# Edited by J. Braunstein and J. R. Selman SECOND INTERNATIONAL SYMPOSIUM

# MOLTEN SALTS

# PROCEEDINGS OF THE SECOND INTERNATIONAL SYMPOSIUM ON

# MOLTEN SALTS

### Edited by

Jerry Braunstein Oak Ridge National Laboratory Oak Ridge, Tennessee J. Robert Selman Illinois Institute of Technology Chicago, Illinois



PHYSICAL ELECTROCHEMISTRY DIVISION

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### PREFACE

The success of the International Symposium on Molten Salts held in 1976 under the auspices of the Electrochemical Society in Washington D.C., prompted the organization of a Second International Symposium on Molten Salts. This Symposium, held in October 1978 during the Electrochemical Society meeting in Pittsburgh, PA, was sponsored by the Physical Electrochemistry Division of the Electrochemical Society. The symposium was dedicated to the memory of Max A. Bredig upon the death, in 1977, of this seminal figure in the development of metal-molten salt solution chemistry.

The co-chairman of the Symposium were Dr. J. Braunstein, Prof. C. T. Moynihan, Prof. J. R. Selman, and Dr. S. J. Yosim.

The Symposium covered all aspects of molten salt chemistry, technology and engineering. Twenty-eight of the papers presented at the Symposium are collected in the present volume. The original editor of this Symposium Volume, Dr. Jerry Braunstein, was unable to carry this task to completion; at his request I have undertaken the final editing of the volume. It is a pleasure to acknowledge the cooperation of the Electrochemical Society editorial staff, headed by Mrs. S. Kilfoyle, in this task.

> J. Robert Selman May 1981

### DEDICATION

### Max Albert Bredig June 20, 1902-Nov. 21, 1977

During the planning stage of this Symposium, the molten salt community lost one of its most active, enthusiastic, energetic and fruitful members. There is no need to review here Max Bredig's accomplishments. A glance at the Table of Contents shows that his work touched a large number of the topics discussed here, and of the participants in this Symposium. In addition to his contributions to molten salt chemistry through his studies of phase equilibria, electrical conductivity and thermodynamic properties of alkali metal-alkali metal halide systems, and the pioneering work on X-ray and neutron diffraction studies of the structure of molten alkali halides, at Oak Ridge National Laboratory, his earlier efforts included studies of ionization in gases, solid state chemistry and mineralogy. The influence of his early days at the Institutes of Fritz Haber in Berlin and of James Franck in Gottingen, providing contact with Nernst, Planck and other giants of the 1920's, were always evident. Max's father was Professor Georg Bredig of Karlsruhe, perhaps most remembered now for the Bredig method of preparation of colloidal suspensions of metals. Bridging the gap to his father's research, Max's work was crucial in demonstrating that metals could form true solutions in molten salts, rather than be dispersed only as colloids. In his relations with other scientists, Max's warmth, sincerity, encouragement, approachability and patience-he was impatient only with sloppy thinking-won him both friendship and respect. Important as were his contributions to the understanding of electronic conduction mechanisms, coordination and packing in molten salts, at least equally important were his great critical faculty, and the insight with which he penetrated to the core of a problem, even in areas where he professed little expertise. It is fitting that this volume be dedicated to the memory of Max Bredig. He will be remembered as a scientist, a colleague and a friend.

J. Braunstein

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### NUCLEAR MAGNETIC RELAXATION IN MOLTEN

### In-InI, MIXTURES

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### ABSTRACT

Nuclear magnetic relaxation data are presented for molten  $\ln_{1-x}I_x$  mixtures in the range  $0.50 \leq x \leq 0.75$ . The results include spin-lattice relaxation times  $(T_1)$  and spin-spin relaxation times  $(T_2)$  of  $^{115}$ In and, for  $x \simeq 0.50$ , of  $^{127}$ I. The observed relaxation behavior is attributed to two competing processes: electric quadrupolar relaxation which decreases with temperature and increases with x, and magnetic relaxation due to thermal fluctuations to the magnetic valence state  $\ln^{2+}$ . The fluctuations result from an electron hop from  $\ln^+$  to a neighboring  $\ln^{3+}$ . The magnetic valence fluctuation the most stable when  $x \simeq 0.67$  ( $\ln I_2$ ). Measurements in the range 0 < x < 0.50 yielded two-line spectra characteristic of liquid-liquid phase separation up to the maximum temperatures studied (>1000°C).

### I. INTRODUCTION

The decade from the middle 1950's to the middle 1960's was a period of intense effort in the study of solutions of liquid metals with their molten salts. Bredig's comprehensive and insightful review article (1964) summarized much of the work of this period and has become a basic reference in the field.<sup>1</sup> The next decade saw a gradual decline of research activity on these solutions, but renewed interest has developed very recently.<sup>2</sup> Current interest in molten metal-salt solutions has arisen within the context of study of electronic transport and the metal-nonmetal transition in structurally disordered materials. From this point of view, the metal-salt solutions are important because of their striking metal-nonmetal transformations as the composition is varied and because electronic localization can occur in particularly simple forms such as the metal ion of low oxidation state ("subhalide" formation).

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The need to understand the microscopic details of electronic structure and dynamics motivates application of truly microscopic experimental probes. Thus, nuclear magnetic resonance (NMR) data are particularly useful since they can reveal static and dynamic properties of the electronic states and, in addition, often contain useful information concerning the dynamic liquid structure such as molecule or complex ion formation, dissociation, diffusion, Nuclear magnetic relaxation studies employing transetc. ient NMR techniques are especially promising since the nuclear spin relaxation rates are directly influenced by the time-dependent local environment. This paper is concerned with one such study, a transient NMR investigation of liquid In-InI3 mixtures. A more extensive description of this work has been published elsewhere.<sup>3</sup>

### II. NUCLEAR MAGNETIC RELAXATION

Transient NMR measurements of nuclear relaxation rates are performed by first disturbing the nuclear spin system with a short pulse of radio frequency power at the nuclear Larmor frequency  $\omega_0$  and then following the magnetization as it recovers to its equilibrium value. In liquids the nuclear magnetization component M<sub>2</sub> along the direction of the applied magnetic field recovers to the equilibrium value M<sub>2</sub><sup>O</sup> according to

$$M_{z}(t) - M_{z}^{o} = [M_{z}(0) - M_{z}^{o}]e^{-t/T_{1}}$$
 (1)

where  $M_Z(0)$  is the initial magnetization following the disturbing pulse and  $T_1$  is the "spin-lattice" relaxation time. Similarly, following establishment of a non-vanishing transverse component  $M_X(0)$  by, say, a rotation of the magnetization with a "90°-pulse", the component  $M_X$  decays to zero according to

$$M_{x}(t) = M_{x}(0)e^{-t/T_{2}}$$
 (2)

where T<sub>2</sub> is the transverse or "spin-spin" relaxation time.<sup>4</sup>

The real value of the measurement derives, of course, from the fact that the relaxation times are determined by properties of the fluctuating local environments of the nuclei. This relationship can be concisely expressed in terms of time-dependent correlation functions for the fluctuating interactions of the nuclei with local fields 5 produced by nearby electric charges and magnetic moments. The fields affecting the nuclei are expressed by the Hamiltonian operator for the spin system in the form

$$= \mathcal{H}_{o} + \mathcal{H}'(t) \tag{3}$$

where  $\mathcal{H}_{o}$  is the interaction energy of the spins with the applied static magnetic field and  $\mathcal{H}'(t)$  is the fluctuating interaction.

If the interaction takes the form of a fluctuating local magnetic field, we can define correlation functions  $G^{1}(t)$  and  $G^{0}(t)$  for interactions involving, respectively, the transverse and longitudinal spin components:

$$G^{1}(t) = \overline{\mathcal{H}'_{+}(t)} \mathcal{H}'_{-}(0)$$
(4a)

$$G^{0}(t) = \overline{\mathcal{H}'_{z}(t)} \mathcal{H}'_{z}(0).$$
(4b)

Then the relaxation rates (inverse relaxation times) are

$$1/T_1 = 2J^1(\omega_0)$$
 (5a)

$$1/T_2 = J^1(\omega_0) + \frac{1}{2}J^0(0)$$
 (5b)

where  $J^{0}(\omega)$  and  $J^{1}(\omega)$  are spectral density functions (Fourier transforms) of the correlation functions:

$$J^{i}(\omega) = \int_{-\infty}^{\infty} dt e^{-i\omega t} G^{i}(t).$$
 (6)

Another example which is of central importance for molten salts is the case in which  $\mathcal{H}'(t)$  is the timedependent electric quadrupolar interaction between the nuclear electric quadrupole moment and the fluctuating local electric field gradient (e.f.g.). Application of a similar formalism leads to an explicit expression for the relaxation rates:<sup>6</sup>

$$(1/T_1)_Q = (1/T_2)_Q = \frac{3}{40} \frac{2I+3}{I^2(2I-1)} \omega_Q^2 \tau_c$$
 (7)

3

where I is the nuclear spin,  $\omega_Q$  is a frequency describing the strength of the quadrupole interaction, and  $\tau_C$  is a correlation time characterizing the rate of fluctuation of the local structural arrangement of the liquid.

If the liquid is highly associated so that the resonant nucleus is located in a molecule or complex ion, the coupling frequency is related to the asymmetry parameter  $\sigma$  and principal component q of the molecular electric field gradient:

$$ω_Q = (1+\sigma^2/3) (e^2 qQ/h)$$
 (8)

where Q is the nuclear quadrupole moment. The correlation time can be approximated by an expression analogous to the Debye relaxation time for a spherical molecule of radius  $r_0$ :

$$\tau_{\rm c} = \frac{4\pi r_{\rm o}^3}{3} \frac{\eta}{k\rm T}$$
(9)

### where n is the viscosity.

For a dissociated liquid, Eq. 7 is only a rough approximation in which  $\omega_Q^2$  is determined by the mean square local e.f.g. value and  $\tau_C$  is related to the complicated diffusional and vibrational modes of ionic motion. The value of  $\tau_C$  in a dissociated liquid should be on the order of 1 psec whereas the slower diffusion and rotation of polyatomic structures leads to  $\tau_C$  values on the order of 10-100 psec. Thus while the e.f.g. may not be strongly affected by the degree of association, longer values of  $\tau_C$  lead to significant enhancement of the quadrupolar relaxation rates in associated molten salts.

The degree of dissociation should also influence the temperature dependence of the quadrupolar relaxation rate. For rotating molecules or polyatomic ions, Eq. 9 predicts that the rates should decrease rapidly with temperature due to the decreasing viscosity. If an exponential (Arrhenius) representation of the temperature dependence of the rate is employed, the variation of  $\eta$  in typical associated salts leads to activation enthalpies of several kilocalories per mole.<sup>8</sup> The temperature dependence is much weaker where polyatomic species are absent. For NaCl, for example,  $1/T_1$  is independent of temperature between the melting point (801°C) and 1050°C.<sup>9</sup>

### III. EXPERIMENTAL RESULTS AND DISCUSSION

The phase diagram of the In-InI<sub>3</sub> system contains three well-defined solid compounds: InI<sub>3</sub>, InI<sub>2</sub> and InI. A region of liquid-liquid immiscibility separates pure In from molten InI. The behavior of the electrical conductivity across the system is illustrated in Fig. 1.<sup>10</sup> The conductivity of liquid InI is more than three orders of magnitude smaller than that of liquid In and is roughly comparable with the conductivity of molten KI and CSI.<sup>8</sup> ISince the ionic radii of In<sup>+</sup> and K<sup>+</sup> are about the same, this result suggests that InI melts to form a dissociated liquid of In<sup>+</sup> and I<sup>-</sup> ions. With increasing I concentrations, the conductivity drops and structural studies of molten InI<sub>3</sub> indicate the presence of In2I<sub>6</sub> molecular dimers.<sup>12</sup>, I<sup>3</sup> However, the conductivity of liquid InI<sub>3</sub> is still relatively high so that there is probably partial dissociation to form In<sup>3+</sup> and I<sup>-</sup>. In addition, in the related system GaI - GaI<sub>3</sub> there is evidence for the complex ion (GaI<sub>4</sub>)<sup>-</sup> at intermediate compositions<sup>14</sup> so that we might expect the presence of (InI<sub>4</sub>)<sup>-</sup> in the present system. Infrared spectroscopy of crystalline InI<sub>2</sub> shows that this complex is present in the solid state.<sup>15</sup>

Nuclear relaxation measurements were made for  $^{115}$ In and, where possible,  $^{127}$ I close to the composition of the three stoichiometric crystalline compounds: InI (two samples), InI<sub>2</sub> and InI<sub>3</sub>. The samples were prepared by melting weighed amounts of In metal (99.9999%) and InI<sub>3</sub> (Alfa-Ventron "ultra-pure") in evacuated quartz ampoules. In most cases the melting was carried out in situ in the high temperature NMR probe. Sample temperatures were determined by a Pt vs. Pt-10% Rh thermocouple located in a re-entrant well protruding into the sample cell.

In addition to the nearly-stoichiometric single-phase melts, three samples were studied whose compositions lay in the region of the liquid-liquid phase separation. These samples invariably exhibited two <sup>115</sup>In resonance lines close to the positions found for pure liquid In and single-phase InI, respectively. This doublet spectrum persisted to temperatures above 1000°C indicating that the critical temperature for phase separation is well above this temperature and that at lower temperatures, therefore, there is no continuous metal-nonmetal transition in this system. Data obtained in the two-phase region are discussed in detail elsewhere.<sup>3</sup>

Nuclear relaxation data for single-phase samples InI,

 $InI_2$ , and  $InI_3$  are presented in Figs. 2, 3, and 4, respectively. The results are quite different for each composition but some systematic behavior can be observed. First, features expected for nuclear quadrupolar relaxation (Eq. 7) are observed for  $^{115}$ In in InI<sub>3</sub> and InI<sub>2</sub> at sufficiently low temperatures and for  $^{127}$ I in InI. These features are the equal values of  $T_1$  and  $T_2$ , rates which decrease with increasing temperature, and rates which are independent of the NMR frequency employed. The  $127_{I}$ resonance could not be detected in InI2 and InI3 indicating that the rates in these compositions are greater than the maximum limit of about 1  $\times$  106 s<sup>-1</sup> imposed by the time resolution of the pulsed NMR spectrometer. The quadrupolar relaxation in InI<sub>3</sub> is roughly an order of magnitude stronger than in InI<sub>2</sub>. We attribute this difference, as well as the apparent tendency of the 127I rates to increase with increasing I content, to the general trend toward a more associated liquid as the composition varies from InI to InI3. An estimate of the magnitude of the relaxation rate for molecular In216 was made using Eqs. 7-9 and quadrupole coupling parameters for crystalline InI3.16 The result was about an order of magnitude larger than the observed rate, thus supporting the evidence given by the electrical conductivity for partial dissociation of InI3. The prediction of Eqs. 7 and 9 for the temperature dependence of the relaxation rate was evaluated from the experimental viscosity data<sup>8</sup> and compared with experiment in Fig. 4. The predicted variation is stronger than that observed but this can be explained as the effect of a second relaxation process which increases with temperature. It can also be expected, of course, that partial dissociation should weaken the temperature dependence relative to the prediction of the simple molecular model.

The second and most striking general feature of the relaxation rate data is the unexpected presence of an additional 115In relaxation process which increases with temperature. As shown in Figs. 2-4 the temperature dependence can be represented as thermally activated. The process is so powerful that it dominates the quadrupolar relaxation in InI at all temperatures and in InI<sub>2</sub> and InI<sub>3</sub> at the higher temperatures investigated. In contrast to the quadrupolar process, the rates for this additional process depend on the NMR frequency (magnetic field), and T<sub>1</sub> and T<sub>2</sub> are not equal. At least for InI for which both 115In and 127I rates can be measured, the process is specific to 115In (Fig. 2).

These features of the additional <sup>115</sup>In relaxation process are, in most respects, similar to those associated with nuclear relaxation via coupling to a localized unpaired electron spin.<sup>17</sup>,<sup>18</sup> The inequality of  $T_1$  and  $T_2$  and the appearance of frequency-dependent rates occur when nuclei are relaxed by interaction with electron spins of Larmor frequency  $\omega_s$  such that  $\omega_s \tau > 1$  where  $\tau$  is the correlation time for the electron-nucleus interaction. The correlation time might be either the duration of association of the nucleus and the localized spin or the inverse rate of fluctuation of the spin, whichever is shorter.

We propose that the localized unpaired electrons responsible for the additional relaxation in  $In-InI_3$  result from magnetic valence fluctuations of the form

$$\ln^{3+} + \ln^{+} = 2\ln^{2+}$$
. (10)

This reaction describes a single electron hop from an  $In^+$ ion to a neighboring  $In^{3+}$  ion leaving a pair of strongly magnetic  $In^{2+}$  ions in the  $5s^1$  configuration. For In, a relatively heavy metal, a single 5s electron produces a magnetic hyperfine field at the nucleus on the order of  $10^7 \text{ G.} 1^9$  The field on a neighboring I<sup>-</sup> ion is of course, much weaker. Thus the relaxation process associated with the fluctuation is highly preferential to the 115In nuclei.

