilst the V/t oscillograms give valuable information about the delay time of oxygen evolution, the corresponding V/q oscillograms give more information about the electrochemical reactions occurring at the electrodes. In Figure 4(g) is shown a typical V/q oscillogram at a temperature of 1200° C and a current density of $0.083A/cm^2$. The Y-axis reading gives the voltage across the working-reference electrode combination and the X-axis reading gives the quantity of electricity passed into the capacitor and cell at any particular point.

The oscilloscope trace may be divided into four parts: After the very rapid rise due to the glass resistance the voltage rises nearly linearly (stage 1); at a voltage of about 0.45V there is a break in the curve when the voltage continues to increase at a lower rate (stage 2); then there is a second, more rapid, linear rise (stage 3); finally the oxygen evolution plateau is attained (stage 4). The gradient of the trace in stage I may be easily found. Measuring the Xaxis displacement and multiplying by the capacity of the capacitor (100µF) gives the charge accumulated in stage 1 as 400µC; dividing by the voltage rise of 0.45V gives a value of $889 \mu C/V$ for the gradient, or 889μ F using the familiar relationship Q = CV for the capacitor. This value of the gradient is usually regarded as the capacity of the double layer at the electrode in the early stage of the electrolysis and, by dividing by 0.3cm^2 , a value of $2963 \mu\text{F}/\text{apparent cm}^2$ is obtained for the double layer capacity under these conditions. Using a similar method the charge accumulated during the next slower stage - stage 2 may be found and works out at 600μ C or 2000μ C/apparent cm². The gradient of the graph in stage 3 is found to be $400\mu C/V$ or $1333\mu C/V$ per apparent cm^2 . Finally, the oxygen evolution voltage is found to be 1.20V measured, of course, from the end of the rapid voltage rise due to the glass resistance.

The various parameters which we have considered are fairly reproducible, and the oxygen evolution voltages particularly so. We measured the various parameters on a sample of 22 different oscillograms at the same current density of 0.083A/cm², photographed at various times during a three week experiment in which the crucible and its contents were cycled many times between 900 and 1350°C. We used the Coefficient of Variation to compare the various parameters. This is the sample standard deviation divided by the mean, and it measures the spread of the individual results; it is expressed as a percentage and is dimensionless.

The parameters considered were the following (with the coefficients of variation in parentheses): the double layer capacity of stage 1 (14.1%); the voltage increase to the start of stage 2 (12.9%); the charge increment during stage 2 (16.9%); the gradient of stage 3 (8.7%); the oxygen evolution voltage (2.32%). Whilst the variation in all the parameters except the oxygen evolution voltage is of the size expected for this type of electrochemical measurement, the value of the coefficient of variation for the oxygen evolution voltage is exceptionally small at 2.3%. Indeed, the calculation of the 95% Confidence Interval of the mean gives a value of (1.21y,1.19V) and this implies that there is a 95% probability that any sample reading of oxygen evolution voltage will be between these two values. For further information on this point see reference (3).

There is another aspect of reproducibility apart from the above: it concerns what happens to the oscillograms after a period of dc polarisation. Figure 4(h) shows successive traces photographed over a period of lminute after an initial dc polarisation of 30seconds at a current density of 0.083A/cm². The trace is first displaced to the left on the application of the dc but then returns over a period of about lmin to the original steady position it had on the screen before the dc polarisation was applied. It is known that, provided the glass is not polarised, the oscilloscope tracks are steady and reproducible; but this experiment shows that even if the glass is polarised by direct current, the oscilloscope trace returns to its original position fairly rapidly when the dc polarising current is removed.

The various parameters which we have discussed above were measured at different current densities between $0.017A/cm^2$ and $1.333A/cm^2$ at $1200^{\circ}C$, and the results of this work are shown in Table IV:

Current Density	Double Layer Capacity stage l	Volts. Inc. to start of stage 2	Charge Inc. in stage 2	Gradient of stage 3	Oxygen Evolution Voltage in stage 4
A/cm²	µF/app.cm ²	v	$\mu C/app.cm^2$	µC/app.cm²/V	v
0.017	2223	0.42	2400	1333	1.16
0.025	2540	0.42	2533	1480	1.16
0.033	2610	0.46	2333	1480	1.18
0.083	2963	0.45	2000	1333	1.20
0.167	2267	0.50	1600	1853	1.20
0.250	2000	0.60	1200	1840	1.26
0.333	2191	0.70	867	1667	1.30
0.500	1167	0.80	933	1333	1.40
0.667	1003	0.95	800	1500	1.50
1.000	800	1.00	667	1067	1.60
1.333	667	1.00	800	1333	1.80

Table IV Variation in the Parameters of the V/q Oscillograms with Current Density at 1200°C

In this table the current density range of 0.250 to 0.333 A/cm² seems to form a natural dividing line for the data: below this line most of the parameters are roughly of the same order, but above this limit they vary - for example, the double layer capacity (column 2) starts to decrease at current densities above the range 0.250 - 0.333 A/cm². This is not surprising in view of Figure 4(i) which is a V/q oscillogram at 0.333 A/cm²: the initial part of the track - stage l - is curved, and the double layer capacity concept is of doubtful validity under these conditions. On the other hand, the stage 3 part of the trace is still linear, and this is reflected in the relative

constancy of the values in column 5 of Table IV. The charge increment during stage 2, given in column 4, shows a drift downwards above a current density of $0.083A/cm^2$ with the values of roughly the same order below it. The parameters which do show a systematic change are the voltages measured in columns 3 and 6: both the voltage increment to the start of stage 2 and the oxygen evolution voltage increase steadily.

The changes which occurred in the V/q parameters when the temperature was changed were also measured and the results are given in Table V:

Temperature	Double Layer Capacity	Volts. Inc. to start of	Charge Inc. in stage 2	Gradient of stage 3	Oxygen Evolution Voltage in
°C	stage l µF/app.cm²	stage 2 V	µC/app.cm ²	µC/app.cm²/V	stage 4 V
900	3333	0.82	600	750	1.50
1000	3187	0.67	1467	1000	1.37
1100	2760	0.58	2133	1250	1.32
1200	2083	0.48	2600	1764	1.20
1300 1350	1587 1043	0.42 0.32	2467 2200	2200 3214	1.14 0.96

Table V Variation in the Parameters of the V/q Oscillograms with Temperature at a Current Density of 0.025A/cm²

The current density used was the low one of 0.025A/cm^2 , chosen because it was difficult to exceed this current density at the lowest temperatures. As the temperature was increased most of the parameters decreased. This was true of the double layer capacity (col 2), but not the gradient of stage 3; the voltage increment to the start of stage 2 (column 3) and the voltage of oxygen evolution (column 6). The charge increment during stage 2 was different (column 4): it was low at 900° and at 1000°C, but at a temperature of 1100°C and above was of the same order as the values given in Table IV at the lower current densities. It should be noted from Figure 4(j) that the trace for stage 1 is curved at 1000°C and also that the length of stage 2 is small.

Molybdenum-Soda Lime Silicate Glass

In Figure 5(a) is shown a V/t oscillogram using the sulphate free glass: the upper trace shows the change in the working electrode (anode) voltage with time, and the lower trace is the current track. The point at which the voltage rise starts after the horizontal blanking period is shown, as usual, by the letter "s", and the rise is extremely rapid compared with the rise at a platinum electrode. For example, from Figure 4(c) the time to oxygen evolution at a current density of 0.083A/cm^2 is shown as 50 msec, and from Table II the delay time before oxygen evolution at 0.033A/cm^2 (the nearest current density recorded for Pt to the 0.042A/cm^2 value for the Mo) was found to be 108 msec. There is obviously a great difference between the electrochemical reactions at the two metals.

This conclusion is confirmed by the photograph of Figure 5(b) showing the decay times found using the second circuit with the same glass melt. The remarkable feature of this photograph is the value of the voltage which is attained during the growth part of the track: it is roughly 20V and, moreover, remains at approximately the same size although the current density was varied over the large range of from 0.017 to 0.083A/cm². These features are not a mistake nor an error from a single photograph since similar values of the voltage were found on several other photographs. The final voltage attained is nearly 20 times greater than that attained at a platinum anode at a current density of 0.083A/cm² (Figure 4(e)), also using the second circuit. Two other contrasting features between Mo and Pt are that the decay at the Mo electrode is almost instantaneous while, with a Pt electrode discharging into a short circuit, the decay time is approximately 20msec (Figure 4(e)). Additionally, the voltage attained in the growth part of the trace is hardly increased at all above 20V in the case of Mo by the increase in current density shown in Figure 5(b) but an increase in current density increases this voltage considerably in the case of a Pt electrode (Figure 4(f)).

In Figure 5(c) oscillograms are shown in a glass to which sulphate has been added, Table I, for the working electrode with respect to a Mo reference electrode and a Pt reference electrode, and also with the oscilloscope probes connected across the working and auxiliary electodes. The oxygen evolution voltages corresponding to these three conditions are 1.3, 2.0 and 3.7V, respectively, measured from the end of the blanking period to the flat part of the plateaux. Again, the rise to oxygen evolution is extremely rapid; and also the decay tracks display the same features as those shown by the sulphate free glass (Figure 5(a,b)).

An unusual feature emerges when the tracks obtained using steady dc at a current density of $0.042A/cm^2$ and shown in Figure 5(d) are compared with the pulsating current oscillograms shown in Figure 5(c): the dc oxygen evolution voltages, while slightly higher than the corresponding pulsating current ones, do not differ greatly from them. This is in marked contrast to the results found with platinum electrodes. There the oxygen evolution voltages found using pulsating current inputs and dc inputs do differ considerably: for example, at current densities of 0.083 and 0.167A/cm² the voltages measured were 2.9 and 9.3V, respectively, using a dc input, while they were both 1.2V with a pulsating current input at the same current densities.

The oxygen evolution voltages in the sulphate free glass and the glass to which sulphate has been added have been measured both with pulsating and direct current inputs, and the results are given in Table VI. In these measurements no correction for the voltage change due to the glass resistance has been made. However, by multiplying the glass resistance, measured with the ac bridge at 1000Hz, by the current passing through the cell and subtracting from the measured voltages such a correction may be made (the glass resistance is 8Ω at 1200°C).

Current Density A/cm ²	Oxygen Evolution Voltage(pc) Sulphate Free V	Oxygen Evolution Voltage(dc) Sulphate Free V	Oxygen Evolution Voltage(pc) Added Sulphate V	Oxygen Evolution Voltage(dc) Added Sulphate V
0.008	1.00	1.15	0.40	0.52
0.013	1.20	1.40	0.56	1.00
0.017	1.30	1.50	0.72	0.84
0.025	1.60	1.80	0.92	1.16
0.033	1.80	2.20	1.30	1.40
0.042	2.20	2.40	1.50	1.70
0.050	2.60	3.00	2.10	2.80
0.067	3.20	3.60	3.00	3.70
0.083	4.00	4.40	3.60	4.20
0.100	6.50	8.00	4.20	5.00
0.133	9.00	11.00	5.40	6.80
0.167	11.00	13.00	6.80	10.00

Table VI Effect of Current Density on Oxygen Evolution Voltage in Glasses with and without Sulphate Refiner at 1200°C

It is clear from the table that the oxygen evolution voltages increase steadily in all cases with increases in current density. Moreover, while the dc values are always slightly higher than the pulsating current values at all current densities, they do not differ greatly from them. A further point is that the values are always lower for the sulphate containing glass than they are for the sulphate free glass, and this is to be expected since the sulphate is a glass refining agent. Another striking feature is that the oxygen evolution voltages attained at the higher current densities are quite large compared with the values which are obtained at platinum electr-For example, at a current density of 0.167A/cm² the pulsed odes. and dc values in the sulphate free glass are 11 and 13V, respectively, at the molybdenum electrode; the comparable figures at a platinum electrode at the same current density are only 1.2 and 9.3V, respectively (Table IV).

All of the measurements made against a Mo reference electrode are a few tenths of volts below the values obtained using a Pt reference electrode, and this is not surprising since there is a difference of 0.2-0.3V between the two reference electrodes at 1200°C measured under static conditions, without any current input, before and during the experiments.

The effect of change of temperature on the oscillograms was also examined, and the results are shown in Table VII:

Temperature	Oxygen Evolution Voltage(pc)	Oxygen Evolution Voltage(dc)	Oxygen Evolution Voltage(pc)	Oxygen Evolution Voltage(dc)
°C	V	V	V	V V
1000	4.6	5.0	2.2	2.4
1050	3.6	4.0	1.6	2.0
1100	3.0	3.1	1.4	1.6
1150	2.5	2.9	1.1	1.2
1200	2.0	2.2	1.1	1.3
1250	2.0	2.4	1.1	1.3
1300	1.8	2.4	0.8	0.9

Table VII Effect of Temperature on Oxygen Evolution Voltage in Glasses with and without Sulphate Refiner at 0.025A/cm²

All the voltages for all the glasses decreased with increasing temperature both with pulsating current and with dc inputs. Again the dc values are slightly higher, but comparable in size to those obtained with a pulsating current at all the temperatures considered; the voltages are always higher in the sulphate free glass than it is in the glass to which sulphate has been added.

A striking feature is the size of the voltages in the sulphate free glass at the lower temperatures. These values are much greater than the corresponding values measured at a platinum electrode also in a sulphate free glass (Table V). For example, at 1000°C with a pulsating current input the value at the Pt electrode is 1.37V, while from Table VII the value at a Mo electrode at the same current density of $0.025A/cm^2$ is 4.6V; the value in the glass to which the sulphate has been added is lower at 2.2V.

A series of V/t oscillograms for sodium disilicate, diborate and diphosphate melts were recorded at different current densities and temperatures, and the time to oxygen evolution measured in each case; V/q oscillograms were not examined to the same extent because they were ill-defined in the case of the diborate. The effect of dc polarisation on the various melts was considered in some detail.

Platinum-Sodium Disilicate

In Figure 6(a) is shown an oscillogram at $1200^{\circ}C$ and a current density of $0.083A/cm^2$. The track has the same general charecteristics as those found in the silicate glass melts: there is an almost linear, rapidly ascending region (stage 1) with a break at 0.4V; this is then followed by a short plateau (stage 2) before another rise (stage 3) to the oxygen evolution plateau (stage 4) at 0.9V.

Table VIII Effect of in	of Current Density Sodium Disilicate	on Time to Oxygen Evolution at 1200°C
Current Density	Time to Oxygen Evolution	Current Density x Time
A/cm ²	msec	C/apparent cm²
0.017	74	1.26×10^{-3}
0.033	57	1.88×10^{-3}
0.050	27	1.35×10^{-3}
0.067	18	1.21×10^{-3}
0.083	20	1.66×10^{-3}
0.100	15	1.50×10^{-3}
0.133	9	1.20×10^{-3}
0.167	7	1.17×10^{-3}
0.200	5.5	1.10×10^{-3}
0.267	5	1.34×10^{-3}
0.333	3.5	1.17×10^{-3}

In Table VIII are given the times to oxygen evolution at the var-

ious current densities used.

The time to oxygen evolution decreases with increase in current density in the usual way, and the product of the current density and the time to oxygen evolution remains fairly constant. Comparison with Table II where the results for the soda lime silicate glass are given shows that the oxygen evolution times are less for the disilicate than for the silicate glass at the same current densities, and this applies also to the product of the current density and time.

In Table IX the effect of change of temperature is shown:

Table IX Effect of Temperature on Time to Oxygen Evolution in Sodium Disilicate at a Current Density of 0.05A/cm²

Temperature	Time to Oxygen Evolution	Current Density x Time
°C	msec	C/apparent cm ²
900	33.3	$1.67 \times 10^{-3}_{-2}$
1000	33.3	1.67×10^{-3}
1100	36.0	1.80×10^{-3}
1200	36.2	1.81×10^{-3}
1350	36.7	1.84×10^{-3}

The times to oxygen evolution are remarkably constant as is the product of the current density and time. Comparison with the results in Table III for the soda lime silicate glass should be treated with

some caution since these results in silicate glass were measured at the lower current density of 0.025A/cm^2 . However, the times to oxygen evolution in Table IX were still less than those for the silicate glass given in Table III even though the former values were measured at the higher current density of 0.05A/cm^2 . The same applies to the product of current density and time: the values for the disilicate were all lower than those found for the silicate glass.

As did the silicate glass previously studied, the present system recovered rapidly after dc polarisation. This is shown in Figure 6(b) where successive anodic tracks are recorded over a period of about 10sec after a dc polarisation of 30sec at 0.083A/cm²; the final shape and position of the oscilloscope track is similar to that of Figure A similar behaviour is recorded at the auxiliary electrode or 6(a). cathode, shown in Figure 6(c): the track is first displaced towards the lower left hand corner and then recovers to its original position and shape. This cathodic track is shown sloping downwards and away from the anodic track rather than close to it as in Figure 4(d), for clarity, and this was achieved by the simple method of reversing the polarity of the oscilloscpe amplifier internally. Next, after dc polarisation both the electrodes recover rapidly within a few seconds in sodium disilicate melts. Similar results were obtained when the polarisation with dc was extended to 5 minutes.

The oscillogram shown in Figure 6(d) is particularly interesting and was made using the second circuit. The cell was polarised initially for 30sec by passing a dc current through the cell of current density 0.083A/cm², and then photographs were rapidly taken of successive, single 100msec pulses discharging into a short circuit. Immediately after the dc polarisation the tracks appear near the upper left hand corner of the photograph, but as time goes on (a few seconds) the tracks move more towards the centre and eventually appear as those in Figure 4(e,) when no dc polarisation was used. The interesting thing about Figure 6(d) is that after dc polarisation there is no evidence at all of any of the detail which is present prior to oxygen evolution when the first circuit with pulsating current is used (Figure 6(b)) and the dc polarising conditions are the same. Indeed, the same tracks are completely featureless in Figure 6(d) in this part of the oscillogram and have exactly the same shape as if no dc polarisation was present: there is a steady smooth, curved rise in the voltage with no breaks or direction changes in the graph until oxygen evolution sets in. The decay time of the current is about 20msec into the short circuit and is thus similar to the decay time found in the silicate glass. Figure 6(e) and (f) show the decay tracks using the Pt reference electrode. It is clear from 6(f) that it is the potential of the auxiliary electrode which reverses direction on discharge into a short circuit; and from 6(e) that the discharge is slow into an open circuit.

Platinum-Sodium Diborate

In Figure 7 the oscillograms (a) and (b) are V/t and V/q traces, respectively. Both are featureless compared with the oscillograms in

Figure 6 for the sodium disilicate melt: there are no pronounced breaks in the curves corresponding to oxide film formation.

The effect of change in current density on the time to oxygen evolution is shown in Table X below:

Current Density	Time to Oxygen Evolution	Current Density x Time
A/cm ²	msec	C/apparent cm²
0.050	22	1.10×10^{-3}
0.083	20	1.66×10^{-3}
0.100	14	1.40×10^{-3}
0.133	13	1.73×10^{-3}
0.167	10	1.67×10^{-3}
0.267	6	1.60×10^{-3}
0.333	7	2.33×10^{-3}

Table X Effect of Current Density on Time to Oxygen Evolution in Sodium Diborate at 1200°C

The oxygen evolution voltages decrease with increasing current density, as usual, and the product of the current density and time is roughly constant as before.

Figure 7(c) shows the oscillogram at the large current density of $0.200A/cm^2$ and it can be seen that now there are present quite pronounced breaks in the curve. These breaks also occur when the experiment at the lower current density of $0.83A/cm^2$ is repeated after all the experiments at the higher current densities needed to construct Table X had been carried out; this is seen by a comparison of Figures 7(a) and (d). The latter oscillogram shows a pronounced break, while the former does not; the time to oxygen evolution for 7(d) is smaller - about 4msec - compared with a value of about 20msec for 7(a); the oxygen evolution is large - about 1.2V - for 7(d) compared with about 0.55V for 7(a). When the charge required for oxygen evolution is calculated from 7(d) it works out at about 0.33×10^{-3} C/apparent cm² and this is considerably less than the value of 1.66×10^{-3} recorded in Table X for the oscillogram 7(a).

The effect of change in temperature on the time to oxygen evolutionat a constant current density is shown in Table XI:

Temperature	Time to Oxygen Evolution	Current Density x Time
°C	msec	C/apparent cm²
900	21	1.05 x 10 ⁻³
1000	22	1.10×10^{-3}
1100	26	1.30×10^{-3}
1200	21	1.05×10^{-3}

Table XI Effect of Temperature on the Time to Oxygen Evolution in Sodium Diborate at a Current Density of 0.05A/cm²

With change in temperature at the same current density the time to oxygen evolution and the product are fairly constant as for the disilicate,

An experiment was carried out in which the cell was subjected to adc 5min polarisation immediately after which the anodic and cathodic V/t oscillograms were recorded. These are shown in Figure 7(e) and (f), and it can be seen that the anodic oscillograms of 7(e) ressemble those in 7(d) and not those in 7(a) which were recorded at the same current density at the start of the series of measurements. The upper track of Fig 7(e), when the voltage was measured across the whole cell, is permanently displaced above the lower track measured across the working and reference electrode: the reason for this is that the cathodic track is distorted by the polarisation as is clear from Figure 7(f). This distortion in the cathodic track remains for some time: the track had not returned to its original position, which is similar in shape to the cathodic track shown in Figure 7(c), 5min after the end of the dc polarisation.

This prolonged distortion suggests that there is some permanent polarisation occurring at the cathode, and this is borne out by the photograph shown in Figure 7(g). This is a photograph of the cell after the experiment and there is evidently some permanent reaction product round the cathode – that is, at the electrode on the left hand side of the picture. Microscopic and Energy Dispersive Analysis showed this to consist of discrete Pt particles about 0.7 μ m in diamater. Such reaction products were never observed after prolonged experiments followed by pulsating current electrolysis in disilicate melts.

Platinum-Sodium Diphosphate

While the oscillograms for sodium disilicate and diborate have some similarities the oscillograms for the sodium phosphate melts are completely different. Figure 8(a) shows a V/t oscillogram in this electrolyte at a temperature of 1200° C and a current density of $0.083A/cm^2$. The difference between this photograph and those for the disilicate (Figure 6(a)) and the diborate (Figure 7(a)) is immediately apparent: there is no linear rise to a short plateau followed by another rise to oxygen evolution; on the contrary the voltage rises slowly over a relatively extended time period and then rises rapidly and directly to oxygen evolution. There are none of the breaks and plateaux on the graphs before oxygen evolution finally occurs which there are with the disilicate and diborate melts (in the later ones, at least).

The times to oxygen evolution are different also. Table XII is a table giving the change in this parameter with change in current density; the values given in the table are the means from several oscillograms.

Time to Oxygen Evolution	Current Density x Time
msec	C/apparent cm²
40	$0.68 \times 10^{-3}_{-3}$
24	0.79×10^{-3}
11	0.73×10^{-3}
9	0.75×10^{-3}
5.3	0.53×10^{-3}
4.7	0.63×10^{-3}
3.3	0.55×10^{-3}
2.4	0.48×10^{-3}
1.8	0.48×10^{-3}
1.4	0.47×10^{-3}
	Time to Oxygen Evolution msec 40 24 11 9 5.3 4.7 3.3 2.4 1.8 1.4

Table XII Effect of Current Density on Time to Oxygen Evolution in Sodium Diphosphate at 1200°C

It is clear that the time to oxygen evolution decreases with increasing current density as it did in the sodium disilicate and the diborate melts, and also that the product of current density and time does not change greatly although there is a slight drift downwards in value as the current density increases. However, the times to oxygen evolution for the diphosphate at corresponding current densities are much smaller, and the product of current density and time for the diphosphate is about half the size it is for the disilicate and the diborate.

The behaviour with change in temperature is similar in this electrolyte to that in the first two electrolytes studied. Table XIII gives the change in oxygen evolution time with increase in temperature.

Temperature	Time to Oxygen Evolution	Current Density x Time		
°C	msec	C/apparent cm ²		
600	25	1.25×10^{-3}		
700	15	0.75×10^{-3}		
800	9	0.45×10^{-3}		
900	8.5	0.43×10^{-3}		
1000	10	0.50×10^{-3}		
1100	9.5	0.48×10^{-3}		
1200	10.5	0.53×10^{-5}		

Table XIII Effect of Temperature on Time to Oxygen Evolution in Sodium Diphosphate at a Current Density of 0.05A/cm²

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The sodium diphosphate melted at a lower temperature than the disilicate and the diborate, and it was possible to make measurements at 600° C with this electrolyte. Apart from the measurements at the lowest temperatures of 600 and 700°C, the times to oxygen evolution are of the same order and the product of current density and time fairly constant; Figure 8(b) is an oscillogram at 600° C.

The time to oxygen evolution is not the only measurement in the diphosphate melt to give rise to discrepancies compared with the other two melts: the oxygen evolution voltage does this also. In Table XIV are given the oxygen evolution voltages for the three electrolytes at various current densities, measured, of course, against the Pt reference electrode.

Table XIV Comparison of Oxygen Evolution Voltages at Various Current Densities in Sodium Disilicate, Diborate and Diphosphate at 1200°C

Current	Oxygen Evolution	Oxygen Evolution	Oxygen Evolution		
Density	Voltage	Voltage	Voltage		
	Na ₂ 0.2SiO ₂	Na20.2B203	Na20.2P205		
A/cm ²	V 2	V	V 2 3		
0.017	0.6	0.48	0.44		
0.033	0.8	0.46	0.48		
0.050	0.7	0.48	0.48		
0.067	0.7	0.62	0.46		
0.083	0.9	0.76	0.48		
0.100	0.9	0.90	0.52		
0.133	0.9	1.05	0.50		
0.167	1.0	1.05	0.52		
0.200	1.1	1.10	0.52		
0.277	1.1	1.15	0.51		
0.333	1.1	1.20	0.50		

The difference between the three is immediately apparent: while the oxygen evolution voltages for the disilicate and the diborate increase with increasing current density, the values for the diphosphate hardly change and are much smaller than the other two at all current densities and do not increase much with increase in the c.d.

These smaller values of the oxygen evolution voltage persist for diphosphate melts when the temperature is varied. In Table XV the values of the oxygen evolution voltages are given for the three electrolytes from 600 to 1300° C, measured against the Pt reference electrode. The values for the disilicate and diborate melts decrease with increase in temperature as usual, but the oxygen evolution voltages in the diphosphate melts are again much smaller at all temperatures and show only a very slight drift downwards above 800° C.

Temperature	Oxygen Evolution Voltage Na ₂ 0.2SiO ₂	Oxygen Evolution Voltage Na ₂ 0.2B ₂ 0 ₃	Oxygen Evolution Voltage Na ₂ 0.2P ₂ O ₂	
°C	V V	V	V Z J	
700	_	_	0.62	
800	_	-	0.54	
900	1.3	1.2	0.52	
1000	1.2	1.0	0.48	
1100	1.04	0.6	0.48	
1200	0.92	0.48	0.44	
1300	0.72	_	-	

Table XV Comparison of Oxygen Evolution Voltages at Various Temperatures in Sodium Disilicate, Diborate and Diphosphate at a Current Density of 0.05A/cm²

The lower values of the oxygen evolution voltages in sodium diphosphate may have something to do with the decay characteristics of platinum electrodes observed in this electrolyte. In Figure 8(e) the decay after a l00msec pulse at $0.083A/cm^2$ is shown into an open circuit, and also into a short circuit, Figure 8(f). Comparison with Figures 4(a) for the soda lime silicate glass melt shows that the decay in the diphosphate is slower than that in the silicate glass melt when discharge is into an open circuit. The most unusual feature, though, is that the voltage reverses polarity when the cell is discharged into a short circuit in the diphosphate melt (Figure 8(f); when a similar discharge occurs in the soda lime silicate glass melt it is the current which reverses polarity (Figure 4(e)).

Finally the behaviour after dc polarisation was examined in the diphosphate electrolyte. Figure 8(c) is a V/t oscillogram taken 10 minutes after a 30sec dc polarisation at 0.083A/cm², and it can be seen, by comparison with Figure 8(a), that the lower track for the working-reference electrode combination has returned to its original shape and position - though with a lengthening of the period before oxygen evolution - while the track for the working-auxiliary electrode combination has not done so. Again, as in the case of the diborate, this is due to a permanent polarisation of the cathode as is clear from Figure 8(d): the track has the sharp outline characteristic of a polarised cathode compared with the non-polarised cathode track shown in Figure 8(a). When the cell was removed from the furnace it was found that the cathode was surrounded by a layer of reaction product similar to that shown in Figure 7(g) for the diborate melt.

The results of a more detailed dc polarisation experiment on both the easily depolarised disilicate melt and the hard to depolarised diphosphate are given in Table XVI:

Polarisation Conditions Na ₂ 0.2SiO ₂	Cell Volts V	Anodic Volts V	Cathodic Volts V	Polarisation Conditions Na ₂ 0.2P ₂ O ₅	Cell Volts V	Anodic Volts V	Cathodic Volts V
Before After 5min dc	1.94	1.04	0.90	Before After 30sec dc	1.24	0.64	0.60
at 0.083A/cm ²	1.08	1.04	0.04	at 0.083A/cm ²	0.68	0.64	0.04
2min later	1.43	1.07	0.36	2min later	0.70	0.66	0.04
5min later	1.80	1.00	0.80	5min later	0.68	0.64	0.04
10min later	1.84	1.00	0.84	10min later	0.74	0.64	0.10

Table XVI Recovery after DC Polarisation of Cell, Anodic and Cathodic Voltages for Sodium Disilicate, Diborate and Diphosphate melts at 1200°C and 0.083A/cm²

The disilicate was polarised for the longer time of 5min at 0.083 A/cm^2 dc while the diphosphate was given a shorter polarisation of only 30sec at the same current density. To study the recovery of the electrodes after these polarisations the anodic and cathodic voltages were measured at intervals - the cathodic voltage chosen being that corresponding to the steady, horizontal part of the track. In all cases the cell voltage recorded is the calculated arithmetical sum of these two values.

In the disilicate the cell voltage drops under dc polarisation and this is due to a reduction in the anodic voltage- and a much larger reduction in the cathodic voltage from 0.90 to 0.04V. On removal of the direct current input the anodic voltage recovers almost immediately and the cathodic voltage also in about 2-5min to near its original value (column 4). The behaviour in the diphosphate is completely different. The cathodic voltage drops from 0.6 to 0.04V after only 30sec dc polarisation and has still only recovered to 0.1V 10minutes later (column 8); the anodic voltage hardly changes.

DISCUSSION

The V/t oscillogram of Figure 4(b) shows clearly that the time to oxygen evolution is 2.6msec at a current density of $0.6A/cm^2$ and a temperature of $1350^{\circ}C$. This is greater than the lmsec half cycle time of a 500Hz sine wave and less than the l0msec half cycle time of a 50Hz sine wave. Consequently oxygen gas bubbles do not have time to form at the platinum electrodes during the positive half cycle of a 50Hz electrical input before the polarity is reversed, but they do have time to do so during the positive half cycle of a 50Hz input before its polarity is reversed. Thus the fact, recorded in reference (1), that platinum electrodes do not corrode appreciably at 1350°C and $0.6A/cm^2$ with electrical inputs of frequency 500Hz but do corrode extensively with a similar input at a frequency of 50Hz Of course, when the temperature and current density are both decreased we would expect the time to oxygen evolution to increase, and that this does actually occur is clear from the oscillogram of Figure 4(c) at the lower temperature of 1200° C and the lower current density of $0.083A/\text{cm}^2$: the time to oxygen evolution, measured from 4(c), is 50msec.

The current density seems to affect the the time to oxygen evolution more than the temperature. Thus, from Table II, the time to oxygen evolution decreases twelve-fold - from 122 to 10msec - when the current density is increased from 0.017 to $0.333A/cm^2$; and it then decreases a futher seven-fold - down to 1.4msec - when the current density is further increased to $1.333A/cm^2$. The behaviour with change in temperature is different: apart from the value at the lowest temperature of 900°C, the time to oxygen evolutionis remarkably similar at all the other temperatures at the fixed current density of $0.025A/cm^2$. This lack of variation with temperature is unusual in an electrochemical reaction in molten glass.

The really remarkable features of both Tables II and III, however, are the figures shown in columns 3 of both tables which give the products of the current densities and the time to oxygen evolution. Apart from the two values at the lowest and the highest current densities in Table II, these remain constant within the limits of experimental error during a forty-fold change in current density from 0.025 to 1.000A/cm². The same is true when the temperature is changed: from Table III the product of current density and time remains constant within the limits of experimental error as the temperature changes from 900° to 1350°C.

The constancy of the product of current density and time means that the same quantity of electricity is deposited during the electrochemical reaction under all the different conditions of current density and temperature in Tables II and III, and implies that exactly the same electrochemical reaction is occurring under all these conditions. The most likely electrochemical reaction to be occurring in the molten glass is the discharge of non-bridging oxygen ions during pulsating current electrolysis to give oxygen gas.

This unusual phenomenon of constant charge deposition under a wide range of experimental conditions is not confined to pulsating current electrolysis, however, but also occurs with ac sine wave inputs.

Thus Eden(6) electrolysed soda lime silicate glass between platinum electrodes at 1290° C under ac conditions and found that when the current density was high $-5A/\text{cm}^2$ - then the discolouration of the glass melt started at the high frequency of 2000Hz. The cycle time is then 0.5msec, the charge deposited per cycle is 2.5 x 10 ° C/apparent cm², and this is the charge required for extensive corrosion to start. In our own work on the corrosion of platinum in molten soda lime silicate under ac conditions described in reference (1), we found that discolouration of the melt started at 250Hz at the lower current density of 0.6A/cm² at a temperature of 1350°C. Then the cycle time was 4msec and the charge necessary for attack to occur was 2.4 x 10^{-3} C/apparent cm². We conclude that this is the quantity of electricity required for extensive attack to occur in molten soda lime silicate glass under ac conditions of electrolysis.

It is also the amount required for extensive attack to occur in a different type of glass with a different modifying oxide-high flint glass with composition 58% SiO_2 , 40% PbO, with minor amounts of the alkali metal oxides. This was shown by Hupfer (7) who electrolysed this glass at 1100°C with ac between platinum electrodes. He also found that at lower current densities the frequency had to be correspondingly lower - and thus the cycle time longer - for attack to occur. Thus at frequencies of 250, 500 and 1000Hz he found that the minimum current densities for attack and darkening to occur were 0.625, 1.25 and 2.5A/cm², respectively, and in each case these values correspond to the deposition of a quantity of electricity of 2.5 x 10^{-3} C/apparent cm². He also noted that the start of this attack coincided with the start of vigorous evolution of oxygen gas at the electrodes.

It is instructive to compare this figure of 2.5 x 10^{-3} C/apparent ${\rm cm}^2$ obtained with ac sine wave inputs with the values found in column 3 of Table II for pulsating current inputs. As we have seen these values are reasonably constant and an average value taken from all the recorded values in column 3 is 3.3 x 10^{-3} C/apparent cm². Considering the great difference between the pulsating current conditions and the sine wave alternating current conditions the agreement between the two figures of 3.3 x 10^{-3} and 2.5 x 10^{-3} C/apparent cm² is good. It could be argued, of course, that oxygen gas evolution is only possible_during the positive half cycle and that hence the figure of 2.5×10^{-3} should be halved. However, if there is any irreversibility in the process - oxygen gas not removed during the negative half cycle - then this reversal of current will not affect the evolution of oxygen gas, and certainly not the corrosion. Furthermore, the analogy should not be pushed too far: the quantity, current density x time was called by Hupfer the density of charge and was used by him purely as a measure of the onset of corrosion.

We can say that for corrosion in soda lime silicate glass and flint glass under ac sine wave conditions that 2.5×10^{-3} C/apparent cm² of electricity is the minimum required for corrosion of the platinum to occur associated with the evolution of oxygen gas; and that 3.3×10^{-3} C/apparent cm² is the minimum quantity of electricity for oxygen evolution to occur under pulsating current conditions. It would thus seem that under both pulsating current and ac sine wave conditions basically the same overall electrochemical reaction is occurring - and this is the discharge of, probably, non-bridging oxygen ions to form oxygen gas which then causes extensive attack on the hot platinum metal. Whether or not corrosion actually occurs is determined by the relationship between the time to oxygen evolution determined by the pulsating current method and the half cycle time of the ac input as we described at the start of this discussion inconnection with the corrosion results at 1350°C and a current density of $0.6A/cm^2$.

We consider now some papers of Hickling who worked at room temperature in aqueous solutions, in order to compare his results with our results at high temperatures. In Figure 9(a) is shown an oscillogram he obtained with a platinum wire anode in $N-H_2SO_4$ at a current density

of 0.01A/cm^2 (8). We will discuss the details of this photograph later, but the feature which we wish to consider now is the overall guantity of electricity required for oxygen evolution to occur. In the original photograph it was arranged that a displacement of lmm on the horizontal axis corresponded to IV. Thus, knowing the value of the series capacitor - $6\mu F$ - and the fact that Figure 9(a) is a two times reduction of the original photograph, it is possible to calculate the amount of electrical charge deposited from the start of the track to the onset of oxygen evolution at the second, upper horizontal plateau. This works out at 3.06 x 10^{-3} C/apparent cm² and, astonishingly, is almost equal to the mean value of 3.3 x 10^{-3} C/apparent cm² found from Table II for molten soda lime silicate glass at 1200°C. Furthermore the values for the charge required for oxygen evolution in neutral and alkaline solution (N-NaOH) work out at 3.06 x 10^{-3} and 3.24 x 10^{-3} C/apparent cm², respectively. This close agreement between the two sets of results in aqueous solution at room temperature and in molten glass at 1200°C strongly suggests that the electrochemical reaction occurring in the two systems is basically the same: the discharge of monovalent hydroxyl ions or of bivalent, non-bridging oxygen ions to give diatomic oxygen gas.

This agreement between the results in aqueous solutions and in molten glass is not confined to platinum but occurs also for other noble metals such as gold (9), and also the more reactive metals: nickel (10), cobalt (11) and silver (12), that Hickling and his co-workers studied. In Table XVII we have calculated the quantity of electricity required for the onset of oxygen evolution at these different metals - Pt, Au, Ni, Co, Ag and also Cu (13) invarious electrolytes of different pH. For the more reactive metals only alkaline NaOH solutions have been considered -apart, that is, from various buffer solutions which will be discussed later in connection with the diborate and diphosphate results we found in molten glass. We have quoted only alkaline solutions because Hickling found that in acid solutions all the metals, apart from platinum and gold, simply dissolved at their respective dissolution A further complication is that some of the metals used potentials. Co, Ag and Cu - were used in plated form and the accessible or true surface area was many times greater than the geometric, apparent surface area (see Table XVII, column 5). For platinum and gold wire electrodes. Hickling took the ratio of the true to the apparent surface area to be 2, and we have used this value as our standard. We have reduced the experimentally determined values of the charge for oxygen evolution recorded at the higher true surface areas to this common ratio of 2 even though the actual ratio of the true to the apparent surface area for a particular metal may be much larger. In this way we compare the different metals on the same basis, and it is these reduced values of the quantity of electricity required for oxygen evolutionwhich are given in column 4 of Table XVII.

From an examination of the results in N-NaOH for all the metals, it is clear that the quantity of electicity required for oxygen evolution is of the same order for all these metals except copper when it is much larger. Hickling and Taylor (13) concluded that a 6 - 7 molecule thick poorly protective layer of CuO formed on the copper electrode during electrolysis and then dissolved in the N-NaOH. Support for this came from the experimentally observed facts that the oscillograms were greatly dependent on changes in current density, temperature and concentration of NaOH, unlike the other metals: Table XVIIshows that as the concentration of NaOH is decreased to 0.3N the charge necessary for oxygen evolution decreases to a figure of 3.65×10^{-3} C/apparent cm² which is near the usual figure found for the other metals in N-NaOH. The figures shown in Table XVII for gold electrodes are less than those for platinum because, for gold, the initial part of the oscillogram due to adsorbed hydrogen is absent.

This remarkable similarity in the charge required for oxygen evolution to start strongly suggests that the process occurring at all the metals is basically the same - in alkaline solutions, at least (but modified by the high solubility of the CuO in the case of copper)-and consists in all cases of the formation of an oxide film on the metal just prior to the start of oxygen gas evolution.

When the alkalinity of the electrolyte is decreased by using buffer solutions and, ultimately, acid solutions, the value of the charge required for oxygen evolution usually decreases for the more reactive metals however, for the noble metals - platinum and gold - this does not occur, and the value of the charge remains the same in alkaline, neutral and acid solutions. Thus, narrowing down the discussion to the noble metals, and platinum in particular, we conclude that the quantity of electricity required for oxygen evolution to occur is the same for platinum electrodes in aqueous solutions (alkaline, neutral and acidic) and in molten glass at 1200°C. Since the overall electrochemical reactions are the same, we consider that the detailed steps of these reactions must have great similarities in aqueous solutions and in molten glass, and we now compare these detailed steps for platinum electrodes in aqueous solutions and in molten glass.

The two oscillograms which we choose to compare these two systems are the V/q oscillograms for Pt in $N-H_2SO_4$ at 18°C of Figure 9(a) and that for Pt in molten glass at 1200°C shown in Figure 4(g). Hickling divided the track of Figure 9(a) into three stages before oxygen evolu-Stage 1 consisted of the initial, curved part of the tion started. trace below about 0.25V, and he ascribed this to the ionisation of free and adsorbed hydrogen following Butler and Armstrong (14). Stage 2, the steeply ascending part between 0.25 and 0.87V, he ascribed to the charging of an electrical double layer of capacity $200\mu F/apparent \ cm^2$. Stage 3 is the most important part of the track and started at a potential of 0.87V. Grube (15) had found that the reversible potential of platinous oxide (PtO) against platinum in 2N-sulphuric acid was 0.9V and this, by applying the usual equation for the variation of potential with hydrogen ion concentration, gave a static potential of 0.88V in IN-H₂SO₄. Hickling thus concluded that the break recorded in the oscillogram at 0.87V corresponded with the onset of PtO formation on the electrode. This was also true for neutral and alkaline solutions (Table XVII) because the potentials of the breaks in the oscillograms of 0.50 and 0.06V, respectively, recorded for these solutions corresponded closely

with the static oxide potentials of 0.49V and 0.07V calculated from the results of Grube in these electrolytes.

The lengths of the tracks from this break in the curve up to the start of oxygen evolution are extremely important. The quantity of electricity calculated from this is found to be $1000\mu C/apparent cm^2$ for all the solutions - acid, neutral and alkaline - and this is sufficient for the liberation of approximately 3.1 x 10^{15} atoms of oxygen. Taking the specific gravity of platinum to be 21.4, the diameter of the platinum atom is calculated to be approximately 2.5 x 10^{-8} cm, and hence there should be about 1.6 x 10^{15} atoms of metal per square cm at the Hickling took the ratio of the true to the apparplatinum surface. ent surface area to be 2, and this was based on the work of Bowden and Rideal (16) who compared the capacities at different metal electrodes with that at a mercury electrode in the same solution for which the true surface area was assumed equal to the apparent surface area. Using this true surface area, the number of platinum atoms on this accessible or true surface area of 3.2 x 10^{15} is almost equal to the number of atoms of oxygen - 3.1 x 10^{15} - liberated by electrolysis, and thus stage 3 was taken to correspond to the formation of a monomolecular layer of platinous oxide, PtO, on the surface of the electrode.

We now ask how these conclusions compare with the results we have found at platinum electrodes in molten glass. In Figure 4(g) there is, of course, no part of the curve corresponding to the ionisation of hydrogen stage in aqueous solutions, but we may still divide the track into three stages before oxygen evolution starts. First, there is stage 1, a rapidly ascending region which extends to a voltage of about 0.45V when there is a break in the curve which corresponds to the onset of stage 2. During this stage the potential grows more slowly and the track extends to a considerable length across the photograph. Eventually, however, there is another break in the curve when the track starts to ascend rapidly again; this is denoted as stage 3 and immediately preceeds oxygen evolution which starts at about 1.2V.

We ascribe stage 1 (which corresponds to Hickling's stage 2) to the formation of an electrical double layer as in the aqueous case. By measuring the x-axis displacement and recalling that the series capacitor used is 100μ F, the charge accumulated in this stage is calculated to be 400μ C and, by dividing by the voltage rise of 0.45V to the start of stage 2, the capacity of the double layer is calculated to be 889μ F or 2963μ F/apparent cm². This is much greater than the $200-300\mu$ F/apparent cm² found by Hickling (8) but is not surprising in view of the difference between the dielectric constants of the two systems (100 and 6μ Fused).

Table IV shows that the value of the double layer capacity remains fairly constant at current densities below $0.333A/cm^2$, but that after this it drops. This is not surprising inview of Figure 4(i) at the high current density of $0.333A/cm^2$: the track is curved in the stagel region and hence the double layer capacity concept is of doubtful validity at and above this current density. This is also a feature of Figure 4(j) and may explain, to some extent, why the double layer capacities at the lower temperatures of 900° and 1000°C are different from the rest at higher temperatures in Table V.
The start of stage 2 occurs at a voltage of 0.45V where the track inFigure 4(g) changes direction, and we now ask what this means. We may calculate the voltage required for the formation of the oxide PtO₂ from the thermodynamic work of Alcock and Hooper (17) on the formation of this oxide. They measured the vapour pressure of PtO₂ at several temperatures between 1100°C and 1550°C and expressed their results by the free energy equation:

$$\Delta G^{O} = 39270 \pm 340 - T(0.93 \pm 0.21) \text{ cal/mole.}$$
[1]

At a temperature of 1200°C (1473°K) ΔG^{O} lies between 38,540 and 37,251 cal/mole. and using the relationship:

$$\Delta G^{O} = n E^{O} F, \qquad [2]$$

the voltage at which the reaction:

$$Pt + O_2 = PtO_2$$
[3]

would be expected to occur lies between 0.42 and 0.40V. These results have been confirmed by Schafer and Tebben (18): at 1208°C they measured a free energy of formation of PtO_2 of 37,777 cal/mole. corresponding to a potential of 0.41V. Since the voltage at which the break in the curve occurs is 0.45V on the oscillogram, the agreement between prediction and experiment is good, and this supports the conclusions from the work of Alcock and Hooper. These calculations thus strongly suggest that the oxide of platinum which forms at the break in the oscillogram track is the oxide PtO_2 .

From Table IV it is clear that the voltage at the start of stage 2 increases with current density away from the reversible, thermodynamic value of Alcock and Hooper. This is to be expected as the system will depart more and more from the reversible state as the current density is increased. Table V shows, on the other hand, that this voltage decreases with increase in temperature and this not unexpected. However, the equation [1] of Alcock and Hooper predicts that the voltage of PtO_2 formation should vary but slightly with increase in temperature: at $1100^{\circ}C$ the mean calculated value is 0.403V, and at $1350^{\circ}C$ the value is 0.407V.

We now enquire how much of the oxide, PtO_2 is formed on the electrode surface during stage 2. From the measurements from Figure 4(g) we found that the charge accumulated during stage 2 was 2000μ C/apparent cm². Using a value of the Faraday of 96,500 C/gm equivalent and Avogadro's Number of 6.023×10^{23} atoms/gm atom, we calculate that this is sufficient for the liberation of 6.2×10^{15} atoms of oxygen. Taking the specific gravity of platinum to be 21.4 and its atomic weight as 195.23 we calculate, using a solid sphere model, that the diameter of the platinum atom is approximately 2.5×10^{-8} cm and therefore there should be about 1.6×10^{15} atoms of metal per geometric cm² of surface. Taking the ratio of the true or accessible surface area to the apparent or geometric surface area to be 2, after Hickling, we have that there are 3.2×10^{15} atoms of platinum per true cm². Thus for every platinum atom on the surface there are two oxygen atoms and stage 2 thus corr-

-espond to the formation of a monomolecular layer of PtO_2 on the platinum surface. This is in contrast to the case in aqueous solution where a monomolecular layer of the lower oxide, PtO, forms. However, since both oxides are monomolecular layers, the times to oxygen evolution will be the same in each case, and this explains why the figures in column 3 of Table II for the high temperature system and column 4 of Table XVII for the aqueous system N-NaOH are of the same order. The formation of these oxide films - PtO₂ in the molten glass case, and PtO in the aqueous case - explains why the onset of oxygen evolution is delayed during electrolysis; and the occurrence of this delay also explains why it is that corrosion of the Pt by oxygen gas occurs with a 50Hz ac input but not with a 500Hz input (see reference (1) and also Figure 4(b).

The position is not quite as clear cut as it looks, however, in the light of some later work by El Wakkad and Emara (19) on the platinum electrode in solutions of varying pH. In order to determine more accurately what is happening during the various stages of the overall process, they passed constant currents of very low current density typically 17 μ A/apparent cm² - using freshly plated platinised platinum electrodes of geometrical surface area 1.8cm². However they, in this work found a ratio of true to apparent surface area of 180 and so their current density was the extremely low one of 0.094 μ A/cm². They used a direct potentiometric method to measure the voltage and they found that at the low current densities they were using they took over an hour to plot the full graph.

One of their graphs for $0.1N-H_2SO_4$ is shown in Figure 9(b), curve A. It can be seen from this figure that its general features agree with the oscillograms of Hickling shown in Figure 9(a). However, in Figure 9(b) there are two breaks in the curve before oxygen evolution occurs and not one, as in Figure 9(a) at a much higher current density, and using the oscilloscopic method. These two breaks occurred at potentials of 0.82 and 1.05V, respectively, and these values agree well with the static equilibrium potentials of 0.82V and 1.1V calculated from the work of Grube (15) for the system Pt-PtO and Latimer (20) for the system Pt0-PtO_2. It appears, therefore, that PtO is not the only oxide which can form at the platinum electrode during pulsating current electrolysis in aqueous solutions, but that PtO_2 can form also as in the molten glass case.

This oxide is unstable, however: El Wakkad and Emara studied the decay of polarisation after oxygen evolution had been attained and the curve they obtained is shown as curve B in Figure 9(b). This shows that when the circuit is broken the potential drops to a break in the curve at just under 1.0V where the unstable PtO_2 decomposes to PtO.

The potential then levels out at about 0.8V which is the potential of the couple Pt-PtO, and then this oxide persists. When oxygen evolution has occurred and the anodically polarised anode is made cathodic then the curve C of Figure 9(b) is obtained. This shows that now there is only one break in the curve starting at about 0.7V and corresponding to the reduction of PtO. This reduction is over in a short time and then the potential drops rapidly to zero. These results

show clearly that a reverse current polarisation - such as that which occurs with the pulsating current method - is necessary to strip all trace of the oxide film from the surface, and that it is not sufficient to rely only on the natural discharge for this to occur. The same two oxides were also found in neutral and alkaline solutions - at different electrode potentials, of course.

In addition to this work, El Wakkad and Emara also used the oscilloscopic method of Hickling at Pt electrodes in $0.1N-H_2SO_4$, using Pt wire electrodes of apparent area $0.1cm^2$ and a current density of $100\mu A/$ apparent cm^2 . They found that the formation of PtO occurred at a potential of 0.8V, and that of PtO₂ at 1.07V.

There is some doubt about which process is occurring in stage 3. One possibility is that higher oxides of platinum form. This was considered by Schneider and Esch (21) by measuring the vapour pressure of platinum oxides formed by passing a mixture of argon and oxygen over platinum metal heated to 1200° C. They found that PtO₃ formed between oxygen pressures of 311 and 810mm Hg and PtO₄ at pressures greater than 890mm. The measured free energies of formation of the two oxides were 48,609 and 60,095 cal/mole, respectively, and these correspond to voltages of 0.53 and 0.65V. As stage 3 starts at a voltage of about 0.7V from Figure 4(g) this suggests that the formation of PtC₄ during stage 3 is a possibility.

This conclusion is not supported by what is occurring during stage3 however, with respect to the quantity of electricity passed. The charge accumulated during this stage is 667µC/apparent cm², corresponding to the liberation of 2.0 x 10^{15} atoms of oxygen per apparent cm² or 1.0 x 10^{15} atoms of oxygen per true cm². Since there are 1.6 x 10^{15} atoms/cm² at the platinum surface, this can only add one atom, at most, to the PtO2 to give PtO3. Since the thermodynamic calculations do not favour the formation of this oxide, but rather the formation of PtO_4 , we are forced back to the conclusion that another, higher oxide is not formed during stage 3 but that this stage corresponds to the formation of an additional monatomic layer on top of the PtO2 film already present on the electrode. In addition, the curve is steep during this part of the track and ressembles the rapidly rising part due to the charging of the double layer as is apparent from an examination of Figure 4(g). Not only this, but from Table IV, column 5, the gradient of stage 3 is one of the most stable parameters found and this contrasts with the variability of the charge increment shown in column 4 which decreases at the higher current densities, and which is associated with the growth of the PtO, film. Thus the evidence given above would seem to suggest that, on balance, additional oxides do not form during stage 3 of Figure 4(g) for a platinum electrode in molten silicate glass, but that rather the formation of an additional double layer of oxygen ions on the PtO, film already on the electrode is favoured prior to oxygen evolution.

It is seen from an examination of Table IV that the gradient of stage 3, measured in $\mu C/V$, is among the most stable parameters measured as the current density changes, and this true also of the oxygen evolution voltages given in column 6 of Table IV. Below a current density

of $0.25A/cm^2$ these hardly change at all, but there is a small, progressive increase after this at high current densities; no linear plots of V against lnI or I could be obtained from this data, however.

In an experiment on reproducibility using 22 different oscillograms at the same current density of 0.083A/cm², it was found (1) that the oxygen evolution voltage had the smallest coefficient of variation of 2.3% of any of the parameters measured; and the 95% Confidence Interval for this measurment was (1.19, 1.21V). This constancy of the oxygen evolution voltage under pulsating current conditions contrasts strongly with its variability with dc inputs. For example, with a pulsating current of 0.083A/cm^2 the oxygen evolution voltage was 1.20V, while with dc it was 2.9V; with a pulsating current of 0.167A/cm^2 the voltage was again 1.20V, while with dc it was 9.3V. There thus seems to be a large amount of polarisation at the electrode, using dc - probably due to the accumulation of oxygen gas round the electrode due to the high viscosity of the melt. This does not occur to the same extent during the pulsating current electrolysis because of the shortness of the oxygen evolution plateaux, and the fact that the electrode reactions are reversed and the electrode returned to its original condition every cycle. Thus the pulsating current method gives much more realistic and reliable values for the oxygen evolution potentials than does the dc method.

The work we have done indictates that the platinum electrode is a reliable reference electrode. When the three tracks on the photograph of Figure 4(d) were discussed it was noted that the sum of the Y-coordinates for the trace of the working against the auxiliary electrode was equal to the sums of the values for the tracks of working against reference electrode and reference electrode against auxiliary electrode. This is to be expected, of course, but the important observation from these traces is that there is no curvature in opposite senses in the two latter tracks, particularly towards the end of the pulse when oxygen evolution is occurring. If such an effect had been observed it would have meant that the potential of the platinum wire electrode was This is because if it does change at all in whichever dirchanging. ection, positive or negative, it must change in the opposite senses with respect to the working and the auxiliary electrodes. The fact that no such curvature is observed means that the potential of the platinum electrode remains constant during the electrolysis.

This constancy of the electrode potential of the platinum electrode means that it may be used as a reference electrode, and indeed many authors have so used it - for example, Plumat and his collaborators (22-24) in molten glass, and Janz, Cohen and Segusa (25) in molten carbonates. If the potential of the platinum electrode is taken at all temperatures to be zero then the voltages of the working and auxiliary electrodes are their potentials on the platinum electrode scale. Α drawback to this is that the variation of the potential of the platinum electrode with concentration of oxygen ion is not known in molten salt solutions. Its great virtues are its simplicity and robustness comppared with reference electrodes based on yttria/zirconia or calcia/ zirconia. Furthermore there are drawbacks to using these reference electrodes because Tran and Bungs (26-28) concluded from an extensive

investigation that the Y_2O_3/ZrO_2 reference electrode was the only one that could be used in molten glass between 1000°C and 1350°C since the CaO/ZrO₂ electrode corroded rapidly and the MgO/ZrO₂ cubic structure was unstable below 1400°C.

One of the most important features of the pulsating current method is that the oscilloscope tracks are very stable: they may be recorded hours or days after the start of electrolysis with the same result. They also recover rapidly and permanently after dc polarisation. Figure 4(h) shows successive tracks recorded after a 30sec dc polarisation. Starting from the upper, left-hand corner of the photograph, the curves move down slowly across the screen towards the centre until they occupy a central position which corresponds with the track before the dc polarisation and where they remain indefinitely.

These curves deserve futher consideration. The first couple of curves photographed after the dc polarisation have very little detail in them, but appear rather like the single pulse tracks shown in Figure 4 (e) and (f). As time goes on breaks begin to appear in the tracks, and they grow larger and less steep. Since the dc polarisation liberates large amounts of oxygen at the electrode it seems not unreasonable to suppose that for the first few traces the large reverse current is removing this oxygen either in the form of oxygen ions or adsorbed oxygen ions, or even PtO3 if, indeed, it forms on the electrode. Consequently there is not much reverse charge left to remove the monomolecular layer of PtO2 which is present on the electrode and so it is only partially removed. When the next positive pulse is applied most of the PtO2 oxide film is still on the electrode, and so the length of stage 2 - during which the PtO_2 film is formed - is short. Eventually, as the excess oxygen gas disappears, the reverse charge strips away more and more of the oxide film and so, during the next positive pulse, more and more PtO₂ oxide film is formed: thus the stage 2 part of the track lengthens. Ultimately the track settles down to an equilibrium condition in which the monomolecular layer of PtO₂ is formed and stripped completely away every cycle. It should be noted that the gradient of of stage 2 changes during recovery from the dc polarisation - it becomes less steep - while the gradient of stage 3 remains constant. This is a further reason for distinguishing between what happens during stage 2 and 3: PtO_2 oxide film formation during stage 2 and adsorption of oxygen ions and not formation of PtO_3 during stage 3. It is also worth noting that Hickling (8) using Pt electrodes in N-H₂SO₄ found a similar increase in the slope of his stage 3 - due to PtO formation - after an initial dc polarisation, and that the original trace was only restored if the electrode was swung all the way between oxygen and hydrogen evolution; if the amplitude control (the series capacitor size) was adjusted so that this condition was not met and the swing of the electode potential was restricted then the gradient of the trace could not be reduced to its original value before polarisation. This is strong evidence that with the pulsating current method under normal working conditions the electrode is brought back to its original condition before electrolysis every cycle.

This type of mechanism may explain, to some extent, why it is that the charge increment in stage 2 decreases with current density as shown in column 4 of Table IV. It may be that at these higher current densities there is an excess of oxygen gas formed at the electrode and a large part of the reverse current charge is used up in re-ionising this rather than stripping the PtO2 oxide film away. Consequently on the subsequent cycles some of the oxide film remains on the electrode and hence the charge increment during stage 2 is less than before. It is interesting to note again that the charge increment per volt during stage 3, when oxygen adsorption is considered to occur and not further oxide film formation, remains fairly constant as the current density is increased to its highest value. It is interesting to note also that when the current density is constant, as it is in Table V, then the charge increment is also of the same order, at least for the higher temperatures above 1000°C. At the lower temperature of 1000°C stage 2 is preceeded by a very curved stage I and the double layer concept is, consequently, of doubtful validity here.

We have seen from Figure 4(h) that when the Pt electrode is anodically polarised with dc the first few following pulsating current tracks have no breaks in them but that after this, in subsequent tracks, breaks occur. No such breaks in the tracks have ever been observed in single pulse experiments with the second circuit - and the tracks of Figure 4(e) and (f) are typical of this behaviour. It was noted in the Results section that the voltage attained in the single pulse experiment of Figure 4(e) was 0.9V at a current density of $0.083A/cm^2$ and a temperature of 1200°C after allowing 0.2V off for the glass resistance; on the other hand, a voltage of 1.5V was recorded for the pulsating current experiment shown in Figure 4(c) at the same current density and temperature. It was tentatively assumed that in the single pulse experiment oxygen evolution was never attained. However, it may be that the cause of this discrepancy is different. It may be due to the fact that there is no PtO2 oxide film formation in the single pulse experiment because it is already present there on the electrode before the electrolysis starts: only in the pulsating current electrolysis is the oxide film stripped away during the high reverse current pulse and so only during the anodic pulse of this electrolysis can an oxide film form. Thus the fact that there are always breaks present in the pulsating current tracks, but none ever present in the single pulse tracks receives a logical explanation. This would also explain the difference in oxygen evolution voltage of 0.9V and 1.5V for the single and the pulsating current electrolyses: if the voltage rise of about 0.5V shown in Figure 4(c), and due to the formation of the PtO₂ film, is discounted then the oxygen evolution voltage is reduced to about 1.0V, which is similar to the value found in the single pulse experiment.

We summarise this part of the work as follows: In the pulsating current electrolysis at platinum electrodes in molten silicate glass, an average quantity of electricity of 3.3×10^{-3} C/apparent cm² is required for the commencement of oxygen evolution under the various conditions of current density and temperature which we have described. This value is of the same order as that required at room temperature for

the evolution of oxygen to occur in acidic, neutral and alkaline aqueous solutions at platinum electrodes, and at other various metals: Au, Ni, Co and Ag in N-NaOH solution.

As a result of this there is a delay before oxygen evolution starts and the cause of this is , first, the charging of an electrical double layer followed by the formation of a monomolecular oxide film which covers the electrode – of composition PtO_2 in the molten glass, and PtO in the aqueous solutions. This film is completely stripped away by the large reverse current, except at the highest currents used, and this is the characteristic feature of the technique, distinguishing it from the other methods, such as the single pulse method, where this stripping does not occur. The oscilloscopic tracks obtained using this method are remarkably stable and recover rapidly after dc polarisation.