Now, except at the precise stoichiometries InI and InI3, we can expect solutions in the range InI-InI3 to contain both In<sup>+</sup> and In<sup>3+</sup> with fractional concentrations  $c(In^+)$  and  $c(In^{3+})$ , respectively. If a given  $In^{3+}$  ion in the matrix of I<sup>-</sup> anions is neighbor to an average number z of In<sup>+</sup> ions, and if  $\Delta G_2$  is the free energy change associated with the fluctuation, then the instantaneous probability that an <sup>115</sup>In nucleus will be in an In<sup>2+</sup> ion is

$$P = z c (In^{+}) c (In^{3+}) exp[-\Delta G_{2}/2RT].$$
(11)

The relaxation rates should be proportional to P. The concentration factors, especially  $c(\ln^{3+})$ , may be temperature dependent due to the dissociation of units such as  $\ln_2 I_6$  and  $(\ln I_4)^-$ . Thus the probability can be expected to vary with temperature according to

$$P = p_{exp} [-\Delta H/RT]$$
(12)

where  $\Delta H$  contains a term  $\Delta H_2$  from Eq. 11 and a term  $\Delta H_3$ , the enthalpy of reaction for whatever reaction controls

the concentration  $c(In^{3+})$ . The prefactor  $p_0$  depends only on concentration and should be maximum near the composition of InI<sub>2</sub> and zero for InI and InI<sub>3</sub>.

The powerful 5s-electron hyperfine interaction is comparable with the electron Zeeman energy. This requires modification of the standard theory.<sup>17,18</sup> for nuclear relaxation by paramagnetic centers in liquids. The generalization to include the effect of the nucleus on the energy levels of the electron spin is straightforward but rather detailed.<sup>3</sup> For the purposes of the present paper, it is sufficient to express the results in the following schematic forms of Eqs. 5a and 5b:

$$\frac{1}{(T_{1})}_{VF} = \frac{PA^{2}}{2(2I+1)} \sum_{i,j} a_{ij} \frac{\tau}{1 + \omega_{ij}^{2}\tau^{2}}$$
(13a)

$$\left(\frac{1}{T_{2}}\right)_{VF} = \frac{\gamma_{2}(\frac{1}{T_{1}})_{VF}}{+ \frac{PA^{2}}{4(2I+1)}} \sum_{i,j} b_{ij} \frac{\tau}{1 + \omega_{ij}^{2}\tau^{2}}$$
(13b)

where A is the hyperfine coupling energy,  $\omega_{ij}$  are frequencies separating eigenstates of the combined electronnucleus system, and the coefficients  $a_{ij}$  and  $b_{ij}$  are determined by the matrix elements separating the eigenstates labeled i and j. Both the coefficients and frequencies depend on the applied field. The field dependence of the rates can thus differ depending on  $\tau$ . The value of  $\tau$  also affects the ratio  $(1/T_2)/(1/T_1)$  which is, in general, greater than one although it approaches one when  $\omega_{ij}\tau << 1$ for all  $\omega_{ij}$ .

The model of magnetic valence fluctuations summarized by Eqs. 13a and 13b accounts for all the major features of the additional relaxation process observed for 115In. The selectivity for 115In and the activated temperature dependence have already been discussed. The frequency dependence and the ratio  $(1/T_2)/(1/T_1)$  can be fitted to Eqs. (13a) and (13b) to obtain parameters A and  $\tau$  for each sample except InI<sub>3</sub> for which the rapid relaxation rates prohibited measurement of  $T_1$ . The hyperfine coupling values  $A = 8 \pm 1$  GHz and 5.0  $\pm$  0.5 GHz for InI and InI<sub>2</sub>, respectively, are of the same order as the value A = 9.362 GHz reported<sup>19</sup> for In<sup>2+</sup> in crystalline ZnS. The correlation times  $\tau = 14 \pm 3$  and  $7 \pm 1$  for InI-1 and InI-2, respectively, increase markedly to  $\tau = 200 \pm 50$  ps for InI<sub>2</sub>. In each case these correlation times are independent of temperature. Since this time represents a lower limit on the lifetime of the  $\rm In^{2+}$  state, this result indirectly suggests a trend toward greater stability of  $\rm In^{2+}$  in the more I-rich medium.

Once having determined A and  $\tau$ , values of  $p_0$  and  $\Delta H$ were obtained from the magnitude and temperature dependence of the relaxation rates using Eqs. (12) and (13).\* The variation of the probability prefactor  $p_0$  with composition shown in Fig. 5 demonstrates that, as expected,  $p_0$  is much higher for InI<sub>2</sub> than for either of the other two compositions studied. This figure also provides an explanation for the fact that the valence fluctuation process is observed at all in our samples of InI and InI<sub>3</sub>. Strictly speaking,  $c(In^{3+})$  and  $c(In^{+})$  should vanish, respectively, at these compositions. It can be seen that the finite values of  $p_0$  can be explained by very small ( $^{\wedge}_{<}$  1%) deviation from stoichiometry in these samples.

The variation  $\Delta H$  is shown in Fig. 6. This quantity is smallest for InI (about 7 kcal/mole), greatest for InI<sub>2</sub> (14 kcal/mole) and decreases again for InI<sub>3</sub> (9 kcal/mole). We attribute the larger values for the latter two cases to contributions from the temperature dependence of c(In<sup>3+</sup>) due to dissociating species. If we assume that InI is fully dissociated on melting, on the other hand, then the value of  $\Delta H$  should be approximately  $\frac{1}{2}\Delta H_{\frac{1}{2}} \simeq 2\Delta H \simeq 14$  kcal/mole (~0.6 eV/atom).

### IV. SUMMARY

Nuclear relaxation in single-phase In-InI<sub>3</sub> solutions in the range InI - InI<sub>3</sub> is governed by two processes: (i) electric quadrupolar relaxation affecting both <sup>115</sup>In and <sup>127</sup>I and (ii) relaxation by magnetic valence fluctuations which is effective only for <sup>115</sup>In. The quadrupolar relaxation indicates a general tendency toward formation of associated structures as the I-content increases. The existence of the magnetic valence fluctuations proceeds in two steps: a single-electron transfer from In<sup>+</sup> to In<sup>3+</sup> to form a pair of In<sup>2+</sup> ions followed by a second transfer at a time <u>at least</u>  $\tau$  later. If the second transfer proceeds in the same direction as the first, the result is an

For InI<sub>3</sub> it was assumed that  $\tau$  and A are the same as for InI<sub>2</sub>. The value of  $\Delta H$  was determined from the temperature dependence of  $1/T_2$  after correcting for the effects of quadrupole relaxation using Eqs. 7 and 9. The decomposition is shown in Fig. 4.

effective interchange of the In<sup>+</sup> and In<sup>3+</sup> ions. The effect on electronic transport is the same as the <u>simultaneous</u> two electron transfer proposed for the conduction mechanism in Bi-BiI<sub>3</sub> solutions by Raleigh.<sup>20</sup> In the case of In-InI<sub>3</sub> solutions, the electronic conductivity estimated from experimental values of  $\tau$  and P is overwhelmed by the ionic conductivity, e.g.  $\kappa_{elec} \sim 4 \times 10^{-8} ~ (\Omega cm)^{-1}$  for InI<sub>2</sub> at 500°C. Thus the nuclear relaxation measurements provide a means of selectively measuring the electronic conductivity and, further, reveal microscopic details of the transport process.

### ACKNOWLEDGEMENT

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Figure 1. Logarithm of the electrical conductivity vs. composition for molten  $In_{1-x}I_x$  mixtures at 365°C (Ref. 10). Shaded region denotes range of liquid-liquid phase separation.



Figure 2. Semi-log plot of nuclear relaxation rates vs. 1/T for  $115_{In}$ and  $127_{I}$  in two molten samples of nominal composition InI. Open points:  $1/T_1$ ; closed points:  $1/T_2$ . NMR frequencies are 16.0 MHz for  $127_{I}$  and for  $115_{In}$ , 16.0 MHz ( $\blacksquare$ ,  $\square$ ), 9.5 MHz ( $\triangle$ ,  $\blacktriangle$ ), and 5.5 MHz ( $\blacklozenge$ ).



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Figure 3. Semi-log plot of nuclear relaxation rates vs. 1/T for 115In in molten  $InI_2$ . Designation of s bols is the same as in Designation of sym-Figure 2.



Figure 5. Probability prefactor p (Eq. 12) vs. com- 12) vs. composition in range position in range  $InI - InI_3$   $InI - InI_3$ . (0.50<×<0.75).



Figure 4. Semi-log plot of nuclear relaxation rates  $1/T_2$  for 115In in molten InI3. Designation of NMR frequencies is the same as in Figures 2 and 3. Dotdash line: temperature dependence of quadrupolar relaxation (Eqs. 7 and 9) normalized to data at 250°C. Additional relaxation after subtraction of quadrupolar relaxation from total rate is also shown (x).



Figure 6. Enthalpy  $\Delta H$  (Eq.

CORRELATIONS BETWEEN <sup>L</sup>HNMR SPECTROSCOPY AND TRANSPORT PROPERTIES IN MOLTEN ASYMMETRIC PYRIDINIUM HALIDES

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### Abstract

The Equivalent Conductance, viscosity and HNMR spectra of 2 and 3 methylpyridinium chloride and 2 and 3 methylpyridinium bromide were measured as a function of temperature. These asymmetric salts were found to be considerably lower melting, more viscose and less mobile than their respective symmetric isomers. However, they exhibited the same chemical shift reversal of the nitrogen proton that was observed in the molten symmetrical systems. From these data details of the dynamics of motion in the melts are suggested.

### Introduction

Molten pyridinium salts are of considerable practical importance and theoretical interest. In an earlier study we correlated transport properties with structure and HNMR spectra of symmetrical pyridinium halides (1,2). Here we extend this investigation to include asymmetrical salts and it will be shown that pyridinium salts naturally divide into two classes based upon their transport properties; the symmetrical salts being far more mobile than the asymmetrical salts.

The equivalent conductance,  $\Lambda$ , viscosity,  $\gamma$ , and <sup>1</sup>HNMR spectra of molten 2-methylpyridinium chloride (2mepyr/HCl) and bromide (2-mepyr/HBr) as well as molten 3-methylpyridinium chloride (3-mepyr/HCl) and bromide (3-mepyr/HBr) were measured as a function of temperature over an approximately 50 °C temperature range. These salts together with their melting points are shown in Fig.1.

From the substantial increase in viscosity and decrease in conductivity accompanying the changing of a methyl group from the four position to either the two or three position on the ring, inferences about the dynamics of motion in these melts can be drawn. In addition, the contribution of the labile nitrogen proton to the conductivity can be assessed.

### Experimental Background

The density, conductivity and <sup>1</sup>HNMR measurements as well as the general procedures for handling the compounds were similar to those described by Newman and Banjoko (1). The synthesis of the four salts can be summarized by the equation



(1)

The viscosity was measured as a function of temperature using a Cannon-Fenske Viscometer. This viscometer was easy to clean, precise enough for our purposes and much more durable than the Ostwald viscometer used in earlier studies.

Dry solid salt was introduced into a large reservoir attached to one arm of the viscometer which was then immersed in the constant temperature bath. The salt was then melted and allowed to fill the viscometer. Viscosity readings were taken at  $5^{\circ}$  intervals after letting the bath equilibrate for twenty minutes at each temperature. Three series of measurements were made with each salt.

### Results and Discussion

The best least squares fit of the equivalent conductance as a function of temperature for each salt are listed in Table I and the densities as a function of temperature are listed in Table II.

Table I. Equivalent Conductance as a function of temperature for asymmetrical pyridinium halides.

 $\ln \Lambda = a + b T^{-1}$ 

Salt	<u>a</u>	b	temperature range (K)
2-mepyr/HCl 2-mepyr/HBr	10.21 12.85	-3526 -4514	363 - 408 350 - 395
3-mepyr/HCl	10.37	-3508	369 - 419
2-mepyr/nor	10.21	-3449	5/0 <del>-</del> 415

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Table II. Density as a function of temperature

	$\rho$ (g/cm <sup>3</sup> ) =	a + bT(K)			
Salt	ι <u>a</u>	<u>-(b x 10<sup>3</sup>)</u>	temperature	range	<u>(K)</u>
2 mepyr/HCl 2 mepyr/HBr 3 mepyr/HCl 3 mepyr/HBr	1.334 1.711 1.329 1.690	0.5657 0.7279 0.5525 0.6890	363 - 408 350 - 395 374 - 419 370 - 415		

Figure 2 shows a graph of  $\ln \eta$  vs T<sup>-1</sup> for the four melts and it should be noted that there is a slight, but distinct curvature in the plots which is reminiscent of the behavior of partially associated liquids like molten silicates. Figure 3 shows the HNMR spectrum of 2-mepyr/HCl at 100°C relative to an external standard of DMSO and Fig. 4 shows the spectrum of 3-mepyr/HCl at the same temperature relative to the same external standard. There was no change in chemical shift or peak narrowing greater than 0.02 ppm which is at the limit of experimental error. Comparing our proton chemical shifts in the 2-mepyr/HCl melt with the chemical shifts in the same melt reported by Angell and Shuppert (3) we agree within experimental error on the location of the  $\alpha$ ,  $\beta$ ,  $\gamma$  and methyl peaks, but differ by 1 ppm on the N-H chemical shift, theirs being further down field than ours. One possible reason for this discrepancy is that a trace of water may still be present in our melts, but not in theirs. This water molecule would tend to lie on or at the N-H proton and shield it from the magnetic field. On the other hand, they used an internal standard of  $(NH_3)_{\downarrow}NC1$  which both exchanges with the N-H and supplies Cl fons. These factors could tend to deshield the  $N-H^+$  and cause it to resonate in the more acidic region of the spectrum. The There does not seem to be any other melt spectra in the literature to compare our data with. Our melting point of 89°C for the 2-methyl salt is exactly the same as that reported by Angell, Hodge and Cheeseman (4) and our specific conductances also agree within experimental error with theirs. Table III lists the chemical shifts for the four asymmetric pyridinium salts corrected to TMS.

Table III.	ð in	ppm vs Tl	1S		
Salt	<u>-СН</u> 3	X	ß	8	> <u>N-H</u>
2 mepyr/HCl 2 mepyr/HBr 3 mepyr/HCl 3 mepyr/HBr	2.92 3.13 2.59 2.78	8.93 9.01 9.04 9.21	8.08 8.26 8.18 8.40	8.71 8.93 8.65 8.84	16.12 15.78 16.37 15.80

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The  $\delta$ s in Table III exhibit the same  $N-H^+$  shift reversal shown by the symmetric melts (1). The  $N-H^+$  is more deshielded in the chlorides than in the bromides, but the ring protons and CH<sub>2</sub> group are further downfield in the bromide melts than in the chloride melts. We again think this shift reversal is due to the formation of complexes between the pyridinium ion and the halide ion in the melts. The  $N-H^+$  forms a stronger bond to the Cl than it does to the Br and this overcomes the deshielding due to crowding that affects the ring protons and methyl groups.

In Table IV we list the equivalent conductance, viscosity, and energies of activation for each salt in a standard state of 1:1 times the melting point in degrees Kelvin. The Eq is obtained from the best least squares fit of the ln $\gamma$  vs T curves and is therefore only an approximation. There are several striking features of these data. The  $\land$  for 3-mepyr/HBr is slightly greater

Table IV. Transport properties at 1:1  $T_M$  (K)

Salt		<b>∧</b> (cm <sup>2</sup> <b>S</b> <sup>-1</sup> eq <sup>-</sup>	<sup>(c p.)</sup>	E <b>7</b> (kj(mole)	$E_{\Lambda}(kj/mole)$
2 py:	r/HCl	3.88	7.06	36.2	29.3
2 py:	r/HBr	3.19	10.87	44.7	37.5
3 py:	r/HCl	5.63	6.33	34.2	29.2
3 py:	r/HBr	5.89	8.26	32.9	28.6

than the  $\blacktriangle$  for 3-mepyr/HCl at 1.1  $T_{\rm M}$  and as far as we know this is the only molten salt system in which a bromide is more mobile, albeit slightly, than the corresponding chloride. An explanation for this peculiar behavior will be suggested shortly. A second interesting observation is that the asymmetric salts are considerably poorer conductors and are considerably more viscose than their symmetrical isomers. A third observation is that the 3-methyl salts are better conductors than the corresponding 2-methyl salts.