Platinum-Sodium Disilicate

A comparison of Tables VIII and II shows that the quantity of electricity required for oxygen evolution is much less at platinum electrodes in molten sodium disilicate than in the soda lime silicate glass at all the current densities studied. A comparison of the V/q oscillograms for the disilicate melt from Figure 6(a) and the silicate glass from Figure 4(a) shows why this is so: the length of stage 2 during which the oxide film is forming over the electrode is much less for the sodium disilicate electrolyte than for the silicate glass one. The charge accumulated during stage 2 for the sodium disilicate is only 750 μ C/apparent cm², from Figure 6(a) compared with a charge of 2000 μ C/ apparent cm^2 for the silicate glass melt from Figure 4(a), and we might thus conclude that the surface of the platinum is only 38% covered with PtO₂ in the disilicate melt. However, since the concentration of Na₂O is much higher in the disilicate, at 34%, than it is at 11% in the silicate glass, the concentration of free, non-bridging oxygen ions must also be much higher in the disilicate. It is thus difficult to see how a smaller amount of oxide film forms on the platinum electrode in the disilicate than in the silicate glass electrolyte. A much more likely explanation is one similar to the one we used to explain the oscillograms for the platinum electrodes in the silicate glass after dc polarisation: that is, that in the sodium disilicate electrolyte, since there are more free, non-bridging oxygen ions present, there is more oxygen present at the electrode, and that some of the reverse current is used up in reducing the oxygen molecules to oxygen ions and desorbing them so that there is less charge available for stripping away the Pt0, film. Consequently there is some Pt0, film remaining on the electrode after the reverse pulse has ended, and during the next positive half cycle only a part of the PtO, has to be replaced. Thus the charge devoted to doing this is correspondingly less.

This conclusion is certainly supported by the oscillogram in Figure 6(b), which shows successive tracks after 30sec dc polarisation. Just as for the disilicate glass electrolysis in Figure 4(h), the first few tracks after the dc polarisation are almost featureless with very short plateaux due to the oxide film formation; and as the effects of the dc polarisation wear off the length of the plateaux increase until, finally, the original shape before dc polarisation is restored. We explained this previously, in the case of the silicate glass electrolyte, as being due to the progressive removal of the excess oxygen gas round the electrode, which was generated from the dc polarisation, and the same explanation will apply in this case for the disilicate. Finally, when the stable position of the track has been reached, the length of the plateau will still be less than in the silicate glass case: there is then still some excess oxygen on the electrode in the disilicate electrolyte due to the high concentration of free, non-bridging oxygen ions present in the melt, and part of the reverse current is used to remove this - hence there is less charge to remove the PtO₂ film and thus it is not completely removed.

We could never completely remove the oxide film plateaux from the pulsating current tracks by using a large amount of dc polarisation; but on the other hand, we never succeeded in introducing any breaks and plateaux into the curves we obtained using single anodic pulses. This is clear from Figure 6(d) which shows several successive single shots using the second circuit after 30sec dc polarisation: in none of the tracks is there the slightest suggestion of any breaks due to oxide film form-We conclude that this is because, in the single pulse experiation. ments, there is already an oxide film present on the platinum electrode before the start of electrolysis and that only in the pulsating current method is the oxide film stripped off from the electrode during the large, negative reverse current pulse. The pulsating current method is thus unique in providing an electrode in the same reproducible state at the start of every anodic pulse.

The oscillogram of Figure 6(c) shows the successive tracks after a 30sec dc polarisation at the auxiliary electrode and should be compared with the anodic tracks at the working electrode shown in Figure 6(b). The recovery at the auxiliary electrode after the dc polarisation is rapid as it is at the working electrode, but the values in Figure XVI show that the auxiliary electrode recovers more slowly than the working electrode. In the light of this experiment the single pulse oscillograms shown in Figure 6(e) and (f) are very interesting. Figure 6(f) shows that the voltage of the auxiliary electrode reverses polarity during the discharge into a short circuit and this suggests that there is some product on the electrode which is decaying. One possibility is that there is a slight amount of alloying occurring at this electrode due to the large reverse current - Figure 17(b) of reference (1) shows that such alloying of silicon with platinum can take place during prolonged ac electrolysis with a superimposed dc bias.

This result may go some way towards explaining the single pulse oscillogram of Figure 4(e). There we saw that when the cell is discharged into a short circuit the current reverses its direction. We thought originally that this was due to the decay of the PtO_2 oxide film on the working electrode, but in the light of Figure 6(f) - and assuming that the same thing happens in silicate glass as in the disilicate electrolyte - we conclude that this reverse current is caused by the decay of a product at the auxiliary electrode and not at the

working electrode, and that this current is driven through the oxide film on the working electrode which, being thin, will have a low resistance. Thus the conclusion which we reached in the last paragraph but one that the PtO₂ oxide film remains on the platinum electrode after a single pulse is supported by this fresh evidence.

Some of the other parameters for disilicate melts differ considerably from those for the silicate glass, while others do not. When they do so the difference can usually be explained as due to the differing concentrations of Na $_2$ O in the two electrolytes and, hence, the differing amounts of free oxygen ions present.

This probably explains why the double layer capacity of stage l cal-culated from Figure 6(a) is so low at 1245 μ F/apparent cm², and comparable to the value of 1038 μ C/apparent cm²/V for the gradient of stage 3 in the same figure. Since there is a large amount of PtO₂ film remaining on the electrode after the reverse pulse, the process in stage l during the next positive half cycle may be predominantly adsorption of oxygen ions on this film as in stage 3.

Again, the oxygen evolution voltage of 0.9V is low compared with the 1.2V recorded for the silicate glass melt, (Figure 4(a)), and this is true at all the current densities considered, as a comparison of Tables IV and XIV for the silicate glass and the disilicate will show. This again is not unexpected at the higher concentration of free nonbridging oxygen ions in the disilicate electrolyte because the reversible electrode potential is decreased by increase in oxygen ion concentration. Denoting the reversible electrode potentials in the silicate glass and the disilicate as E_1 and E_2 , respectively, and the standard electrode potential of the oxygen electrode as E^0 we have, from the Nernst Equation, that

$$E_{1} - E_{2} = E^{\circ} - \frac{RT}{nF} \ln [O_{1}^{"}] - E^{\circ} + \frac{RT}{nF} \ln [O_{2}^{"}]$$
[4]

$$E_{1} - E_{2} = -\frac{RT}{nF} \ln \frac{[O_{1}']}{[O_{2}']} .$$
 [5]

We have used the European Convention for the sign of the electrode potential because these particular results are more clearly explained in this way since the sign of the standard electrode potential of the oxygen electrode is positive on this convention. If we make the very crude approximation that the concentration of free, non-bridging oxygen ions is proportional to the concentration of Na₂O we have

$$E_1 - E_2 = -0.029 \log \frac{(11)}{(34)}$$
 [6]

$$E_1 - E_2 = -0.029 \log (0.3235)$$

= 0.014V,

or

and so

$$E_0 = E_1 - 0.014.$$
 [7]

Thus the reversible electrode potential in the silicate glass is redused by increasing the concentration of free, non-bridging oxygen ions to the higher value in the disilicate melt, and thus we might expect the potential for the irreversible evolution of oxygen to be reduced also. The voltage for oxygen evolution in the disilicate is reduced by increasing the temperature as shown in Figure XV, and this behaviour is similar to that found for the silicate glass electrolyte in Table V; the values in the disilicate are always less than the corresponding ones in the silicate glass at all temperatures, however.

The parameter which does remain constant in both the electrolytes is the potential at the start of stage 2: this is 0.45V in the silicate glass melt compared with 0.44V in the disilicate, and this similarity is not surprising since both represent the start of PtO_2 formation on the electrode.

We summarize this part of the work as follows: The pulsating current electrolysis in the disilicate electrolyte is similar to that in the silicate glass glass melt in that a roughly constant amount of electricity has to be supplied to obtain oxygen evolution at all the current densities and temperatures considered. The difference is that the quantity of electricity required is less in the disilicate than it is in the silicate glass composition: an average of 1.3×10^{-3} C/apparent cm² is sufficient for oxygen evolution in the disilicate, but an average of 3.3×10^{-3} C/apparent cm² is necessary for the silicate glass. This is because the PtO₂ oxide film is only partially stripped away from the electrode during the reverse current pulses, and this itself is due to the higher concentration of oxygen at the electrode at the end of the positive half cycles due to the higher concentration of free, non-bridging oxygen ions in the disilicate melt.

The recovery after dc polarisation is rapid in the disilicate melt as it is in the silicate glass electrolyte, and a comparison of the pulsating current and single pulse electrolyses shows that, once again, only in the pulsating current method is there any stripping away of the PtO₂ oxide film.

Platinum-Sodium Diphosphate

We consider the diphosphate melt before the diborate one because it is the one which differs the most from the disilicate and silicate glass electrolytes which are similar to one another. The long initial, curved region in the oscilloscope tracks for diphosphate shown in Figure 8 (a) and (b) at temperatures of 1200° and 600°C are best explained as being due to the dissolution of the electrode in the melt to give platinum phosphate and the deposition of a phosphate salt film on the electrode prior to oxygen evolution. We could never induce the breaks and plateaux indicating oxide formation which we observed so often in silicate melts, and this was true even though we changed the current density 20-fold and the temperature from 600° to 1350°C.

The formation of a platinum phosphate film is certainly possible chemically since there is evidence in the literature that platinum can dissolve to a greater extent in phosphate glass melts than in silicate or borate glass ones. Thus, Rindone and Rhoades (29) added platinum as PtCl₄ solution to sodium silicate, borate and phosphate glass composi-tions containing l mole of the modifying oxide to 4 moles of the glass former in each case. When the glass had been formed on fusing they found that in the phosphate glass the platinum at a concentration of 0.1% gave a yellow colouration indicating ionic dissolution, but a grey colour, indicating colloid formation, at concentrations of 0.01% and 0.001% in the silicate glass and the borate glass, respectively. This evidence supports the view that during the anodic pulse platinum dissolves in the phosphate melt and then precititates on the electrode as a salt film.

That such a salt film does indeed form on the electrode is strongly suggested by the decay curves shown in Figure 8(f) for discharge into a short circuit. This shows clearly that the voltage of the anodic working electrode reverses direction during the discharge in the diphosphate melt, and it differs from Figure 4(e) for the silicate glass in this respect in that, for that oscillogram, the anodic voltage did not reverse its voltage but the current did. The fact that the polarity of the working electrode changes sign during the discharge suggests that there is some product present on the electrode which decays during the discharge, and that this is more substantial than the oxide film present on the electrode in the disilicate since there was no reversal of polar -ity of the working electrode in that electrolyte after a single pulse (Figure 6(f)). Close examination of Figure 8(f) shows that there are actually two tracks appearing on the photograph after the positive single pulse has ended, and the second track must correspond to the decay of the voltage on the auxiliary electrode without reversal of polarity.

The presence of a phosphate film on the electrode could explain the results shown in Tables XII to XV. Thus the quantity of electricity required for oxygen evolution in the diphosphate electrolyte is less than that for the disilicate at the various current densities studied, as comparison of Tables XII and VIII will show. In the diphosphate case there is no oxide film formation to delay the onset of oxygen evolution; the same thing is true at different tempertures, as an examination of Tables XIII and IX will show.

Another feature of oxygen evolution voltages in diphosphate melts is that they remain at the same low value as the current density and temperature are varied, and this is in contrast to the values in the silicate melts where the oxygen evolution voltages are not only larger but also change appreciably with change in current density and temperature (see Tables XIV and XV). This may easily be explained if there is a thick phosphate salt film on the electrode of large surface area: such a film would would decrease the true current density emormously and would result in a lower oxygen evolution voltage under all conditions. This film cannot be of a very permanent and protective character, however because Table XVI shows that after dc polarisation the voltage of the working electrode reduces rapidly to its value before dc polarisa-It is the polarisation of the auxiliary electrode shown in coltion. umn 8 of Table XVI which is the cause of the long term change in the track with the oscilloscope across the cell from working to auxiliary electrode shown in Figure 8(c); the relatively permanent polarisation

at the auxiliary electrode is shown in Figure 8(d). We have seen that alloying may explain some of the results at the auxiliary electrode or cathode during the reverse pulse in the disilicate electrolyte and, to anticipate the borate results, alloying at the cathode occurs to a considerable extent there. It may well be that something similar may happen at the cathode in the diphosphate and explain the prolonged polarisation which, from Table XVI, is there some considerable time after the polarisation.

The work of Hickling and Spice on the polarisation of nickel anodes in aqueous solutions (10) throws further light on what is occurring in molten phosphates. In Figure 10(a) and (b) are shown the tracks obtained in N-NaOH and 0.2M-KH₂PO₄ + 0.2M-Na₂HPO₄ buffer solution of pH 6.8 The oscillogram for N-NaOH shows an initial, very at room temperature. rapidly ascending region followed by a break at 0.55V indicating the start of Ni203 formation, which forms a film slightly thicker than 1 molecule thick before oxygen evolution starts at about 0.85V. The oscill -ogram for the phosphate buffer is completely different, however: the voltage rises directly to oxygen evolution without any break due to oxide film formation and with only a small curvature; the cathodic track is similarly featureless showing only a small peak before hydrogen evolution. Figure 10(c) shows the result of an experiment to find out what is happening in the early stages of the electrolysis. First the nickel electrode was polarised cathodically at 0.01A/cm² for about 3min to free the surface from any existing film; then the pulsating current was switched on and the first few tracks photographed. They are shown as numbers 1 to 4 in Figure 10(c). In 1 a process, probably of simple dissolution of nickel phosphate, occurs at a potential of -0.1V; this is repeated in 2, but is followed by a rapid rise in voltage; in 3 the voltage rises to oxygen evolution almost immediately and 4 is the normal form of the track shown in 10(a), and this remains unchanged thereafter. Hickling and Spice concluded that, on being made anodic, the nickel dissolves to form an insoluble phosphate which coats the electrode forming a protective and conducting film which subsequently remains stable. This film could, however, be removed by continous dc cathodic treatment for after such treatment the sequence of tracks could again be observed.

While this is a perfectly logical explanation for the results found by these authors it is not sufficient to explain our results as exemplified in Figure 8(a) and (b). The anodic tracks there are permanent and stable and the track of working electrode against reference electrode may be considered to be intermediate between tracks 2 and 3 of Figure 10(c) of Hickling and Spice which we have just discussed. This would suggest that the anodic track of Figure 8(a) corresponds to the initial dissolution of platinum to form platinum phosphate followed by the formation of a partially stable and semi-protective film. It is possible that on reversal of the current the film is completely stripped away, but it is more probable that it is only partially stripped off from the electrode. This is because Hickling and Spice calculated that more than $10,000\mu$ C/apparent cm² had been used in the formation of the stable phosphate salt film obtained in their experiment and this

is equivalent to the dissolution of about 30 x 10^{15} nickel atoms in the bivalent state, or rather more than 4 atomic layers from the electrode We did not repeat this experiment, but the quantity of elecsurface. tricity corresponding to the initial, curved part of the track in Figure 8(a) is about $1417\mu C/apparent \ cm^2$ and is thus less than the $2000\mu C/apparent cm^2$ required to form a monomolecular layer of PtO₂ on a clean, oxide-free platinum electrode in molten silicate glass electrolyte. If the phosphate salt film is formed and completely removed every cycle then the electrode is never completely covered by the salt film. But the salt film must completely cover the electrode because it protects the surface completely from the formation of any oxide film, and its large surface area reduces the oxygen evolution voltage as shown in Table XIV. A more likely explanation of what is occurring at the electrode is as follows: We assume that the first few tracks at the start of the experiment are similar to numbers 1 and 2 found by Hickling and Spice, and that the central track, for the working /reference electrode combination, which we see in Figure 8(a), is the third and stable position for the subsequent tracks. Then the quantity of electricity used to form the salt film works out at $7250\mu C/apparent\ cm^2$, and this is equivalent to the dissolution of 23 x 10^{15} platinum atoms in the divalent state or rather more than 7 atomic layers from the electrode surface. Rindone and Rhoades (29) are of the opinion that there are some ${\rm Pt}^{4+}{\rm ions}$ in the glass even though the ${\rm PtCl}_4$ they added decomposed to PtCl₂. If this were so then the number of platinum atoms dissolving would be halved as well as the number of atomic layers. This would give a mean value for the number of atomic layers as just over 5; it is probably safe to say that the platinum phosphate salt film, when fully formed is between 5 and 7 atomic layers thick. Once this salt film is established it is protective in the sense that it completely inhibits the formation of an oxide film on the electrode - we never saw any evidence for oxide film formation in any of our experiments in diphosphate melts under any conditions; and it must also be of large surface area to explain the low values of the oxygen evolution potentials found in However, our track is unlike the static trace of Hickling Table XIV. and Spice shown in Figure 10(b) which corresponds with a compltely stable salt film. The fact that there is evidence of metal dissolution before salt film formation for every positive half cycle in Figure 8(a) - the first, slowly curving part of the track - must mean that during the negative half cycle some of the film dissolves away - helped, of course, by the large, negative reverse current. Thus the salt film is partially removed during every reverse cycle and then built up again during the next positive half cycle; but it never completely disappears from the electrode.

We summarize the results found in this section as follows: In sodium diphosphate electrolyte, in contrast to sodium disilicate, there is no oxide film formation occurring under any of the conditions we have considered. However, there is present on the electrode a protective phosphate salt film, several atomic layers thick and of large surface area, which is partially removed and replaced during every cycle of the pulsating current.

Platinum-Sodium Diborate

The behaviour of a platinum electrode in sodium diborate electrolyte is intermediate between its behaviour in sodium disilicate and in sodium diphosphate.

Thus in the V/t and V/q oscillograms shown in Figure 7 there is very little detail in 7(a), the V/t oscillogram, prior to oxygen evolution and almost none in the V/q oscillogram of 7(b). At the higher current density of 0.200A/cm², however, there is a well marked break in the curve followed by a plateau - shown in Figure 7(c) - and this corresponds to the formation of an oxide film on the surface of the electrode. The really interesting photograph in this series, however, is Figure7(d) which is a repeat oscillogram of 7(a) at the same current density of 0.083A/cm^2 , but taken after all the other measurements at the higher current densities had been made. It is clear from the tracks that now, in contrast to Figure 7(a) and (b), there is a well defined break in the curve followed by a plateau before the final rapid ascent to oxygen ev-These features show that there is an oxide film forming on olution. the electrode surface during cycling.

The length of this plateau is small - it is finished in about 2msec - and this corresponds to a quantity of electricity of only $167\mu C/appar$ -ent cm². If we assume, as in the case of the silicate glass melt,that a charge of about $2000\mu C/apparent$ cm² represents full coverage of the electrode surface with a monomolecular layer of PtO₂, then we must conclude that the electrode is only 8.5% covered in the diborate melt and this seems unlikely. There is always the possibility, of course, that the oxide is only partially stripped away during the reverse cycle as in the sodium disilicate melt, and the charge we are seeing on the osc-illogram is merely the charge necessary to cover the rest of the partially stripped surface.

Hickling and Spice (10) found a similar shortening of the time to oxygen evolution at nickel anodes in N-NaOH when the electrolyses were carried out in 0.1N-Na₂B₄O₇ solutions. Thus the length of the tracks before oxygen evolution in Figure 10(a) in N-NaOH was reduced, on the original photograph, from about 51mm to 30mm when the NaOH was replaced by $0.1N-Na_2B_4O_7$ solution; this corresponded with a reduction in the charge required for oxygen evolution of from $5400\mu C/apparent cm^2$ to 3180µC/apparent cm². Hickling and Spice did more that this: they cathodically polarised an electrode for 3min with dc at 0.01A/cm² in the $0.1N-Na_2B_4O_7$ solution before examining the first few pulsating current tracks. The results are shown in Figure 10(d) and it can be seen that the first track marked "1", shows no detail, but that the second track 2 shows a well defined break due to oxide film formation. The length of this break in the track 2 before oxygen evolution is about 25mm on the original photograph and corresponds with a quantity of electricity of about 2600μ C/ apparent cm², which is somewhat less than the 3180μ C/apparent cm² found under steady state, continuous running conditions. They had shown previously that $4500\mu C/apparent cm^2$ was sufficient to form a monomolecular layer of Ni₂O₃ on the nickel electrode in N-NaOH solution and the comparable value of 2500μ C/apparent cm² for the borate corresponds to a 0.55 surface coverage. Thus track I corresponds to the formation of a salt film on the surface of the electrode which is only partially protective since since in one cycle it gives way to an oxide film partially covering the surface, which is cyclically formed and removed during the pulsating current electrolysis.

This cannot be the explanation of what is occurring in the molten sodium diborate, however, because the tracks in Figure 7(a) and (b), which we ascribe to the formation and removal of a salt film, are repetitive and the oscillograms are stable; only when high currents of $0.200A/apparent cm^2$ are applied does the formation of oxide films start and continues thereafter at the lower current densities. We ascribe the tracks in Figure 7(a) and (b) to the formation of a salt film on the surface of the platinum electrode. From Table X, the quantity of electricity required for oxygen evolution is $1660\mu C/apparent$ cm² at a current density of 0.083A/apparent $\rm cm^2$ and we calculate that this amount of charge corresponds to the dissolution of 5.2 X $10^{15} \rm atoms$ in the bivalent state or a salt film of just over 12 molecules thick, using a sp-When the high current density of 0.200A/appecific gravity of 21.4. arent cm² is applied the film ruptures and is then replaced by an oxide film forming and reforming as shown in Figure 7(c). The quantity of electricity corresponding to the break in the curve is only 300µC/apparent cm², and this represents only 15% coverage of the electrode surface with the oxide film. We note from the initial part of Figure 7(c)that the track is curved and, as are the tracks for diphosphate - this indicates dissolution of metal. This dissolution may be one reason for the rupture of the salt film at the higher current densities, but another may be the formation of platinum - boron alloys on the electode during the large negative pulses of the reverse half cycle. It is well known that boron alloys easily with platinum at high temperatures (30) and this may be the reason for the extensive attack shown in Figure 7(g)at the cathode; if a similar slight attack takes place at the working electrode during high current density pulses then this could sensitise the surface and perhaps allow the formation of oxide films there. The tracks in Figure 7(d) are almost identical with those formed at the last and highest current density of 0.333A/apparent cm² used, in that the plateau due to oxide film formation is so short - about 2msec - as is the It could be that on the passtime to oxygen evolution - almost 4msec. age of the highest current density there is a slight amount of alloying of the working electrode which sensitises the surface and allows a stable oxide film to form over most of it; then the cyclic formation and removal of the oxide film occurs which only corresponds to a coverage of the surface of about 8.5%. If a part-boron oxide does form on the electrode surface then it will be stable since the strength of the boron oxygen bond is greater than that of the silicon-oxide one: the values are 119 and 106kcal, respectively, according to Sun (31).

Support for the idea outlined above comes from the photograph of Figure 7(e) which was taken immediately after 5min dc polarisation at $0.083A/apparent \text{ cm}^2$. Although there must be a large amount of oxygen round the electrode the track of working against reference electrode is almost identical with that in 7(d) showing that the over-riding factor

determining the shape of the curve is the effect of the past application of a very high current density and not the dc polarisation; if there had been partial stripping of the film at the electrode then we would have expected dc polarisation to have had a very great effect on the shape of the pulsating current tracks as in the case of the silicate glass and the disilicate melts. There is polarisation at the auxiliary electrode as shown in Figure 7(f) and this displaces the track of the working electrode against the auxiliary electrode upwards in Figure 7(e).

The behaviour of platinum in sodium diborate electrolyte is complicated, but we summarize the results in this section as follows: At the lower current densities protective salt films form on the platinum elctrodes and there is no evidence of oxide film formation. At the higher current densities, however, breakdown of the salt film occurs as well as, possibly, some alloying of boron with the platinum of the working electrode. When this occurs a stable oxide film forms on the electrode surface, only a small amount of which is periodically stripped away and reformed during the pulsating current cycle.

Molybdenum-Soda Lime Silicate Glass

If the reaction at a platinum electrode is characterised in silicate, borate and phosphate melts by the formation of thin oxide or salt films then, for a molybdenum electrode, nearly all the evidence points to the conclusion that its behaviour is dominated by the presence on the electrode of a more or less permanent, thick oxide film.

Certainly the metal oxidises very easily in air or oxygen: Stroud (32) describes molybdenum electrodes used in glass melting furnaces some parts of which must be protected from oxidation by an inert gas atmosphere at temperatures as low as 500°C. At higher temperatures of 1300°C and above Bartlett (33) found that cylindrical molybdenum rods decreased in diameter by the large amounts of 0.36 and 2mm per hr at pressures of 0.1 and latm, respectively, and this corresponded to reaction rates of 1 x 10^{-4} and 6 x 10^{-4} cm/sec at the two pressures. The attack on the metal by free, non-bridging oxygen ions in melts may be even greater than this since Rosner and Allendorf (34) maintain that the attack of molybdenum by oxygen ions can exceed that due to gas molecules by two orders of magnitude. Certainly both the extent and the velocity of the reaction of molybdenum with oxygen is much greater than that of platinum. Thus Gulbransen, Andrew and Brassart (35) found a value of -104 kcal/mole for the standard free energy at 1200 °C of the reaction:

$$2 Mo + 3/20_2 = 2 MoO_3$$
 [8]

and this should be compared with the positive value of +38kcal/mole found by Alcock and Hooper (17) for the oxidation of Pt to PtO_2 . Again Gulbransen and his co-workers found that the linear reaction rate for the oxidation of molybdenum in oxygen was $530mg/cm^2/hr$ and this is enormously greater than the value of $0.23mg/cm^2/hr$ found for the oxidation of platinum in oxygen by Fryberg and Petrus (36), again at $1200^{\circ}C$.

Oxide films form on molybdenum electrodes in glass melts with and without the passage of electrical current. Thus, Boffe, Delzant and Plumat (37) concluded that the film they observed on Mo rods heated for 65hr in sulphur-free soda lime silicate glass at temperatures from 1000°C to 1300°C were oxides of molybdenum; they also found a concentration of MoO_3 in the glass of up to 3.78wt%. The most extensive attack on molybdenum electrodes occurs, however, when refining agents such as SO_3 , Sb_2O_3 or As_2O_3 are added to the glass. Thus, Hierl, Hanke and Scholze (38) found that Mo electrodes corroded about twice as rapidly in soda lime silicate glass melts containing Sb₂O₃ at 1250°- 1350°C than they did without any added refining agent; and when the Sb₂O₃ was replaced by added sulphate the extent of the reaction increased a further three times. They identified reduced antimony on the electrode using EDAX and they found a Mo-S compound on the electrode using the electron This work was carried out using an applied ac current of microprobe. 50Hz which caused anodic oxidation during the positive half cycle accord -ing to the authors; and the extent of the reaction increased with current density.

The glasses in which the greatest reaction occurs, however, are the lead silicate glasses. Matej, Truhlavora and Rycl (39) electrolysed a glass of composition 21% PbO, 65% SiO₂ and 14% K₂O between heated Mo electrodes at current densities from O to $3A/cm^2$ at $1200^{\circ}C$ and $1400^{\circ}C$. They found reduced Pb on the electrodes on top of the oxides of molybdenum at both temperatures, and with and without current; there was also liquid lead on the bottom of the crucible from the electrode. The composition of the layer of product on the electrode was found to be 60%Mo, 11%Pb and 4%K; the corrosion increased with increasing current density. These results are not surprising since we calculate from the linear free energy table of Coughlin (40) that the standard free energy of the reaction:

$$Mo + 3 Pb0 = Mo0_{2} + 3 Pb$$
 [9]

is -66.4kcal/mole of MoO₃ at 1200°C.

In the light of the results which we have discussed it seems probable that during pulse electrolysis there is present on the molybdenum electrode a thick film of oxide which determines the type of oscillogram obtained. Thus the voltage rise shown in Figure 5(b), found using the single pulse circuit, is no less than the extremely high value of 22V at a current density of 0.042A/apparent cm² in the sulphate free glass. This is an extremely large voltage change to encounter compared with the value of 2.2V found from the pulsating current oscillogram of Figure 5(a)at the same current density. It is not due to an observational error because similar voltages were found from several other, different oscillograms. Furthermore, this latter value of 2.2V from the pulsating current circuit is itself greater than the more usual value lying between 1.18 and 1.2V found for a platinum anode at current densities of 0.033 and 0.083A/apparent cm² (Table IV). We measured the resistance of the glass in the cell at a frequency of 1000Hz using platinum electrodes and found it to be 8Ω . Thus we assign a voltage drop due to the

resistance of the glass of 8x0.042x.6=0.20V. If we take the actual voltage required for oxygen evolution to be, say, the 1.2V needed to evolve this gas at a platinum electrode having on its surface the low reistance monomolecular layer of PtO2 then the most we can ascribe to glass resistance and oxygen gas evolution is 1.4V. Subtracting this from the 22V we have measured in Figure 5(b), we are left with 20.6V to account for. Even if we subtract the 2.2V for oxygen evolution found in Figure 5(a) for the pulsating current electrolysis using the first circuit, we are still left with 19.8V. It seems to the author that the only way these large voltage drops can be satisfactorily explained is that they are due to the presence on the electrode of a high resistance molybdenum oxide layer, probably MoO3(35). If this is so we may calculate its resistance by dividing by the current of 0.042x0.6=0.025A passing through the cell and, doing this, we obtain resistance values of 824 and 7920 corresponding to voltages of 20.6 and 19.8V, respectively. This is a very high resistance for such a small area (0.6 cm^2) film and it would have been useful to have calculated its thickness knowing its resistivity. Unfortunately, however, the most probable oxide occurring at these temperatures is MoO3 according to Gulbransen, Andrew and Brassart (35) and this has a melting point at 795°C and sublimes at 1155°C (41). Above 800°C, indeed, the above authors found that the oxide MoO_3 volatilised as fast as it was formed if the oxygen pressure was latm. That is not to say, though, that the gas phase reaction they studied is exactly comparable with the electrolytic system we are concerned with. Indeed, although Gulbransen and his co-workers are of the confirmed opinion that MoO₃ is the oxide forming throughout their investigation, other authors give thermochemical data such as the standard free energy up to a temperature of 1727°C (see Coughlin (40) and King, Weller and Christensen (42)) for the oxide MoO2. It is possible that a film of MoO_3 can form on the electrode surface and remain there at the high temperatures we are using since the oxide is encapsulated in the glass and is dissimilar to a system of a flowing stream of oxygen gas at latm pressure. That some thick film is present on the Mo electrode even before electrolysis is shown by a measurement of the glass resistance we made at 1200°C and 1000Hz using the molybdenum electrodes. We found a resistance of 130Ω which is very much greater than the 8Ω we found with platinum electrodes under the same conditions. There is certainly a thick film on the Mo electrode after electrolysis: Figure 2 and 3 of reference (5) shows such a film on the electrode. The photograph there is a 2/3 reduction of the original and the bars on the original are each 8µm long. Consequently the average thickness of the film is about 40µm. The film was shown to be an oxide film by wave length dispersive analysis. It is probable then that the large voltage risegot with the single pulse experiment (Figure 5(b)) is simply due to the voltage drop across the large resistance of a very thick film of oxide already present on the electrode before eletrolysis begins. This explains the shape of the tracks: the voltage rises and decays extemely rapidly and there are none of the slowly ascending tracks and slow decays associated with platinum electrodes in silicate glass or sodium disilicate, or even diphosphate.

We turn now to a consideration of the pulsating current tracks in Figure 5(a). In the upper track showing the voltage of the working electrode there are none of the delays characteristic of the polarisation at a platinum electrode and due to the formation and decay of a thin oxide film; rather the voltage jumps almost immediately from its rest value to oxygen evolution - as, indeed, it does for the single pulse experiment shown in Figure 5(b). Since the voltage jump of about 2.2V for the pulsating current is much less than the 22V found with the single pulse oscillogram, we are forced to the conclusion that any oxide film with the pulsating current electrolysis must be very much thinner. If we subtract 1.4V as before to allow for the glass resistance and the voltage needed for oxygen evolution at a metal such as platinum where there is only a thin, low resistance film present, then then we are left with 0.8V to accountfor, and this corresponds to a film with a resistance of only about 30 Ω . At first sight these two figures of 30 Ω and 824 Ω for the resistances of the two films for a pulsating current and a single pulse, respectively - and at the same current densities also - may seem to be contradictory. However, it should be borne in mind that there is a very high current spike passed through the cell in the reverse direction in the pulsating current electrolyses and this will have the effect of reducing the thickness of the oxide on the electrode.

The thickness of the film on the molybdenum electrode must increase with increasing current density because, as column 2 of Table VI shows, the oxygen evolution voltage increases with increasing current density. Thus, at current densities of 0.083 and 0.167A/apparent cm^2 the oxygen evolution voltages are 4 and 11V, respectively, and subtracting 0.4V and (since the oxygen evolution voltage at a platinum electrode is 0.8V still 1.2V from Table IV), we have for the film resistance, values of 48 and 90 Ω for the two current densities. These resistances correspond to films which are thicker than the 30Ω one at a current density of 0.042A/apparent cm², but they are much thinner than the filmwith resistance 824Ω from the single pulse experiment shown in Figure 5(b)-also at a current density of 0.042A/cm^2 . We might still explain this difference as being due to the reduction of the oxide thickness on the Mo electrode by the reverse current. But if we do this, how are we to explain the figures in column 3 of Table VI which show that the dc oxygen evolution voltages are only slightly higher at all the current densities than the pulsating current ones? There is no reverse current operating in this case and so why are the two sets of voltages - and, by implication, the resistances of the films - of roughly the same size? It can only be that the over-riding factor which is controlling the oxygen evolution voltage and the film thickness is not the reverse current pulse but the actual evolution of oxygen gas on the electrode, with the consequent sublimation of some of the volatile MoO3. It does not seem possible that the negative reverse current pulse can remove films of the thickness we envisage by itself, alone - certainly not if the films are of MoO₂ which, according to Coughlin (40) is a solid at 1727°C. The presence of MoO3 on the electrode, which may voltilise in the gas stream and does so according to Gulbransen, Andrew and Brassart (35), seems to be the only way to explain the results we have obtained.

We conclude that the mechanism of the reactions occurring at the anodic molybdenum working electrode are as follows: Initially, due to the high negative free energy of the reaction, there is formed on the molybdenum electrode a thick film of the oxide MoO3 not free to move from the surface of the electrode because of the constraints imposed by the presence of the surrounding molten glass. When a single pulse is applied the resistance of this film determines the shape and size of the oscilloscopic tracks and, since only a single pulse is applied, the film is not altered or disturbed. When an anodic dc current is flowing, however, the thickness of the film is reduced to a value depending on the current density by the extensive evolution of oxygen gas at the electrode, which allows some of the MoO3 to volatilise away in the gas stream. The same thing occurs when the pulsating current is applied, but helped to a small extent by the current reversal during the negative half cycles.

Oscillograms obtained with a pulsating current input in the glass with added sulphate are shown in Figure 5(c). They are of the same basic shape as those found for sulphate free glass 5(a) and (b) and, as is clear from Figure 5(d), the oxygen evolution voltages are similarly only less than the dc values by a small amount. Potentials in the two photographs are given with reference to a Pt reference electrode and also a Mo reference electrode, and it can be seen that there is a difference between the two: this is due to the 0.2-0.3V recorded under static, reversible conditions using a digital voltmeter for the difference between a Pt and Mo electrode.

The oxygen evolution voltages for glass containing added sulphate are less than those for sulphate free glass under all the different conditions of current density and temperature which we examined and which are shown in Tables VI and VII. It would be surprising if it were otherwise since sulphate is added to molten glass as a refining agent to aid the removal of oxygen gas bubbles by itself providing a source of SO₂ and O₂ gas. It can be seen by comparing columns 4 and 5 in these tables that the dc values are again slightly higher than the pulsating current values as they were in the sulphate free glass. The two sets of values are so similar, indeed, that we may ascribed the same mechanism of film formation and stability to both - with the added complication in the case of the sulphate containing glass, of course, that the gas SO₂ is involved in the removal of the MoO₃ film as well as oxygen gas.

While it is considered that the oxide is the main component of the film surrounding the anodic working electrode, nevertheless sulphides can also form on the molybdenum electrodes. Most of the authors we have quoted with respect to molybdenum and, notably Hierl, Hanke and Scholze (38); Matej (43); Boffe, Delzant and Plumat (37) find sulphides present on their electrodes in one form or another as well as oxides. Certainly the formation of sulphides is thermodynamically possible for Stubbles and Richardson (44) found the standard free energy of the reaction:

$$4/3Mo + S_2 = 2/3Mo_2S_3$$
 [10]

to be -32kcal/mole of $\mathrm{Mo}_2\,\mathrm{S}_3$ at 1200°C, using the linear free energy equation:

$$\Delta G^{O} = -85,700 + 36.4T.$$
 [11]

SUMMARY

The pulsating current technique which we have described allows the measurement of many of the parameters involved in the electrochemical reactions occurring at polarising electrodes: the time to oxygen evolution (crucial as the deciding factor in whether a platinum electrode corrodes or not with an alternating current input); the quantity of electricity required for oxygen evolution; the capacity of the electrical double layer; the type and thickness of any oxide or salt film formed on the electrode; the reproducible values of the oxygen evolution potential, free from the polarising effects which are almost inseparable from dc measurements made in high temperature viscous melts.

The quantity of electricity required for oxygen evolution is usually constant for any one particular electrode/electrolyte combination and is independent of changes in current density and temperature within the limits of experimental error. The details of the reactions which occur before oxygen gas evolution then depend upon both the electrode material and the electrolyte. For platinum electrodes in molten silicate glass there is the complete removal of a mono molecular layer of the oxide PtO₂ every cycle followed by its fresh replacement; for sodium disilicate the replacement and removal are partial. For molten sodium diphosphate there is the partial removal and re-formation of a protective salt film on the electrode surface every cycle; for sodium diborate there is the initial formation of a partially protective salt film followed by breakdown and oxide film formation at the higher current densities. When the electrode material is changed to the reactive molybdenum the electrode kinetics are dominated by the permanent presence on the electrode of a thick oxide film.

The technique thus enables a detailed picture of the fast electrochemical reactions which are occurring to be built up, and in this the method is far superior to single pulse techniques. Its unique advantage over such methods is that it returns the electrode to its initial condition at the end of every cycle either completely stripped of oxide and salt film or in an equilibrium, partially stripped condition. It is the author's opinion that this pulsating current technique has been greatly neglected by electrochemists in comparison with the enduring interest shown in the other method which Hickling pioneered: the electronic potentiostat (45-48). Whenever basic data on the electrochemical reactions occurring at polarising electrodes is required which is free from bulk diffusion effects the method has a great deal to recommend it. It is ideally suited to the study of corrosion reaction mechanisms, but it may also be used to study cathodic processes such as electrodeposition; and it can be used with porous as well as bulk electrodes.

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NOTES I RELAY IS SHOWN OPERATED, WHICH IS NORMAL CONDITION BEFORE TIMED PERIOD STARTS

Figure 2 Single Pulse Circuit



Figure 3 High Temperature Electrolysis Cell



Pt Electrode-Soda Lime Silicate Glass





Pt Electrode-Soda Lime Silicate Glass







Mo Electrode-Soda Lime Silicate Glass



Figure 6

Pt Electrode-Sodium Disilicate

$s = \frac{1}{(a) \frac{1200^{\circ}C}{0.083A/cm^{2}}; 50\mu F}}$ (b)

T=5msec/d W(MP4)...R(MP2) A(MP1)...R(MP2) Anodic/Cathodic







(c) 1200°C 0.083A/cm²; 50μF Y=0.2V/d T=5msec/d A(MP1)...R(MP2) Successive shots after 30sec dc at 0.083A/cm² Cathodic



Figure 6 (cont)











Figure 7 (cont)

Pt Electrode-Sodium Diborate



(e) 1200°C 0.083A/cm²; 50µF Y1=Y2=0.5V/d T=2msec/d W(MP4)...R(MP2) W(MP4)...E Immediately after 5min dc at 0.083A/cm²



(f) 1200°C 0.083A/cm²; 50µF Y=0.5V/d T=2msec/d A(MP1)...R(MP2) Immediately after 5min dc at 0.083A/cm²



(g) Reaction at Cathode on Left after Electrolysis in Sodium Diborate Melt

560











Figure 9 Pt Electrode-Sulphuric Acid



N-H₂SO₄
0.01A/cm²; 6μF
Oscilloscopic;
Platinum Wire



b) 0.1N-H₂SO₄ 17μA/cm²; 5μF Direct Potentiometric; Platinised Platinum

Figure 10 Ni Electrode-Alkaline and Buffer Solutions



(a) N-NaOH 0.01A/cm²; 10.6µF



(b) 0.2M-KH₂ PO₄ +0.2M-Na₂ HPO₄ (pH6.8) 0.01A/cm²; 10.6μF



(c) 0.2M-KH₂ PO₄ +0.2M-Na₂ HPO₄ (pH6.8) (d) 0.1N-Na₂ B₄ O₇ (pH9.2) 0.01A/cm²; 10.6µF After cathodic polarisation at 0.01A/cm² for 3min



0.005A/cm²; 10.6µF After cathodic polarisation at 0.01A/cm² for 3min
ANODIC REACTION ON NICKEL IN A MOLTEN CsF-NH4F-HF SYSTEM

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ABSTRACT

The anodic reaction on nickel was investigated in the temperature range of 50 ~ 80 °C using a molten CsF-NH_F-HF system. The addition of cesium fluoride (CsF) into the molten electrolyte reduces the corrosion of the nickel anode. Anodic reaction on nickel seemed to vary with increasing potential, permitting division into four regions as follows: Anodic dissolution of nickel in Region I (0~ 1 V vs. H_2), deposition of a Ni(II) compound containing oxide on nickel in Region II (1~ 3 V), oxidation of Ni(II) film to Ni(II) and/or Ni (IV) compounds in Region II (3~ 5 V), and electrochemical fluorination of NH_a in Region IV (more positive than 5 V). The anode gas was composed of nitrogen trifluoride (NF_a) and nitrogen (N_2) with a small amount of cygen (0_2), nitrous oxide (N_2O), difluorodiazine (N_2F_2), and tetra-fluorohydrazine (N_{F_4}).

INTRODUCTION

A large amount of gaseous fluorine compounds such as nitrogen trifluoride (NF₃), sulphur hexafluoride (SF₆), and tungsten hexafluoride (WF₆) are consumed by the electronics industry in Japan. Highly pure NF₃ (99.99 %) free from carbon tetrafluoride (CF₄) is produced by electrolysis of molten NH₄F·2HF with a nickel anode to meet such demand.

However, the high consumption of nickel anodes is troublesome. The corrosion of the nickel anodes in NH₄F·2HF results in electrolytic current losses of more than 3 % at 120°C, resulting in deposition of nickel fluoride (NH₂) and ammonium nickel fluoride (NH₄NiF₃) on the cell bottom and increase of the operating cost.

The objective of this work is to analyze the anodic reaction on nickel in molten $CsF-NH_{4}F-HF$ system, and to clarify the advantage of the addition of cesium fluoride (CsF) into a melt, i.e., the reduction of the anodic dissolution of nickel.

EXPERIMENTAL

A small PTFE (poly-tetrafluoro-ethylene) cylinder-type cell of 0.45 dm³ in volume was provided for the electrochemical measurements and the corrosion test of nickel under operating conditions. The cell configuration was described in the previous paper [1] in detail. A rod anode having an effective area of 0.07 cm² was located at the center of the cell passing through the cell cover. A nickel sheet anode (purity of 99.9 %) having an effective area of 1 cm² was also used in some cases. A large area nickel counter cathode was used. Although the electrode potential was measured against the static potential of a platinum wire immersed in the same molten electrolyte, it was calibrated to a new scale referred to the potential for hydrogen evolution, and was presented in volts vs. H₂. The cell was positioned in a chamber filled with dry nitrogen to avoid moisture, and was warmed with a mantle heater to 50 or 80° C.

Figure 1 illustrated the production cell. A Ni working anode of 50 cm^2 in effective area located at the center of a cylinder-type copper cell (1.5 dm³ in volume) was separated by a copper skirt from the cell wall at which electrolytic hydrogen was evolved. The cell bottom was insulated by a PTFE sheet to avoid mixture of hydrogen with anode gas. The anode gas was treated with sodium fluoride (NaF) to eliminate HF. Its sample gas was fractionated by means of gas chromatography, and analyzed by infrared spectroscopy. The current efficiencies with respect to these constituents were evaluated from the results of gas analysis and the overall flow rate of anode gas.

Pre-electrolysis at low current density mainly with a carbon anode was conducted for many hours until NF₃ was generated and the electrolytic cell was stabilized before polarization measurement and/ or the corrosion testing. A Ni working electrode washed with water was rinsed with methanol to remove trace water prior to weighing. The anode was weighed before and after electrolysis to evaluate weight loss and the corresponding current losses. In this case, the concentration of water in the electrolyte could not be determined, but it might be less than 0.02 wt% [2].

In experiments of production cell, electrolyte was also prepared in a dry box with highly pure HF (99.99 %), NH₄F·2HF (purity of 99.7 %), and cesium fluoride (purity of over 99 %), but the cell was positioned in the atmosphere. Electrolysis was conducted soon after the electrolyte was charged in the cell. In our experiments, the concentration of water in the melt could not be either determined, but it might be higher than 0.02 wt%.

RESULTS AND DISCUSSION

Electrolysis

Molten CsF·NH₄F·4HF at 80°C was electrolyzed at 20 mA·cm⁻², and cell gas generated at the anode was collected and analyzed. In this case, anode potential stayed in the potential range of $4.2 \sim 4.8$ V vs. H₂. While a large amount of O₂ was evolved for the first 25 hours from decomposition of residual water in the melt, the gas composition was stabilized thereafter, as illustrated in Figure 2. It is clear that N₂ and NF₃ are main products with a small amount of O₂, N₂O, N₂F₂, and N₂F₄ being present. The current efficiency of NF₃ formation was about 37 %.

The limiting current density caused by diffusion of water was calculated from the equation of Fick's first law, as represented in Equation 1. The density of molten CsF+NH_F+4HF at 50 $^{\circ}$ C was ca. 2.06

g·cm⁻³. If the concentration of water in this melt might be 0.02 wt% (200 ppm), it would correspond to 22.9 mmol·dm⁻³.

$$i_{\rm L} = n FDC/\delta \tag{1}$$

where, i_{\perp} is the limiting current density (A·cm⁻²), *n* is number of electron in the discharge process of water, *F* is Faraday's constant (C ·mol⁻¹), *D* is Diffusion constant (cm² s⁻¹). *C* is the concentration of water in an electrolyte (mol·cm⁻³), and δ is the thickness of diffusion layer (cm). When we substitute the values such as F = 96,500 C·mol⁻¹, $D = 10^{-5}$ cm²·s⁻¹, $C = 22.9 \times 10^{-6}$ mol·cm⁻³, and $\delta = 10^{-3}$ cm in Equation 1, we can get $i_{\perp} = 88.4$ and 44.2 mA·cm⁻² in *n* = 4 and 2, respectively. This result indicates that the direct discharge of water in the melt and/or the oxidation of the film formed on Ni anode as well as the electrochemical fluorination of water could take place on the nickel anode according to Reactions $2 \sim 5$.

2H₂0	>	0₂ + 4H⁺ + 4e ⁻	(2)
2H₂O + 4F⁻	\rightarrow	0 ₂ + 4HF + 4e ⁻	(3)
NiF ₂ + 2H ₂ O	>	NiO + ½O₂ + 2HF + 2H⁺ + 2e⁻	(4)
3NiO + H₂O	>	Ni₃O₄ + 2H+ + 2e ⁻	(5)

Under the conditions of interest, $NH_{4}{}^{+}$ and NH_{3} are in the equilibrium of Eqs. 6 and 7,

NH₄F	+	nHF		$NH_4^+ + F(HF)_n^-$	(6)
NH₄⁺	+	mHF	₹	$NH_3 + H(HF)_m^+$	(7)

where F(HF),⁻ and H(HF),⁺ are the solvated ions of F⁻ and H⁺, respectively, and now written as F⁻ and H⁺ for simplicity. Amount of NH₃ in the melt is generally considered negligible. Nitrogen trifluoride and nitrogen are evolved at the anode by Reactions $8 \sim 10$ [3].

NH₄⁺	+	6F-	>	NF3	. +	· 3HF		- H+	+	6e-	(8)
2NH₄+	+	6F-	\rightarrow	N2	+	6HF	+	2H⁺	+	6 e ⁻	(9)
	21	lH₄+	>	N 2	+	8H+	+	6 e -			(10)

However, the side reactions, $2 \sim 4$ and $11 \sim 13$, may also proceed in parallel to form minor components, eq., O_2 , N_2F_2 , N_2F_4 , and N_2O .

2NH₄⁺ + 8F⁻ —	→	N ₂ F ₂ + 6HF + 2H ⁺ + 8e ⁻	(11)
2NH₄+ + 10F	→	N₂F₄ + 6HF + 2H⁺ + 10e⁻	(12)
2NH₄⁺ + H₂O + 8F⁻	→	N₂O + 8HF + 2H⁺ + 8e⁻	(13)

Anodic Polarization Measurements

Figure 3 shows the potential sweep curves of a nickel anode in CsF·NH₄F·4HF at 50°C. A large current caused by anodic dissolution of Ni flowed at the potential range of 0.3 \sim 0.5 vs. H₂ when a fresh Ni anode was polarized (Curve 1), but it was subsequently passivated in the potential range of 1.5 \sim 3 V (Region II). The current increased again by oxidation and/or fluorination of the anode surface in the

range of $3\sim 5$ V (Region III). At potentials higher than 6 V (Region IV), gas was evolved from the anode, and the current increased.

Curve 2 shows the polarization curve of the same specimen at the second run. No electrolytic current was observed over a wide range of potential until gas evolution took place at ca. 6 V since the electrode surface was covered with a stable film. The surface film was not removed even if the electrode was left at the static potential for several minutes. Potential scanning in the range of 0 to ca. 9 V was repeated many times. Curve 3 in Fig. 3 is the polarization curve after fifty runs. A large current was observed at potentials more positive than 3 V. The current density moved up and down with the potential scan toward the positive direction through a maximum of ca. 82 mA·cm⁻² at 4.3 V and a minimum of 50 mA·cm⁻² at 5 V, and increased thereafter. The polarization curve varied with the history of electrode.

Figure 4 shows the potential sweep curves of a nickel anode at 50 °C in CsF·NH₄F·4HF without pre-electrolysis. The shape of waves was very similar to that in Fig. 3, but three remarkable differences between Figs. 3 and 4 were observed as follows; The anodic current peak at ca. $0.3 \sim 0.5$ V in Fig. 4 was much larger than that in Fig. 3, and in contrast, the current density at potentials more positive than 3 V in Fig. 4 was smaller than that in Fig. 3. Besides, the muximum current density at 4.3 V was not observed, but the limiting current density at potential range of $4.5 \sim 6$ ' was observed in Fig. 4 (see Curves 1 and 3). These facts indicate that the anodic current densities observed on nickel are affected with the concentration of water in the melt.

Molten CsF+NH₄F+4HF after pre-electrolysis was electrolyzed with a fresh anode at given potentials, and the corrosion rate of the Ni anode was measured. The experimental results are summarized in Table 1. Note that the experimental was conducted under potentiostatic conditions whereas the polarization measurements such as shown in Fig. 3 were carried out by a potentiodynamic method. This causes different current density under equal potential in the two cases (Fig. 3 and Table 1). Generally, the higher the sweep rate of potential the higher is the current density. As shown in Fig. 3, a large current caused by active dissolution of nickel was observed at 0.37 V. Table 1 shows that the electrolytic current was almost 100 % consumed by the anodic dissolution. In passive region, $1.5 \sim 3 \text{ V}$ vs. H₂, the overall current density was small with no dissolution of Ni. The current density incresed with increase of the anode potential above 5 V. Although the corrosion rate of nickel anode also incresed, the current losses were almost unchanged at 1.1 \sim 1.8 %. Electrolytic gas evolution took place at potentials more positive than 5 V in Region IV of Fig. 3.

The potentiostatic polarization curve was shown in Figure 5 with the potential sweep curve (First run) with a sweep rate of 5 mV·s⁻¹ together. The comparison with both curves also revealed that the anodic current density in Region III incresed with a course of time.

It is difficult to identify the passive film or oxide layer on the anode surface since the fluorine-containing nickel compound formed in the melt is decomposed when it is exposed to the atmosphere. However, its surface film is stable in the melt, and it built up by repeatition of potential scanning, resulting in roughness.

With these experimental results and visual observation, we can evaluate the electrochemical processes occurring on the anode. After the virgin surface is dissolved in Region I, the anode is covered with a protective film, probably composed of a Ni (I) compound, either oxide or fluoride or both, in Region II. Nickel (II) film is oxidized to Ni(II) at potentials more positive than 3 V. In the intermediate region, $3 \sim 5 V$ (Region III), a component of film. NiO, would be possible to form a spinel (Ni₃O₄) layer, which is electrochemically active and electrically conductive [4], and hence the electrolytic current of Curve 1 in Figs. 3 and 4 increases. Its layer is further oxidized to NiO_{2-x}, where x varies with the polarization potential; the higher the potential the smaller x.

In order to prove it, the potential sweep curves of a nickel anode at 50 °C in CsF·NH₄F·4HF without pre-electrolysis was also determined at the potential range of 0 ~5 or 6 V, and shown in Figure 6. The limiting current density at potential range of $4.5 \sim 5.5$ V was also observed on Curve 1 at first run scanned toward the positive direction, but the cathodic current density was not observed on the curve scanned toward the negative direction. Besides, the limiting current density disappeared on Curve 2 obtained in second run, and the current density increased at the potentials more positive than ca. 5 V. This means that the limiting current density would be due to the oxidation of the film formed on the Ni anode rather than due to decomposition of residual water to 0_2 .

The potential sweep curves in Figs. 3 and 4 were again analyzed. In the potential range more positive than 6 V (Region IV), gas evolution takes place preferentially on the surface containing oxide. Once the film containing oxide is formed during the first run of positive potential scanning, the oxide in the layer is apparently not reduced even if the potential is scanned negatively, and hence no current flows in the potential range of 0 \sim 6 V in the second run with the exception of a very small current for passivation. The film containing oxide becomes thick by repetitive potential scanning in the wide range of 0 \sim 9 V. Its brittle layer may crack and the nickel substrate is exposed to the melt, resulting in a large surface at high rate (high current density) and relatively negative potential, ca. 5.5 V vs H₂.

Figure 7 shows the chronopotentiograms of a fresh nickel electrode at 50 °C in molten CsF·NH₄F·4HF after pre-electrolysis. At 25 mA·cm⁻² (top figure), the anode potential jumped to some 10 V υ s. H₂ 20 minutes after switch-on, then dropped to 5 V. It indicates that the formation of stable film containing oxide requires 20 minutes or some 30 coulombs per cm². At 10 mA·cm⁻² (bottom figure), on the other hand, the film containing oxide was only formed after 9 hours. The potential fluctuated extensively after dropping to 5 V, probably because of degradation and regeneration of the layer composed of oxide and/or fluoride. In parallel with these processes, fluorination of NH₃ to NF₃ takes place at ca. 5 V υ s. H₂.

CONCLUSION

Anodic reaction on nickel in molten CsF-NH₄F-HF system seemed to vary with increasing the potential, permitting devision into four regions stated as follows. The reaction in Region I (0 \sim 1 V vs. H₂) is anodic dissolution of nickel. The Ni(II) compound containing oxide is deposited on nickel and the nickel anode is covered with a stable film, so that the nickel anode is passivated at the potential range of $1 \sim 3$ V (Resion II). Nickelous film on nickel is further oxidized and/or fluorinated to form the Ni(Π) and/or Ni(Π) compounds containing oxide in Region \mathbbm{H} , and electrochemical fluorination of NH₃ to NF₃ takes place at the potentials more positive than 5 V (Region IV). The composition of film formed on the nickel anode changed with a course of time and its resistance decreased, so that electrochemical fluorination of NH₃ to NF₃ could also take place at ca. 4.2 ~4.8 V vs. H₂ after electrolysis for longer duration. The addition of CsF into the molten electrolyte is effective on the reduction of the corrosion of nickel anode, resulting in the loss of electrolytic current.

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- Fig. 1 Experimental setup for electrochemical fluorination.
 - W: Working electrode, Ni sheet,
 - C: Counter electrode, Cell wall,
 - RE: Reference electrode, Pt wire,
 - S: Skirt,
 - G: Gasket, PTFE,
 - A: HF absorber, NaF pellets,
 - P.G.: Potentiostat-
 - Galvanostat,
 - R: Recorder.



Fig. 2 Change of anode gas composition during galvanostatic electrolysis in molten $CsF \cdot NH_4F \cdot 4HF$ at 20 mA $\cdot cm^{-2}$ and 80 °C as a function of time. Conditions: Anode: Nickel, surface area = 50 cm², Cell voltage: $4.2 \circ 4.9$ V, Anode potential: $3.7 \circ 4.3$ V vs. Pt.



Fig. 3 Potential sweep curves of a nickel anode at 50 °C in molten $CsF\cdot NH_4F\cdot 4HF$ after pre-electrolysis; sweep rate = 200 mV·s⁻¹. 1: First run, 2: Second run, 3: 50th run.



Fig. 4 Potential sweep curves of a nickel anode at 50 °C in molten CsF·NH₄F·4HF without pre-electrolysis; sweep rate = 200 mV·s⁻¹. 1: First run, 2: Second run, 3: 50th run.

Anode	Overall Current	Corrosion	Current Losses
Potential	Density	Rate	caused by Ni
/V vs. H ₂	/mA·cm ⁻²	/mg·cm ⁻² ·h ⁻¹	Dissolution /%
0.07	0.0114	0.00455	63.3
0.37	2.00	2.30	105
3.07	0.212	0.00	0
5.07	255	0.94	1.34
6.47	420	5.15	1.12
7.56	1180	16.8	1.30
9.47	3505	69.6	1.81

Weight losses of a nickel anode in molten $\texttt{CsF} \cdot \texttt{NH}_4 \texttt{F} \cdot \texttt{4HF}$ at 50 °C and given potentials. Table 1





- Obtained at 100 °C with a sweep rate of 5 mV·s⁻¹ by the potential sweep method,
 Obtained at 50 °C by the potentiostatic method.



Fig. 6 $CsF \cdot NH_4F \cdot 4HF$ without pre-electrolysis; sweep rate = 200 mV \cdot s⁻¹.



안

Time / hours

Electrochemical Formation of Thin Carbon Film from Molten Chloride System

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ABSTRACT

Cathodic reduction of carbonate ion in LiCl-KCl eutectic melt was investigated at $400-500^{\circ}C$ (mainly at $450^{\circ}C$) using cyclic voltammetry and chronopotentiometry. In the voltammogram, two cathodic peaks were observed at 0.8V and 0.5V(vs.Li/Li'), respectively. The former was ascribed to the reduction of carbonate ion to form elementary carbon and the latter was ascribed to the intercalation of reduced lithium into the electrodeposited carbon layer. On the other hand, three anodic peaks were observed. The peak observed at the most negative potential was ascribed to the anodic dissolution of intercalated lithium and the other two, at 1.8V and 2.1V(vs.Li/Li') respectively, were concluded to be due to the irreversible anodic oxidation of carbon, through a series of the slow back reactions of

(a) $CO_3^2 + 2e^- = CO_2^2 + O^2^$ and

(b) $CO_2^{2-} + 2e^- = C + 2O^{2-}$. Diffusion coefficient of carbonate ion was estimated to be $1.66(\pm 0.05) \times 10^{-5}$ cm²s⁻¹ at 450°C, and the activation energy of diffusion was estimated to be $1.43(\pm 0.15)$ kJ mol⁻¹. By potentiostatic and galvanostatic macroelectrolysis, various

types of film were obtained at the cathode depending on the electrolytic conditions. From the analysis by RBS,ESCA, X-ray diffraction and Raman spectroscopy, these films were concluded to be amorphous carbon.

INTRODUCTION

The electrochemical formation of carbon film from molten halide is an interesting research subject since this can be considered as one of the candidate electrochemical CO_2 fixation processes to obtain valuable product. The CO_2 fixation can be achieved through the following two steps : First, CO_2 gas is supplied into molten halide containing oxide ion, to form carbonate ion. And then, by the electrolysis, cathodic reduction of carbonate ion takes place to form various types of carbon film on the cathode, depending on the electrolytic conditions. This report describes the results of experiments conducted by using LiCl-KCl eutectic melt containing carbonate ion which exemplified the possibility of the latter step of the above process. The results obtained here also provide useful information for considering the electrodeposition of metal carbides from halide melts containing the mixture of oxyanion of the metal and CO_3^{2-} ion.

EXPERIMENTAL

First of all, the electrochemical behaviour of carbonate at nickel cathode in LiCl-KCl eutectic melt was ion investigated at 400-550°C (mainly at 450°C) using cyclic voltammetry and chronopotentiometry, in order to realize that the aimed reaction can really occur, as well as to clarify the reaction mechanism. All chemicals were of reagent grade (Wako Chemicals Co., Ltd.) and were dried under vacuum for several days at 200°C. After melting the salt, argon gas was bubbled into the melt for severl hours to remove contaminated water further. By this procedure, residual cathodic current density could be reduced to less than $2 \times 10^{-3} \text{ A} \cdot \text{cm}^{-2}$ at $1.3 \text{ V}(\text{vs.Li/Li}^+)$ at a scan rate of 0.1Vs⁻¹. An Ag/Ag⁺ electrode was used as the reference electrode, which comprises a silver wire and chloride(1mol% AgCl) that were both contained in a pyrex glass tube which had a very fine tip. The potential of this reference electrode was calibrated against an alkali metal electrode, Li/Li^{*}, that was prepared by the electrodeposition of Li on a nickel wire [1]. Unless otherwise stated, all potentials are reported with respect to the potential of $\mathrm{Li}/\mathrm{Li}^*$ couple in the melt. Glassy carbon rod was used as an anode. After preparing the solvent melt, vacuum-dried pottasium carbonate was added to a oncentration of 0.02 - 1.0 %.

After a series of cyclic voltammetry and chronopotentiometry experiments, potentiostatic and galvanostatic macroelectrolysis were conducted using several kinds of cathode materials including nickel and aluminum. The electrolytic conditions were determined based on the voltammograms as well as the chronopotentiograms obtained in the above experiments. The electrodeposited samples were taken out of the cell, washed with distilled water, dried and kept in a desiccator. The samples were then subjected to analysis using SEM, EPMA, EDX, ESCA, RBS, XRD and Raman spectroscopy.

RESULTS AND DISCUSSION

1. Reaction Mechanism

Typical cyclic voltammogram is shown in Fig.1[2]. Two cathodic peaks B and C are observed at 0.8V and 0.5V, respectively. And three anodic peaks, D, E and F are also observed.