Assuming the same sort of complex is forming in the asymmetric salts as in the symmetric salts (1), the most reasonable explanation for the higher conductivity of the 3-methyl salt than the corresponding 2-methyl salt is that the labile nitrogen proton is contributing to the conducivity (4), but this contribution is a larger fraction of the 3-methyl salt's conductivity than it is of the 2-methyl salt's conductivity. This happens because the 2-methylpyridine is more basic than the 3-methylpyridine (5) and therefore attracts the labile proton more strongly and reduces its concentration. A second reason is that

the methyl group on the two position of the ring partially, if not totally, blocks the N-H and prevents it from readily transferring to the halide ion. Since the densities of the 2 and 3 mepyr/HCls are virtually identical (Table II), as are the densities of the 2 and 3 mepyr/HBrs, and the molecular dimensions are so similar, a difference in liquid free volume by itself would be unable to account for the substantial differences in conductance between the two pairs of salts. To a ∧s of the rough approximation then, the difference between the 2-mepyr/HCl and 3-mepyr/HCl or the 2-mepyr/HBr and the 3-mepyr/ HBr is equal to the contribution of the proton to the conduct-ance. At 1.1  $T_M \wedge_{H^+}$  is 1.75 ( $\Re$  eq)<sup>-</sup> cm<sup>-</sup> in the chloride<sub>2</sub> system while in the bromide system  $\wedge_{H^+}$  is 2.70 ( $\Re$  eq)<sup>-</sup> cm<sup>2</sup>. Whether or not an actual Grotthuss mechanism, in which there is a transfer of charge or virtual movement without an actual proton diffusion, as is thought to be present in, say, aqueous HCl solutions occurs, or a hopping mechanism in which a given proton is "hopping" from site to site and during one of its excursions reaches an electrode, occurs cannot be ascertained with confidence at this time. Nevertheless, some protonic contribution to the conductance must be taking place.

This conjecture is further supported by the fact that the 3-mepyr/HBr is a slightly better conductor than the 3-mepyr/HCl at l.l  $T_M$ . Hydrogen bonding is considerably stronger in the chloride melt than in the bromide melt which reduces the contribution of both H and Cl to the conductivity in the chloride melt relative to the contribution of Н' and Br to the bromide melt's conductivity. In addition, the greater size of the Br increases the stringency of the packing requirements and allows the melt fewer degrees of freedom so that if a concerted Grotthusslike mechanism consisting of the partial "in plane" rotation of the pyridinium ring accompanied by the passing of its proton to a Br which in turn collides with another proton, etc. were to occur, it would be favored in the Br melt. This possible mechanism contributing to the high bromide conductivity is illustrated in Fig. 5 and is consistant with the suggestion that the dominent associated species is the (3-mepyr-H...X.. H-pyr me-3)  $\top$  ion (1,3). Two predictions based on this mechanism are that the viscosity of the 3-mepyr/HBr melt is also greater than the viscosity of the 3-mepyr/HCl melt, and the  $E_{\Lambda}$  for 3-mepyr/HCl is greater than  $E_{\Lambda}$  for 3-mepyr/HBr. Both of these predicitions are borne out if the salts are compared in the same standard state of 1.1 T (Table IV). The bromide melt has the greater viscosity because the packing is tighter and the liquid layers cannot pass over eachother easily. On the other hand, the chloride melt has the greater  $E_{A}$  because part of this energy must go toward the breaking of stronger hydrogen bonds.

Finally, the extraordinarily large difference in conductance and viscosity between the symmetric and asymmetric salts which results from very slight differences in molecular size and melt density probably arises because there is very little free volume and molecular motion must be highly correlated. In all likelihood there are at least three contributions to the mobility, besides the protonic contribution, and each one requires an energy of activation. The first, and most obvious mode of motion is one salt layer passing by another "in plane", as it were. The second mode is an inplane rotation of the pyridinium ion and the third is an out of plane rotation of the pyridinium ion and the Both the in and out of plane rotations share the primary responsibility for the large difference in transport properties between the symmetrical and asymmetrical melts. It is during these rotations, coupled with the translational motion that the asymmetric pyridinium ions interfere with eachother and also block the passage of the halide ions.

### Conclusions

By changing the structure of the pyridinium melts in a systematic way and correlating these changes with transport properties and HNMR spectra, inferences about the dynamics of mass transfer in these melts may be made. As an example we are able to conclude there are at least four distinct contributions to the conductance. These are an in and out of plane rotation, an inplane translation of one layer past another and a hopping or Grotthusslike movement of the acidic proton.

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Figure 4.  $^{1}$ HNMR spectrum of 3-mepyr/HCl at 100 $^{\circ}$ C vs DMSO



Figure 5. Possible mechanism for proton transfer in pyridinium halide melts

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### CORRELATIONS BETWEEN EQUIVALENT CONDUCTANCE AND <sup>1</sup>HNMR SPEC-TROSCOPY IN MOLTEN 4-METHYLPYRIDINIUM HALIDES

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### Abstract

The equivalent conductance and <sup>1</sup>HNMR spectra of several symmetrical molten pyridinium halides were measured as a function of temperature. Correlations between change in chemical shift and changes in conductance allowed inferences about the melt's structure to be drawn. From these inferences we conclude that complex ions exist in the 4-methyl salts. Approximate values of the association constants for these complexes were obtained.

### Introduction

Molten pyridinium salts are of considerable importance as the electrolyte in batteries and as the solvent for synthetic and mechanistic studies of organic and inorganic compounds. They are also potentially useful as the heat storage media in solar heating and air conditioning systems. In addition to these practical applications, pyridinium salts are of considerable interest to people seeking a basic understanding of the molten state because the relatively low melting points of these salts make them accessible to NMR techniques as well as conventional transport measurements. The structure of the pyridinium melts can be changed systematically by substituting different groups on the pyridine ring, adding to the basic nitrogen and varying the anion. Correlations can be found between changes in "HNMR spectra, changes in molecular structure and the changes. The dynamics of molecular motion in these melts can then be understood in terms of these correlations.

In an earlier study (1) we found the equivalent conductance,  $\Lambda$ , of 4-methylpyridinium bromide to be about 8% lower than the conductance of N-methylpyridinium bromide over approximately the same temperature range. We suggested this surprising result is due to complex formation in the 4-methyl salt which reduces the number of charge carriers per unit volume relative to the N-methyl salt. The HNMR spectrum of 4-methylpyridinium bromide showed no line width broadening greater than 0.02 ppm over the nearly  $50^{\circ}$  temperature range indicating the barrier to complex formation was less than about 40 kj/mole. There was however, a concommittant change in chemical shift as the anion is changed from Br to Cl that correlates well with the conductivity data and this will be discussed later. Herein we extend the investigation to include other symmetrical pyridinium salts and assess the magnitude of the complex ion's association constant in 4-methyl bromide and in 4-methyl chloride. 4-Methylpyridinium chloride and N-methylpyridinium chloride are shown in Fig. 1.

### Experimental Details

All transfer operations were carried out in a drybox in which  $N_2$  was circulated over molecular sieves to remove water. A fiber optic light pipe was used to conduct light into the Dow Corning 710 oil which served as the heat bath. The flexible light pipe greatly facilitated the density and viscosity readings. The bath temperature was held constant to  $\pm$  0.1°C.

### Preparation of the Salts

The salts were synthesized in essentially the same way as in our previous investigations using a technique described by Rozdhestvenski and Brode (2) and modified by Newman et. al. (3). The syntheses can be summarized by Eq.1



The purity of each salt was determined by C, H, and N analysis, halide analysis and melting point.

### Conductivity Measurements

The specific conductance,  $\chi$ , of each salt was measured as a function of temperature using an Industrial Instruments model RC-18 bridge at a frequency of 1000 Hz. The salts were contained in a Pyrex capillary cell as described by Newman et. al. (3). Cell constants ranged from 200 to 500 cm<sup>-1</sup>. The conductivity readings were taken at 5° intervals, and at least three sets of measurements of the conductivity of each salt were made. The time allowed for the system to equilibrate at each temperature was at least twenty minutes. The molten salt densities used to obtain  $\Lambda$ , from X were taken from a previous study (4).

## HNMR Spectroscopy

The <sup>1</sup>HNMR spectra of all four salts were obtained using a Varian CFT-20 NMR spectrometer equipped with a variable temperature proton probe. In order to negate any possible solvent effects, an external standard was used in these experiments. A 1 mm i.d., capillary tube containing the external reference was inserted into the standard 5 mm NMR tube, surrounded by salt, so that the longitudinal axes of both tubes were parallel. This minimized errors due to bulk magnetic susceptibility differences between the sample and standard. Dimethyl sulfoxide (CH<sub>3</sub>SO<sub>2</sub>CH<sub>3</sub>) or dimethyl sulfone (CH<sub>3</sub>SO<sub>2</sub>CH<sub>3</sub>) were used as standards depending upon the temperature range of the salt studied. The NMR machine maintained a constant temperature to within  $\pm 1^{\circ}$  during spectral measurements as determined by standardizing with ethylene glycol at each temperature reading.

### Results and Discussion

Figure 1 shows a plot of ln  $\wedge$  vs T<sup>-1</sup> for 4-methylpyr/HCl and N-methylpyr/Cl. It is obvious from this graph that the N-methyl salt is a better conductor than the 4-methyl salt and that the results first observed in the bromide melts are even more pronounced in the chloride melts. Again, because isomers are being compared and the N-methyl salts are actually slightly more dense than the corresponding 4-methyl salts the most reasonable explanation for the difference in  $\wedge$  is that there are fewer charge carriers per unit volume in the 4methyl salts than in the corresponding N-methyl salts.

Figure 2 shows the <sup>1</sup>HNMR spectrum of 4-methyl pyridinium iodide at  $172^{\circ}$ C relative to an external standard of CH<sub>3</sub>SO<sub>2</sub>CH<sub>3</sub>. There was no discernable peak narrowing or chemical shift<sup>2</sup> change as a function of temperature greater than 0.02 ppm in any of the melts so only one 4-methylpyridinium ion spectrum need be shown. The chemical shifts relative to CH<sub>3</sub>SO<sub>2</sub>CH<sub>3</sub> for the three 4-methyl pyridinium halides are listed in Table I.

TABLE I

Proton Chemical Shifts, S, of 4-Methylpyridinium Halides in ppm Relative to an External Standard of CH<sub>3</sub>SO<sub>2</sub>CH<sub>3</sub>.

Melt	<u> </u>	ß		<u>N-H</u> +	$\Delta$ (H- $\alpha$ )	<u>Δ(ζ-β</u> )
4-mepyr/HC1	6.25	5.28	-0.18	13.68	7.43	0.97
4-mepyr/HBr	6.42	5.44	0.03	12.66	6.24	0.98
4-mepyr/HI	6.62	5.67	0.19	11.66	5.04	0.95

These data show a striking "reversal" of  $\delta$  for the >N-H proton relative to the ring protons. That is, the  $\prec$ ,  $\beta$  and CH<sub>2</sub> protons are all deshielded in the order I > Br > Cl<sup>-</sup> as was the case for the N-methyl salts (1), but the > N-H proton is deshielded in the reverse order, i.e., Cl > Br > I<sup>-</sup>. The most plausible explanation for these results, when combined with the conductivity data, is that the packing or crowding of the ions in the melt is still important, but that a complex species must also be forming in the melts. The formation of this complex involves the nitrogenic proton and the halide ion and can be described by the equation.



A similar complex was thought to be present in pyridinium chloride, 2-methylpyridinium chloride and mixtures of pyridinium chloride with either ZnCl<sub>2</sub> or AlCl<sub>3</sub> by Angel and coworkers (5,6,7,). These authors sited as part of their evidence the existence of a crystalline compound corresponding AlCl<sub>4</sub> found in the  $\checkmark$  PyHCl.AlCl<sub>3</sub> phase diagram and its existence lends further credence to the complex described by Eq. 2. Assuming this to be the proper equation for complex formation, we obtain an estimate of the size of the complex ion's formation constant by means of the following agrument. If there was no complex formation in the 4-methyl melts, the equivalent conductance of a particular 4-methyl halide would be about the same as the equivalent conductance of the corresponding N-methyl isomer. In the N-methyl salt it is assumed there are relatively few, if any complexes. We therefore use the Arrhenius notion that  $\checkmark$ , the degree of dissociation is  $\Lambda/\Lambda_0$  and we take  $\Lambda_0$  to be the equivalent conductance of an N-methyl salt in a standard state of 1.1 times its melting point while  $\Lambda_0$  is the equivalent conductance of the corresponding 4-methyl halide at 1.1 times its melting point. The association constant for the complex in Eq. 2 is

$$K_{A} = \frac{1 - \alpha}{2 \alpha^{3} c^{2}}$$
(3)

where c is the concentration in moles/lit. The values for  $K_A, \mathcal{A}$ ,  $\bigwedge_{A} G$  and the appropriate  $\Lambda$  s and densities are summarized in Table II

### TABLE II

Salt	Λ 1	:1 T <sub>M</sub>	(K) X	(g/cm <sup>3</sup> )	K <sub>A</sub> Z	∆G (kj/mole)
N-mepyrCl	18.18	464		1.12		
4-mepyr/HCl	15.02	484	0.826	1.06	2.2x10 <sup>-3</sup>	24.5
N-mepyrBr	15.51	467		1.418		
4-mepyr/HBr	14.43	478	0.930	1.368	$7 \times 10^{-4}$	29

The K<sub>A</sub>s represent a small but significant complex ion contribution to the structure of the Br and Cl melts and in all likelihood will be present, albeit to a smaller extent, in the I melts as well since the 4-methylpyridinium iodide shows a similar chemical shift reversal to that found in the corresponding chloride and bromide melts. Our estimate of K<sub>A</sub> for the 4-methylpyridinium chloride complex should be compared with Angel and Shuppert's estimated value of K<sub>A</sub>.  $\sim 2 \times 10^{-10}$  for the formation of the similar pyridinium chloride complex (py-H..Cl..H-py)<sup>T</sup>.

### Conclusion

The chemical shift reversal of the >N-H relative to the ring protons found in bromide and chloride melts using an internal standard is found to also exist in the iodide melts and is reconfirmed in the Cl and Br melts using a more reliable external standard. Its presence in these melts suggests that in the molten state hydrogen bonding probably occurs with I as well as Br and Cl. This hydrogen bonding causes a reduction in  $\Lambda$  due to complex ion formation.

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Figure 1. Ln  $\wedge$  vs T<sup>-1</sup>



Figure 2. The <sup>1</sup>HNMR spectrum of 4-methylpyridinium iodide at 172°C.

# THE ELECTROREACTIVITY OF TRANSITION METAL IONS IN MOLTEN SALTS

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# ABSTRACT

Electrochemical investigations of transition metal ions in molten inorganic salts are generally accompanied by two main classes of chemical complications.

The first class results from solvent-solute interactions that is, the effect of solvent anion/cation composition upon the volatilisation and the disproportionation of solutes, and cluster formation. The second class includes those chemical reactions coupled to electron transfer steps of which there are many types. However, two principal types may be distinguished a) kinetic and b) catalytic.

The effects of these chemical complications are discussed in general terms with respect to the transition metals and highlighted by some of our observations on tungsten (VI) and (V) chloride species in LiCl-KCl at  $400^{\circ}$ C.

# GENERAL ASPECTS

Many investigations of the electrochemical behaviour of transition metal ions in molten inorganic salts have had, as their long term aim, the production of dense, coherent metal deposits. Hence attention has been paid to electroreduction and oxidation mechanisms and pathways as well as to the electrocrystallization and growth of the deposits. (Some typical reaction pathways and the questions which may be posed concerning these mechanisms are shown in figures 1 and 2.) Nevertheless, there is a need to develop a better understanding of the basic chemistry of the solute-solvent interactions.

The focus of interest in systems such as  $Pb^{2+}/Pb(1)$  is the high electron transfer rates and the, probably related, adsorption of the  $Pb^{2+}$  ions in the (ionic) multilayer at the electrode surface. Likewise for example the  $Ag^+/Ag(s)$  couple has been investigated from the point of view of the high charge transfer rates and the electrocrystallization and nucleation phenomena. In the case of metals which give rise to multivalent ions (i.e. the transition metals) interest tends to be centred on the role of chemical reactions coupled to the electron transfer process, i.e. dimerization, disproportionation, etc. Such complications are to be welcomed since additional chemical information is obtained from electrochemical experiments but this advantage is offset by the resulting complications and ambiguities. However, it should be noted that transition metal halide compounds and their salts have received relatively little attention with regard to their synthesis, physical and chemical properties and, in particular, their reactions in molten salts. We believe that electroanalytical experiments play an important role in this area but they must always be complemented by structurally orientated techniques such as spectroscopy, magnetic susceptibility and by simultaneous spectroscopic/electrochemical investigations.

Obviously the subject of the electrochemistry and chemistry of transition metal compounds in molten salts is very broad. The various advantages and disadvantages of molten salt solvents and the processes researched have been reviewed quite extensively (1-4). In this paper our aim is to summarise some of the chemical complications which arise from such studies and to report on some of our initial experiments on tungsten and its compounds.

Two main complications arise in our studies of transition metal compounds in molten salts: a) melt stability problems and b) chemical reactions coupled to electron transfer.

# a) Melt stability problems.

i) Volatilisation of solutes. In all studies it is necessary to achieve a stable solution. In the case of high oxidation state metal ions the solvent anion/cation composition has proved to be the dominating factor. The solvent anion composition produces a first order effect. In general the 'all' fluoride systems exhibit greater stability than the 'all' chloride systems. Such effects may be conveniently described in terms of a SHAB concept in which the 'hard' fluoride ion forms stronger complexes with the higher oxidation states than the 'softer' chloride ion. Even small additions of fluoride to an 'all' chloride system have significant effects (5).

The anion composition also determines the nature of the electrodeposit. The all-fluoride melts developed by Senderoff and Mellors at Union Carbide produce structurally sound deposits except in the case of Ti (3,6); however in the presence of chloride ions dendritic and/ or powdery deposits are formed. On the contrary, molybdenum, along with chromium, may be successfully plated from chloride baths (7,8).

Solvent cation composition only produces a second order effect although, for a particular anionic solvent, their effects are quite marked. For example, the partial pressures of Ti(IV), Zr(IV) and Hf (IV) in LiCl approach  $10^3$  torr, but above CsCl the vapour pressures are only of the order of 1 torr at 1000K (9). The form of electrodeposit is also affected (10). Increase in melt stability with increasing size of the solvent alkali metal cation for a given temperature is well illustrated in the case of MoCl<sub>3</sub>-containing melts (11,12). Thus at  $750^{\circ}$ C a NaCl:KCl (20 m/o: 80 m/o) solvent gave optimum stability.

<u>ii) Disproportionation of solutes.</u> A particular aspect of transition metal chemistry is the onset of disproportionation reactions at relatively low temperatures. Homogeneous or heterogeneous equilibria may exist in chloride melts, for example

and  $3Ta_6Cl_{18} + 16Cl^- \iff 4Ta + 14TaCl_5^2$  heterogeneous equilibrium.

<u>iii)</u> Formation of cluster compounds. Cluster compounds are a particular feature of the low oxidation states of transition metals. Syntheses of these compounds have utilised alkali chloride melts (13-15). Such soluble or insoluble cluster compounds may therefore result from the electrochemical reduction of the higher oxidation states.

The formation of a soluble cluster compound may lead to the enhancement of solute stability (for example the vapour pressure of MoCl<sub>3</sub> decreases as its concentration increases (7), which is probably due to the formation of  $Mo_2Cl_9^{-1}$  species).

Insoluble cluster compounds can lead to electrode passivation; such phenomena have been invoked to explain the inability to oxidise Mo anodically in  $AlCl_3$ -KCl melts (16) and W in (Li,K) Cl melts (17).

The systems (in alkali chloride melts) in which these phenomena (i-iii) have occurred in our own work are indicated in Table 1.

# b) Chemical reactions coupled to electron transfer.

For the purposes of the present discussion we have excluded reactions such as "ionic adsorption" (adsorption of this type occurs within the electrode multilayer and is in any event probably fast and therefore non-rate-determining) and also reactions involving insoluble solids at interfaces.

Homogeneous bulk reactions are numerous and there are many complications possible but two principal classes may be distinguished.

1.	kinetic	i.e.	문	••I →	ο		
			0	+	ne	<b>→</b>	R
and 2.	catalytic	i.e.	0	+	ne	<b>→</b>	R
			R	+	æ	<b>→</b>	0

(The chemical and electrochemical reactions may of course be either reversible or irreversible to varying degrees.) The electroreduction of Mo(III) is a classic example (18) where the overall rate of electrodeposition in chloride melts was shown to be controlled by the rate of a coupled chemical process,

viz.  $Mo_2^{6+}$  (complex  $\rightarrow 2 Mo^{3+}$  (slow)  $Mo^{3+} + 3e \rightarrow Mo$  (fast)

Some of these complications are evidenced for the W(VI) and W(V) systems in LiCl-KCl below.

### TUNGSTEN.

Tungsten is one of the most technologically important metals as it has a wide range of applications, particularly as a high temperature alloy. In view of its high melting point, powder metallurgical fabrication techniques are generally used. Commercial extraction processes employ aqueous leaching techniques and finally the hydrogen reduction of its oxide. The resultant powder needs to be of high purity and fine controlled grain size, which necessitates numerous closely controlled processing steps.

Alternative processes employing molten salt electrowinning, plating and forming techniques have received considerable attention. Among the many solvents investigated have been fluorides (6), chlorides (19), and phosphate/borate (20)melts, using a variety of tungsten sources, tungstates (21), oxides (22), fluorides (23) and chlorides (24).

Our interest in tungsten is to produce a controlled high purity metal powder via an electrochemical reaction. Some of our interim results and observations on the tungsten oxidation states (VI) and (V) as chlorides in LiCl-KCl eutectic at  $400^{\circ}$ C are given below.

# Aspects of tungsten chemistry.

Tungsten may exist in a variety of oxidation states ranging from +2 to +6. Some of the halides are listed in Tables 2 and 3 and the alkalimetal compounds in Table 4. As with most high oxidation state refractory halides, disproportionation reactions occur at relatively low temperatures, i.e.

 $WCl_6(g) \rightleftharpoons WCl_5(s) + \frac{1}{2}Cl_2$ 

 $\mathbf{or}$ 

Metal atom clusters are particularly common in tungsten chemistry, particularly in the lower oxidation states, i.e.  $K_3W_2Cl_9$  and  $W_6Cl_{12}$ . From a study of refractory metal halides it is quite apparent that the change in oxidation state is accompanied by striking structural changes. In the case of tungsten halides, the diversity of structural

 $3WX_{a}(s) \rightleftharpoons "WX_{a}"(s) + 2WX_{s}(g) X = C1, Br.$ 

types ranges from the simple monomeric (WCl<sub>6</sub>) to the polynuclear  $(W_6Cl_{12})$ . The reactivity of a halide is to a certain extent dependent upon its structure, a decrease in reactivity usually paralleling an increase in the polymeric nature of the halide.

# Experimental.

The LiCl-KCl eutectic mixture was prepared by mixing Analar grade KCl and laboratory grade LiCl (anhydrous) in the correct proportions and slowly drying under vacuum up to  $300^{\circ}$ C. Dry HCl gas was then passed through the mixture until fusion occurred, and further bubbled through the melt for one hour. This was followed by bubbling with Cl<sub>2</sub> for one hour and finally sparging with Ar. Heavy metal ions were removed by vacuum pre-electrolysis at 2.5 V between a graphite anode and a stainless steel cathode for 4 hours. The melt was then filtered and collected in a pyrex glass pot and cooled under vacuum. The purified salt was kept over  $P_2O_5$  in a dry box until required.

The melt was contained in a pyrex pot within a pyrex envelope which had a water-cooled brass cell head. Seven holes in the cell head enabled entry of the electrodes and other components. Vacuum tightness was ensured by '0'-ring seals. The cell and electrodes were dried prior to, and subsequent to, adding the purified salt under vacuum for about 12 hours. The experiments were conducted under a slight positive pressure of purified Ar.

Pt or Au flag electrodes were used. The vitreous carbon electrode consisted of 3mm rods held by a graphite connector which were allowed to dip into the melt to a depth of about 2mm. A graphite or Pt counter electrode was used. The reference electrode was based on the Ag/Ag(I) couple, contained in a thin pyrex membrane.

Tungsten species were added to the melt in the form of small pellets of  $WCl_6$  and  $KWCl_6$ .

Commercial WC1<sub>6</sub> (solid) was purified by several vacuum sublimations at 120°C to remove volatile oxyhalides. The remaining compound was then sealed into a pyrex ampoule and the temperature increased to  $200^{\circ}$ C. Pure WC1<sub>6</sub> sublimed to the cool end of the ampoule (held at room temperature)<sup>6</sup> leaving an impure residue in the hot zone.

 $\rm KWCl_6$  was synthesised according to the technique used by R.N. Dickenson et al (25) based upon the reaction

 $KI + WCl_6 \rightarrow KWCl_6(s) + \frac{1}{2}I_{2(g)} \text{ at } 100^{\circ}C.$ 

Both compounds were characterised by x-ray analysis.

The special solute addition assembly has been described pre-

viously (11). Prior to the addition of solutes, the solvent was checked for purity using cyclic voltammetry.

#### Results

a) General observations.

Addition of WC1 to the solvent resulted in a vigorous reaction with the evolution of chlorine gas. Thus solvent oxidation occurs which may be described by the reactions:

 $W^{VI}(s) + Cl^{-}(soln) \rightarrow W^{V}(soln) + \frac{1}{2}Cl_{2(g)}$ and/or  $W^{VI}(s) + 2Cl^{-}(soln) \rightarrow W^{IV}(soln) + Cl_{2(g)}$ 

As a first approximation, the resultant primary oxidation state in solution may be estimated by its colour. Complete reaction yielded a yellow/green solution at  $400^{\circ}$ C which tends to suggest an oxidation state of +5 (a similar colour is observed upon adding KWCl<sub>6</sub>). A further possible complication arises from the reaction with any unreacted WCl<sub>c</sub>, i.e.

$$W^{VI} + W^{IV} \rightarrow 2W^{V}$$

which has indeed been used for synthesising  $w^{5+}$  and  $w^{4+}$  (25). Volatilization occurs with the formation of WCl<sub>6</sub> on the cool parts of the cell (observed with both solutes); there was an estimated 25% loss over a 3-day period.

Upon standing the solutions overnight, disproportionation occurs which is evidenced by a very bright metallic film on the surface of the container and any other surfaces in the melt. X-ray analysis of this film indicated that it was  $W_{30}$ , the coupled oxygen is thought to be a result of either a) washing the product or b) interaction with the pyrex glass.

A possible reaction describing the disproportionation is:

 $6W^{V} \rightarrow W^{\circ} + 5W^{VI}$   $5W^{VI} + 5C1^{-} \rightarrow 5W^{V} + 5/2 C1_{2}$   $W^{V} + 5C1^{-} \rightarrow W^{\circ} + 5/2 C1_{2}$ 

b) Cyclic voltammetry.

(i) <u>WCl</u> solute. In general one broad reproducible reduction wave was observed on different electrode materials at approximately -150 to -250 mV w.r.t. ref. electrode (Fig. 3). However, significantly different behaviour is observed with increasing concentration. At a 6.5 x  $10^{-3}$  molal concentration, the absence of reoxidation waves is observed for the range of scan rates  $(0.02 - 10 \text{ vs}^{-1})$  used. Examination of the current functions shows that a plot of i <sup>c</sup> vs v<sup>2</sup> is linear with zero intercept (Fig. 4). However, the more sensitive plot of i <sup>c</sup> / v<sup>2</sup> vs. v shows a distinct decrease at slow sweep

 $p^{p}$  rates, but then i  $/v^{2}$  becomes virtually independent of v at higher sweep rates (Fig. <sup>p</sup>5). Anodic shifts in the peak potential (E) occur at sweep rates greater than 0.4 Vs<sup>-1</sup>. The variation of the half peak width (E  $-E_{p/2}$ )with log y shows unusual behaviour (Fig. 6); at sweep rates less than 150 mVs<sup>-1</sup> a constant  $E_{p-E_{p/2}}^{-E_{p/2}}$  is indicated, whereas higher sweep rates result in a maximum at about 2-3 Vs<sup>-1</sup>. On the basis of the behaviour of the functions which involve currents (e.g.  $i_{p}/v^{2}$ ) catalytic reaction with irreversible charge transfer mechanism may be inferred, although the shift in peak potential is not expected on the basis of this scheme.

$$0 + ne' \rightarrow R + Z \rightarrow 0$$

At more cathodic potentials a further wave is observed whose appearance tends to be highly variable (Fig. 3). It is probably subject to the condition of the electrode surface, particularly if the previous reduction product is insoluble.

At a higher concentration of  $3.6 \times 10^{-2}$  molal complex behaviour is observed on Pt and vitreous carbon electrodes. However, using a gold microelectrode, reproducible behaviour occurs with the appearance of a reoxidation wave. A plot of

 $i_{p}^{c}/v^{\frac{1}{2}}$  vs. v

was a horizontal line. On the other hand the  $i_p^{a}/i_p^{c}$  function

increases towards unity with increasing sweep rate, the increase being greater at low sweep rates (Fig. 7). A cathodic shift in E occurs at slow sweep rates but it tends to become independent (of sweep rate) at the higher sweep rates. The data appear to be consistent with a reversible charge transfer followed by an irreversible chemical reaction mechanism.

$$\begin{array}{ccc} 0 &+ & \mathrm{ne'} \rightarrow \mathrm{R} \\ & & \mathrm{k_f} \\ \mathrm{R} & \rightarrow & \mathrm{Z} \end{array}$$

<u>ii)  $KWCl_6$  solute</u>. Similarly to the WCl<sub>6</sub> solute, a single reduction wave at a potential of about -200 to-300 mV w.r.t. Ag/Ag(I) is observed on the platinum electrode upon addition of  $KWCl_6$ . Over the concentration range studied (8.4 to 34.4 x 10<sup>-3</sup> molal) the absence of any associated reoxidation waves or transition times is noteworthy.

At a concentration of 8.4 x  $10^{-3}$  molal, the i vs.  $v^{\frac{1}{2}}$  plot is linear with a zero intercept on the y-axis. The more sensitive i  $v^{\frac{1}{2}}$ 

parameter is likewise independent of sweep rate,  $(0.02 - 0.4 \text{ Vs}^{-1})$ (see Fig. 8). The peak potential remained constant as did the half peak width  $E_p-E_{p/2}=70$  mV). At the higher concentration  $(20.2 - 1)^{-3}$  molal positive intercepts on the y-axis of the  $i_p^{-C} \text{ vs } \text{ v}^2$ plots occur, the  $i_p^{-C}/\text{v}^2$  relationship decreasing at slow sweeps and becoming constant at higher values (Fig. 9).

The peak potential shifts cathodic by approximately 150 mV for a tenfold increase in sweep rate, while the corresponding half peak width remained constant at about 65 mV.

### c) Chronopotentiometry of KWCl6

Balco carried out a more extensive chronopotentiometric investigation in LiCl-KCl, using WCl<sub>6</sub> and WBr<sub>5</sub> as the solutes. He obtained virtually identical results for both solutes (see above) although he observed two reduction processes; a consideration of these results led him to suggest w(W) = 0 = w(TTT)

$$W(V) + 2e \rightarrow W(III)$$

W(III) + 3e → W

as the most likely mechanism. As noted above the second wave observed in our linear sweep voltammetric studies was generally poorly defined. Chronopotentiometry has been applied in a limited way only. A single ill defined reduction wave only was observed up to the cathodic limit with no discernible reverse transition time over the range of current densities used  $(3.52 - 41.3 \text{ mA/cm}^2)$ .

 $\Upsilon^{\frac{1}{2}}$  vs. i<sup>-1</sup> plots are linear with a positive intercept on the y-axis and the product i $\Upsilon^{\frac{1}{2}}$  increases with increasing current density (Fig. 10). These observations tend to suggest film formation.

### Conclusions

The possibility of irreversible electron transfer may indeed by inferred by the absence of reoxidation waves within the available solvent limit. However, it is more likely that this is due to the transformation (by a chemical reaction) of the primary electroreduction product to a species which cannot subsequently be electrooxidised or by the blocking of the electrode surface by an insoluble product.

At this stage of the research it is not possible to put forward and confirm definite mechanistic pathways. A major bottleneck is the inability to determine a reliable 'n' value (the number of electrons involved in the process) for the overall reduction in the presence of disproportionation, when the process under investigation is diffusion-controlled.

The main general conclusions to be drawn are:

- 1. The solution chemistry is markedly dependent upon solvent composition.
- 2. The absence of chemical information for many of the refractory

metals leads to uncertainties concerning the exact nature of the initial oxidation state in solution.

- 3. Electrochemical reductions are generally associated with coupled chemical reactions.
- 4. The formation of insoluble clusters (as films) on the electrode after the first reduction stage determines the course of subsequent steps and vitiates the interpretations of the electrochemical data.

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# TABLE 1.

Volatilization of solute	₩ √	Mo √ MoCl <sub>3</sub>	Cr x (CrCl <sub>2</sub> )	Ti x (TiCl <sub>2</sub> )	Ta √ TaCl <sub>5</sub> TaCl <sub>4</sub>
Disprop. of solute	1	x	x	$\checkmark$	√
Cluster Cpds.	√	√ soluble	?	$\checkmark$	1

All these phenomena are solvent melt dependent.