1.1 Cathodic Reaction

Figure 2 shows relation between peak current density of Peak B and the concentration of added carbonate ion, and Figure 3 shows relation between peak current density of Peak B and potential scan rate. These linear relations suggest that the reaction is diffusion controlled. As for Peak C, it seems to appear due to the formation of intercalation compound between electrodeposited carbon and lithium [3]. Thus, cathodic peak concerning the reduction of carbonate ion is only Peak B. And as will be described later, electrodeposition of elementary carbon was confirmed by the analysis of the product obtained at the peak potntial of B. Then, cathodic reduction of carbonate ion is simply expressed as :

$$CO_3^2 + 4e^- = C + 3O^2 - (1).$$

Figure 4 shows relation between the potential of Peak B and potential scan rate v. The peak potential shifts to the negative direction linearly with log \sqrt{v} [4]. This indicates that the following theoretical relation for the irreversible reaction [5] can be applied :

$$\frac{dE_P}{d(\log\sqrt{v})} = -2.303 \frac{RT}{\alpha n_a F}$$
(2)

, where n_{a} is the number of electrons involved in the rate determining elementary step. From the slope of the line in Fig.4, αn_{a} for Peak B is estimated to be $1.04(\pm 0.20)$. The αn_{a} value can be also estimated from the peak width. This was determined to be 0.89 (\pm 0.13), according to the following equation [5]:

$$E_{P} - E_{P/2} = -1.859 \frac{RT}{\alpha n_{a}F}$$
(3).

These two values are in fairly good agreement.

1.2 Anodic Reaction

Let us then consider Peak E which appears at the anodic scan, applying the theoretical relation :

$$E_{Pa} - E_{Pa/2} = \Gamma \frac{RT}{(n - ana) F}$$
(4).

Here, n is the number of electrons involved in the total reaction, and n_a is the number of electrons involved in the rate determining elementary step.

This relation is derived for the case of anodic reaction of the product formed at the electrode surface by the cathodic reduction of complex ion with coordination number m. Γ in eqn(4) is a constant which is given as :

 $\Gamma = 1.839, 2.588, 3.288 (m = 1, 2, 3)$

, depending on the coordination number m [5]. From the width of Peak E, 0.13 (\pm 0.007), (n - α n,)is calculated to be :

$$n-\alpha n_a = 0.88 (\pm 0.05), 1.24 (\pm 0.07),$$

and $1.58 (\pm 0.09)$

, for the m value of 1,2 and 3, respectively. Accordingly, n is calculated to be 1.77, 2.13 and 2.47 for m = 1, 2 and 3, respectively. These values are all arond 2, which is very different from the value 4 for the number of electrons for reaction (1). This can be understood if we assume that the reaction (1) proceeds through 2 electron reaction steps (5) and (6). That is, in Fig.1, carbonate ion in the solution is reduced to divalent carbon, which is immedeately reduced to elementary carbon. But at Peak E which corresponds to the

reverse reaction of Peak B, reaction from divalent to tetravalent carbon does not proceed even when elementary carbon is reduced to divalent carbon, and divalent ion is considered to diffuse to the bulk solution. Chemical form of divalent corbon ion may be CO_2^{2-} , as proposed by Delimarskii et al [6]. Thus, Peak F is considered to be ascribed to the anodic oxidation of CO_2^{2-} to form CO_3^{2-} ion.

$$\frac{Q}{CO_3}^{2-} + 2e \frac{(s \mid ow)}{(s \mid ow)} CO_2^{2-} + O^{2-}$$
(5)
$$CO_2^{2-} + 2e \frac{(fast)}{(s \mid ow)} C + 2O^{2-}$$
(6).

Concludingly, Peak B corresponds to the forward reaction of (5) + (6), Peak E corresponds to the back reaction of reaction (6), and Peak F corresponds to the back reaction of reaction (5).

As reactions (5) and (6) are both elemetary processes and thus $% \left(\left\{ {{{\mathbf{x}}_{i}} \right\} \right\}$

$$n_a = n = 2$$

, peak potential differenece can be written as:

-

$$E_{Pa} - E_{P} = 2.53 \frac{RT}{nF} + \{-(2.303 + 0.215\alpha) \log \Lambda - 5.69 + 6.17\alpha\} \times \frac{RT}{\alpha (1 - \alpha) nF}$$
(7).

From this equation, reversibility parameter Λ defined by euation (9) can be obtained. And from equation (8) and the peak potential of Peak B, $E_{\rm P}$ = 0.743V, standard potential E° can be determined. Furthermore, standard rate constant k° can be also determined from the Λ value, according to equation (9).

$$E_{P} - E_{\cdot}^{*} = -1.16 \frac{RT}{nF} + 2.303 \{ log \wedge +2.475 \} \frac{RT}{a nF}$$
(8)

$$k^* = \sqrt{\frac{nF}{RT}v} \cdot \Lambda \tag{9}.$$

Here, E_{\circ} and k_{\circ} are defined as:

$$E^* = \frac{RT}{nF} \, \ell n \left(\frac{kf}{k_b^*} \right) \tag{10}$$

and

$$k^{\circ} = k \ell^{\circ 1 - \alpha} k \delta^{\circ \alpha} \tag{11}$$

Reversibility factor Λ are obtained as:

$$log \wedge (5) = -5.53$$

and

$$log \Lambda^{(6)} = -4.50$$

, respectively, since potential diffences between Peak B and Peak C, and Peak B and Peak F are 1.07 and 1.38(V), respectively, at the scan rate of $0.4Vs^{-1}$. Furthermore, E° 's are determined to be 1.27 and 1.11, respectively, and k° 's are determined to be 1.06×10^{-5} and $1.13\times10^{-4}\,({\rm cm\cdot\,s^{-1}}),$ respectively.

Figure 5 shows the comparison between experimental and calculated voltammogram[4]. The calcuation was conducted using the paramenters obtained above. The fairly good agreement suggests that the above discussion is reasonable.

Figure 6 shows typical chronopotentiogram. Only one plateau can be observed here, which also shows the appropriateness of the above conclusion that the cathodic rection (1) proceeds by single step or by a consective step involving slow rection (5) immedeately followed by fast reaction (6).

2. Diffusion Coefficient of Carbonate Ion

From the experimental data of cyclic voltammetry shown in Figs.2 and 3, diffusion coefficient of carbonate ion D_{\circ} is estimated to be:

$$D_o = 1.6 (\pm 0.4) \times 10^{-5} (cm^2 s^{-1})$$

, with the use of equation (12):

$$i_{P} = -0.4955 n F A C o^{x} \sqrt{\frac{\alpha n_{a} F}{RT} D o}$$
 (12).

Figure 7 shows relation between transition time τ and $(C_{\rm o}/i)^2$ obtained by chronopotentiometry. As equation:

$$\sqrt{\tau} = \frac{\sqrt{\pi D_o \, n F A C_o}}{2 \, i} \tag{13}$$

holds for both reversible and irreversible reaction, diffusion coefficient of carbonate ion is thus estimated to be:

 $D_{\circ} = 1.66 (\pm 0.05) \times 10^{-5} (cm^2 s^{-1}).$

This value is coincident with the value obtained by cyclic voltammetry.

Figure 8 shows Arrhenius plot of diffusion coefficient. From this figure, activation energy of the diffusion is estimated to be:

 $\Delta E_a = 1.43 (\pm 0.15) (kJ mol^{-1}).$

3. Electrodeposition of Carbon Film

Figures 9 and 10 show SEM images of film potentiostatically electrodeposited on Ni substrate and Figures 11 and 12 show those potentiostatically electrodeposited on Al substrate [7]. Figure 13 and Figure 14 show those galvanostatically electrodeposited on Al substrate. Various morphologies are obtained depending on the potential. Especially, it is interesting to see fiber like carbon in Figs. 10 and 15. Figures 16,17,18 and 19 show an example of RBS spectrum, ESCA spectrum, XRD pattern and Raman spectrum of film, respectively. These data show that the electrodeposited films are amorphous carbon.

CONCLUSION

Cathodic reduction of carbonate ion in LiCl-KCl eutectic melt was investigated at $400-550^{\circ}C$ (mainly at $450^{\circ}C$) using cyclic voltammetry and chronopotentiometry. Cathodic reduction of carbonate ion to form elementary carbon is concluded to proceed by single step reaction:

$$CO_3^{2-} + 4e = C + 3O^{2-}$$

, or by a consective reaction involving slow reaction:

$$CO_3^{2^-} + 2e \xrightarrow{(slow)} CO_2^{2^-} + O^{2^-}$$

, immedeately followed by:

$$CO_2^{2^-} + 2e \xrightarrow{(fast)} C + 2O^{2^-}$$
.

On the other hand, anodic dissolution of carbon to form carbonate ion is concluded to proceed through a series of the slow back reactions of the latter two.

Diffusion coefficient of carbonate ion was estimated to be $1.66(\pm~0.05)\times~10^{-5}~{\rm cm^2}\cdot~{\rm s^{-1}}$ at $450^{\circ}{\rm C}$, and the activation energy of diffusion was estimated to be $1.43(\pm~0.15){\rm kJ}\cdot~{\rm mol^{-1}}$.

By potentiostatic and galvanostatic macroelectrolysis, various types of film were obtained depending on the electrolytic conditions. From the analysis by RBS, ESCA, XRD and Raman spectroscopy, these films were concluded to be amorphous carbon.

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- Fig.1 Voltammogram LiCl-KCl, 450°C, Ni electrode, [CO₃²⁻] : 0.2mol%, Scan rate : 0.2V·s⁻¹
- Fig.2 Relation between Current Density of peak B and [CO₃²⁻] LiCl-KCl, 450°C, Ni electrode, Scan rate V·s⁻¹



Fig.3 Relation between Current Density of peak B and scan rate LiCl-KCl, 450°C, Ni electrode, $[CO_3^{2-}]$ (mol%) $\blacksquare:0.1, +:0.2, \diamond:0.4, \land:0.7$



Fig.4 Potential of peak B against $log \sqrt{v}$ LiCl-KCl, 450°C, Ni electrode, $[CO_3^{2-}]$ (mol%) O:0.1, +:0.2, ×:0.4, \bullet :0.7





Fig.6 Chronopotentiogram LiCl-KCl, 450°C, Ni electrode, Current: 20 mA \cdot cm⁻² \cdots : $[CO_3^{2-}]: 0.1$ mol% \cdots : blank data A : Reduction of carbonate ion B : Reduction of lithium ion



Fig.7 Relation between τ and $(C_{o}/i)^{2}$ LiCl-KCl, 450°C, Ni electrode,



Fig.8 Arrhenius plot of diffusion coefficient of ${\rm CO}_{\,3}{}^{2-}$ LiCl-KCl. Ni electrode



Fig.9 Surface SEM Image of Carbon Deposits on Ni Substrate (0.5V vs. Li/Li*)



Fig.10 Surface SEM Image of Carbon Deposits on Ni Substrate (1.0V vs. Li/Li⁺)



50 µ m

Fig.11 Surface SEM Image of Carbon Deposits on Al Substrate (0.9V vs. Li/Li*)



50µm Fig.12 Surface SEM Image of Carbon Deposits on Al Substrate (1.0V vs. Li/Li*)



50µm

Fig.13 Surface SEM Image of Carbon Deposits on Al Substrate $(1.0 \text{mA} \cdot \text{cm}^{-2})$



50 µ m

Fig.14 Surface SEM Image of Carbon Deposits on Al Substrate $(2.0\text{mA}\cdot\text{cm}^{-2})$



1 *µ* m

Fig.15 Surface SEM Image of Carbon Deposits on Al Substrate $(2.0 \mbox{mA} \cdot \mbox{cm}^{-2})$



Fig.16 RBS Spectrum of Film Electrodeposited at 0.6V







Fig.18 X-ray Diffraction Pattern (Co-Kα) of Film Electrodeposited at 0.4V



MELTING BEHAVIOR FOR POWDERS/ HYDRATE MELT (CaCl₂·*n*H₂O; *n*=6.00, 7.35) COEXISTING SYSTEMS

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ABSTRACT

The melting behavior of CaCl₂·nH₂O (n=6.00, 7.35) coexisting with the inorganic powders was investigated with DSC measurement. For α -Al₂O₃ powder/CaCl₂·6.00H₂O coexisting system, the melting point of the hydrate was lowered and the molar enthalpy of melting decreased both with the decreases of the liquid content and with the increase of the specific surface area of the powder. The observed melting point correlated to the transition point obtained by the electrical conductivity. For α -SiC powder/CaCl₂·6.00H₂O coexisting system, the melting point and the molar enthalpy of fusion for hydrate were constant in the range of 17.2-48.0 vol% of the hydrate content. These behaviors led that the phase transition of hydrate mear the surface of the solid phase was significantly influenced by the hydrophilicity of solid phase surface.

Introduction

The thermodynamical properties of the melt at the temperature range near the melting point were attractive in the viewpoint of the utilization of them, such as crystal growth, heat accumulation and so on, and have been investigated (1, 2). Some researches on the thermal cycles of the various kinds of hydrates have been carried out with differential scanning calorimetry (DSC) by Cantor (3, 4). Recently, we have investigated on the physical properties of the liquid phase in the solid-liquid coexisting system and reported on the electrical conductivity and its temperature dependence for α -Al₂O₃ powder/CaCl₂·nH₂O system(5). In the present paper, we studied on the melting behavior of hydrate in the inorganic powder (α -Al₂O₃ α -SiC)/CaCl₂ hydrate coexisting system to measure with DSC. Also, the relationship between the thermodynamical properties of the liquid phase of the solid phase were discussed.

Experimental

The solid phase used in this study were high-purity α -Al₂O₃ powder and high-purity α -SiC powder which had various surface areas. The physical aspects of them are shown in Table 1. The methods of the pretreatment and characterization of powders have been reported(6). CaCl₂ hydrates were prepared from CaCl₂·2H₂O (supplied Nakalai Tesque

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Species	Sample no.	Specific surface area [m ² /g]	Particle size [µm]	Grade
α-Al ₂ O ₃	2 5 7 9	0.6 3.0 5.0 25.3	75 0.7 0.4 0.6	Showa calcined Showa low soda Showa ultra pure Showa ultra pure
α-SiC	s	1.1	<19	Kishida (#800)

	Tab	le I.	Ph	ysical	asp	ects	of	powd	ers
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Inc.) and double distilled water as a liquid phase. $[H_2O]/[CaCl_2]$ ratios, *n*, in used hydrates were 6.00 and 7.35.

For DSC measurement, α -Al₂O₃ powder was mixed thoroughly with the hydrate by using an agate mortar and immediately sealed in an aluminum pan. The volume fractions of the liquid phase were ranged in 17.2-48.0 v/o. The measurement was carried out for the frozen sample on heating from -80 to 60°C with DSC/20 thermal calorimeter (Seiko Instruments & Electronics Ltd.).

The Scanning speed was 5° C/min. The temperature calibration was carried out by using the melting points of 1,2-dichloroethylene (m.p.: -35.3° C) and diphenylether (m.p.: 30° C). The area of the endothermic peak on DSC curves, attributed to melting of CaCl₂-6H₂O, was calculated with the Kambe's method (6). The volume fraction was calculated by the same method as described previously (7).

The obtained DSC curve included the heat capacity of the powder and hydrate with the latent heat of fusion as a base line. It was corrected to determine the heat of fusion for the hydrate by subtracting the base line. In order to discuss the influence of the solid phase on the melting behavior of the hydrate, the DSC curves were represented as the heat balance for the liquid phase per unit area of the solid phase, $(\Delta Q_s/\Delta T)$, which was calculated as follows;

$$(\Delta Q_{\perp}/\Delta T) = (\Delta Q/\Delta T) / (S_{\rm w} \cdot W)$$
^[1]

where $(\Delta Q/\Delta T)$, S_w and W are the heat balance of the sample, thespecific surface area and the weight of the powder, respectively.

Because the hydrate is lied on the solid surface with having a certain thickness as mentioned in Ref.5., the apparent average thickness of the liquid phase layer, *d*, was defined as following;

$$d = V_{\text{lig}} / (S_{\text{w}} \cdot W)$$
^[2]

where $V_{\text{lig.}}$ is the total volume of the liquid phase.

Then the molar enthalpy of melting, $\Delta H_{\rm m}$, was calculated as follows,

$$\Delta H_{\rm m} = \frac{-M \int_{T_1}^{T_{\rm h}} (\Delta Q_s / \Delta T) dT}{d \cdot \rho}$$
[3]

where *M* is the molecular weight of CaCl₂·6H₂O (219.1), ρ is density of the hydrate melt above the melting point, and *T*₁ and *T*₁ are temperatures of the higher end and the lower end of the peak, respectively. The calculated value is regarded to the heat of fusion for the hydrates.

Results and Discussion

The DSC curves for various kinds of α -Al₂O₃ powders/CaCl₂·6.00H₂O coexisting systems are shown on Figure 1. For each sample, the endothermic peak assigned to melting was observed. The peak shifted toward the lower temperature with the decrease of the liquid content.



Fig.1. DSC curves for α -Al₂O₃ powder/ CaCl₂·6.00H₂O coexisting system. α -Al₂O₃ powder in (a): no.5 and in (b): no.9.

For the system which contains α -Al₂O₃ (*no.* 5) powder (Fig.1(a)), the variation of the endothermic peak area was not linearly proportional to the content of the liquid phase. Especially, for 25.5 v/o of the liquid phase, the endothermic peak was very small. Also, the DSC curves at the lower end of the peak were overlapped for each samples. In order to discuss on the melting behavior, the models of the liquid layer near the solid surface were presented at Figure 2. It is suggested that the melting of the hydrate starts from the vicinal region on the powder surface at a lower temperature than the ordinary melting point. The smaller peak than that expected for the system containing little hydrate, which is in a state of the thin layer on the powder surface, led to the decrease of the molar enthalpy of melting for the hydrate near the powder. In contrast, the peak area was remarkably large for the system with the higher hydrate content. It is suggested that the molar enthalpy change for melting was close to that of the bulk state at the distant region from the solid surface. Thus, the molar enthalpy change for melting of the hydrate was correlated with the distance from the solid surface. The DSC curves for the system containing α -Al₂O₃ (*no. 9*) powder are shown in Figure 1(b). It shows that the diminution of the peak area is promoted with the increase of the specific surface area of the α -Al₂O₂ powder. These results suggested that the phase transition of the hydrate near the powder surface was influenced by the existence of the solid phase.

The relationship between the total enthalpy of the melting, $\Delta H_{m}^{\text{total}}$, with a normalized



Figure 2. Models for the vicinal layer.



Fig.3. (a) Relationships between $\Delta H_m^{\text{total}}$ and the content of the hydrate for α -Al₂O₃ (*no. 2*) powder/ CaCl₂·6.00H₂O coexisting systems. (b) Variations of ΔH_m with the liquid content for various kinds of α -Al₂O₃ powders/ CaCl₂·6.00H₂O coexisting systems.

surface area, per 1.0 m², of the powder and the content of the hydrate for α -Al₂O₃ (*no.* 2) powder/ CaCl₂·6H₂O coexisting systems was shown in Figure 3(a). The $\Delta H_m^{\text{total}}$ increased with the amount of the hydrate phase, but is not proportional with the amount of the hydrate phase near the solid surface differs from that in the bulk region. The molar enthalpies for the melting of the hydrate, ΔH_m^{-1} , in the various kinds of α -Al₂O₃ powder/ CaCl₂·6H₂O coexisting systems was shown in Figure 3(b). It is

shown that ΔH_m increased with the hydrate content and was levelled off in the composition range above *ca.* 40 v/o of the liquid phase. ΔH_m also decreased with the increase of the surface area of α -Al₂O₃. If it can be assumed that the molar enthalpy change for melting of CaCl₂·6H₂O is constant, these results suggest that the hydrate melt partially solidifies in the vicinity of the surface of α -Al₂O₃ powders.

On the basis these results, the existence of the non-frozen liquid phase, ϕ_{NFL} , can be defined thermodynamically as follows,

$$\phi_{\rm NFL} = 1 - \Delta H_{\rm S/L} / \Delta H_{\rm bulk} \qquad [4]$$

where, ΔH_{sfL} and ΔH_{pulk} were the molar enthalpies of melting of the hydrate for the solid/ liquid coexisting system and the bulk system, respectively. Thus, variations of ϕ_{NFL} with the hydrate content for α -Al₂O₃ (*no.* 2 and *no.* 9) powders/ CaCl₂· 6.00H₂O coexisting system



Fig.4. Variations of ϕ_{NFL} with the liquid content for α -Al₂O₃ powders/CaCl₂·6.00H₂O coexisting systems.

are shown in Figure 4. The decrease of the hydrate content led to the relative increase of the region of the non-frozen liquid phase. It indicates that the freezing of the hydrate was hindered by the solid surface. In the solid/liquid coexisting system, it is known generally that the solid particle acts as a seed for crystalline nucleation. However, in this case, the melt was stabilized by too many solid particles.

The non-frozen liquid contributes to form the electric conduction path at a temperature even below the melting point, whereas the solidified crystalline hydrate behaves as the electric insulator. According to the results of the electric conductivity (5), the deflection of the conductivity was observed at the melting point on the plots of $\ln \sigma vs. 1/T$ during heating. However, during cooling, the solidification did not occur and the deflection point was not observed. So, the electrical conductivity measured in the cooling process were that of the supercooled hydrate. The ratio of the electrical conductivities on cooling to that on heating, $\sigma_{coag}/\sigma_{mpl}$, at the various temperatures indicates the extent of the decrease of paths owing to the solidification of the hydrate.

The molar entropy of melting means the structural change of the hydrate for the phase transition. Generally, the molar entropy of melting, ΔS_m , can be calculated by the following equation for the crystalline solid,

$$T_{\rm m} = \Delta H_{\rm m} / \Delta S_{\rm m}$$
 [5]

where, T_m was the melting point of the crystalline solid. However, in this system, the peak profile was broadened and the melting point varied with the liquid content. Thus, the value of ΔS_m cannot be simply calculated. In this case, ΔS_m was calculated by the same manner as that for the ΔH_m , by using Eq. [6].

$$\Delta S_{\rm m} = - \frac{M \int_{T_{\rm l}}^{T_{\rm h}} \left(\frac{\Delta Q_{\rm s}/\Delta T}{T}\right) \, \mathrm{d}T}{d \cdot \rho} \quad [6]$$

As shown in Eq.[6], if the melting proceeds only at a certain temperature, T_m , T_m Eq.[5] was applied. The variations of ΔS_m with thehydrate content for various kinds of ΔS_m systems are shown in Figure 5. These results is showed that the phase transition did not fully of change its structure. Comparing with Figure 3(b), the same tendency was observed as ΔH_m . Also, the decrease of ΔS_m was constant below *ca.* 40 v/o of the liquid phase. The value of ΔS_m lowered to the 20 v/o of that in the bulk state for the system containing the powder of which the specific surface area is stion of the liquid phase near the solid phase AI was hindered, and the extent of structural is



Figure 5. Variations of ΔS_m with the hydrate content for various kinds of α -Al₂O₃ powders/ CaCl₂·6.00 H₂O coexisting systems.

change depends on the distance from the powder surface.

Under solidification, CaCl₂·7.35H₂O immediately gives two phases, *i. e.*, CaCl₂·6.00H₂O cyrstalline hydrate and saturated CaCl₂ aqueous solution. Therefore, the endothermic peak of melting was observed at two temperatures. For the bulk system, these two peaks appear at -51° C, corresponding to a eutectic melting temperature for the mixture of ice and CaCl₂·6H₂O, and 27°C, corresponding to an end point of melting for the hydrate. The DSC curves for α -Al₂O₃ (*no. 9*) powder/ CaCl₂·7.35H₂O coexisting system are shown in Figure 6. The endothermic peaks were observed at *ca.* -60°C and 25°C. Both temperatures were lower than those in bulk state. The endothermic peak area at *ca.* 25°C proportionally increased with the hydrate content. However, the shift of the endothermic peak with the liquid content was observed only for the peak at -60°C, whereas that was barely observed for the peak at 25°C.

It is well-known that aluminum oxide has a hydrophilic surface and whereas silicon carbide has a hydrophobic surface. In order to discuss the dependence on the hydrophilicity of the solid surface for the thermal behavior, the DSC curves for α -SiC powder/ CaCl₂·6H₂O coexisting systems were measured, as shown in Figure 7. The melting point did not vary with the hydrate content. The endothermic peak area proportionally increased with the liquid content. It is suggested that the phase transition of the hydrate near the solid surface was not affected by the solid surface. The variations of ΔH_m and ΔS_m for α -SiC powder/ CaCl₂·6H₂O coexisting systems with the liquid content were shown on Figure 8. The values of ΔH_m and ΔS_m were nearly constant with the content of the liquid phase, and were nearly equal to that of bulk liquid (32.94 kJ·mol⁻¹ and 108.7 J·mol⁻¹K⁻¹). It suggested that the hydrate was wholly coagulating near the solid phase.

On discussing the relationship between the properties of the hydrate and that of the powder surface, the wettability of the powder with the liquid phase is very important. In general, the hydrophilic property of the surface of the inorganic compound was represented by the heat of immersion as the surface enthalpy or the surface energy. It was reported by some reserchers that the heat of immersion by water of α -Al₂O₃ powder was ranged in 0.9 to 1.2 J·m⁻² (8). On the other hand, that of SiC powder was ranged in 0.3 to 0.6 J·m⁻² (9), which was smaller than that of α -Al₂O₃ powder. Those results may be the analogous to those for the CaCl₂ hydrate as the liquid. If the influence of the solid phase apprared by a contact of the solid phase and liquid one, the wettability remarkably affects on them. Therefore it is suggested that the influence of the solid surface was relatively small for the system containing α -SiC powder. Thus, the phase transition of hydrate near the surface of the solid phase was influenced by the hydrophilicity of solid phase surface.

Conclusions

The melting behavior of CaCl₂·nH₂O coexisting with the inorganic powders was investigated to be measured with differential scanning calorimetry (DSC). For α -Al₂O₃ powder/CaCl₂·6.00H₂O coexisting system, the melting point of the CaCl₂·6.00H₂O lowered, and ΔH_m decreased with both the decreases of the hydrate content and the increase of the specific surface area of the powder. The non-frozen liquid phase was observed near the solid surface. The relationship between the amount of the non-frozen liquid, ϕ_{NFL} , and the electrical conductivity was observed. For α -Al₂O₃ powder/CaCl₂·7.35H₂O coexisting system, the separated solid phase was formed when the hydrate solidified. Two endothermic peaks were observed at *ca.* -60°C and 25°C. The endothermic peak at 25°C proportionally increased with the liquid content. For α -SiC powder/CaCl₂·6.00H₂O coexisting system, the melting point and the molar enthalpy change of hydrate on meltingwere constant in the range of 17.2-48.0 v/o of the liquid content. These behavior showed that the phase transition of hydrate near the surface of the solid phase was influenced by the hydrophilicity of solid surface.



Figure 6. DSC curves for α -Al₂O₃ (*no. 9*) powder/ CaCl₂· 7.35H₂O coexisting system.



Temperature [°C]

Figure 7. DSC curves for α -SiC (1.1 m^2/g) powder/ CaCl₂·6.00H₂O coexisting system.



Liquid content [vol%]

Figure 8. Variations of ΔH_m and ΔS_m with hydrate content for α-SiC (1.1 m²/g) powder/ CaCl, 6.00H2O coexisting system.

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TRANSFERENCE NUMBERS IN MOLTEN FLUORIDES BY AN OPERATIONALLY DEFINED *emf* METHOD

by

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A new method has been proposed for determination of transference numbers from *emf* measurements in systems having one degree of freedom. The method is applied to molten fluorides, using literature data. Data for the system NaF-AlF₃-Al₂O₃(sat) gives the relative movement of the Na⁺ ion with respect to a fixed frame of reference. A consistent data set is given for t_{Na} from different concentration cells. The transference number is also discussed for different frames of reference. *Emf* measurements for a cell containing NaF and AlF₃ give transference numbers which are physically unlikely.

INTRODUCTION

This work presents an extended discussion of a new method for evaluation of transference numbers of concentration cells. The method has been developed for concentration cells with ion exchange membranes (1). It was already applied and briefly discussed for cells with molten fluorides (2). Some additional applications are shown in this work. Transference numbers in fluoride melts are needed for calculations of cell potentials and local heat productions at the electrodes during aluminium electrolysis (3).

PRINCIPLES

Our approach to electrochemistry is operational; i.e. the quantities used are all measurable (4). We shall consider a cell consisting of three compartments. The left-hand side half cell (I), the right-hand side half cell (II), and the junction compartment. In compartments (I) and (II) there is no gradient in concentration. The *emf* is derived from the flux equations of irreversible thermodynamics. No other assumptions than those inherent in the Onsager reciprocal relations are involved. This leads to the expression for

the emf of isothermal cells:

where $\Delta \varphi$ is given in units J mol⁻¹ of electric charge (J F⁻¹), $\Delta \varphi = EF$, *E* is the *emf* in Volts, and *F* is the Faraday constant (F=96485 C mol⁻¹). What is essential in equation [1] is that **i** is an electrically neutral component, not an ion. Thus the chemical potential μ_i (units J mol⁻¹) is a well defined quantity. Correspondingly, t_i is a *transference coefficient* of a neutral component referring to a chosen frame of reference. (see equations [4]). The transference coefficients describe the change in composition in the electrolyte by charge transfer, irrespective of the mechanism. i.e. they are operational. Thus changes by electrode reactions are included in the transference coefficient.

The integral of equation [1] will hereafter, be given without the integration limits.

The transference number of the ion **j**, t_j , is defined as the fraction of the electric current density, *j*, carried by the ion in a solution of uniform composition i.e. $\Delta c = 0$, (see e.g. refs. (5-8)):

$$t_{j} = \left| z_{j} J_{j} / j \right|_{\Delta c=0}$$
^[2]

where z_j and J_j are charge and flux respectively of the ion. J_j is given in mol m⁻² s⁻¹ and *j* in mol of electric charge m⁻² s⁻¹ or F m⁻² s⁻¹.

Other names for t_j are "transport number" or "electrical transport number". The fraction is positive by definition; it does not show the direction of transport. Transference numbers are called "internal" when another ion of the system or a neutral solvent is the frame of reference. "External" transference numbers have a porous plug or a wall reference. From the definition [2] it follows that:

$$\sum_{j} t_{j} = 1$$
 [3]

The transference coefficient for a neutral component i is defined as the number of moles of i, Δn_i , transferred, divided by the number of moles of electric charge, ΔQ , passing a cell of uniform composition, in the limit $\Delta Q \rightarrow 0$:

$$t_{i}^{H} = \lim_{\Delta Q \to 0} (\Delta n_{i} / \Delta Q)$$
[4a]

In a Hittorf type experiment Δn_i , and hence t_i^{H} , is referred to a fixed amount of a compound or ion. Superscript H means Hittorf type experiment. In aqueous solutions, water is often chosen as the frame of reference. Another common choice for the frame of reference used together with equation [4a] is the wall or a porous plug. If one of the ions, e.g X⁻ is used as the reference, it is indicated in the superscript as t_i^{H,X^-} .

$$L^{H,X-}_{i} = \lim_{\Delta Q \to 0} (\Delta n_i / \Delta Q)$$

$$(4b)$$

A modification of the Hittorf transference coefficient is obtained by using one of the ions e.g X⁻, as a fixed frame of reference. This is then a quasi lattice of immobile X⁻ ions, that is, we consider the transport of all other ions with respect to the X⁻ ions. The transference coefficient of a component i is then defined as:

$$t^{L,X_{-}}_{i} = (J_{i} / j)_{\Delta c=0}$$
 [5]

where J_i expresses the transfer of the neutral component i from left to right. Superscript L means a quasi lattice reference. We shall use this definition in the present derivation (see equations [10a,b,c]).