# TABLE 2.

# Non-cluster halides of tungsten

Valency	Fluoride	Chloride	Iodide	Bromide
6	WF <sub>6</sub>	WC1 <sub>6</sub>		WBr <sub>6</sub>
5	WF <sub>5</sub>	WC15		WBr <sub>5</sub>
4	WF4	WC14	WI4	WBr <sub>4</sub>
3			WI 3	

# TABLE 3.

Anhydrous	cluster halides of	tungsten
Chloride	Bromide	Iodide
<sup>W</sup> 6 <sup>C1</sup> 18	<sup>W</sup> 6 <sup>Br</sup> 18	<sup>W</sup> 6 <sup>I</sup> 15
W <sub>6</sub> C1 <sub>12</sub>	<sup>W</sup> 6 <sup>Br</sup> 16	<sup>W</sup> 6 <sup>T</sup> 12
	<sup>W</sup> 6 <sup>Br</sup> 14	
	<sup>W</sup> 6 <sup>Br</sup> 12	

•	
4	1
Ξ	
AB	1
F	I

Halide	Valency	Sodium	Potassium	Rubidium	Caesium	Colour
Fluoride	9	NaWF7	KWF <sub>7</sub>	RbWF <sub>7</sub>	CSWF <sub>7</sub>	White
Fluoride	9	Na <sub>2</sub> WF <sub>8</sub>	K <sub>2</sub> WF <sub>8</sub>	$Rb_2WF_8$	Cs 2WF 8	White
Fluoride	ũ		K <sub>3</sub> WF <sub>8</sub>	$Rb_{3}WF_{8}$	Cs WF8	1
Fluoride	5	NaWF <sub>6</sub>	KWF <sub>6</sub>	RbWF <sub>6</sub>	CsWF <sub>6</sub>	ı
Chloride	ß		KWC1 <sub>6</sub>	RbWC1 <sub>6</sub>	CsWF <sub>6</sub>	light green
Chloride	4		K <sub>2</sub> WC1 <sub>6</sub>	Rb <sub>2</sub> WC1 <sub>6</sub>	Cs <sub>2</sub> wc1 <sub>6</sub>	purple/red
Bromide	4		$\mathbf{K_2^{WBr}_6}$	${ m Rb}_2{ m WBr}_6$	$c_s_{2}^{WBr_6}$	green
Chloride	e		K <sub>3</sub> W <sub>2</sub> C19	$Rb_3W_2C1_9$		
			(yellow-			
			(maa.18			

# FIGURE 1.

Typical questions.

1.	Z Do complex species/clusters exist in the melt?
	What is their structure/energetics of formation?
2	D.u. What are the values of D and $\mu$ ? What are the diffusive and
	migrative mass transfer mechanisms?
з.	$\overline{Z} \rightarrow 0$ What is the rate and mechanism of this chemical step?
4	ne What is the rate and mechanism of this charge transfer step?
	How does it depend on the structure of the metal/melt interphases?
5.	Does adsorption intervene? i.e. Oads Zads
6.	Is ne preceded by the formation of a surface film?
7.	Does R form a non-conducting film?
8.	Does $[R] \rightarrow R_{e}$ occur?
9.	What is the structure of $[R_f]$ ?
10.	Is <u>kr</u> a surface process?

# FIGURE 2

Typical reaction pathways for cathodic reaction of complex ion  ${\rm Z}$  .





Figure 3

Figure 4



Figure 5

- <u>Fig. 3</u>. Cyclic voltammogram for the reduction of tungsten ions on a Pt electrode in LiC1-KC1 eutectic at  $400^{\circ}$ C [WC1<sub>6</sub>] = 6.5 x 10<sup>-3</sup> molal, Pt electrode = 0.241 cm<sup>2</sup>, sweep rates - 0.15, 0.2, 0.3, 0.4 Vs<sup>-1</sup>.
- <u>Fig. 4</u>. Peak Current  $(i_p^c)$  versus (sweep rate)<sup> $\frac{1}{2}$ </sup> at a Pt electrode [WC1] = 6.5, 20.0, 36.0 x 10<sup>-3</sup> molal. Pt electrode = 0.241 cm<sup>2</sup>.
- <u>Fig. 5</u>.  $i_p^{C/v_2^2}$  versus (sweep rate) for reduction of tungsten ions on a Pt electrode  $[WC1_6] = 6.5 \times 10^{-3}$  molal.



Fig. 6. Peak potential  $(E_p^c)$  and half peak width  $(E_p^{-E_{p/2}})$  versus ln (sweep rate)  $[WC1_6] = 6.5 \times 10^{-3} \text{ molal}$ , Pt electrode = 0.241 cm<sup>2</sup>. Fig. 7. Current functions  $\left(\frac{i_p}{4}\right)$  and  $\left(\frac{i_p}{2}\right)$  versus (sweep rate) for

the reduction of tungsten ions on Au electrode (0.10 cm<sup>2</sup>)  $\begin{bmatrix} WC1_6 \end{bmatrix} = 3.6 \times 10^{-2} \text{ molal.}$ 



# THERMODYNAMICS OF THE Li/A1/FeS SYSTEM

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# ABSTRACT

In order to predict heat generation rates during the charge and discharge of the Li/Al/FeS battery, it is necessary to quantify the thermodynamics of the system. The direct measurement of the open circuit potential as a function of temperature provides the most convenient method for the determination of the free energy, enthalpy and entropy changes of the reaction. The entropic contribution defines the intrinsic heat generation during operation of the cell. Reproducible variations of the cell potential with temperature have been measured using an iron wire electrode previously anodized at 1.55V vs. Li/Al in a lithiumsulfide-containing LiCl/KCl eutectic melt. The observed temperature coefficient of the EMF is in reasonable agreement with that determined for a Gould 178Ah cell which had been maintained at  $500^{\circ}C$  for 12 hours.

Calculations of the predicted temperature excursions of the 178Ah cell during a  $60mA/cm^2$  discharge indicate only a  $30^{\circ}C$  temperature increase to the 1V cut-off potential.

The Li/Al/iron sulfide battery which uses a LiCl/KCl molten salt electrolyte at 700°K is currently being advanced for both the load leveling and vehicular propulsion markets (1). At the present time, the "lower plateau" cell based upon a nominally FeS positive electrode is most favored.

Despite the advanced stage of development of this system, relatively little work has been directed toward assessing temperature variations during charge and discharge. It is desirable to keep the operating temperature between 430 and 470°C to inhibit corrosion and self-discharge. To address this problem requires the characterization of thermodynamics with particular emphasis on the determination of the entropy. Heat generation during charge and discharge of the battery is determined both by irreversible voltage losses as well as entropy changes between the initial and final states of the electrochemical reaction (2). The small magnitude of the irreversible losses associated with high-temperature molten salt cells increases the relative importance of the entropy change in the thermal analysis. <u>Experimental</u>: All experimental work was conducted under an argon atmosphere in a modified Vacuum Atmospheres glovebox capable of reducing contamination levels to less than 1 ppm. Broken 25W light bulbs generally showed lifetimes of about 100h. The LiCl/KCI molten salt was prepared at Gould Laboratories; it melted at 362°C, being slightly richer in LiCl than the eutectic. The molten salt was contained in crucibles of Mg0, ZrO, viterous carbon, or tungsten. Pyrex glass was generally avoided because of its reactivity toward the melt containing lithium sulfide (3).

Iron wire and rod supplied by Alfa Inorganics were 99.99% pure. Iron sulfide and lithium sulfide were used as supplied by Fisher and Alfa Inorganics, respectively. Current-voltage curves were obtained with a Wenking H.P. 40 potentiostat in association with a P.A.R. 175 function generator. Potential measurements were carried out against a Li/Al reference electrode prepared electrochemically in the eutectic.

Results: Cyclic voltammograms for the sulfidation of iron were obtained with an iron wire immersed in the LiCl/KCl melt containing a known amount of added Li<sub>2</sub>S. A typical profile is shown in Figure 1. The voltage was scanned initially anodic from 1.0V up to a voltage just prior to iron The oxidation reaction constitutes a typical charge cycle dissolution. and is characterized by two peaks indicating at least two major processes taking place. Associated reduction peaks were obtained by reverse scan. By selecting appropriate scan reversal potentials it is possible to establish that more anodic oxidation is associated with the more anodic In view of the complexity of the reactions, no reduction peak. quantitative analysis was attempted; however, the reaction was further investigated using a rotating iron cylinder electrode. The concentric counter electrode was a tungsten crucible with the base "blocked" by a watch glass.

Typical diffusion-limited behavior was obtained at low concentrations of Li<sub>2</sub>S (Figure 2). Plots of the plateau current <u>vs</u>.  $\omega^{0.71}$  were linear and passed through the origin. From the expression derived by Eisenberg <u>et al</u>. (4) a value of 9 X 10 cm ·s <sup>1</sup> was derived for the diffusion coefficient of the sulfide ion. As the concentration of the lithium sulfide was increased, the current-voltage curve observed on the rotating iron cylinder resembled more closely that obtained at higher sweep rates on a stationary iron electrode. Moreover, no diffusion-limited control was observed. The surface nature of the rate-limiting step was confirmed by potentiostatic pulse experiments in which an iron wire was maintained at 1.0V vs. Li/Al for several minutes before being pulsed into the active potential region. The maximum shown by the current transient as the final potential was increased from 1340mV to 1380mV (Figures 3a-3c) was typical of rate-controlling film growth. More anodic final potentials resulted in a second current maximum (Figures 3d and 3e), indicating the formation of a second film.

Significantly, in the rotating iron cylinder case, the observation of a reduction current indicated the formation of an iron sulfide film of low solubility during the oxidation reaction; the quantities of electricity in the oxidation and reduction reactions were identical. Therefore, it was possible to anodize an iron wire at 1.55V for 30s to yield an Fe/FeS electrode which was responsive to sulfide ions. The temperature dependence of the potential of this electrode at various lithium sulfide concentrations is shown in Figure 4. Increasing sulfide concentration and decreasing temperature results in lower potentials. At lower temperatures some of the plots were curved; however, in the linear region between 450°C and 500°C there was good agreement with the Nernst equation, which indicates the reversible nature of the electrode (Figure 5). The extrapolated values of E° (with no correction for the activity of Li in Li/Al) were 1.128 and 1.122V at 500° and 450°C, respectively. Figure 6 indicates that a temperature coefficient of  $-0.17 \pm 0.01$ mV/°C was obtained in a melt saturated with lithium sulfide.

Values for the solubility of lithium sulfide were found from the intersection of the saturated and unsaturated cell potential-temperature plots. Table 1 shows the temperature dependence of the solubility. A plot of the logarithm of the solubility against the reciprocal of the absolute temperature was linear. From the slope of the line a value for the heat of solution was derived as 49  $\pm$ 9kJ/mol, in agreement with literature values (3,5).

As a verification that the behavior of the anodized iron wire could be reproduced with commercially available iron sulfide, some material from Fisher was introduced into a magnesia crucible along with powdered iron and lithium sulfide. Within 95% confidence limits, the potential variation with temperature was the identical to the behavior of the anodized wire. Discharging the electrode at low current density to 30% depth of discharge did not result in any significant variation of the potential at 430°C.

To study the applicability of the results to the behavior of engineering size cells, GLER (Gould Laboratory Energy Research) cell No. X2 was equilibrated at 430°C. When the temperature was lowered, the cell potential rose; this behavior resembled that of the iron wire in a melt saturated with lithium sulfide. However, increasing the temperature above 430°C also resulted in an increase in the potential (Figure 7). Maintenance of the temperature 500°C resulted in a slow decrease in the potential, and after a 12-hour period the temperature was decreased and the temperature coefficient was negative throughout the temperature range.

<u>Discussion</u>: The cyclic voltanmetry and rotating iron cylinder results have indicated a two-step mechanism for the positive electrode charge/discharge reaction. At low sulfide concentrations the rate-determining step at more anodic potentials is mass transport; however, as the concentration increases, film growth becomes rate determining. Potentiostatic pulse work at almost saturated lithium sulfide concentrations has identified the growth of two distinct sulfide films, consistent with the reaction mechanism:

Fe + 2 
$$\text{Li}_2$$
S =  $\text{Li}_2$ FeS<sub>2</sub> + 2Li<sup>+</sup> + 2e<sup>-</sup>

The overall reaction can be simply represented as:

$$FeS + 2Li/A1 = Fe + Li_2S + 2A1$$

Values for the free energy of formation of FeS and Li<sub>2</sub>S at 700°K are -101kJ/mol(6) and -418kJ/mol(7), respectively, which yields a value for the cell potential with a pure lithium negative of 1.642V. Applying the correction for the reduced lithium activity<sup>8</sup> gives a value of 1.350V for the cell potential, about 0.011 greater than the experimentally derived value. The temperature coefficient of -0.17mV/°K translates to an entropy change of -33Jmol<sup>-1</sup>°K<sup>-1</sup>.

The curvature in the cell potential-temperature plots of the melt containing unsaturated lithium sulfide was not consistently observed; however, the reproducibility of the line during temperature cycling indicated that the curvature was not due to irreversible changes in the electrolyte. It is possible that the curvature arises either as a direct result of phase changes in the iron sulfide or as a secondary effect of these phase changes, e.g., sulfide depletion of electrolyte within the pores of the film.

The results determined for the GLER 178Ah cell above  $430\,^{\circ}$ C differ from those determined on the iron wire, in that a positive entropy is indicated. Holding the cell at 500\,^{\circ}C for 12 hours, however, resulted in behavior similar to that of the wire electrode throughout the temperature range, although the cell potential was lower as a result of self-discharge.

The positive entropy change observed in the cell above 450°C may indicate an active-material phase change or the unsaturation of the electrolyte with respect to lithium sulfide. Holding the cell at 500°C for twelve hours may have changed the EMF/temperature dependency due to a change in the state of charge as a result of self-discharge. This could alter both the nature of the active material and the concentration of lithium sulfide in the cell.

On the basis of the evidence presented here, it is not possible to determine what is responsible for the positive temperature coefficient of the EMF at high temperatures. However, the value of the temperature coefficient of the EMF observed for the cell above  $430^{\circ}$ C (i.e., +0.29mV/°C) closely corresponds to the value predicted for an unsaturated solution containing 0.0175m lithium sulfide (i.e.,  $0.28 \sim 0.32$ mV/°C) which would become saturated at approximately  $430^{\circ}$ C.

Charge-discharge curves for the GLER cell X21 (capacity 178Ah) are shown in Figure 8. The cell was discharged at 25A (60 mA/cm<sup>2</sup>) and charged at 10A (24mA/cm<sup>2</sup>). Using the thermodynamic values obtained experimentally, together with a charge-discharge curve, heat generation rates may be determination from the equation (2).

$$-dq/dt = I [-(T/nF) (\partial S/\partial \xi)_{P,T} + E-V]$$
(1)

where -dq/dt is the heat generation rate,  $(\Im S/\Im \xi)_{P,T}$  is the rate of change of entropy with respect to the reaction progress, T is the current and is taken positive for discharge and negative for charge, E is the reversible cell potential, and V is the operating cell potential. Heat generation rates calculated from equation (1) assuming both positive and negative values of the entropy change are shown in Figure 8. The  $\Delta T$  values on the figure represent the predicted temperature rise assuming adiabatic conditions. For a cell exhibiting a negative EMF temperature coefficient, the temperature would rise from 430°C to 490°C during discharge and fall to 420°C during charge. A positive temperature coefficient of EMF would be associated with a 500°C temperature at the end of charge and a 423°C temperature at the end of discharge.

At such high operating temperatures, losses through insulation considerably modify the temperature excursion. We have considered the particular case of cell X21 completely encapsulated by a 1 cm thickness of vacuum foil insulation (Linde) with a thermal conductivity of  $6.9 \times 10^{-10}$ W/m°C. The analysis assumed the thermal conductivity of the cell to be infinite and convection to be the only heat transfer mechanism to the surrounding atmosphere, assumed to be at 25°C. The time dependence of the temperature is shown in Figure 9.

Only in the case of the discharge in which a negative entropy change is assumed does the predicted temperature of the cell increase. These predictions compare favorably with experimental data obtained with the Li/SiFeS cell(9) and indicate that only minimal cooling, if any is required at these discharge rates.

Further work is ongoing in these laboratories to test these predictions and to determine the origin of the observed positive temperature coefficient of EMF.

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# Table I. Solubility of Li2S

Solubi	lity (mol/kg)	Temp	erature	(°C)
	30 x 10 <sup>-3</sup>		465	
	25 X 10 <sup>-3</sup>		447	
	$17.5 \times 10^{-3}$		423	
	$12.4 \times 10^{-3}$		<b>3</b> 93	

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FIGURE 1 CYCLIC VOLTAMMOGRAM ON Fe WIRE IN LiCI/KCI +  $Li_2S$ 



FIGURE 2 ROTATING Fe CYLINDER IN LICI/KCI + Li<sub>2</sub> S



FIGURES 3a, b AND c POTENTIOSTATIC PULSE EXPERIMENTS ON Fe WIRE: INITIAL POTENTIAL, 1.0V, 30mM Li\_2 S, AREA,  $0.31cm^2$ 







FIGURE 4 THE TEMPERATURE DEPENDENCE OF THE Fe/FeS/S<sup>2 -</sup> ELECTRODE E.M.F.



FIGURE 5 NERNST RELATIONSHIP FOR ANODIZED FeWIRE IN UNSATURATED Li<sub>2</sub> S



FIGURE 6 TEMP. DEPENDENCE OF EMF FOR ANODIZED Fe WIRE IN SAT. Li<sub>2</sub> S



FIGURE 7 TEMPERATURE DEPENDENCE OF EMF FOR CELL X2







# ELECTROLYSIS OF MOLTEN NaNO<sub>3</sub>-Agno<sub>3</sub> AS TEST OF A MODEL OF TRANSPORT IN BATTERIES\*

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# ABSTRACT

Concentration changes resulting from electrolysis of 0.8 NaNO<sub>3</sub>-0.2 AgNO<sub>3</sub> mixtures between silver electrodes have been measured by: (i) potentiometric analysis during electrolysis (with current interruption); (ii) emf relaxation following electrolysis; (iii) chemical analysis of sections of frozen electrolyte. Enrichment in NaNO<sub>3</sub> at the cathode and in AgNO<sub>3</sub> at the anode are observed. The measurements confirm predictions from a model of component separation in mixed molten salt batteries with faradaic, migrational, and diffusional flows analogous to those in Li/LiCl-KCl/S batteries.

### INTRODUCTION

Binary and multicomponent mixtures of molten salts are used as the electrolyte in some high temperature batteries.<sup>1</sup> Under the influence of the high current densities at which these batteries operate, changes in composition within the electrolyte may arise from the electrode reactions and from ionic migration. Concentration changes near the electrodes, resulting from transport phenomena, have been studied in aqueous electrolytes. Brenner<sup>2</sup> obtained concentration profiles near the electrode, during electrodeposition from copper sulfatesulfuric acid mixtures, by freezing the solution and subsequent analysis. More recently, high resolution interferometric measurements<sup>3,4</sup> of concentration and distance provided transient concentration profiles of CuSO4 in sulfuric acid solution supporting electrolyte at a copper electrode. Changes in composition of the electrolyte in porous electrodes also have been widely studied  $^{5,6}$  because of the deleterious effect on the battery performance when the "supporting electrolyte" is depleted at the pore mouth.<sup>6</sup> For molten salt media there is also experimental evidence of component separation induced by current flow. During discharge of a A1/Cl<sub>2</sub> battery with A1Cl<sub>3</sub>-NaCl-KCl mixture as

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the electrolyte, solid AlCl $_3$  precipitates  $^7$  at the aluminum anode. Significant difference in the Li/K ratio at anode and at cathode has been observed<sup>8,9</sup> during electrolytic separation of <sup>6</sup>Li and <sup>7</sup>Li in fused LiBr-KBr mixtures between Br2/C electrodes. (The isotopic separation is itself an example of component separation by virtue of differing electrical mobilities.) A previous analysis<sup>10</sup> of transport in binary mixtures during current flow predicted the establishment of concentration gradients in two-component melts such as those employed as electrolytes in molten salt batteries. Since variations of the potential difference between LiAl and FeS<sub>2</sub> electrodes 11, 12 for reasons other than changes of the Li/K ratio in the LiCl-KCl electrolyte may tend to obscure in situ potentiometric observation of the change of the Li/K ratio, there was a need to find suitable analog experiments for testing the validity of the predictions. Composition changes resulting from electrolysis of  $KN0_3$ -AgNO<sub>3</sub> melts between silver electrodes have been reported previously.<sup>13</sup> New measurements of composition changes in NaNO<sub>3</sub>-AgNO<sub>3</sub> mixtures provide a more accurate test of the model because the diffusion coefficient,  $^{14}$  the transference number,  $^{15}$  and the activity coefficient  $^{16}$  are independently known in this system. Furthermore, NaNO3-AgNO3 is more suitable for analysis of the changes in the cation ratio by SEM-EDX because of better separation of the Na and Ag peaks than of the K and Ag peaks.

### MODEL AND BASIC EQUATIONS

The model of mass transport in binary molten salt mixtures considers the Faradaic processes at the electrodes, the ion flows by electromigration, and interdiffusion of the components. Figure 1 shows the analogy between the ion flows during electrolysis of  $AgNO_3$ -KNO<sub>3</sub> mixture between two silver electrodes and the ion flows in a Li/S battery with LiCl-KCl as the electrolyte. In both cases, one of the two like-charged ion reacts at both electrodes. Silver (or lithium) enters the electrolyte at the anode and leaves it at the cathode.

The one-dimensional diffusion migration equation for a constant volume system  $\mathrm{is}^{10}$ 

$$\frac{\partial C_{Na}}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C_{Na}}{\partial x} \right) - \frac{I}{F} \frac{d t_{Na}^{NO_3}}{d C_{Na}} \frac{\partial C_{Na}}{\partial x}$$
(1)

where  $C_{Na}$  is the number of Na equivalent per cm<sup>3</sup>, D the interdiffusion coefficient of the two components, I the current density,  $t_{Na}^{NO3}$  the internal transference number of sodium ions (relative to the common anion NO<sub>3</sub><sup>-</sup>), x the distance from electrode (anode), t the time, and F the Faraday.
The boundary conditions at both electrodes are:

$$\frac{\partial C_{Na}}{\partial x} = \frac{I}{FD} t_{Na}^{NO3}$$

In the AgNO<sub>3</sub>-NaNO<sub>3</sub> mixture, the interdiffusion coefficient<sup>14</sup> and the transference number<sup>15</sup> have been independently measured and are composition dependent. Equation (1), which is a nonlinear partial differential equation is solved numerically. A finite difference scheme developed previously gives the composition profile between anode and cathode at any time.<sup>17</sup>

## EXPERIMENTAL

Figure 2 shows a typical silica cell used for the electrolysis and measurement of concentration changes at the electrodes in molten salt mixtures. The molten electrolyte is contained in the coarse silica frit. Silica frits 0.25-0.7 cm thick are fused to one end of a silica tube. Two planar silver electrodes of  $0.5 \text{ cm}^2$  area are placed against opposite faces of the frit. The upper electrode, inside the tube, has a known area in contact with the melt which impregnates the frit. The upper electrode is used as an anode or as a cathode in different experimental runs. The electrolyses are done between the two planar electrodes. The third silver electrode dips in the nonelectrolyzed melt contained in the outer tube, carries no current and serves as a reference electrode. The level of the molten mixture is adjusted to just touch the bottom of the upper electrode to help define the area in contact with the melt and the current path. The cell is contained in an aluminum block for uniformity of temperature. A Leeds and Northrup Electromax Controller was used to maintain the furnace to within ±0.1°C of the desired temperature. Two kinds of measurements have been performed and a third is being developed. In the first kind, the frit after electrolysis is quickly cooled and is cut into slices. The salt is extracted with a 0.01 N HNO3 solution. The total weight loss gives the weight of mixture contained in the slice. Solutions containing, typically,  $1 \times 10^{-3}$  g of salt per cm<sup>3</sup> are analyzed for both cations. Sodium is analyzed by flame spectroscopy, silver by spark source mass spectroscopy. In the second kind of measurement the composition change at an electrode, caused by electrolysis, is measured potentiometrically. The relaxation with time of this composition change also is followed potentiometrically. The third method is scanning electron microscopy with energy dispersive X-ray fluorescence (SEM-EDX) of a cross section through the axis of the cylindrical frit; this will be reported on later.

### RESULTS

Composition profiles predicted to arise from current flow are calculated from the diffusion-migration equation and boundary conditions (1) and (2). The composition dependent interdiffusion coefficient  $^{14}$  may be well represented by the equation

$$D/cm^{2}s^{-1} = 1.7 \times 10^{-5} + 5.937 \times 10^{-5} (X_{Na} - 0.4)^{2}$$
  
- 8.594 x 10<sup>-5</sup> (X<sub>Na</sub> - 0.4)<sup>3</sup> (3)

where  ${\rm X}_{Na}$  is the mole fraction of NaNO3. The composition dependent transference number^{15} of silver relative to nitrate is represented by

$$t_{Ag}^{NO_3} = 1 - t_{Na}^{NO_3} = 1.6 x_{Ag}^2 - 1.9636 x_{Ag}^2 + 1.3636 x_{Ag}^3$$
 (4)

where  $X_{Ag}$  is the mole fraction of AgNO<sub>3</sub>.

## Chemical Analysis

A frit of 0.584 cm thickness, containing an 0.8  $\rm NaNO_3-0.2~AgNO_3$  mixture at 300°C was electrolyzed at 0.6 A cm^-2 for 7 seconds. After rapid cooling, the frit was cut into seven slices from which salt was extracted for analysis. The model predicts compositions, at anode and cathode, respectively, at the end of the electrolysis,  $X_{AgNO_3} = 0.33$ and  $X_{AgNO_3} = 0.032$ . The predicted composition profile shows sharp changes of composition with distance near the two electrodes over a distance of about 0.05 cm, and the initial composition ( $X_{AgNO3} = 0.2$ ) in the middle part. Analysis of the salt extracted from six slices in this middle part, at distances of 0.03  $\rm cm$  to 0.5  $\rm cm$  from the anode, gives a composition  $X_{\rm AgNO3}$  = 0.2  $\pm$  0.005. For the end slice, situated at the cathode and 0.07 cm thick, the analysis gives a composition  $X_{AgN03} = 0.175$ . The predicted average composition of this slice,  $X_{AgN03} = 0.180$ , is in excellent agreement with the measured composition. The slice touching the anode fragmented during the cutting, preventing analysis of the salt. A second frit, of thickness 0.660 cm, was electrolyzed with the same salt mixture for 30 s at 0.3 A cm<sup>-2</sup>. After cooling, the frit was cut into ten slices. The general shape of the predicted profile is similar to that in the previous experiment. It extends from  $X_{AgNO3} = 0.34$  at anode to  $X_{AgNO3}$ = 0.04 at cathode. Eight central slices, located at distances of 0.1 to 0.58 cm from the anode, have compositions  $X_{AgNO3} = 0.2 \pm 0.004$ . The slice near anode (distance: 0.03 cm to 0.09 cm) has a composition  $X_{Ag}$  = 0.215. The predicted average concentration,  $X_{AgNO3}$  = 0.211, is in excellent agreement with the measured concentration. The slice touching the cathode (0.066 cm thick) has a measured composition  $X_{AgNO_3} = 0.163$ . The predicted composition,  $X_{AgNO_3} = 0.150$ , is in

good agreement with the measured one.

Although better resolution of the distance would provide a more accurate test of the shape of the predicted profile, these results clearly show an increase in the AgNO<sub>3</sub> content at the anode and a decrease of the AgNO<sub>3</sub> content at the cathode. The direction and the magnitude of the observed composition changes confirm these predicted from the model. Analyses by SEM-EDX, under way, should provide better tests of the predictions for profile shapes.

#### Potentiometric Determinations

The potential difference on open circuit, between one electrode and the reference electrode in the melt of initial composition is directly related<sup>18</sup> to the silver nitrate composition,  $X_{el}$ , at the electrode by

$$E_{el} - E_{ref} = \frac{1}{F} \int_{X_{ref}}^{X_{el}} \frac{t_{Na}^{NO3}}{1 - X_{Ag}} d\mu_{AgNO_3}$$
(5)

where  $\mu_{AgNO_3}$  = RT ln  $X_{Ag}$   $f_{AgNO_3}$  and the activity coefficient of  $AgNO_3$  at 300°C is taken from reference (16) as

RT ln 
$$f_{AgNO_3} = B_2 (1 - X_{Ag})^2 + B_3 (1 - X_{Ag})^3 + B_4 (1 - X_{Ag})^4$$
 (6)

with  $(J \text{ mol}^{-1})$ :  $B_2 = 12.22 \times 10^3$ ;  $B_3 = -18.03 \times 10^3$ ;  $B_4 = 9.25 \times 10^3$ . After a known time of electrolysis the current is cut off and the diffusional relaxation to the uniform initial composition is followed by measuring the potentials of cathode and of anode, relative to the reference electrode, as they decay back to zero. Typically, the potential difference between two electrodes prior to electrolysis is  $\pm 0.02$  mV. After electrolysis the decay from 20 mV to few hundredths of a millivolt is recorded with a 7046 A Hewlett-Packard X-Y recorder. This decay is virtually complete within about 30 minutes after the cutoff of the current. At zero time of relaxation, the potentials give the compositions reached at both electrodes at the end of electrolysis. The potential relaxation curves reflect the composition profile at the end of the electrolysis since the solution of the diffusion equation during relaxation includes the composition profile at the end of electrolysis as the initial condition. Figure 3 shows experimental and calculated potential relaxations together (in the upper part) with the corresponding calculated composition profiles at the end of electrolysis. The two runs are electrolyses of differing duration and differing current density such that the number of Coulombs is constant. The comparison of the experimental data from the two runs shows: first, that the concentration at the electrode after electrolysis does

not depend only on the number of coulombs, as would be the case if only the faradaic processes at electrodes were involved (i.e., with no contribution from diffusion and migration); second, there is little difference in the quality of the fit of the model to the experimental data between the run at 30 seconds and the run at 2 minutes of electrolysis. This suggests that convection (not yet taken into account in the model) does not eliminate the separation, likely because of the containment of the melt by a silica frit; however, at long relaxation times the potentiometrically measured composition gradients relax faster than predicted, probably because of convection. Experimental emf relaxations after electrolysis at 0.15 A  $cm^{-2}$  at differing duration are summarized in Figure 4. Experiments have been made with frits of thickness in the range 0.250-0.350 cm. The symbols for the experimental data indicate the time of electrolysis. On the right-hand side, the emf values are converted into compositions at the electrodes with equations (4), (5), and (6). Table I gives the silver nitrate compositions at the electrodes after electrolysis. The zero time concentrations are calculated from graphical extrapolations of the experimental potentials plotted against square root of time.

Time of Electrolysis (s)	0	2.5	7.5	15	20
X <sub>AgNO3</sub> Cathode	0.200	0.174	0.160		0.140
X <sub>AgNO3</sub> Anode	0.200	0.222		0.253	

Table I

As the time of electrolysis increases, the  $AgNO_3$  concentration decreases at the cathode and increases at the anode. Changes in composition of the order of 30% are observed after a time of electrolysis of 20 seconds. The calculated curves are in excellent agreement with the measured ones for the entire relaxation. It should be noted that no adjustable parameters were used in the calculation.

Although no attempt was made to fit the model to the data with adjustable parameters, the magnitudes and trends observed for the deviations of the predictions from experiment may be compared with the expected effects of factors not incorporated in the model. Thus, convection should cause the relaxing emf to lie closer to zero than the predicted emf, and this deviation should increase with length of electrolysis and relaxation time. Dendrite formation at the cathode and "chunking" at the anode should decrease the measured change of concentration from its initial value by decreasing the effective current density from the value calculated with the geometric electrode area. On the other hand, partial blocking of the electrode surface by the solid portions of the porous frit should increase the current density and the concentration change. Finally, tortuosity in the frit would decrease the effective diffusion coefficient of the mix-Table II summarizes standard deviations, calculated for 15ture. 20 points, along several anodic and cathodic relaxation curves, following electrolyses of differing duration (column 2). The third column gives the signs of the deviations of the absolute values of the electrode potentials from the experimental." The five last columns give the signs of the deviations expected from convection, dendrite formation, chunking, blocking by the frit and poor contact angle. Column 2 shows that the "fits" at the anode are very slightly better than those at the cathode. The deviations at the anode change sign during the electrolysis, but in the opposite sense for the two runs, thus giving no indication of a systematic trend.

	Ti Elec	me of trolysis	Standard	Sign o	f	Sig	n of ( E <sub>cal</sub>	_  -  E <sub>exp</sub>  ;	expected	from:
	and in	Symbol Fig. 4	(mV)	$( \mathbf{E}_{calc}  -  \mathbf{E}_{calc} )$	exp )*	Convection	Dendrites	Chunking	Blocking	Poor Contact Angle
e	2.5	(0)	.47		-	+	+		-	-
hoc	7.5	(4)	.07		-	+	+		-	-
Cat	20.0	(□)	.83		+	+	+		-	-
le	2.5	(•)	.19	short time long time	+ -	+		+	-	-
Anoc	15.0	(•)	.54	short time long time	- +	+		+	-	-

Table II

The signs of the deviations in the three cathodic runs remain unchanged throughout a run, but are negative for short electrolysis times and positive at the longer electrolysis time, in the direction expected from convection and/or dendrite formation. With the effective current density in the computation reduced by 20%, the standard deviation drops from 0.83 to 0.77 and some deviations, in the middle part of the relaxation curve, become negative. On the other hand, a decrease in the effective current density in the calculation at the anode leads to larger standard deviations. A systematic difference also may arise

\*The sign of  $|E_{calc}| - |E_{exp}|$ , whether for anode or cathode, indicates whether the relaxing emf is closer to zero (positive) or farther from zero (negative) than the calculated emf.

from the porosity of the silica matrix, which increases the effective diffusion path. An increased effective electrode separation would lead to significant changes in the predicted profiles at current densities and electrolysis times such that the diffusion layers at the two electrodes interfere;<sup>10</sup> however, calculations for our experimental conditions of current density and of electrolysis time show that the diffusion layers are independent.<sup>19</sup> A decrease in the diffusion coefficient would not change much the predicted relaxation curves. Experiments are under way under conditions such that the diffusion layers are expected to interfere in order to study the effect of tortuosity in the frits. It appears that the effects of convection and changes of effective electrode surface area are not large, and are partly compensating in this system.