Both transference coefficients, equations [4,5] depend on the electrodes used, and for the specific choice of electrodes, they are related. When X^- is not involved in the electrode reaction, they are identical. The definition [5] is often convenient to describe cells with solid electrolytes. The *emf* of an electrochemical cell is of course invariant to our choice of the frame of reference. A more extensive discussion of the types of frame of reference is given in refs. (2,9).

THE SYSTEM NaF-AlF₃-Al₂O₃

The solvent for Al_2O_3 in the industrial electrolysis of aluminium is a molten mixture of NaF and AlF₃, with a composition in the neighborhood of cryolite Na₃AlF₆. A large number of studies of the thermodynamics of the mixture NaF-AlF₃-Al₂O₃ has been carried out. In all studies relevant in this context, the system has been saturated with Al_2O_3 .

The dissociation of the cryolite according to:

$$AIF_6^{3-} = AIF_4^{-} + 2F^{-}$$
 [I]

was first estimated by Grjotheim (10) from phase diagram analysis. Spectroscopic evidence for cryolite dissociation was first obtained by Ratkje and Rytter (11). The following reaction is likely at high concentrations of oxide (12,13):

$$3 \operatorname{NaF}(l) + \operatorname{AlF}_{3}(l) + \operatorname{Al}_{2}O_{3}(s) = 1\frac{1}{2} \operatorname{Na}_{2}\operatorname{Al}_{2}O_{2}F_{4}(l)$$
[II]

At low oxide concentrations another complex is formed:

$$Al_2O_2F_4^{2-} + 2 AlF_4^{-} = 2 Al_2OF_6^{2-}$$
 [III]

The first experimental evidence for the complex ions, $Al_2OF_6^{2-}$ and $Al_2O_2F_4^{2-}$ was given by Førland and Ratkje (12,13) for dilute solutions of cryolite and oxide in NaF. Their experiments showed that complexes of the type $AlOF_3^{2-}$ were negligible and that $Al_2OF_6^{2-}$ will be present only at low oxide concentrations, or high AlF_3 concentrations. Their results were further confirmed by enthalpy data at higher concentrations by Julsrud (14), and by Raman spectroscopy by Gilbert et al. (15). For the composition in the industrial cell, the ions Na⁺, F⁻, AlF_4^{-} , AlF_6^{3-} and $Al_2O_2F_4^{2-}$ are probably most important. Sterten (16) has calculated melt compositions assuming an ideal Temkin model over extended concentration ranges.

Derivation of transference numbers from emf measurements of concentration cells

The *emf* has been measured at 1000° C in cells [a] and [c] by Sterten et al. (20) and in cell [b] by Yoshida and Dewing (19) and by Thonstad and Rolseth (25).

$$Na(Pb)(l)|(NaF, AlF_3, Al_2O_3(sat))_1||(NaF, AlF_3, Al_2O_3(sat))_{II}| Na(Pb)(l) [a]$$

$$Al(l) | (NaF, AlF_3, Al_2O_3(sat))_I || (NaF, AlF_3, Al_2O_3(sat))_{II} | Al(l)$$
 [b]

$$O_2(g) | (NaF, AlF_3, Al_2O_3(sat))_1 | | (NaF, AlF_3, Al_2O_3(sat))_{11} | O_2(g)$$
 [c]

The basic components of the electrolyte are NaF, AlF₃, and Al₂O₃. For the derivations, we may choose any combinations of these to make a new set of neutral components. The most practical choice of components in this system turns out to be NaF, AlF₃, and Al₂O₂F₂. This choice is made because the fluoride lattice frame of reference is convenient. Furthermore, Al₂O₂F₂ is chosen due to the presence of the group Al₂O₂F_x as expressed in equations [II,III]. We shall derive the transference numbers for the Na⁺ ion using these components.

Since the fused mixture is saturated with alumina, we have the following formal equilibrium:

$$AlF_3 + Al_2O_3(sat) = 1\frac{1}{2} Al_2O_2F_2$$
 [IV]

This gives the stoichiometric relationship:

$$\Delta n_{\rm AlF_3} = -\frac{2}{3} n_{\rm Al_2O_2F_2} \tag{6}$$

where Δn_{AlF_3} is the change in the content of AlF₃ by the reaction [IV],

and the relationship between the chemical potentials:

$$d\mu_{Al_2O_2F_2} = \frac{2}{3} d\mu_{AlF_3}$$
^[7]

The system consists of 3 components and 2 phases. At constant temperature and pressure there is only one degree of freedom, i.e. there is only one independent transference coefficient or one independent ionic transference number. The Gibbs-Duhem equation for this system gives:

$$n_{\text{NaF}} d\mu_{\text{NaF}} + n_{\text{AlF}} d\mu_{\text{AlF}} + n_{\text{AlsO}} d\mu_{\text{AlsO}} = 0$$
[8a]
By introducing equations [6] and [7] into the Gibbs-Duhem equation we obtain:

$$d\mu_{AIF_3} = -n_{NaF} d\mu_{NaF} / n^{\circ}_{AIF_3}$$
[8b]

where the original content of AlF₃, $n^{\circ}_{AlF_3} = n_{AlF_3} + \frac{2}{3} n_{AlsOsF_3}$.

The electrode reactions on the right hand side electrode for the cells are:

For Na electrodes:
$$Na^+ + e^- = Na(Pb)(l)$$
 [V]

For Al electrodes:
$$\frac{1}{3} \text{Al}^{3+} + e^- = \frac{1}{3} \text{Al}(1)$$
 [VI]

For O₂ electrodes:
$$\frac{1}{2} Al^{3+} + \frac{1}{4} O_2(g) + e^- = \frac{1}{4} Al_2 O_2^{2+}(l)$$
 [VII]

Equation [3] for the three cells gives:

$$t^{\text{L,F-}}_{\text{Na+}} + t^{\text{L,F-}}_{\text{Al}^{3+}} + t^{\text{L,F-}}_{\text{Al}^{2+}} = 1$$
[9]

The relations between the transference coefficients and the transference numbers differ for the three cells. For known ionic equilibria, we obtain for:

Na electrodes:
$$t^{L,F_{-}}_{NaF} = t^{L,F_{-}}_{Na+} - 1$$
, $t^{L,F_{-}}_{AIF_{3}} = \frac{1}{3} t^{L,F_{-}}_{AI^{3+}}$ [10a]
and $t^{L,F_{-}}_{AbO_{2}F_{2}} = \frac{1}{2} t^{L,F_{-}}_{AbO_{2}^{2+}}$

Al electrodes:
$$t^{1_{3}F_{-}}_{NaF} = t^{1_{3}F_{-}}_{Na+}, t^{1_{3}F_{-}}_{AIF_{3}} = \frac{1}{3} t^{1_{3}F_{-}}_{AI^{3+}} - \frac{1}{3},$$
 [10b]

O₂ electrodes:
$$t^{L,F_{-}}_{NaF} = t^{L,F_{-}}_{Na+}$$
, $t^{L,F_{-}}_{AIF_3} = \frac{1}{3} t^{L,F_{-}}_{AI^{3+}} - \frac{1}{2}$, [10c]
and $t^{L,F_{-}}_{AbOF_2} = \frac{1}{2} t^{L,F_{-}}_{AbO2^{2+}} + \frac{1}{4}$

From equations [9] and [10], we obtain the same relationship between transference

and $t^{L,F-}_{Al_2O_2F_2} = \frac{1}{2} t^{L,F-}_{Al_2O_2C_2+}$

coefficients for all the three cells:

$$t^{L_{F_{Alb}}}_{NaF} + 3 t^{L_{F_{Alb}}} + 2 t^{L_{F_{Alb}}}_{Albo} = 0$$
[11]

For any of the cells (a,b,c), the emf can be expressed according to equation [1] as:

$$\Delta \varphi = -\int (t^{\text{L},\text{F}_{-}}_{\text{NaF}} d\mu_{\text{NaF}} + t^{\text{L},\text{F}_{-}}_{\text{AIF}} d\mu_{\text{AIF}} + t^{\text{L},\text{F}_{-}}_{\text{AbOxF}} d\mu_{\text{AbOxF}})$$
[12]

By introducing equation [7] into [12] we obtain:

$$\Delta \varphi = -\int \{ t^{L_{r}F_{-}}_{NaF} d\mu_{NaF} + [t^{L_{r}F_{-}}_{AIF_{3}} + \frac{2}{3} t^{L_{r}F_{-}}_{AbO_{2}F_{2}}] d\mu_{AIF_{3}} \}$$
[13]

The *independent* transference coefficient is here $t^{L,F-}_{NaF}$. Only the *sum* of the two others, $[t^{L,F-}_{AIF_{1}} + \frac{2}{3} t^{L,F-}_{AIG_{1}F_{2}}]$, can be obtained.

By introducing equations [8b] and [11] into [13] we obtain:

$$\Delta \varphi = -\int \{ t^{\text{L,F-}}_{\text{NaF}} / (1 - x_{\text{NaF}}) \} d\mu_{\text{NaF}}$$
[14]

where x_{NaF} is the equivalent fraction of NaF in the system, defined as:

$$x_{\text{NaF}} = n_{\text{NaF}} / (n_{\text{NaF}} + 3 n_{\text{AlF}_3} + 2 n_{\text{AlgO}_{F_2}}) = n_{\text{NaF}} / (3 n_{\text{AlF}_3}^\circ + n_{\text{NaF}})$$
[15]

Cells [b] and [c] have identical *emfs* because for both these cells, $t^{L,F_{NaF}} = t^{L,F_{NaF}}$. (see equations [10b,c,14]). For cell [a], $t^{L,F_{NaF}}$ is different and therefore $\Delta \varphi_{Na} \neq \Delta \varphi_{AI} = \Delta \varphi_{O_2}$, where the subscript represents the electrode used.

The transference numbers of Na⁺ ions for the three cells can thus be expressed as:

$$t^{L,F-}_{Na+} = 1 - (1 - x_{NaF})(d\phi_{Na}/d\mu_{NaF})$$
 [16a]

$$t^{\text{L},\text{F}-}_{\text{Na+}} = -(1-x_{\text{NaF}})(\mathrm{d}\varphi_{\text{Al}}/\mathrm{d}\mu_{\text{NaF}})$$
[16b]

$$t^{L,F-}_{Na+} = -(1-x_{NaF})(d\phi_{Oz}/d\mu_{NaF})$$
 [16c]

An alternative choice of components, NaF, AlF₃ and Al₂OF₄, leads to the same equations [16]. The expression for $t^{L,F_{-}}_{Na+}$ is thus independent of the specific choice of aluminium-oxygen-complex.

The experiments are performed in the following way. The composition of compartment I is kept constant while the composition of compartment II varies. The *emf* of the cell is measured for each composition difference. The incremental change in *emf*, $d\phi$, is due to the change $d\mu_s$, in compartment II. The slope of the plot of $\Delta\phi$ against μ_s in this compartment, gives $t^{L,F}$ as a *continuous* function of concentration in compartment II.

Literature data (19,20,25,27) were used to plot *emf* as a function of $\Delta \mu_{\text{NaF}}$ in cells [a,b,c]. Plots using data for cells [b] and [c] are shown in Fig.1. A similar plot for cell [a] gives approximately constant $d\phi_{\text{NaF}} = +0.02 \pm 0.004$. The transference number of Na⁺, $t^{\text{L,F-}}_{\text{Na+}}$ is obtained from equations [16a,b,c] and shown in Table I.

Table I.Transference number of Na⁺ t^{L,F^-} Na⁺, in the system
NaF-AlF₃-Al₂O₃(sat) for cells [a,b,c].

The *emf* results are taken from Sterten et al.(O₂ and Na electrodes) (20), and Yoshida and Dewing (Al electrodes) (19). Activity data are from ref. (20). The derivatives $d\phi_0/d\mu_{NaF}$ and $d\phi_{AI}/d\mu_{NaF}$ are taken from Fig.1, and $d\phi_{Na}/d\mu_{NaF} = 0.020 \pm 0.004$. The error in the derivatives are estimated from the uncertainty of the *emf* and μ_{NaF} .

 $t^{L,F-}_{Na+}(av)$ is the average from the results of the three cells and $r = n_{NaF}/n_{AlF}$.

Elec- trode:	(O ₂) t ^{L,F-} _{Na+}	(Al) t ^{L,F-} _{Na+}	(Na) t ^{L.F-} _{Na+}	t ^{LF-} Na+(av)
	± 0.06	± 0.06	± 0.004	
r				
1.4	1.14	1.01		
1.6	1.09	1.04		
1.8	1.05	1.03		1.04 ± 0.02
2.0	1.00	1.00	1.00	1.00 ± 0.01
2.2	0.97	0.96	0.99	0.97±0.02
2.4	0.93	0.92	0.99	0.94 ± 0.05
2.0	0.90	0.85	0.98	0.91±0.06
3.0	0.84	0.82	0.98	0.88±0.07
3.2		0.79		
3.4		0.76		
3.6		0.73		
3.8		0.71		
4.0		0.69		

In Table II the results from cell [b] are further analyzed. The transference number of Na⁺ is shown with two reference choices, L₂F⁻ and L₂Al³⁺. For the latter frame of reference, the derived expression is:

$$t^{L,Al3+}_{Na+} = -\{x_{NaF}/(1-x_{NaF})\} - (d\varphi_{Al}/d\mu_{NaF})$$

Table II. Transference number of Na⁺ in the system NaF-AlF₃-Al₂O₃(sat) for cell [b].

Two different reference frames are shown. The emf values are from Yoshida and Dewing (19) for 2 < r < 4 and from Thonstad and Rolseth (25) for r > 4. Activity data are from ref. (20) and $r = n_{\text{NaF}}/n_{\text{AlF}}$. The error in the derivative $d\phi_{\text{Na}}/d\mu_{\text{NaF}}$ is estimated from the uncertainty of the emf and μ_{NaF} .

r	$\Delta \phi/kJ F^{-1}$	dq/d $\mu_{\rm NaF}$	t ^{L,F-} Na+	t ^{L,AI3+} Na+	:
	± 1	± 0.06	± 0.06	± 0.06	
2	15.9	-1.47	1.00	0.80	
2.4	6.9	-1.47	0.92	0.67	
3	0.3	-1.63	0.82	0.63	
3.5	-4.8	-1.78	0.82	0.61	
4	-7.5	-1.37	0.58	0.03	
4.5	-9.1	-1.47	0.63	-0.03	
5	-10.6	-1.68	0.63	0.01	
5.5	-11.6	-1.92	0.68	0.09	
6	-12.6	-2.19	0.73	0.19	
7	-14.5	-2.69	0.81	0.36	
8	-15.9	-3.13	0.85	0.46	
9	-17.4	-3.49	0.87	0.49	
10	-18.8	-3.79	0.87	0.45	
12	-20.3	-4.23	0.85	0.23	
14	-21.7	-4.84	0.85	0.17	
		· · · · · · · · · · · · · · · · · · ·			

THE SYSTEM NaF-AlF₃

The molten mixture of NaF and AlF_3 has been investigated at 1020°C using the concentration cell (25)

$$Al(l) | (NaF, AlF_3)_{I} || (NaF, AlF_3)_{II} | Al(l)$$
 [d]

The electrolyte has two components and one phase. At constant P and T this means that also in this case we have only one degree of freedom; i.e. only one independent transference number. Using a similar procedure as above, the transference number of Na⁺ ions for this cell is expressed as:

$$t^{L_{\rm AF}}_{\rm Na+} = -(1 - x_{\rm NaF})(\mathrm{d}\varphi_{\rm AI}/\mathrm{d}\mu_{\rm NaF})$$
[17]

where x_{NaF} is the equivalent fraction of NaF in the system defined as:

$$x_{\text{NaF}} = n_{\text{NaF}} / (3 n_{\text{AlF}} + n_{\text{NaF}})$$
[18]

The same form of the equation for the transference number of Na⁺ is obtained as for the ternary electrolyte, compare equations [17] and [16b]. This means that a difference in *emf* between cells [d] and [b] is due to the participation of oxygen-containing complexes in the charge transfer.

Equation [17] is used to calculate t^{LF}_{Na+} in cell [d] from *emf* data of Saget et al. (26) and activity data from Sterten and Mæland (29). The results are given in Table III.

Table III. Transference number of Na⁺, $t^{L,F-}_{Na+2}$ in the system NaF-AlF₃ for cell [d].

The *emf* values are from Saget et al. (26) and activity data are from ref. (29). $r = n_{\text{NaF}}/n_{\text{AlF}}$.

r	$\Delta \phi/kJ F^{-1}$	$\mathrm{d} \varphi / \mathrm{d} \mu_{\mathrm{NaF}}$	t ^L a ^{F-} Na+
	± 4	± 0.5	± 0.5
20	15	_1 3	0.8
2.0	13	-1.2	0.7
2.4	9	-1.5	0.7
2.8	3	-2.3	1.2
3.0	0	-2.6	1.3
3.4	-6	-3.1	1.5
3.7	-9	-3.2	1.5
4.0	-12	-3.2	1.4

DISCUSSION

The method

One advantage of the operationally defined method described above is that it allows consistency checks of different experiments. This is demonstrated by the results of Table I. Results from the different cells [a,b,c] should yield the same values for $t^{L,F-}_{Na+}$. When this is the case, we may have more confidence in the results. We have thus calculated average value for $t^{L,F-}_{Na+}$ from the different cells in the concentration range where approximately the same values are obtained. According to the derivations $\Delta \phi_{AI} = \Delta \phi_{O,}$. Fig. 1 shows a significant difference in the value of the *emf* for cell [b] and cell [c] in a concentration range of low *r*-values. The error may be due to an irreversible reaction between aluminium metal and the electrolyte (2). Also, the results in Table III, indicate large errors in the reported *emfs*. There is a need for further investigations.

One further advantage of the method is that the definition of the transference coefficients includes the frame of reference. Knowledge of the relative velocities makes further analysis of the data possible. For example, a value of t^{1,F^-}_{Na+} close to unity does not imply that the F⁻ ions does not carry current in the melt. Recalculation of t^{1,F^-}_{Na+} to another frame of reference in Table II demonstrates this. The same physical phenomena must explain the data in the two columns in this table. It is more easily seen from the Al³⁺-reference choice that fluoride ion moves, and has a velocity different from that of Na⁺. The point that cne measures relative movements has been neglected in the literature. A frequent statement is that the Na⁺ ions carries approximately all current, without a definition of the frame of reference.

Another advantage of the method is that the transference number is obtained as a continuous function of melt composition. Frequently, only average values have been reported for ranges of composition. The lack of continuity shown in the data of Table II for data from cell [b], imply that these experiments contain errors. We have previously discussed (2) the uncertainties in the experiments by Thonstad and Rolseth (25).

Furthermore, it is a necessity that the limiting value of the transference number of Na⁺, $t^{L,F-}_{Nat}$ is unity when $x_{AIF_2} \rightarrow 0$.

The difference between transference numbers obtained from the two systems described above should give information on the participation of oxygen-containing complexes in the charge transfer. Unfortunately such a comparison cannot be carried out due to uncertainty in *emf* measurements for cell [d].

Transference numbers of Na⁺ in molten fluoride melts

Table I give reliable values for the transference number of Na⁺ only in the narrow concentration range 1.8 < r < 2.2. This is, however, the range of interest for industrial electrolysis of aluminium. For 2.2 < r < 3 the error is $< \pm 0.07$. For 3 < r < 4 we use values obtained with Al(I)-electrodes.

Given the limiting value $t^{L_{r}F_{Na+}} = 1$ when $x_{AIF_{r}} \rightarrow 0$ and the values of Table II, we see that the transference number as a function of concentration passes a minimum. This can be understood by considering a frame of reference $L_{r}Na^{+}$. In this frame of reference, we may assume that the velocity of the F⁻ ions to the left is larger than that of the Al³⁺ containing negative species e.g AlF₄⁻, Al₂O₂F₄²⁻. This gives a movement of the Al³⁺ species to the right, relative to the sum of the separate F⁻ ions and the F⁻ ions in the negative complexes. This effect vanishes as $x_{AIF_{r}} \rightarrow 0$. Thus the transference numbers $[t^{L_{r}F_{-AI34}} + \frac{2}{3} t^{L_{r}F_{-AI024}}]$ may have a maximum, giving a minimum for $t^{L_{r}F_{-Na+}}$.

Table III give values of $t^{L,F-}_{Na+} > 1$ which means that $t^{L,F-}_{Al3+}$ is negative. This is physically unlikely in a L,F⁻ frame of reference. However, the uncertainty in the *emf* values is so large that the values of the transference numbers are not reliable.

CONCLUSION

We have applied a method of data analysis for finding transference numbers in systems having one degree of freedom according to the phase rule. The method has been applied to molten fluoride mixtures and several advantages of the method are pointed out. The transference coefficient of NaF has been derived as a function of the derivative $d\phi/d\mu_{NaF}$ and the equivalent fraction of NaF, in mixtures of NaF-AlF₃ and NaF-AlF₃-Al₂O₃(sat). We have used the electrochemical cell theory of Førland et al.(4). The applicability of this theory has thus been further demonstrated.

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Fig. 1. The *emf*, $\Delta \varphi$, of the cell:

E | (NaF, AlF₃, Al₂O₃(sat))₁ || (NaF, AlF₃, Al₂O₃(sat))₁₁ |E

for different electrodes, E, as a function of the activity of sodium fluoride, $\Delta \mu_{\text{NaF}}$, as given by Sterten et al. (20).

Results for oxygen electrodes, from Sterten et al. (20), are given by filled circles, while results for aluminium electrodes, from Yoshida and Dewing (19), are given by empty circles. The temperature is 1273 K and the cryolite ratio is in the range 0.8 < r < 3.0.

THERMODYNAMICS OF Li₂O - LiF - CaF₂ MELTS

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ABSTRACT

Processing of aluminum-lithium alloys by electrochemical method was investigated. Thermodynamics of solubility of lithium oxide in Li₂O-LiF-CaF₂ melts was studied as a function of temperature and it was found to increase from 10.6 wt% at 1058 K to 14.8 wt% at 1133 K. The liquidus temperature of 4LiF.CaF₂ + Li₂O (saturated) melt was determined to be 1004.5 \pm 2.5 K. The equilibrium phase and activity of Li₂O in the melts as a function of temperature was determined. The calculated activity coefficients of Li₂O in the melts exhibited a negative deviation from Raoult's law.

INTRODUCTION

There is an evergrowing demand for the use of aluminum-lithium alloys in the aerospace industry, because of their light-weight and improved modulus. The increase in demand was due to rapid escalation of fuel costs; higher thrust for more fuel efficient aircraft and improved overall structural properties for Al-Li alloys over the existing aerospace structural Al-alloys of AA 2xxx and 7xxx series. Reduction in aircraft weight is one means of decreasing fuel consumption. Since majority of aircraft frames are made out of aluminum alloys, development of low-density structural aluminum alloys is of paramount interest. Each weight percent lithium added to an alloy reduces the density 3 percent and increases the elastic modulus by 6 percent(1). Addition of lithium to aluminum also improves the corrosion resistance(2). Presently two types of Al-Li alloys viz., AA 2090 and 8090 are commercially available. The present commercial method for production of Al-Li alloys is by powder metallurgy or melting and casting methods involving the use of pure metallic lithium which is added to the molten aluminum(3). Production of Al-Li alloys by mixing the pure metal is an energy intensive and expensive process. The principal objective of the described research is to develop physico-chemical information that can be applied to the direct production of Al-Li alloys by electrochemical method.

To study the viability of a process for obtaining a metal from its oxide, it is necessary to obtain sufficient information on the solubility characteristics of the oxide in the fluoride melt. While extensive studies have been done for Al_2O_3 - cryolite system (4-7), very little work has been done for other oxide-halide systems. Belyayaev (8) found that mixed fluorides, particularly cryolite (Na₃AlF₆) are good solvents for metal oxides while Stern (9) found that molten chlorides have a very limited solubility for metal oxides. Haupin (10) studied the solubility of Al₂O₃ in AlCl₃ - LiCl melts and predicted a simple model for the reaction between the oxide and chloride to form the dissolved species. He predicted the dissolved species to be AlOCI and found that the Al_2O_3 solubility increases with the cube root of activity of AlCl₃. Wai and Blander (11) studied the solubility of Al₂O₃ in eutectic LiCl - KCl containing dissolved AlCl₃ using a proton activation technique. The presence of AlO⁺ complex species in the melt was identified and a formation constant for the AlO⁺ was deduced. From the solubility data, they obtained a value of 300 KJ/mole for the specific bond free energy for the Al^{3+} and O^{2-} ions.

In the present study, a systematic investigation was undertaken to measure the solubilities of Li_2O in LiF - CaF_2 melts at different temperatures and also to find the liquidus temperature of $4LiF.CaF_2 + Li_2O$ (saturated). The solubility of Li_2O in LiF - CaF_2 electrolytes must be significant because it is the only dissolved oxide in the complex oxyfluoride form which is available for reduction at the anode during electrolysis. Also, it is necessary to find the liquidus temperature of $4LiF.CaF_2 + Li_2O$ (saturated) in order to determine the optimum temperature for electrolysis of Li_2O in $4LiF.CaF_2$ melts.

EXPERIMENTAL

The solubility of Li_2O was investigated as a function of temperature in the range of 1058 to 1133 K in $4LiF.CaF_2$ electrolyte. The liquidus freezing temperature of ternary $Li_2O-LiF-CaF_2$ melt was measured. The experimental set-up and procedure were described elsewhere (12,13) and only a brief description is given here.

Materials :

Calcium fluoride of 99.9% purity and lithium fluoride of 99.9% purity were weighed and mixed in stoichiometric proportions of 4:1 to form 75 grams of CaF_2 - LiF mixture. Lithium oxide of 99.8% purity was used.

Apparatus and Procedure :

The apparatus used for the solubility studies consisted of a 11.5 cm diameter stainless steel chamber with ports for evacuation, argon gas outlet and oxide additions. The chamber was heated by a 10 cm diameter kanthal wire-wound cylindrical resistance furnace. A schematic diagram of the set up used is shown in Figure 1. The CaF₂ - LiF mixture in 4:1 ratio was dried in dynamic vacuum at 423 K for 6 hours and then melted at 1073 K under a dry argon atmosphere for one hour in a graphite crucible. The solidified mixture was crushed and remelted under dry argon atmosphere at the required temperature till a homogeneous melt was obtained. Li₂O, 20% by weight of electrolyte mixture (15 g) was added to the melt. The molybdenum tube containing purified argon gas was passed at a rate of 60 to 80 cm³/min by immersing it into the melt to provide a stirring effect. Samples were withdrawn through a graphite tube at selected time intervals after the addition of oxide. The solidified samples were grounded to less than 100 mesh size in an alundum vial to obtain a homogenized mixture and the powder was analyzed for the constituent elements viz., Ca, Li, F and O.

<u>Liquidus Temperature of $4\text{LiF.CaF}_2 + \text{Li}_2\text{O}$:</u>

In order to determine the optimum temperature for electrolysis of Li_2O in $4LiF.CaF_2$ melts, the liquidus temperature of $4LiF.CaF_2 + Li_2O$ (saturated) melt was determined. For this, the melt was held at 1093 K for

6 hours after the addition of excess Li₂O, using same set up discussed in the preceding section, and then cooled at the rate of 0.5 K/minute. Three sets of heating and cooling cycles were performed. A liquidus temperature of 1004.5 ± 2.5 K was obtained with a thermal arrest time of 3.5 to 4.6 minutes as shown in Table 1. The cooling curve of the sample showing a thermal arrest temperature of 1006 K and a thermal arrest time of 4.6 minutes is shown in Figure 2.

RESULTS AND DISCUSSION

Solubility of Li₂O in Li₂O-LiF-CaF₂ Melts :

The experimental data on the solubility of Li_2O as a function of temperature are presented in Table 2. It can be seen that the solubility of Li_2O increases with increase in temperature of the melt. For example, the solubility of Li_2O increased from 10.6 wt% at 1058 K to 14.8 wt% at 1133 K. The calculated mole fraction of Li_2O in the melt as a function of temperature is plotted in Figure 3. A linear relationship between ln mole fraction of Li_2O and temperature was obtained and given by :

$$\ln X_{\text{LizO}} = 2.411 - 4567.8/T$$
[1]

with a correlation coefficient of 0.98.

Activity of Li₂O in the Melt :

The liquidus freezing temperature of $4\text{LiF.CaF}_2 + \text{Li}_2O$ (saturated) melt is 1004.5 ± 2.5 K at 11.77 mole % of Li₂O. At any temperature above 1004 K, for $4\text{LiF.CaF}_2 + \text{Li}_2O$ (saturated) melt, solid Li₂O is in equilibrium with the liquid electrolyte. In other words,

$$Li_2O$$
 (liquid, electrolyte) = Li_2O (pure, solid) [2]

The partial molar free energy of Li_2O in the liquid electrolyte, $\Delta G_{Li:O(1)}$, should be equal to the molar free energy of the pure solid Li_2O , $\Delta G_{Li:O(s)}^0$. Hence,

$$\Delta \overline{G}_{\text{LisO}(1)} = \Delta G^{0}_{\text{Li2O}(1)} + \text{RT } \ln a_{\text{LisO}(1)} = \Delta G^{0}_{\text{LisO}(s)}$$
[3]

where $a_{LiO(1)}$ is the activity of Li_2O in the liquid electrolyte with respect to the pure liquid Li_2O standard state. Rearranging terms,

$$RT \ln a_{\text{LisO}(1)} = \Delta G^0_{\text{LisO}(s)} - \Delta G^0_{\text{LisO}(1)} = - \Delta G^0_{\text{m,LisO}}$$
[4]

where ΔG^0_m is the standard free energy of fusion for Li₂O at temperature T K. $\Delta G^0_{m,LixO}$ was deduced from the suggested value of heat of fusion $\Delta H^0_{m,LixO} = 58,576$ J/mole, melting point of Li₂O = 1843 K and the heat capacity data(14). The following expression was obtained:

$$\Delta G^{0}_{m,Li:O} = 33127 - 25.907 \text{ T } \ln \text{T} + 6.264 \text{ x } 10^{-3} \text{ T}^{2} - 9.411 \text{ x } 10^{5}/\text{T} + 165.556 \text{ T } \text{ J/mole.}$$
 [5]

Combining equations 4 and 5, the activity and activity coefficient of Li_2O at several temperatures were calculated and presented in Table 2. As seen from the table, dissolution of Li_2O in $4LiF.CaF_2$ electrolyte melt exhibits a non-ideal behavior and follows a negative deviation from the Raoult's law.

CONCLUSIONS

The following conclusions can be made from the present experimental determination of solubility of Li_2O in $4LiF.CaF_2$ melt :

- 1) Liquidus temperature of $4\text{LiF.CaF}_2 + \text{Li}_2\text{O}$ (saturated) melt is $1004.5 \pm 2.5 \text{ K}$.
- Solubility of Li₂O in Li₂O-LiF-CaF₂ melts increases with increase in temperature, with a value of 10.6 wt% at 1058 K and 14.8 wt% at 1133 K.
- 3) Dissolution of Li_2O in $4LiF.CaF_2$ electrolyte melt exhibits a negative deviation from Raoult's law in the composition range studied.