## CONCLUSIONS

Composition gradients at the electrodes were measured following electrolysis of molten  $AgNO_3$ -NaNO\_3 mixtures between silver electrodes. Potentiometric analysis of the compositions at the electrodes on termination of the electrolysis and during diffusional relaxation of the gradient confirmed predictions from a mass transport model, using independent experimental values of the interdiffusion coefficient, activity coefficients and the transference number. Chemical analysis of quenched electrolyte also confirmed the gradients. The ion flows in this system are analogous to those in a Li/LiCl-KCl/S battery, suggesting that similar gradients could develop - of the order of 30% after 20 seconds of electrolysis at 0.15 A cm<sup>-2</sup>. Such composition changes require consideration in the optimization of electrolytes and in the avoidance of formation of solid phases such as LiCl, KCl, or J-phase in molten salt batteries.<sup>10,20</sup>

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<u>Figure 1</u>. Ion Flow Analogies in Li/S Battery with LiCl/KCl as the Electrolyte (left) and in  $KNO_3$ -AgNO<sub>3</sub> Electrolyzed Between Silver Electrodes (right).



Figure 2. Silica Cell for Electrolysis of Molten Salt Mixture and for Potentiometric Measurement of Composition Changes at Electrodes.



<u>Figure 3.</u> Predicted Composition Profiles at the End of Electrolysis, and Subsequent Potential Relaxation on Open Circuit.

- Top: Predicted Profiles after Electrolyses at 9C  $\rm cm^{-2}$ .
- Bottom: Subsequent Anodic Potential Relaxations.

 $\Delta$ , 0 experimental; - predicted from the model.





# ELECTRONIC CONDUCTION IN MOLTEN POTASSIUM CHLORIDE\*

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# Abstract

The Wagner-Hebb polarization technique, usually applied to solids, has been employed to measure electronic conductivity in molten KCl. Steady-state currents were measured at various applied voltages for the cell

 $Ta(s) + KCl(\ell) + K-Bi(\ell)$ 

Results showed the electronic conductivity to be proportional to the activity of K in KCl at temperatures between 800°C and 860°C and for activities of potassium less than 0.02. The apparent mobility and diffusion coefficient of electrons are reported as well as the activity coefficient of K in KCl and the transference number of ions.

# Introduction

Molten salts generally possess a very high ionic conductivity making them useful industrial and scientific electrolytes. They also have a component of electronic conductivity which can often have important effects on electrochemical measurements. (1-2) In contrast to the ionic conductivity, the electronic component depends strongly on the metal to non-metal ratio of the salt. This work reports on results for molten KC1.

Bredig and Bronstein<sup>(3)</sup> have measured the increase of conductivity of molten KCl with addition of K metal up to a concentration of 10 mole % K. The electronic conductivity was obtained as a function of K concentration. In this work the electronic conductivity is obtained as a function of potassium activity and only quite dilute solutions were studied ( $a_{\rm K} < .02$ ,  $x_{\rm K} < .007$ ). Measurements were performed on the cell

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**(I)** 

where the K-Bi alloy, with known activity of K, acts as a reference electrode and Ta acts as a negative inert electrode. Steadystate currents were measured for applied voltages below those needed to decompose KCl so that ionic currents were suppressed. Under these conditions the steady-state current is given by the expression

$$i = \frac{RT}{FG} \left\{ \sigma_{e}^{\text{ref}} \left[ \exp\left(\frac{EF}{RT}\right) - 1 \right] + \sigma_{h}^{\text{ref}} \left[ 1 - \exp\left(-\frac{EF}{RT}\right) \right] \right\}$$
(1)

where G is the cell constant, E is the applied voltage,  $\sigma_e^{\text{ref.}}$  is the electronic conductivity of KCl equilibrated with the reference electrode and  $\sigma_b^{\text{ref.}}$  the corresponding electron-hole conductivity.

Under very reducing conditions the current, due to electron holes, can usually be neglected so that

$$i = \frac{RT}{FG} \sigma_{e}^{ref.} \left[ exp\left(\frac{EF}{RT}\right) - 1 \right]$$
 (2)

The assumptions used to arrive at equation (2) have been discussed by Wagner<sup>(4)</sup> for solids. The extension to ionic liquids requires that convection be eliminated in the melt. Validity of equation (2) also requires that the metal to non-metal ratio does not deviate considerably from the exact stoichiometric ratio so that only dilute solution of K in KCl can be studied. It is assumed that the Nernst-Einstein equation holds for the transport of electrons

$$\sigma_{\rm e} = \frac{{\rm D}_{\rm e} F^2}{{\rm RT}} \frac{{\rm x}}{{\rm V}_{\rm m}}$$
(3)

where  $D_e$  is the diffusion coefficient of electrons and  $V_m$  is the molar volume of KCl. The electronic conductivity is proportional to the activity of potassium and is given by the expression

$$\sigma_{\rm e} = \left(\frac{\sigma_{\rm e}^{\rm ref.}}{a_{\rm K}^{\rm ref.}}\right) a_{\rm K} \tag{4}$$

Also the activity coefficient of K in KCl is essentially constant over the region of activity studied using cell (I).

Thus by measuring steady-state currents from cell (I), one may obtain  $\sigma_e^{\text{ref}}$  and knowing the activity of the reference electrode<sup>(5)</sup>one calculates the electronic conductivity as a function of K activity.

The diffusion coefficient of electrons and their apparent mobility were also studied. The two quantities are related by the equation

$$D_{e} = \frac{RT}{F} u_{e}$$
 (5)

which is another form of the Nernst-Einstein equation. These quantities were obtained by two methods.

The work of Bredig and Bronstein and this work overlap in their dilute measurements. Since they obtain the electronic conduction as a function of mole fraction of potassium and cell (I) yields  $\sigma_e$  as a function of activity comparison yields the activity coefficient of potassium. Equation (3) may be written in the form

$$D_{e} = \frac{\sigma_{e}^{ref.}}{a_{K}^{ref.}} \frac{RT}{F^{2}} V_{m} \gamma_{K}$$
(6)

since potassium metal dissolves as  $K^+$  ions and electrons. Thus  $D_e$  and  $u_a$  are obtained.

The second method involves transient measurements on cell (I) according to a method discussed by Weiss,  $^{(6)}$  Rickert,  $^{(7)}$  and J. B. Wagner.  $^{(8)}$  After steady-state values of current were reached in cell (I), the applied voltage was removed and the open circuit voltage was measured as a function of time. This voltage is given by the expression

$$E = \frac{RT}{J} \ln \frac{n^{Ta}}{\frac{e}{n_{e}}}$$
(7)

Solution of Fick's second law for the appropriate boundary conditions has been given by Rickert for short time as

$$n_{e}^{Ta}(t) = n_{e}^{Ta}(t=0) \left(1 - \frac{2}{\ell} \sqrt{\frac{D}{\frac{e}{e}}} \right)$$
(8)

From equation (7)

$$E(t) - E(t = 0) = \Delta E(t) = \frac{RT}{F} \ln \left(1 - \frac{2}{\ell} \sqrt{\frac{D}{e}} \frac{t}{\pi}\right)$$
(9)

so that

$$t = \frac{\ell^2 \pi}{4 D_e} \left[ \exp\left(\frac{\Delta E F}{RT}\right) - 1 \right]^2$$
(10)

Thus a plot of  $\left[\exp\left(\frac{\Delta EF}{RT}\right) - 1\right]^2$  vs t yields values of  $D_e$ .

## **Experimental Details**

The experimental arrangement of cell (I) is schematically shown in Figure 1. Since convection in the melt must be eliminated for the measurements, two techniques were used. (1) A capillary of 0.79 mm. diameter with a close fitting tantalum wire was used as the inert electrode. The salt column was 1.4 cm long. (2) An alumina tube of 0.6 cm inside diameter was filled with fine alumina powder for a length of 1.4 cm and a tantalum electrode was fitted over this. Both electrodes dipped into the molten KCl as shown and gave essentially the same results. A three electrode arrangement was used for the measurements on each of the above electrodes so that the refernce electrode would not be polarized. The pool at the bottom of the cup served as a working electrode and the reference electrode consisted of a K-Bi alloy ( $x_K \cong 0.10$ ) contained in an alumina tube with a small hole to connect to the salt and a tantalum wire for electrical connections.

The cell constant for both cell arrangements was obtained by measuring the ac resistance between the pool and the respective inert electrode with an ac bridge. The cell constant was then calculated by the expression

$$\mathbf{G} = \mathbf{R}\,\boldsymbol{\sigma}_{\mathrm{ion}} \tag{11}$$

Values of  $\sigma_{ion}$  were obtained from measurements of Van Artsdalen and Yaffe. (9)

The K-Bi alloys used for both reference and working electrodes were prepared in situ. A glassy carbon electrode (not shown in figure) dipped into the salt. The alloys were generated by electrolysis between previously weighed bismuth pools and the carbon electrode at a potential of about 3.5 volts. A PAR digital coulometer monitored the concentration of K in the Bi of the reference and working electrodes. This concentration was checked occasionally by coulometric analysis. A stainless steel sheathed chromel-alumel thermocouple was used to measure temperature. The entire cell fitted into a larger Vycor container which served to maintain an inert atmosphere of purified argon.

Single crystal KCl of 99. 999% purity was used in the experiments.

# **Results and Discussion**

Steady-state currents measured in cell (I) at various applied voltages are shown in Figure 1 at temperatures of 800°C, 830°C, and 860°C. From equation (2)

$$\log\left(\frac{iFG}{RT}\right) = \log \sigma_{e}^{ref} + \log \left[\exp\left(\frac{EF}{RT}\right) - 1\right]$$
(12)

Thus Figure 1 shows that equation (2) is obeyed and the intercepts give  $\sigma_{e}^{\text{ref}} \cdot \text{at}$  three temperatures. The electronic conductivity may be calculated as a function of potassium activity from equation (4) and results are shown in Table 1.

# Table 1

# Electronic Conductivity of KCl for $a_{\rm K} < 0.02$

T°C	a <sup>ref.</sup> K	σ <sup>ref.</sup> e	σ <sub>e</sub>	$t_{ion}(a_{K} = 0.01)$
800 830	$3.4 \times 10^{-5}$ $4.22 \times 10^{-5}$ $5.10 \times 10^{-5}$	$7.08  imes 10^{-4}$ $1  imes 10^{-3}$ $1.58  imes 10^{-3}$	20 $a_{\rm K}$ 24 $a_{\rm K}$ 31 $a$	0.92 0.91

The activity of K in the reference electrode was obtained at various temperatures by assuming that the excess free energy of mixing K in Bi obtained by Lantratov et. al. was constant with temperature (regular solution). The transference number of ions in KCl is given by the expression

$$\mathbf{t}_{\text{ion}} = \frac{\sigma_{\text{ion}}}{\sigma_{\text{ion}} + \left(\sigma_{\text{e}}^{\text{ref}} \cdot / a_{\text{K}}^{\text{ref}}\right) a_{\text{K}}}$$
(13)

and is shown as a function of  $a_{\kappa}$  in Table 2.

# Table 2

# Transference Number of Ions in KCl as a Function of Potassium Activity

K	<b>x</b> <sub>K</sub>	tion
10 <sup>-4</sup>	$3.8 \times 10^{-5}$	. 999
$5 \times 10^{-4}$	$1.9  imes 10^{-4}$	. 995
10-3	$3.8 \times 10^{-4}$	. 991
$5 \times 10^{-3}$	$1.9 \times 10^{-3}$	. 957
10-2	$3.8 \times 10^{-3}$	. 918
$2 \times 10^{-2}$	7.7 $ imes$ 10 <sup>-3</sup>	. 848

The results of Bredig and Bronstein<sup>(1)</sup> can be represented by the equation  $\sigma_e = 60 x_K$  for  $x_K < 0.01$  and  $T \simeq 820$  °C. Results here show that  $\sigma_e = 23 a_K$  so one obtains  $\gamma_K = 2.6$  for the activity coefficient of K in KCl at 820 °C and  $a_K < 0.02$ . From equation (6) one obtains

 $D_e = 2.9 \times 10^{-3} \text{ cm}^2/\text{sec}$  $u_e = 0.03 \text{ cm}^2/\text{volt} \cdot \text{sec}$ 

Voltage relaxation measurements were also taken on cell (I) and for the packed column they yielded a straight line when  $\left[\exp\left(\frac{\Delta EF}{RT}\right) - 1\right]^2$  was plotted against t. Figure 3 shows one such decay curve. Values of  $D_e$  obtained from several curves at several steady-state potentials ranged in value from  $2\times10^{-3}$  to  $3\times10^{-3}$  in good agreement with results from Bredig and Bronstein. The capillary yielded much smaller values of  $D_e$  and were discarded. It is believed that potassium metal trapped in the upper portions of the capillary interfered with the readings.

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FIGURE 1. EXPERIMENTAL ARRANGEMENT OF CELL (I).





FIGURE 3. VOLTAGE RELAXATION MEASUREMENTS ON CELL (1) AT 800°C,

## A COMPARISON OF REFERENCE ELECTRODES IN

# MOLTEN SODIUM SULFATE

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# ABSTRACT

Four commonly used electrodes in molten sulfate melts have been combined to form six interrelatable galvanic cells. The dependencies of cell emf on sodium oxide activity and oxygen activity of a pure  $Na_2SO_4$  melt at 1200K have been studied and interpreted. Only a platinum wire immersed in the melt provided behavior inconsistent with a simple interpretation, in this case, an equilibrium of molecular oxygen and oxide ions in the melt. An interference of superoxide and peroxide ions, and the formation of corrosion products on the platinum electrode, are suggested as the cause of the inconsistent electrode behavior.

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# Introduction

The study of the effect of molten sodium sulfate on the hot corrosion of superalloys makes extensive use of electrochemical measurements. Previously<sup>1-7</sup> several reference-and indicator-electrodes have been used, but apparently no systematic study of the electrodes has been published.

The electrodes examined in this study are (1) the  $Ag/Ag^+$  electrode, (2) the  $ZrO_2/oxygen$  electrode, (3) the  $SO_2/O_2$  gas electrode, and (4) bare Pt wire and/or foil electrodes in the melt (in some instances Pt was substituted by Au). These four electrodes combine to give six different electrochemical cells.

## Experiment

The basic experimental setup is shown in Fig. 1. The molten  $Na_2SO_4$  was contained in an alumina crucible inside a 15cm OD mullite tube in a vertical electric furnace. The mullite tube had a water-cooled brass flange sealed by epoxy. Brass O-ring couplings were sealed to the flange, and the electrodes were inserted into the melt through these couplings. Also gas inlet and outlet tubes were passed through the brass flange. The electrodes were positioned so that they were inside the alumina crucible and immersed in the  $Na_2SO_4$  when the cell was brought to temperature (1200K). The  $Na_2SO_4$  was dried for several days at 200°C prior to use, and was added to the  $Al_2O_3$  crucible through a quartz or  $Al_2O_3$  addition tube that was inserted through a coupling in the brass flange.

The construction of the electrodes is shown in Fig. 2. Figure 2a shows the  $Ag/Ag^+$  electrode which consisted of a mullite tube (McDaniel MV30) containing a solution of  $10m/o Ag_2SO_4$ ,  $90m/o Na_2SO_4$ . Into this solution was immersed a 1 mm silver wire spotwelded to a platinum wire that served as the lead wire. Rahmel<sup>7,8</sup> reported that evacuation of the tube is not necessary. However, to minimize drift which would be caused by loss of  $SO_3$  from decomposition of the salt, the tube was sealed with a piece of Tygon tubing and a pinch clamp. The ease of fabrication and stability of this electrode, make it well suited for use with molten sodium sulfate. One negative aspect of this electrode is evidence for transport of Ag through the mullite tube. The part of the tube that contained the  $Ag_2SO_4/Na_2SO_4$  mixture became dark in color, and silver could be detected in the  $Na_2SO_4$  in the crucible. Transport of silver through a Na<sup>+</sup> ion conductor has been reported previously at lower temperatures with Pyrex<sup>7</sup> and at high temperatures with mullite <sup>9</sup>.

The  $2rO_2$  oxygen electrode, shown in Fig. 2b was prepared by platinizing the inside of the  $2rO_2$  tube at the bottom. The reference gas on the inside of the tube was air. Electrical contact with the platinized area is obtained by placing a Pt/Pt+lORh thermocouple in an alumina protection tube and spring loading it inside the  $2rO_2$  tube to ensure positive electrical contact. The tubes used were either partially stabilized 3.5 w/o CaO or fully stabilized 7.5 w/o Y $_{2O_2}$  zirconia manufactured by Zircoa. They would break easily from thermal shocks, and great care had to be exercised when heating and cooling the tubes.