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Melt Composition	Liquidus Temperature (K)	Thermal Arrest Time (min.)	
4LiF.CaF ₂ + Li ₂ O (saturated)	1005 <u>+</u> 1	3.5	
"	1006 <u>+</u> 1	4.6	
"	1003 <u>+</u> 1	3.8	

Table 1. Liquidus Temperature of $4LiF.CaF_2 + Li_2O$ (saturated) Melt

Temp. (K)	1/T x 10 ⁴ (K ⁻¹)	Li ₂ O wt%	X _{LizO}	ln X _{Lio}	a _{LizO}	$\gamma_{ m LizO}$
1058	9.450	10.63	0.147	-1.917	0.069	0.469
1078	9.276	11.66	0.159	-1.839	0.077	0.484
1093	9.149	13.20	0.176	-1.737	0.083	0.473
1113	8.985	14.22	0.187	-1.676	0.092	0.494
1133	8.826	14.82	0.193	-1.645	0.102	0.529

Table 2. Solubility, Activity and Activity Coefficient of Li_2O in $4LiF.CaF_2$ Melts at Different Temperatures



11. To vacuum pump



6. Thermal insulating wool



Figure 2. Cooling Curve for $4\text{LiF.CaF}_2 + \text{Li}_2\text{O}$ (saturated) Melt Showing Thermal Arrest at 1006 K.



Figure 3. Variation of $\ln X_{LisO}$ in 4LiF.CaF₂ Melt with Temperature.

NIOBIUM CHEMISTRY IN MOLTEN LICI+KCI EUTECTIC

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ABSTRACT

Redox and acidic properties of dissolved niobium chlorides in the molten LiCl+KCl eutectic melt at 450° C have been investigated. Niobium is stable in the eutectic melt under four oxidation states: 0, III, IV and V in oxoacidic media (very low amount of lithium oxide containing melt). The standard potentials of the corresponding electrochemical systems (potentials expressed in volts, concentrations in mol.kg.⁻¹) have been determined versus the standard chlorine-chloride reference electrode. In oxobasic media, the niobium(II) is stable under the form of NbO(s). This oxide disproportionates in acidic media leading to the formation of metallic niobium and niobium(III). The solubility products of NbO₂(s), Nb₂O₅(s) and LiNbO₃(s) as well as those of the niobium oxychlorides have been also determined. A potential-oxoacidity diagram of niobium is given.

INTRODUCTION.

Among the main applications of molten salts, one of the most promising is certainly their use as reaction media for extractive metallurgy purposes. In fact, fused salts can be employed at working temperature ranging from the high temperatures corresponding to pyrometallurgy and low temperatures relative to the classical hydrometallurgy. Thus molten salt metallurgy cumulates the main advantages of pyrometallurgy that are high kinetics of chemical reactions and the possibility of manufacturing reactive metals and materials, and that of hydrometallurgy that is applying solution chemistry for increasing selectivity of a given process.

The work presented here belongs to a larger investigation concerning the possibilities of chemical treatment of metallic oxides (ores, concentrates or wastes) in molten salts, and in particular their selective chlorinations by gaseous reagents (1-8). In fact, this field of investigation is one of our research topics that we have now developped in our laboratory for several years ago. Within this research topic, the chemical properties of transition and refractory metal ions were determined in the LiCl+KCl eutectic melt (7, 9-15). In particular we have focused our interest on the beneficiation of oxide-based ores and concentrates like for examples the chemical treatment of bauxites for extracting pure aluminium chloride(1-6), ilmenite for titanium tetrachloride(7,12,14,15) and lead and zinc concentrates for recovering tin and indium(16).

More recently, we have envisaged the chemical separation of niobium and tantalum (whose properties were previously determined (17)) from their ores.

This work upon niobium and tantalum is included in a research program concerning the extractive metallurgy, extraction and electrowinning of these two metals (A.R.C.: Procédés de Métallurgie Extractive utilisant les Sels Fondus; projet : extraction et élaboration du niobium et du tantale, n° 8780 N 2031) realized with the financial support of C.N.R.S.(Centre National de la Recherche Scientifique) / P.I.R.S.E.M.(Programme Interdisciplinaire de Recherchers sur les Sciences pour l'Energie et les Matières premières) and A.F.M.E. (Agence Française pour la Maîtrise de l'Energie). The two main objectives of this program are : (i) the selective extraction of niobium and tantalum, and secondly, if possible, obtaining niobium and tantalum compounds suitable for the electrowinning of the corresponding metals.

TECHNICAL.

Preparation of the eutectic melt, apparatus and electrodes.

The eutectic mixture (lithium chloride 58.8 mol% - potassium chloride 41.2 mol%, analytical grade Merck) was melted under vacuum in a pyrex crucible placed inside a Pyrex reactor within a Taner furnace, and purified by the standard method with HCl bubbling(18), and then kept under a dry argon atmosphere. Temperature was controlled by a Gulton 3200 self-tuning controller at $(450\pm1)^{\circ}$ C.

The working electrodes were either tungsten electrode (wire) or niobium rod. The counter electrode was a tungsten wire, and the reference electrode was the silver - silver chloride (0.75 mol.kg.¹) reference previously described (18). In the following, all the potentials will be given versus the standard chloride-chlorine(1 atm) electrode.

Electrochemical techniques.

Chronoamperograms and linear sweep voltammograms were recorded using an EG&G-PAR Model 176 potentiostat-galvanostat connected to an IBM microcomputer via a model 273 interface. Potentiometric measurements were performed with a high impedance Tacussel voltmeter (Aries 10000).

NIOBIUM ELECTROCHEMICAL SYSTEMS.

What are the the basic thermodynamic knowledge we need for conceiving a selective extraction process? They are of two natures. In fact, we have to distinguished those concerning the elements to be recovered, and those concerning the chemical reagents we intend to use.

Firstly, if they are not available in the literature, we have to acquire the solubilities and the redox properties of the chlorides in the melt under consideration, and also their acidobasic properties characterized by the acidity constants and the solubility products of oxides and oxychlorides formed. These data are then summarized under the form of a potential-acidity diagram. It is often of worth to know the possibility of complexing the cations.

As for the chemical reagents, only gaseous reagents - which are widely used because of their unpolluting character regarding the melt and the resulting products - have been considered. For them, we have to know their reactive zones in a potential-acidity diagram in order to choose the more suitable for our purpose in comparing them with the predominance area diagrams of niobium and tantalum. These reactive zones were determined in our previous studies.

This paper deals only with the setting up of the potential-acidity diagram of niobium summarizing its chemistry in the lithium chloride+potassium chloride eutectic melt at 450°C.

The first problem encountered was the knowledge of the stable oxidation states of niobium in melt. In fact, various discrepancies occur in the literature, depending the melt composition and the working temperature. This was reinvestigated using the anodic dissolution of a pure niobium rod for generating niobium cations in melt.

Average valency of niobium solutions and stable oxidation states of niobium.

Anodic dissolution of a niobium rod.

Niobium cations were electrogenerated by anodic dissolution of a niobium rod (ϕ =4.5 mm) whose purity was better than 99.5%, with a fixed current of 50 mA. Anodic current density was then controlled by the immersion depth of the niobium working electrode. From the anodic charges for dissolution and the measured weight losses, it was possible to determine the average valency of the resulting niobium solutions. Fig.1a gives the anodic current density dependence of the average valency when niobium concentration reached in each case is close to 10⁻² mol.kg.⁻¹. The colour of the niobium solutions changes from brown for average valencies lower than 3.8, to yellow-orange for average valencies close to 4.

Steady-state current-potential curve (redox systems).

The chronoamperograms obtained at a tungsten working electrode with a nobium solution of total concentration equal to 9.7.10⁻³ mol.kg.⁻¹ (obtained with a current density of 7.7 mA.cm⁻²) exhibit, for times higher than 10 s, constant current values due to thermal convection. These steady-state potential-dependent current values were used for obtaining the typical sampled-current voltammogram represented in Fig.1b.

Assuming niobium cations have equal diffusion coefficients, the steady state currentpotential curve suggests that niobium stable oxidation states are 0, III, IV and V. The average valency can be calculated from the limiting current densities corresponding to each reduction step (average valency = 3.75 in the case of Fig.1b) and compared to those obtained from the weight losses observed during electrochemical generation of the solutions. We can observe (Table 1) a good agreement between these two kinds of values corresponding to three experiments.

Our results are in good agreement with those obtained by Caton and Freud(19) and Inman et al(20), and more recently by Chemla et al(21), De Lepinay et al(22) and Barhoun and Lantelme(23).

The following step of our research was to determine the standard potentials of the corresponding electrochemical systems.

Standard potentials of the Nb(0)/Nb(III), Nb(III)/Nb(IV) and Nb(IV)/Nb(V) redox systems.

Potentiometric determination of the $Nb(s)/Nb^{3}$ +standard potential.

Niobium(III) solutions were generated by chemical oxidation of metallic niobium (in excess) by silver cations (added as silver chloride) according to the reaction :

$Nb(s) + 3 Ag^{+} = Nb^{3+} + 3 Ag(s)$

When equilibrium was completed, the equilibrium potential was measured both with a silver and a niobium working electrodes (values so measured were identical within 5 mV). By plotting the equilibrium potential versus the niobium(III) concentration, we obtained a linear variation with the theoretical slope for three exchanged electrons (Fig.2a). From this straight line, the standard potential $E^{\circ}(Nb(s)/Nb^{3+})$ of the corresponding electrochemical system was determined :

$$E^{\circ}(Nb(s)/Nb^{3+}) / Volt = -1.44 \pm 0.01.$$

Potentiometric determination of the Nb^{3+}/Nb^{4+} standard potential.

A solution of $1.1.10^{-2}$ mol.kg.⁻¹ Nb⁴⁺ without any Nb³⁺ cations was prepared by anodic dissolution of a niobium rod with a current density equal to 22 mA.cm⁻² (average valency = 4.01). Metallic niobium powder (325 mesh) was then added into the solution in order to realize the following chemical reaction :

 $3 \text{ Nb}^{4+} + \text{Nb}(s) = 4 \text{ Nb}^{3+}$

The observed variation of the equilibrium potential of an inert working electrode (tungsten) as a function of the $[Nb^{4+}]/[Nb^{3+}]$ ratio is given in Fig.2b. This variation is linear and the slope is practically equal to the theoretical one for one exchanged electron. We can then derived the standard potential $E^{\circ}(Nb^{3+}/Nb^{4+})$ of the corresponding electrochemical system :

 $E^{\circ}(Nb^{3+}/Nb^{4+}) / Volt = -1.12 \pm 0.01.$

Determination of the Nb⁴⁺/Nb⁵⁺standard potential by linear sweep voltammetry.

Niobium pentachloride is unstable in the molten mixture. So, the standard potential $E^{\circ}(Nb^{4+}/Nb^{5+})$ of the corresponding electrochemical system was determined from cyclic voltammograms (see for example Fig.3) as being equal to :

 $E^{\circ}(Nb^{4+}/Nb^{5+}) / Volt = -0.32 \pm 0.01.$

These determinations are in very good agreement with those of Barhoun and Lantelme(23).

After that, we were interested in the determination of the solubilities of niobium chlorides.

Solubilities of Nb(III), Nb(IV) and Nb(V),

Solubility of niobium trichloride.

The niobium(III) solubility was determined by analysing the peak curents of cyclic voltammograms (Fig.4) recorded in the case of the oxidation of pure niobium(III) solutions prepared by chemical oxidation of pure metallic niobium powder (325 mesh) suspended in melt with silver chloride. We can observe in Fig.5, a good linearity of the ratio of peak current density with the square root of the niobium(III) concentration even for the highest concentration considered in the experiments. This signifies that the niobium(III) solubility is higher than 1.2 mol.kg⁻¹. The free enthalpy of formation of pure solid NbCl₃ (24) allows us to calculate the standard potential of the redox Nb(0)/NbCl₃(s) couple. The value obtained (-1.465 V) compared with the experimental value found for the Nb(0)/Nb³⁺ redox couple (-1.440 V) gives us the solubility of Nb³⁺, S(Nb³⁺), corresponding to the equilibrium :

$Nb^{3+} + 3 Cl^{-} = NbCl_3(s)$

The value so determined is $S(Nb^{3+}) = 3.0.10^{-1}$ mol.kg⁻¹ which is in agreement with the experimental observation.

Limit of the solubility of Nb^{3+} in presence of metallic niobium. We have to remark here, if we introduce metallic niobium in excess, we observe a decrease in this quantity (Fig.5) corresponding to, the formation of metal cluster compound whose solubility is lower (0.08 mol.kg⁻¹) than that of niobium(III) chloride.

Solubility of niobium tetrachloride.

Now, we have determined the solubility of niobium(IV) chloride from the variation of the limiting current densities of steady state i-E curves corresponding to niobium(IV) solutions of increasing concentrations obtained by anodic dissolution of a niobium rod. We easily observe in Figure 6 that the maximum concentration of niobium(IV) is 1.3.10⁻² mol.kg.⁻¹.

Solubility of gaseous niobium pentachloride.

The solubility of niobium(V) can be deduced from the Henry's constant defined by :

 $K = P(NbCl_5)/[Nb^{5+}]$

corresponding to the equilibrium :

 $Nb^{5+} + 5 Cl^{-} = NbCl_{5}(g)$

and calculated from the free enthalpies of formation of dissolved and pure niobium pentachlorides. The value obtained is : $K = 8.76 \text{ atm.mol.}^{-1}$.kg. This constant corresponds to a low solubility of niobium(V) and enables us to determine the solubility under a given value of the partial pressure of niobium pentachloride. The value corresponding to a residual pressure of 10^{-3} atm. for example is very low (1.14.10⁻⁴ mol.kg.⁻¹).

OXOACIDITY OF DISSOLVED NIOBIUM CHLORIDES.

The last step to set up the predominance area diagram of niobium species is the determination of the stabilities of niobium oxides and oxychlorides. The experimental determination of acidity constants and solubility products of these compounds are made difficult because of their great stabilities. In particular, use of the yttria-stabilized membrane electrode, as an oxide anion indicator, is not possible since this electrode doesn't work for pO^{2-} values higher than 12 or 13(1,25). Therefore, we were obliged to perform titrations with silver oxide as a reagent and also to use other alternative methods.

Experimental Titration of solid Niobium by solid silver oxide.

Silver oxide which is both an oxidizing and oxide anion donor reagent has enabled us to realize the titration of metallic niobium with the formation of niobium oxides of high oxidation states. This titration was monitored with a silver working electrode for controlling the pAg. The titration curve given in Fig.7 [initial amount of Nb(s) : $4.28.10^{-3}$ mole in 100 g of eutectic melt] can be explained by considering that the succeeding reactions are :

 $Nb(s) + [Ag_2O(s)] = NbO(s) + 2 Ag(s)$ $NbO(s) + [Ag_2O(s)] = NbO_2(s) + 2 Ag(s)$

 $NbO_2(s) + [Ag_2O(s)] + Li^+ = LiNbO_3(s) + Ag(s) + Ag^+$

In fact, only the last reaction leads to a change in the pAg value. Moreover, when the titration reaction was stopped at $\alpha = 0.93$ [α : stoichiometric ratio = added Ag₂O(s)/initial amount of Nb(s)], the resulting product was an amorphous dark grey powder, probably NbO(s) whose stability was verified in the melt, and when the titration was stopped at $\alpha = 1.5$, the dark grey product gave the XR pattern of NbO₂(s).

This kind of titration gave important results on the nature of the compounds formed, but unfortunately not quantitative results. Thus we used another approach for determining the stabilities of oxides and oxychlorides.

Calculated Solubility products.

The Gibbs free energies of most of niobium oxide compounds are known(24), and subsequently, taking into account of the solvation activity coefficients of the dissolved niobium chlorides (derived from the corresponding standard potentials in melt and from the chemical potentials of pure chlorides) and that of lithium oxide previously determined(1), as well as the activities of the components of melt, we can calculate the solubility products and equilibrium constants of niobium oxide compounds. This was the case for the niobium monoxide, dioxide, pentoxide and the niobium(IV and V) oxychlorides.

In the case when thermochemical data are not available, we can perform titrations corresponding to the transformation of an oxide into a more basic one in order to have sufficiently low pO^2 -values to be measured, for which the zirconia electrode is worthwhile. This was the case of the formation of lithium niobiate from niobium pentoxide as indicated below.

Titration of Nb₂O₅ by Na₂CO₃.

The potential values of an yttria stabilized zirconia membrane electrode - indicator electrode of the activity of oxide anion(1,9-11,18,25-27) - obtained after successive amounts of sodium carbonate to 100g melt containing $1.85.10^{-3}$ mole of suspended niobium pentoxide are represented in Fig.8. We can notice one equivalence point, so evidencing the formation of lithium niobiate according to the reaction :

 $Nb_2O_5(s) + O^{2-} + 2 Li^+ = 2 LiNbO_3(s)$

The coexistence of the two solids Nb₂O₅(s) and LiNbO₃(s) fixed the pO²⁻ value. This latter was measured (pO²⁻ = 4.85 ± 0.10) and has enabled us to determine the solubility product of lithium niobiate knowing that of Nb₂O₅(s).

CONCLUSION : POTENTIAL-OXOACIDITY DIAGRAM OF NIOBIUM IN THE LICI+KCI EUTECTIC MELT

The chemical properties of niobium in molten LiCl+KCl eutectic at 450°C have been summarized under the form of an equilibrium potential-oxoacidity diagram calculated for the maximum concentrations of dissolved species of niobium (Fig.9).

For high values of potential, the electrochemical window is limited by the oxidation of the oxide anion into oxygen for basic media, and in acidic media by the oxidation of chloride ions into chlorine.

We can notice in Fig.9 the great stability of most of niobium oxides and oxychlorides, and especially niobium(V) compounds whose predominance areas correspond to 80% of the stability domain of oxides and oxychlorides. We have also to note the existence of a little domain of stability of niobium(IV) oxychloride.

On contrast, in acidic media, it is niobium(IV) which has the largest predominance area.

The particular points of the niobium chemistry are the following :

- great stabilities of the oxide compounds : in fact, one has to reach pC²⁻ values higher than 14 for dissolving the oxides and oxychlorides,
 in acidic media, NbO(s) disproportionates into metallic niobium and niobium(III)
- in acidic media, NbO(s) disproportionates into metallic niobium and niobium(III) (pO² > 14.5),
- in very basic media (pO²⁻ < 1), NbO₂(s) disproportionates into lithium niobiate and niobium monoxide.

In order to extract the gaseous niobium pentachloride, we have to impose a pO^2 -value higher than 17.9 which can be only obtained with very strong chlorinating agent such as mixtures of chlorine and carbon monoxide.

Further studies are currently in progress in our laboratory to clarify the formation of metal cluster compounds and for examining the effect of fluoride anion upon the stabilities of niobium oxides and oxychlorides in the eutectic melt at 450°C.

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Table 1 : Anodic dissolution of a niobium rod: comparison of average valency values derived from the weight losses of a niobium rod and from the analysis of the corresponding steady-state current-potential curve (LiCl+KCl eutectic melt at 450°C).

	Average valency				
Anodic current densities	from weight losses	from limiting current densities			
7.7 mA.cm ⁻² 22 mA.cm ⁻² 33 mA.cm ⁻²	3.79 4.01 4.12	3.75 4.05 4.00			



Figure 1: Average valency of niobium solutions and stable oxidation states of niobium: a) anodic dissolution of a niobium rod; b) steady state current-potential curve.



Figure 2: Potentiometric determinations of standard potentials: a) Nb(0) / Nb³⁺ redox couple; b) Nb³⁺/Nb⁴⁺ redox couple.





Figure 4 : Typical voltammograms relative to the oxidation of a pure niobium(III) solution. Working electrode : tungsten (S= 0.16 cm⁻²); concentration of Nb(III) = 3.2.10⁻² mol.kg.⁻¹; sweep rates v = 200, 400, 800 and 1500 mV.s⁻¹.

Figure 5 : Voltammetric measurements of the solubility value of niobium(III).



Figure 6 : Determination of the solubility value of niobium(IV) from limiting current densities of steady state i-E curves.



Figure 7 : Experimental titration of solid niobium with silver oxide.

Figure 8 : Experimental titration of niobium pentaoxide with sodium carbonate.



Figure 9: Predominance area diagram of niobium species (equilibrium potential - oxoacidity diagram).

THERMOGRAVIMETRIC STUDY OF THE 800°C REACTION OF ZIRCONIA STABILIZING OXIDES WITH SO₃-NaVO₃

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A thermogravimetric study was made of the reaction of the zirconia stabilizing oxides, In_2O_3 , Sc_2O_3 , Y_2O_3 and MgO, with molten NaVO₃ at 800°C under SO₃ partial pressures of 10⁻³ to 10⁻⁸ bar. The melt composition is determined by: 2 NaVO₃ + SO₃ \rightleftharpoons V₂O₅ + Na₂SO₄. No reaction of In_2O_3 was found at SO₃ partial pressures up to 5 x 10⁻⁴ bar where the reaction, $In_2O_3 + V_2O_5 = 2 InVO_4$, commenced. Reaction of Sc₂O₃ occurred at about 5 x 10⁻⁶ bar of SO₃, with ScVO₄ formed. Reaction of Y₂O₃ and MgO with the NaVO₃ melt began, on the other hand, at SO₃ partial pressures too low to be measured (< 10⁻⁷ bar). In₂O₃ and Sc₂O₃ are thus potentially superior to Y₂O₃ and MgO as stabilizers for hot corrosion resistant zirconia thermal barrier coatings. Certain other information concerning the thermochemistry of the SO₃-NaVO₃ system was also revealed.

INTRODUCTION

Stabilized zirconia thermal barrier coatings (TBCs) improve fuel economy and component durability in engines, and are widely used in aero gas turbines (1). TBCs are also beginning to be used in industrial diesel and gas turbine engines. Success in these latter applications has been limited, however, in large part because the stabilizers now commonly used for engine zirconia coatings (Y_2O_3 or MgO) react with the molten vanadate-sulfate deposits formed in engines from the sodium, sulfur and vanadium impurities found in industrial (non-aviation) fuels.

The corrosive vanadate-sulfate deposits are composed of the components, Na_2O , V_2O_5 and SO_3 , which are related by reactions [1], [2] and [3]:

$$Na_{2}O(1) + SO_{3}(g) \neq Na_{2}SO_{4}(1)$$
[1]
$$Na_{2}O(1) + V(0, d) \neq 2 Na_{2}V(0, d)$$
[2]

$$Na_2O(1) + V_2O_5(1) \neq 2 NaVO_3(1)$$
 [2]

$$2 \text{ NaVO}_3 (l) + SO_3 (g) \rightleftharpoons \text{Na}_2 SO_4 (l) + \text{V}_2 O_5 (l)$$
[3]

Several research groups have shown that the most critical reaction in the vanadate-sulfate hot corrosion of yttria-stabilized zirconia (YSZ) is:

$$Y_2O_3 (ss) + V_2O_5 (ls) \rightleftharpoons 2 YVO_4 (s)$$
[4]

In reaction [4], the Y_2O_3 is in solid solution (ss) in the ZrO_2 matrix, while the V_2O_5 is in liquid solution (ls) in the deposit melt, and both may thus have activities of well below 1. The YVO₄ product, which occurs as a minimally soluble precipitate, is highly stable (mp 1810°C) and acts as a low activity sink which leaches the Y_2O_3 stabilizer from the ZrO₂ ceramic.

Reactions of a similar type occur for magnesia-stabilized zirconia (MSZ) where, depending upon the MgO-to- V_2O_5 ratio, one may have reactions [5], [6] or [7]:

$$MgO(ss) + V_2O_5(ls) \rightleftharpoons MgV_2O_6$$
[5]

 $2 \text{ MgO (ss)} + V_2 O_5 (\text{ls}) \rightleftharpoons \text{Mg}_2 V_2 O_7 \qquad [6]$ $3 \text{ MgO (ss)} + V_3 O_5 (\text{ls}) \rightleftharpoons \text{Mg}_3 V_3 O_8 \qquad [7]$

The decomposition temperatures for these compounds are about 640°C for MgV_2O_6 , 740°C for $Mg_2V_2O_7$, and 1100°C for $Mg_3V_2O_8$. Dosages of 3 MgO to 1 V_2O_5 , which produce $Mg_3V_2O_8$, give best results when magnesium is used to inhibit high temperature corrosion caused by vanadium in the fuel (2).

In addition to reaction with V_2O_5 , Y_2O_3 (3,4) and MgO may also react with SO₃ in the presence of Na₂SO₄ to produce low melting mixed sulfates as indicated in reactions [8] and [9]:

$$\begin{array}{ll} Y_2O_3 \ (ss) + 3 \ SO_3 \ (g) \ (+ \ Na_2SO_4) \rightleftarrows Y_2(SO_4)_3 \ Na_2SO_4 \ (l) \\ MgO \ (ss) + \ SO_3 \ (g) \ (+ \ Na_2SO_4) \rightleftarrows MgSO_4 \ Na_2SO_4 \ (l) \\ \end{array} \tag{8}$$

Reaction [8] goes readily at 800°C under SO₃ partial pressures as low as 5×10^4 bar (4). The sulfation of MgO by reaction [9] is also highly favored, with SO₃ and V₂O₅ being known to compete for reaction with MgO when magnesium inhibitors are used with low quality fuel (2,5).

Our earlier research indicated that reaction between the TBC ceramic oxides and the corrosive molten deposit oxides is largely controlled by a Lewis acid-base reaction mechanism (6). Working from this basis, we have since identified scandia (7) and india (8) as potential corrosion-resistant stabilizers for zirconia TBCs.

We report here a thermogravimetric study intended to help understand and quantify the reactions between the different zirconia stabilizing oxides and vanadate-sulfate molten deposits. In this study, we consider $NaVO_3$ to simulate an engine deposit

(having a Na/V ratio of 1) that exists in equilibrium with the SO_3 in the combustion gas. The equilibrium is described by reaction [3] above. Thermodynamic calculations by Luthra and Spacil (9) indicate that reaction [3] should be the predominant reaction under gas turbine conditions.

In our experimental approach, we study reaction [3] by equilibrating NaVO₃ with increasing partial pressures of SO₃ in the thermobalance and determining, from weight gain, the concentrations of V_2O_5 , Na₂SO₄ and NaVO₃ produced at each SO₃ pressure. Repeating the NaVO₃ equilibrium experiments, but with the various stabilizing oxides added, then serves to pinpoint the SO₃ partial pressures at which the melt V_2O_5 activity is raised sufficiently by reaction [3] that reaction (i.e., reaction [4]) between the stabilizing oxide and the melt V_2O_5 commences. This procedure provides a ranking of the reaction resistance of the stabilizing oxides, as well as certain information on the thermochemistry of their reaction with vanadate/sulfate melts. It has been applied here to study and compare the zirconia stabilizing oxides, Y_2O_3 , MgO, Sc₂O₃, and In₂O₃.

EXPERIMENTAL

The required low partial pressures of SO₃ were produced by a two-stage SO₂/air dilution system using Tylan FC-260 mass flow gas controllers having 0-10 sccm (for SO₂) and 0-5 slm (for air) flow rate ranges (Fig. 1). After being dried over an indicating anhydrous CaSO₄ drying agent, tank SO₂ (Matheson, 99.98%) and laboratory air were passed into the first stage of dilution where, by using 0.5 sccm of SO₂ and 5 slm of air, dilutions of up to 10⁴ could be achieved. Total dilutions of up to 10⁻⁸ were possible by second stage dilution. The diluted SO₂/air then passed into a manifold, from which samples were withdrawn for analysis by H₂O₂ absorption (10), and finally into a Cahn 1000 thermobalance (Fig. 2). The SO₂/air mixture was equilibrated over a Pt catalyst at temperature, as shown in Fig. 2, with the resultant SO₃ concentration calculated. Controlled (\pm 10%) SO₃ partial pressures over the range of 10⁻³ to 10⁻⁸ bar, along with a balance sensitivity of 0.1 mg, were provided by the system. Furnace temperatures were maintained within \pm 5°C using a three-zone furnace (Applied Test Systems 3210) and electronic temperature controller (Omega CN9121).

The sample sizes were 0.41 millimoles (50mg) for NaVO₃, and 0.10 mmols for the stabilizing oxides, except for MgO which was 0.20 mmols. (Note: the NaVO₃ contained about 2% water, and our practice was to weigh out 51mg of NaVO₃ which reduced to approximately 50mg after H₂O loss on heatup.) The samples were weighed directly into a platinum planchet using a Mettler AE 160 bench balance, and the planchet then transferred to the Cahn 1000 thermobalance. The chemical reagents used were NaVO₃ (Johnson Matthey, 98%), Y₂O₃ (Rare Earth Pdts, 99.999%), MgO (Johnson Matthey, 99.998%), Sc₂O₃ (Rare Earth Pdts, 99.99%), and In₂O₃ (Johnson Matthey, 99.99%). At the end of selected experiments, the specimen samples were ground and subjected to x-ray diffraction to help identify the reaction products.

RESULTS AND DISCUSSION

Reversibility and Reproducibility

Preliminary tests established that reaction [3] was reversible and reproducible at 700 and 800°C. These properties are demonstrated for 700°C in Fig. 3a. (NB, the indicated SO₃ values in Figs. 3a and 3b are only relative, and not absolute, since the Pt catalyst was not at proper temperature in these initial trials.) A sample of NaVO₃ (solid line) was equilibrated with 50 Pa of SO₃, and then the SO₃ pressure reduced to 11 Pa, and the NaVO₃ reequilibrated, with corresponding weight loss, at this new pressure. A second NaVO₃ sample (dashed line) was equilibrated with 11 Pa of SO₃ (coming to the same weight as in the first experiment), and the sample then reequilibrated under 5 Pa of SO₃. Finally, a third NaVO₃ sample (short dashed line) was equilibrated under 5 Pa of SO₃, with the same weight gain as in the second experiment. In each case, identical equilibria were reached, regardless of whether approached from higher or lower SO₃ partial pressure.

Detection of Ceramic Oxide Reaction

Fig. 3b compares the weight gain curves obtained for pure NaVO₃ (from Fig. 3a) with the curves produced when mixtures of 0.1 mmol $In_2O_3/0.4$ mmol NaVO₃ were equilibrated at the same 50, 11, and 5 Pa of SO₃. Note that a pronounced increment of additional weight gain is produced with the In_2O_3 -NaVO₃ mixtures at 50 and 11 Pa of SO₃, but not at 5 Pa of SO₃ where the total weight gain is in fact slightly lower with the presence of In_2O_3 . This behavior results because the melt V_2O_5 activity is increased enough, via reaction [3], at 50 and 11 Pa of SO₃ to allow V_2O_5 reaction with In_2O_3 to form $InVO_4$ (see below). At 5 Pa of SO₃, the critical V_2O_5 activity required for reaction with In_2O_3 is not reached, and so no weight gain or $InVO_4$ formation is seen.

Kinetics of reaction

Note that the rate of weight gain in Fig. 3b, although different for the various SO_3 pressures, is nearly constant until near equilibrium, and that it is not changed when In_2O_3 is present. This implies that the rate-controlling step is associated with the uptake of SO_3 into the NaVO₃ melt, and not with the subsequent reaction between In_2O_3 and V_2O_5 . Division of the weight gain rate by the SO_3 concentration indicates the rate-controlling reaction to be first order with respect to SO_3 , although the weight gain rate/ SO_3 concentration quotient decreases slightly with concentration, going from 0.0312 at 5 Pa of SO_3 to 0.0260 at 50 Pa of SO_3 .
Insuring Equilibrium at Low SO₃ Pressures

Since the rate of reaction is inversely proportional to the SO₃ partial pressure, progressively longer times are required for equilibrium as the SO₃ pressure decreases. This problem was alleviated by driving reaction [3] to near equilibrium under high SO₃ pressure, and then reducing to the test SO₃ level and determining the closeness to equilibrium from the slope of the ensuing weight gain trace. An example is shown in Fig. 4 for Y_2O_3 -NaVO₃ under 0.06 Pa of SO₃ at 800°C. A higher SO₃ partial pressure (of about 200 Pa) was applied in 5 stages, with the ensuing slope under 0.06 Pa of SO₃ being positive up to the fourth stage (at 11.4 mg) where the slope was very slightly positive, and the fifth stage (at 12.1 mg) where the slope was clearly negative. True equilibrium (approached from both below and above) therefore lies at about 11.5 mg weight gain.

Equilibrium of SO3 with Pure NaVO3

Using the technique above for achieving equilibrium, and with the furnace heat zones properly adjusted so that the Pt catalyst was within \pm 5°C of the specimen temperature, we determined the equilibrium weight gain for NaVO₃ at 700° and 800°C under SO₃ partial pressures ranging from approximately 1 x 10⁻³ to 5 x 10⁻⁸ bar. The results are shown in Fig. 5 in terms of SO₃ activity.

Nonideality of Solution Behavior

Using thermodynamic data compiled by Luthra and Spacil (9), one can calculate the Gibbs standard free energy for reaction [3], which is -49.560 kJ and -40.316 kJ at 700° and 800°C respectively. Then, assuming ideal behavior on the part of all species, and knowing the equilibrium SO₃ partial pressures or activities, it is possible to calculate the ideal solution behavior of V_2O_5 for each SO₃ pressure and temperature on the basis of the relationships:

$$\Delta G^{\circ} = -RT \ln K$$
 [10]

and, where K is the equilibrium constant,

$$K = \frac{(a_{Na_2SO_4})(a_{V_2O_5})}{(a_{Na_{VO_3}})^2(a_{SO_3})}$$
[11]

In addition, noting that the SO₃ concentration is below 10^{-3} in the melt and negligible in terms of mole-fraction calculation, one can use the equilibrium weight gain data to determine the experimental V₂O₅ concentration produced for each set of conditions. This

allows a comparison between the ideal and experimental solution behavior for V_2O_5 at 700° and 800°C, as shown in Fig. 6. Note, however, that while this comparison is useful for showing that V_2O_5 deviates significantly from ideal behavior, it provides no information as to the actual V_2O_5 activity.

Observations Concerning Association in the Melt

The SO₃ addition to NaVO₃ can be viewed as being an acid-base "titration" of the polybasic Na₂O-V₂O₅ system. This would be analogous to the neutralization of polybasic acids such as H_3PO_4 by strong bases, where the titration curve of ml of titrant vs. pH takes a multi-step form as a result of the progressive dissociation of the polybasic acid molecule. However, the weight gain vs. log of SO₃ activity curves in Fig. 5 are smoothly monotonic, and show no sign of a step-wise break in slope. This implies, assuming our analogy is correct, that no strong association or dissociation is occurring in the given V_2O_5 -Na₂SO₄-NaVO₃ system within the SO₃ activity range being investigated.

Reaction of In₂O₃ with SO₃-NaVO₃

The reaction of In_2O_3 with SO_3 -NaVO₃ was investigated by experiments similar to those above, but with 0.10 mmols of In_2O_3 added. The 800°C test temperature was chosen because earlier results (8) indicated that there should be little reaction between SO_3 and In_2O_3 at this temperature for the SO_3 levels under study.

The SO₃-In₂O₃-NaVO₃ results are plotted in Fig. 7 along with the "baseline" 800°C SO₃-NaVO₃ equilibrium curve (from Fig. 5). The In₂O₃-NaVO₃ data are essentially parallel (although slightly lower) to the pure NaVO₃ weight curve up to an SO₃ activity of about 5 x 10⁴, where the In₂O₃-NaVO₃ data show an abrupt increase of approximately 5-6mg above the NaVO₃ weight gain curve.

The upward break in the In_2O_3 -NaVO₃ weight curve marks the point at which the melt V_2O_3 activity has been raised high enough, by reaction [3], that In_2O_3 begins to react with V_2O_5 to form $InVO_4$. This is confirmed by comparison of x-ray patterns from specimens A and B (as marked in Fig. 7) with standard patterns for pure $InVO_4$ (synthesized in our laboratory) and cubic In_2O_3 (JCPDS 6-0416). As Fig. 8 shows, the pattern from Spec. A contains the major lines for $InVO_4$, but not those for In_2O_3 , while the pattern from Spec. B agrees well with that of In_2O_3 , but not $InVO_4$. India is therefore the stable indium form up to an SO₃ activity of about 5 x 10^4 , with $InVO_4$ being stable thereafter. The relative intensities of the $InVO_4$ forms with a crystal habit that leads to a high degree of orientation in the powder specimen.

The weight gain behavior is also consistent with an oxide-to-metavanadate transition at the SO₃ activity of 5 x 10^4 . The only source of weight gain in our system

is from SO₃ uptake into the melt, and the maximum possible weight gain for 50mg of NaVO₃ is 16.4mg, which corresponds to complete conversion of the NaVO₃ to Na₂SO₄ and V₂O₅ by reaction [3]. On the other hand, total conversion of 0.10 mmols of In₂O₃, Y_2O_3 , or Sc₂O₃ to the metavanadate via reaction [4] would consume 0.10 mmols of V₂O₅ from the NaVO₃, which would make 0.10 mmols of Na₂O available for reaction with SO₃ by reaction [2], and thus lead to a weight gain of 8.2mg. The weight gain step for In₂O₃-NaVO₃ in Fig. 7 is only 5-6mg, but note that 10mg of weight gain occurs before InVO₄ formation begins (a high V₂O₅ activity is required), and that the final combined weight gain of 15-16mg essentially equals the 16.4mg maximum possible weight gain for the specimen.

If the oxide and metavanadate in reaction [4] are pure solids and their standard energies of formation are known, then the V₂O₅ activity required for the commencement of reaction [4] can be calculated. For example, on the basis of thermodynamic data from Hwang and Rapp (11) and Turkdogan (12), the V₂O₅ activity necessary for reaction with Y₂O₃ to form YVO₄ at 900°C can be calculated to be about 1 x 10⁻⁵. Mittal and Elliott (13) have determined the activity of V₂O₅ in 50 mole-percent Na₂O-V₂O₅ (i.e., NaVO₃) by electrochemical measurement as being 5 x 10⁴ at 850°C. One can predict therefore that Y₂O₃ should react with pure NaVO₃ to form YVO₄ (as in fact we see below).

Unfortunately the standard energy of formation for $InVO_4$ is not known, and so the V₂O₅ activity for $InVO_4$ formation can not be calculated directly. However, from Fig. 7, we know that the V₂O₅ activity for $InVO_4$ formation is higher than the 5 x 10⁴ V₂O₅ activity of pure NaVO₃. If we postulate that interaction of SO₃ with the melt increases the V₂O₅ activity to 5 x 10⁻³ or 5 x 10⁻² (i.e., by 1 or 2 orders of magnitude), the corresponding free energies for $InVO_4$ formation by reaction [4] would be -47.3 kJ or -26.7 kJ, respectively. These two values would then lead, since the known standard energies of formation for V₂O₅ (l) (9) and In_2O_3 (s) (12) are known, to an estimated energy of formation for $InVO_4$ at 800°C of -870 kJ/mole (for 5 x 10⁻³ V₂O₅ activity) or -860 kJ/mole (for 5 x 10⁻² V₂O₅ activity). Furthermore, since the V₂O₅ mole-fraction in the melt at $InVO_4$ formation is approximately 0.3 (as read from Fig. 6 at the critical SO₃ activity of 5 x 10⁻⁴), we can estimate the activity coefficient for V₂O₅ at this concentration to be of the order of 2 x 10⁻² to 2 x 10⁻¹.

Reaction of Sc₂O₃ and Y₂O₃ with SO₃-NaVO₃

Similar experiments with Sc_2O_3 and Y_2O_3 produced the results given in Fig. 9. Note that the predicted weight gain step of about 8mg is seen with these more reactive oxides, especially at the lower SO₃ activities. The critical SO₃ activity for reaction of Sc_2O_3 with the melt V_2O_5 is shown to be about 5 x 10⁻⁶ in Fig. 9. X-ray diffraction confirmed that $ScVO_4$ is the stable scandium phase at SO₃ activities higher than 5 x 10⁻⁶. Some ScVO₄ is detected, however, (although the majority scandium phase is Sc₂O₃) below the critical 5 x 10⁻⁶ SO₃ activity. This is not unexpected since pure NaVO₃ may have sufficient V₂O₅ activity at 800°C to allow ScVO₄ formation (14). The production of ScVO₄ consumes V₂O₅ and lowers the V₂O₅ activity of the NaVO₃ melt (especially if the Sc₂O₃/NaVO₃ ratio is high), so that only limited ScVO₄ formation occurs. When SO₃ is present, at activities above 5 x 10⁻⁶, it reacts with the Na₂O generated in the melt because of V₂O₅ consumption (cf. reaction [2]), and maintains the melt V₂O₅ at a level which drives the conversion of Sc₂O₃ to ScVO₄ essentially to completion.

The reaction behavior of Y_2O_3 with SO₃-NaVO₃ is similar, except that Y_2O_3 , presumably because it is a more basic oxide than Sc₂O₃ (14), reacts more readily than Sc₂O₃ with NaVO₃. There is a substantial conversion of Y_2O_3 to YVO_4 by reaction with NaVO₃ alone, as shown experimentally (6) and predicted by thermodynamics (see above). It is not possible therefore to identify an SO₃ partial pressure that leads to the onset of reaction of Y_2O_3 with NaVO₃. The effect of SO₃ in driving full conversion of Y_2O_3 to YVO_4 can be seen in Fig. 9, however, as manifested by the near 8mg weight gain produced even at SO₃ activities in the 10⁻⁷ range.

Reaction of MgO with SO₃-NaVO₃

The results for the reaction of MgO with SO₃-NaVO₃ are given in Fig. 10. The weight gain curve for SO₃-MgO-NaVO₃ lies above the SO₃-NaVO₃ equilibrium curve at all SO₃ activities, being roughly parallel to the SO₃-NaVO₃ curve at the lowest SO₃ activities, but then diverging upward as the SO₃ activity increases. One may speculate that the weight gain at the lower SO₃ activities results from MgSO₄ formation, with Mg-vanadate formation (perhaps Mg₃V₂O₈ since MgO is initially in excess) then coming into play as the V₂O₅ activity increases. Some evidence of a break in the MgO weight gain curve may be seen, as suggested by the dashed lines in Fig. 10. However, the x-ray diffraction patterns produced by the MgO-melt specimens are complex, and it has not been possible to verify that Mg-vanadate formation in fact commences in the vicinity of the "break point" indicated in Fig. 10.

CONCLUSIONS

The reaction of zirconia stabilizing oxides with molten vanadate-sulfate salts under SO₃ equilibrium can be successfully studied by high temperature thermogravimetry, and the resistance of the individual oxides to reaction with the vanadate-sulfate melt quantitatively evaluated.

The results show Sc_2O_3 , and especially In_2O_3 , to be more resistant than Y_2O_3 and MgO to reaction with 800°C vanadate-sulfate melts. Scandia and india are thus potentially superior to yttria and magnesia for use as stabilizers to produce zirconia

thermal barrier coatings having improved resistance to molten vanadate-sulfate hot corrosion.

The method is limited to SO₃ activities of 10^{-8} and upward, but this covers the range of SO₃ activities likely to be encountered in technology. For example, the SO₃ partial pressure in an industrial gas turbine (CH_{1.7} fuel, 10/1 compression, 30/1 air-to-fuel, 800°C) is of the order of 5 x 10^{-6} for fuel with 0.01% sulfur (aviation fuel allows up to 0.05%) and 5 x 10^{-4} for fuel containing 1% sulfur (typical of industrial fuels). The effect of the Na/V ratio in engine deposits, which may well also be critical, can be studied by changing the Na/V ratio in the thermobalance vanadate specimen.

Thermogravimetric study of SO_3 equilibrium with vanadate-sulfate melts has the potential for providing new information on the thermodynamics and solution chemistry of the technologically important molten vanadate-sulfate salt system.

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Fig. 1 Schematic of SO₂/air gas dilution system.



Fig. 2 Schematic of thermobalance system.



Fig. 3(a)-3(b) Weight gain behavior showing (3a) reversibility and reproducibility of SO_3 -NaVO₃ equilibrium at 700°C, and (3b) reaction of In_2O_3 at 50 and 11, but not 5, Pa of SO₃.



Fig. 4 Weight gain trace illustrating determination of equilibrium of 0.06 Pa of SO₃ with Y_2O_3 -NaVO₃ at 800°C.



Fig. 5 Equilibrium weight gain for SO₃-NaVO₃ reaction as a function of SO₃ activity at 700 and 800°C.



Fig. 6 Mole-fraction of V_2O_5 vs. SO₃ activity, as (1) calculated assuming ideal behavior, and (2) determined from weight gain.



Fig. 7 Comparison of weight gain for pure $NaVO_3$ vs. In_2O_3 - $NaVO_3$ at 800°C as a function of SO₃ activity.



Fig. 8 X-ray diffraction spectra from Specimens A and B of Fig. 7 confirming transition from In_2O_3 to $InVO_4$ at SO₃ activity of 5 x 10⁴.



Fig. 9 Weight gain behavior for Sc_2O_3 -NaVO₃ and Y_2O_3 -NaVO₃ at 800°C as function of SO₃ activity.



Fig. 10 Comparison of weight gain behavior for MgO-NaVO₃ vs. pure NaVO₃ at 800°C as function of SO₃ activity.

MODELS OF ALUMINA DISSOLUTION IN CRYOLITE

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ABSTRACT

Two models for the dissolution of alumina powder in cryolite were formulated and compared with experimental results obtained using modified fast linear sweep voltammetry. The first model, where the rate of dissolution is assumed to be controlled by the rate of chemical reaction at the alumina surface, gave a reasonable fit with the experimental data. The second model, where it is assumed that the rate of dissolution of alumina is mass transport controlled, also gave a reasonable fit with the experimental data. Comparisons of the models with experimental data suggest that the alumina, when added to the electrolyte, forms agglomerates. Heat transfer was shown not to be the dominant rate controlling process in the stirred electrolyte system studied.

1. INTRODUCTION

In the Hall-Heroult process for producing aluminium, refined alumina is added to an electrolyte of molten cryolite (Na_3AlF_6) . The alumina dissolves in the cryolite and is then electrolysed using carbon electrodes to produce aluminium and carbon dioxide. An important consideration in achieving maximum efficiency in production of aluminium is in the rapid dissolution of the alumina in the cryolite bath. Rapid dissolution is necessary to prevent "sludging", the formation of undissolved alumina which settles below the molten aluminium at the bottom of the cell. This sludge is undesirable since in addition to this alumina not being available for electrolysis it causes erosion of the cathode and an increase in cell resistance.

The NaF - AlF₃ solvent is a mixture of hexa- and tetrafluoroaluminate anions and the dissolution of alumina in cryolite may be written (1):

$$Al_2O_3 + AlF_6^{3-} \rightarrow 3AlOF_x^{(1-x)-} + (6-3x)F$$

The composition of the bath used in the alumina dissolution tests had a cryolite ratio (moles NaF/moles AlF₃) of 2.4 with 5 wt% CaF. For this composition the predominant oxyanion species formed in solution from the dissolution of alumina would be $AlOF_2^{-1}$ and $AlOF_3^{2-1}$. These species are the oxygen carrying components of the bath which are reduced at the anode.

In order to better understand the process of alumina dissolution, two simple models for the dissolution of dispersed alumina in a molten cryolite electrolyte have been developed. The first model is one where the rate of reaction depends only on the surface area of the alumina. The dissolving alumina is regarded as shrinking smooth spheres. In this model the rate of dissolution is therefore controlled by the rate of chemical reaction. In the second model it is assumed that the rate of dissolution of alumina is mass transport controlled, so that the concentration of alumina in the electrolyte is important. With the second model the rate depends on the diffusion rate of alumina across a boundary layer at the surface of the alumina.

The predicted shape of the dissolution curves is then compared with the experimental data. This comparison is possible because of the developments in the technique of in situ measurement of alumina dissolution in molten cryolite using a modified form of fast linear sweep voltammetry (2,3,4).

2. EXPERIMENTAL DETERMINATION OF DISSOLUTION RATES

Alumina was added to a stirred electrolyte of cryolite and the dissolution measured with a modified form of linear sweep voltammetry. The equipment setup and the method of dissolution rate measurement have been described elsewhere (3).

Commercial grade alumina was used. This alumina was sieved and the size fraction 63-90 μ m was used for this work. This alumina had an alpha alumina content of 15% and a surface area, as measured by the BET method of gas adsorption, of 66 m²/g. This area includes the internal surface area which is a result of the very porous nature of the alumina.

A set of three dissolution curves obtained from the commercial alumina were used in this modelling work. The amount of alumina used and the electrolyte alumina concentrations are listed in Table I. The curves obtained are illustrated in Figure 1. These curves are typical of a large number of similar dissolution experiments performed as part of a wider experimental programme.

Dissolution Curve	Alumina Added	Initial Alumina Concentration		Surface Area*
	Mo	C_i/ρ_e	Ci	A_0
	(g/kg)	(g/kg)	(g/L)	(m ²)
1	10	7.5	15.8	0.39
2	10	17.5	36.9	0.39
3	18	27.5	58.0	0.71
* based on smooth sphere model				

Table I Initial Mass, Initial Surface Area and Initial Electrolyte Alumina Concentrations for Alumina Dissolutions.

3. HEAT TRANSFER CONTROL

Heat transfer has been postulated as an important process for limiting the dissolution rate of alumina (5, 6, 7). Where this is proposed it has generally been assumed that large agglomerates of alumina form, with a frozen shell of electrolyte around the agglomerate.

The time taken to heat 10 g of alumina, with an effective geometric surface area of 0.39 m² (Table I), from 20°C to 975°C, the liquidus temperature of the electrolyte, can be calculated from Equation [1]:

$$t = \frac{2C_p M}{W h_R A}$$
[1]

where:

t is the time to heat the alumina

- C_p is the molar heat capacity of alumina (79 J K⁻¹ mol⁻¹) M is the mass of alumina (10 g)
- W is the molecular weight of alumina (102 g mol⁻¹)
- A is the effective surface area of the alumina (0.39 m^2)
- h_{B} is the heat transfer coefficient between the electrolyte and the alumina

Heat transfer coefficients have been reported (5,6,7) in the range 400 - 1200 J s⁻¹ m⁻² K⁻¹. Using these heat transfer coefficients in Equation [1] results the alumina remaining out of contact with the molten electrolyte, due to the existance of a frozen shell, for less than 0.1 seconds. This is negligible when compared with the total

dissolution time and can be ignored.

When large agglomerates of alumina form, as is generally assumed in systems studied previously (5,6,7), the heat transfer becomes much more important because the surface area of the alumina exposed to the electrolyte is much reduced. Also, the cooling of the surrounding electrolyte would result in freezing around the agglomerate. If this were the case, one would expect to observe an initiation time between the addition of alumina and commencement of dissolution, due to the need to remelt the frozen electrolyte. This was not observed in these experiments thus supporting the supposition that some, if not all, of the alumina particles are well dispersed in the electrolyte by the action of the stirrer.

4. FIRST MODEL - CHEMICAL CONTROL

4.1 Derivation of equations

The first model which we propose and wish to test states that the rate of dissolution of well stirred dispersed alumina in an electrolyte of molten cryolite is proportional to its surface area. The rate is not mass transport controlled, but rather, depends on the rate of the surface reaction involving the breaking of strong Al-O bonds by complexing with AlF^{6-} . The model assumes that the mass transport is fast relative to the surface chemical reaction.

$$R = kA$$
 [2]

where:

- R is the rate of dissolution, units g s⁻¹
- k is the rate constant, units g s⁻¹ m⁻²
- A is the surface area of the alumina, units m^2

We may suppose that the particles of alumina which are added to the cryolite electrolyte are monodisperse smooth spheres each with an initial radius r_0 . In making this assumption we are supposing that although the alumina is very porous, as shown by the high BET surface area, the electrolyte does not penetrate these pores or if it does then there is no exchange of electrolyte from these pores to the bulk electrolyte. The initial surface area of the total alumina added is then:

$$A_0 = \frac{3M_0}{r_0 \rho}$$
 [3]

where:

 A_o is the initial surface area of the total amount of alumina added M_o is the initial mass of alumina added

 ρ is the particle density

It is readily shown that the surface area of the alumina will decrease as the mass of the undissolved alumina decreases by the relationship:

$$A = A_0 \left(\frac{M}{M_0}\right)^{2/3}$$
 [4]

where:

A is the surface area of all the spheres at time t M is the mass of alumina remaining undissolved at time t

The mass of alumina remaining undissolved can be related to the concentration of alumina in the electrolyte by the relationship:

$$M = M_0 - (C - C_i)V$$
 [5]

where:

 C_i is the initial alumina concentration (g/L) in the cryolite electrolyte C_i is the alumina concentration at time t

V is the volume of the electrolyte

In order to simplify the equations we will call $C' = C - C_i$, where C_i is the initial alumina concentration, prior to each alumina addition. We therefore obtain an expression for the rate of dissolution of alumina, using the shrinking sphere model:

$$R = \frac{dC}{dt}V = kA_0 \left(1 - \frac{V}{M_0}C'\right)^{2/3}$$
 [6]

By rearranging the equation and integrating with respect to concentration and time, then obtaining the integration constant when t=0 and C'=0 we get the following expression:

$$t = \frac{3M_0}{A_0k} \left[\left(\frac{V}{M_0} C' - 1 \right)^{1/3} + 1 \right]$$
 [7]

This can be rearranged to give the concentration of alumina, C':

$$C' = \frac{M_0}{V} \left[1 + \left(\frac{A_0 k}{3M_0} t - 1 \right)^3 \right]$$
[8]

4.2 Comparison with experimental

Using the shrinking sphere model (Equation 8) a set of calculated experimental curves are plotted in Figure 2, along with the experimental data for comparison. The density of crystalline alumina is 4.0 g/cm³, however, the density of the individual alumina particles is approximately 2 g/cm³ due to the high void space within each particle. Based on the estimated median particle diameter of 76.5 μ m, and a density of 2 g/cm³ the surface areas for the alumina additions were calculated as listed in Table I. The rate equation is fitted to the experimental data by a nonlinear regression procedure using a Marquardt-Levenberg algorithm, to obtain a value of the rate constant, k. The values of k which were found to be the best fit are listed in Table II.

The simple first dissolution model proposed above, where the rate is proportional to the surface area of the alumina supposing the alumina to be smooth spheres gives a reasonable fit to the experimental behaviour. The shape of the experimental curve differs from the predicted curve in that the reaction proceeds more rapidly initially. This could be due to the alumina particles not being completely monodisperse, with some particles breaking up and others forming agglomerates.

Alumina Addition	Rate Constant k (g s ⁻¹ m ⁻²)	
1	0.22	
2	0.19	
3	0.11	

Table 2. Rate Constants Obtained for the First Model

5. SECOND MODEL - MASS TRANSPORT CONTROL

5.1 Derivation of equations

The first rate equation (Equation 2) can be modified by taking into account the diffusion of dissolved alumina away from the surface of the alumina into the bulk of the electrolyte. The driving force for this diffusion is the difference in concentration of

dissolved alumina between that at the surface of the alumina (C_{sat}) and that of the bulk of the electrolyte (C). It is assumed that diffusion is one dimensional through a constant thickness boundary layer, δ , where δ is invariant with respect to particle size.

The rate equation may then be written:

$$R = \frac{dC}{dt}V = k_2 A \left(C_{sat} - C\right)$$
[9]

Substituting the expression for area as a function of concentration, (4) and (5), the rate equation becomes:

$$\frac{dC}{dt}V = k_2 A_0 \left(1 - \frac{V}{M_0}C'\right)^{2/3} (C'_{sat} - C')$$
 [10]

where: C' is the concentration of alumina minus the initial concentration C'_{sat} is the saturation alumina concentration for the particular electrolyte composition used minus the initial concentration

This can then be integrated, using algebraic substitution, and the integration constant found for C'=0 when t=0 to yield the expression:

$$t = \frac{2V}{k_2 A_0 a^2 b^2} \left[\frac{1}{2} \ln \frac{(a+u)^2}{a^2 - au + u^2} + \sqrt{3} \tan^{-1} \frac{2u - a}{a\sqrt{3}} - \frac{1}{2} \ln \frac{(a+b)^2}{a^2 - ab + b^2} - \sqrt{3} \tan^{-1} \frac{2b - 1}{a\sqrt{3}} \right]$$
[11]

where:

$$u = \left(C' - \frac{M_0}{V}\right)^{1/3}$$
$$a = \left(\frac{M_0}{V} - C'_{sat}\right)^{1/3}$$
$$b = \left(-\frac{M_0}{V}\right)^{1/3}$$

5.2 Comparison with experimental

The saturation concentration of alumina in the electrolyte used is 164.6 g/L (8). The initial alumina concentration in the electrolyte was $15.8 \text{ g/L} \text{ Al}_2\text{O}_3$ so that the C'_{sat} for the first second and third dissolution curves will be 150.9, 129.8 and 108.7 g/L respectively. When these values are used and Equation [11] is plotted for each of the three dissolution runs then the curves shown in Figure 3 are obtained. The rate constants obtained from computer best fits of the calculated curves with the experimental curves are listed in Table III. The rate constants obtained are similar, as should be expected, at the three different initial alumina concentrations.

5.3 Particle interaction

It has been observed (2,4), from dissolution studies of powder alumina added to a stirred electrolyte of cryolite, that the degree of dispersion of alumina in the electrolyte has a large effect on the dissolution rate of the alumina. This dispersion is controlled by the stirring of the electrolyte, by a stirrer in the laboratory cell and in a commercial cell by electromagnetic forces and gas induced stirring. The second model proposed, assumes that the alumina particles are well dispersed so that the diffusion of dissolved alumina away from each alumina particle is not affected by neighbouring particles. This will clearly not be the case for a real system. Where complete dispersion is not obtained there will be some overlap in the boundary layers of adjacent alumina particles, as represented

Dissolution Run C' _{sat}		Rate Constants Actual C' _{sat}		Adjusted
	C' _{sat} (g L ⁻¹)	k ₂ (m s ⁻¹)	C' _{sat} (g L ⁻¹)	k ₂ (m s ⁻¹)
1 2 3	151 130 109	1.4×10^{-7} 1.5 x 10^{-7} 1.1 x 10^{-7}	80 80 80	2.9×10^{-7} 2.5 x 10^{-7} 1.6 x 10^{-7}
5	109	1.1 X 10	80	1.0 x 10

Table 3. Best Fit Rate Constants Obtained for the Second Model Using the Actual Values of C'_{sat} and an Adjusted Value of C'_{sat} of 80 g L^{-1} .

in Figure 4.

We can test this hypothesis by using a smaller concentration gradient in Equation [11]. This can be done simply by using a smaller value for C'_{sat} , which is equivalent to saying that the effective bulk alumina concentration experienced by each particle is greater. When a lower C'_{sat} is used, as illustrated in Figure 5, a better fit of the model to the experimental data is obtained. These plots are obtained with $C'_{sat} = 80 \text{ g/L } Al_2O_3$.

A better fit still can be obtained using $C'_{sat} = 40 \text{ g/L Al}_2O_3$, as illustrated in Figure 6.

5.4 Estimation of boundary layer thickness from rate constants and diffusion coefficient.

The rate constant, R, for the second model is related to the diffusion coefficient, D, and the boundary layer thickness, δ , by the relationship:

$$k_2 = \frac{D}{\delta}$$
[12]

The diffusion coefficient for alumina under the conditions employed here is approximately $1x10^9$ m² s⁻¹ (9). Therefore a rate constant of $1.4x10^7$ m s⁻¹ gives a calculated boundary layer thickness of $7x10^3$ m. Typically, in a well stirred system, boundary layers are about 10^4 m. This suggests that the value of k_2 obtained with this model is too small or that the surface area calculated is too large. If there was some clumping of the particles taking place then the surface area exposed to the electrolyte would decrease and the rate constant would be smaller. For example a surface area of 0.01 m^2 would give a calculated boundary layer thickness of $1.8x10^4$ m. The initiation

time for dissolution due to heat transfer would in this case be of the order of 1 - 4 seconds, which is still negligible. Some small degree of clumping of alumina is therefore suggested by the comparison of this model with the experimental data. As with the first model, the shape of the experimental curve differs from the predicted curve in that the reaction proceeds more rapidly initially. This could be due to the alumina particles not being completely monodisperse, with some particles breaking up and others forming agglomerates.

6. CONCLUSIONS

Two models for the dissolution of alumina powder in cryolite were formulated and compared with experimental results obtained using modified fast linear sweep voltammetry. The first model, where the rate of dissolution is assumed to be controlled by the rate of chemical reaction at the alumina surface, and is therefore proportional to the surface area assuming smooth spheres, gave a reasonable fit with the experimental data. The shape of the experimental curve differs from the predicted curve in that the reaction proceeds more rapidly initially. This could be due to the alumina particles not being completely monodisperse, with some particles breaking up and others forming agglomerates.

The second model, where it is assumed that the rate of dissolution of alumina is mass transport controlled, also gave a reasonable fit with the experimental data. The shape of the experimental curve differs from the predicted curve in that the reaction proceeds more rapidly initially. The fit was improved if it is assumed that dispersion is not complete so that there some overlap between the boundary layers of adjacent alumina particles. The fit could also be improved if it is assumed that the alumina particles are not completely monodisperse, with some particles breaking up and others forming agglomerates. This is supported by a calculation of the thickness of the boundary layer from the rate constants obtained from the second model, and the diffusion coefficients, which suggest that the alumina is clumping to some extent resulting in a reduced surface area.

Heat transfer was shown not to be the dominant rate controlling process in the stirred electrolyte system studied.

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Figure 1. Experimental Dissolution Curves. 600 g Electrolyte (Cryolite with Ratio of $NaF/AlF_3 = 1.50, 5\% CaF_2$) in 100 cm Diameter Carbon Crucible with Stirrer at 200 rpm, 8°C Superheat (Above Liquidus). Curve 1 and 2 for 1 Mass% Alumina Additions, Curve 3 for 1.8 Mass% Alumina Added. Alumina Added Through a Dropper with a Cone Shaped Spreader, Addition Time Approximately 2 Seconds.



Figure 2. Experimental Curves with Best Fit Curves Obtained Using Equation [7] for the First Model.



Figure 3. Experimental Curves with Best Fit Curves Obtained Using Equation [11] for the Second Model.



Figure 4. Representation of the Overlap of the Boundary Layers of Two Alumina Particles Resulting in an Effectively Lower C'_{sat}.



Figure 5. Experimental Curves with Best Fit Curves Obtained Using Equation [11] for the Second Model with C'_{sat} = 80 g/L Al_2O_3 .



Figure 6. Experimental Curves with Best Fit Curves Obtained Using Equation [11] for the Second Model with C'_{sat} = 40 g/L Al_2O_3 .

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