The  $SO_2/O_2$  gas electrode is basically the same as used by Stroud and Rapp<sup>11</sup>, and is shown schematically in Fig. 2c. A small amount of  $Na_2SO_4$  was placed in a mullite tube (McDaniel MV30). An equilibrated mixture of  $SO_3$ ,  $SO_2$  and  $O_2$  was passed over the salt, and a 20 mil Pt wire was inserted into the  $Na_2SO_4$  as an electrode. The  $SO_2/O_2$  gas preliminarily passed over a catalyst of platinized ceramic material so that by fixing the  $P_{SO_3}$  in the gas phase, the basicity of the  $Na_2SO_4$  was fixed and the electrode should maintain a fixed potential.

The gas used in the electrode was  $SO_2$  (Matheson) containing 1 ppm  $O_2$ . This small amount of  $O_2$  made the electrode potential very sensitive to small

changes in flow rate, indicating that it was difficult to establish the  $SO_3/SO_2/O_2$  equilibrium. Several arrangements were tried in order to ensure establishment of equilibrium within the gas phase. The arrangement used for most of the experiments was that shown in Fig. 2c. Some of the platinized material was crushed into small particles and filled into the gas inlet tube of the electrode. This should have ensured better gas/catalyst contact, but the flow rate dependence still persisted.

Figures 3a and 3b show how the Pt (and Au) electrodes were arranged for large amounts of melt (a) and for small amounts and thin films of sodium sulfate (b). When large amounts of salt were used, one electrode was completely submerged in the melt while the other was about half submerged and half extending out of the melt.

The sodium sulfate electrolyte decomposes according to the reaction

$$Na_2SO_4 = Na_2O + SO_3$$

and the basicity of the melt can therefore be fixed by fixing the  $P_{SO_{\tau}}$  in the gas phase over the melt.

The gas compositions used and the corresponding basicities (activity of  $Na_2^{0}$ ) in the melt are shown in Table I. To extend further the range of  $a_{Na_2^{0}}$ ,  $Na_2^{0}$ 

was added to the melt when pure oxygen was used as the gas; some additions of  $Na_2S_2O_7$  were made to reduce the oxide activity.  $Na_2O_2$  was used rather than  $Na_2O$  because of the hygroscopic nature of  $Na_2O$ . The thermal decomposition was assumed to be rapid, so that the  $Na_2O_2$  addition actually became  $Na_2O$ .

The solid materials dipping into the salt have a finite solubility in the salt. The molten salt will consequently not be completely pure and it is impossible to control accurately the composition of the melt.

## Electrochemical cells and proposed cell reactions

The four electrodes can be combined into six different cells. These cells and their proposed

Nernst equations are:

Cell A The cell arrangement is

and the proposed reactions are:

$$0^{2^{-}}(ZrO_{2}) = 1/2 O_{2}(r) + 2 e^{-} (anode/ZrO_{2})$$

$$0^{2^{-}} = 0^{2^{-}}(ZrO_{2}) (ZrO_{2})' solution)$$

$$Na_{2}O' = 0^{2^{-}} + 2Na^{+'}$$

$$2 Na^{+'} = 2 Na^{+} (mullite) ('solution/Rullite)$$

$$2 Na^{+} (mullite) = 2 Na^{+''} (mullite/''solution)$$

$$2 Na^{+''} + Ag_{2}SO_{4}'' + 2 e^{-} = Na_{2}SO_{4}'' + 2 Ag (cathode)$$

$$Na_{2}O' + Ag_{2}SO_{4}'' = 1/2 O_{2}(r) + Na_{2}SO_{4}'' + 2 Ag (A-1)$$

From the overall reaction involving two electrons one obtains:

$$E_{A} = E_{A}^{\circ} - \frac{2.3RT}{2F} \frac{\log^{\frac{p_{1}^{2}}{2}(r)}}{a_{Na_{2}} o' a_{Ag_{2}} SO_{4}^{''}}$$
(A-2)

since  $a_{Ag} = 1$  for pure Ag. Upon combining the activities of the salt in the Ag/Ag+ electrode and the  $P_{O_2}(r)$  term we obtain

$$E_{A} = E_{A}^{\circ'} + \frac{2.3RT}{2F} \log a_{Na_{2}}^{\circ} O'$$
 (A-3)

where

$$E_{A}^{\circ} = E_{A}^{\circ} - \frac{2.3RT}{2F} = \log \frac{a_{Na_{2}}SO_{4}^{\circ}}{a_{Ag_{2}}SO_{4}^{\circ}} - \frac{2.3RT}{4F} \log P_{O_{2}}(r) \quad (A-4)$$

and  $E^{\,o}_{A} \text{can}$  be calculated from

$$E_{A}^{\circ} = -\frac{1}{2F} \left[ \Delta G_{f}^{\circ}(Na_{2}SO_{4}) - \Delta G_{f}^{\circ}(Na_{2}O) - \Delta G_{f}^{\circ}(Ag_{2}SO_{4}) \right] (A-5)$$
  
if the thermodynamic data are known. Table II gives  
the thermodynamic data that are appropriate for these  
calculations. Most of the data is obtained from  
JANAF<sup>10</sup>, but  $\Delta G_{f}^{\circ}(Ag_{2}SO_{4})$  is not available at 1200K.  
Extrapolation of low temperature data<sup>10-13</sup> gives  
for  $\Delta G_{f}^{\circ}(Ag_{2}SO_{4})$  at 1200 K the value 78,736 cal/mol  
(-328.4kJ/mol) in reasonable agreement with the  
data reported for cell E. The thermodynamic data  
indicate that  $E_{A}^{\circ} = 1.63$  volts and  $E_{A}^{\circ}' = 1.56$  volts.

 $\rm E_A^{\circ}'$  is calculated assuming the 10 m/o  $\rm Ag_2SO_4/Na_2SO_4$  mixture is an ideal solution.

Cell B The cell arrangement is

(-) 
$$G_2(r)$$
, Pt  $ZrO_2(O^{2-})$   $Na_2SO_4'$ ,  $O^{2-4}$ , Pt (+)

and the electrode reactions and equilibria are

$$0^{2^{-}}(ZrO_{2}) = 2 e^{-} + 1/2 O_{2}(r) \qquad (anode/ZrO_{2})$$

$$0^{2^{-}} = 0^{2^{-}}(ZrO_{2}) \qquad (ZrO_{2}') \text{ solution}$$

$$\frac{1/2 O_{2}' + 2 e^{-} = 0^{2^{-}}}{1/2 O_{2}(r)} \qquad (cathode/solution)$$

$$1/2 O_{2}' = 1/2 O_{2}(r) \qquad (B-1)$$

and

\_

$$E_{B} = -\frac{2.3RT}{4F} \log P_{O_{2}}(r) + \frac{2.3RT}{4F} \log P_{O_{2}}(r)$$
(B-2)

For  $P_{0_2}(r) = 0.21$  atm at 1200K

$$E_{\rm B} = 0.040 + 0.0595 \log P_{\rm O_2}^{*}$$
 (B-3)

<u>Cell C</u> This cell combines the gas electrode and  $\text{ZrO}_2$  electrode

for which the Nernst equation is

$$E_{C} = E_{C}^{\circ} - \frac{2.3RT}{2F} \log \frac{a_{Na_{2}}SO_{4}^{\prime\prime\prime} a_{Na_{2}}O^{\prime}}{a_{Na_{2}}^{2}O^{\prime\prime} P_{SO_{2}}^{\prime\prime\prime} P_{O_{2}}^{2} (r)}$$
(C-2)

Upon rearranging (C-2) one obtains

$$E_{C} = \left\{ E_{C}^{\circ} + \frac{2.3RT}{2F} \log \left( a_{Na_{2}O}^{2} p_{O_{2}}^{**} P_{O_{2}}^{1/2}(r) \right) - \frac{2.3RT}{2F} \log a_{Na_{2}O}^{\circ} \right\}$$
(C-3)

with a 
$$\operatorname{Na}_2 \operatorname{SO}_4^{\prime\prime\prime} = 1$$
, where  

$$E_{C}^{\circ} = \frac{-1}{2F} \left[ \Delta G_{f}^{\circ} (\operatorname{Na}_2 \operatorname{SO}_4) - \Delta G_{f}^{\circ} (\operatorname{Na}_2 \operatorname{O}) - \Delta G_{f}^{\circ} (\operatorname{SO}_2) \right]$$
(C-4)

From the thermodynamic data of Table II,  $E_C^{\circ}$  = 1.91 volts. The second term in Eq. (C-3) depends on the composition of the gas in equilibrium with the molten Na<sub>2</sub>SO<sub>4</sub>.

Cell D Cell D combines the  ${\rm Ag/Ag}^+$  electrode and the Pt electrode in the melt

$$O'_2$$
,  $SO'_2$ , Pt mullite  
(-)  $Na_2SO'_4$   $Na^+$  10 mW o  $Ag_2SO''_4$ ,  $Na_2SO''_4$ ,  $Ag$  (+)

$$0^{2^{-}} = 2e^{-} + 1/2 0_{2}'$$
(anode)  

$$Na_{2}O' = 2 Na^{+'} + 0^{2^{-}}'$$
('solution)  

$$2 Na^{+'} = 2 Na^{+} (mullite)$$
('solution/mullite)  

$$2Na^{+} (mullite) = 2 Na^{+''}$$
(mullite/''solution)  

$$2Na^{+''} + Ag_{2}SO_{4} + 2e^{-} = 2 Ag + Na_{2}SO_{4}''$$
(cathode)  

$$Na_{2}O' + Ag_{2}SO_{4}' = 1/2 O_{2}' + 2 Ag + Na_{2}SO_{4}''$$
(D-1)

And the resultant equation for the above equilibrium reaction is

$$E_{\rm D} = E_{\rm D}^{\circ} - \frac{2.3 \text{RT}}{2\text{F}} \log \frac{\frac{{\rm P}_{\rm O_2}^{1/2} \, a_{\rm Na_2} \text{SO}_4^{\prime \prime}}{{\rm a}_{\rm Na_2} \, o' \, a_{\rm Ag_2} \text{SO}_4^{\prime \prime \prime}}$$
(D-2)

where 
$$a_{Ag} = 1$$
. Upon rearranging  
 $E_{D} = \left\{ E_{D}^{\circ} - \frac{2.3RT}{2F} \log \frac{Na_{2}SO_{4}}{a_{Ag_{2}SO_{4}}} \right\} + \frac{2.3RT}{2F} \log \frac{a_{Na_{2}O'}}{P_{O_{2}}^{1/2}}$ 
(D-3)

and

$$E_{D}^{\circ} = -\frac{1}{2F} \left[ \Delta G_{f}^{\circ}(Na_{2}SO_{4}) - \Delta G_{f}^{\circ}(Na_{2}O) - \Delta G_{f}^{\circ}(Ag_{2}SO_{4}) \right]$$
(D-4)

When the thermodynamic data given in Table II are employed,  $E_D^{\circ} = 1.63$  volts, and if the solution of 10 m/o  $Ag_2SO_4$  and 90 m/o  $Na_2SO_4$  is an ideal solution then the second term of Eq. (D-3) is 0.114 volts at 1200K<sub>a</sub> and the term

$$E_{\rm D}^{\circ} - \frac{2.3 \text{RT}}{2\text{F}} \log \frac{-\text{Na}_2 \text{SO}_4}{\text{a}_{\text{Ag}_2 \text{SO}_4}} = 1.52 \text{ volts.}$$

<u>Cell E</u> Cell E is an important cell because it should be independent of the gas and salt compositions of the test melt. The cell is a combination of the gas electrode and the  $Ag/Ag^+$  electrode:

$$2 \text{ Na}_{2}0''' + \text{ SO}_{2}'' = 2 \text{ Na}^{+ '''} + \text{ Na}_{2}\text{SO}_{4}'' + 2e^{-} \quad (\text{anode})$$

$$2 \text{ Na}^{+ i''} = 2 \text{ Na}^{+} (\text{mullite}) \quad (\overset{\texttt{W}}{} \text{ solution/mullite})$$

$$2 \text{ Na}^{+} (\text{mullite}) = 2 \text{ Na}^{+'} \quad (\text{mullite}/\text{ solution})$$

$$2 \text{ Na}^{+'} = 2 \text{ Na}^{+} (\text{mullite}) \quad (\text{'solution/mullite})$$

$$2 \text{ Na}^{+}(\text{mullite}) = 2 \text{ Na}^{+} \text{II} \qquad (\text{mullite/ solution})$$
$$2 \text{ Na}^{+} \text{II} + \text{Ag}_{a} \text{SO}_{4}^{\text{II}} + 2e^{-} = \text{Na}_{a} \text{SO}_{4} + 2 \text{ Ag} \qquad (\text{cathode})$$

$$2Na_2O''+ SO_2''+ Ag_2SO_4''= Na_2SO_4''+ 2 Ag + Na_2SO_4''$$
 (E-1)

$$E_{\rm E} = E_{\rm E}^{\circ} - \left[ \frac{2.3 \text{RT}}{2\text{F}} \log \frac{{}^{\text{a}}\text{Na}_2 \text{SO}_4^{\ \text{i}} - {}^{\text{a}}\text{Na}_2 \text{SO}_4^{\ \text{i}}}{{}^{\text{a}}\text{Ag}_2 \text{SO}_4^{\ \text{i}} - {}^{\text{a}}\text{Na}_2 \text{O}^{\ \text{i}} - {}^{\text{i}}\text{SO}_2^{\ \text{i}}} \right]$$
(E-2)

where

$$E_{\rm E}^{\circ} = -\frac{1}{2F} \left[ \Delta G_{\rm f}^{\circ}(Na_2SO_4) - \Delta G_{\rm f}^{\circ}(Na_2O) - \Delta G_{\rm f}^{\circ}(SO_2) \right] \\ -\frac{1}{2F} \left[ \Delta G_{\rm f}^{\circ}(Na_2SO_4) - \Delta G_{\rm f}^{\circ}(Na_2O) - \Delta G_{\rm f}^{\circ}(Ag_2SO_4) \right]$$
(E-3)

The first term in Eq. (E-3) is equivalent to  $E^{\circ}_{C}$  and the second term is equivalent to either  $E^{\circ}_{A}$  or  $E^{\circ}_{D}$ . Thus

$$E_{\rm E}^{\rm o} = E_{\rm C}^{\rm o} + E_{\rm A}^{\rm o} \tag{E-4}$$

Based on the given thermodynamic data,  $E_E^{\circ} = 3.54$  volts. If the  $Ag_2SO_4/Na_2SO_4$  is ideal, then  $a_{Na_2}SO_4^{"}/a_{Ag_2SO_4}$  remains constant and Eq. (E-2) can be written as

$$E_{E} = \left\{ E_{E}^{\circ} - \frac{2.3RT}{2F} \log \frac{a_{Na_{2}}^{\circ}SO_{4}^{"}}{a_{Ag_{2}}^{\circ}SO_{4}^{"}} \right\} + \frac{2.3RT}{2F} \log \left(a_{Na_{2}}^{2}O_{2}^{"}P_{SO_{2}^{"}}\right) (E-5)$$

where the first term is constant and the second will vary if the flow rate in the gas electrode varies. If the silver sulfate/ sodium sulfate solution is ideal, the constant term becomes 3.43 volts.

Cell F Cell F is equivalent to the cell used by Stroud and Rapp: 14

$$(-) \begin{array}{c} SO_{2}^{\prime\prime\prime}, O_{2}^{\prime\prime\prime\prime} \\ Na_{2}SO_{4}^{\prime\prime\prime\prime} \end{array}, Pt \left| \begin{array}{c} Mullite \\ (Na^{+}) \end{array} \right| \left| \begin{array}{c} Na_{2}SO_{4}^{\prime\prime}, (Na_{2}O) \\ O_{2}^{\prime}, SO_{2}^{\prime}, \end{array} \right| Pt (+)$$

The equilibrium reactions are

$$2 \text{ Na}_{2}\text{O}^{'''} + \text{SO}_{2}^{'''} = \text{Na}_{2}\text{SO}_{4}^{'''} + 2 \text{ Na}^{+m} + 2e^{-} \qquad (\text{anode})$$

$$2 \text{ Na}^{+(''')} = 2 \text{ Na}^{+} (\text{mullite}) \qquad (''\text{solution/mullite})$$

$$2 \text{ Na}^{+} (\text{mullite}) = 2 \text{ Na}^{+'} \qquad (\text{mullite/'solution})$$

$$2 \text{ Na}^{+'} + \text{O}^{2-'} = \text{Na}_{2}\text{O'} \qquad ('\text{solution})$$

$$1/2 \text{ O}_{2}^{+} + 2e^{-} = \text{O}^{2-'} \qquad (\text{cathode})$$

$$2 \text{ Na}_{2}0^{\prime\prime} + \text{ SO}_{2}^{\prime\prime} + 1/2 \text{ O}_{2}^{\prime} = \text{ Na}_{2}\text{SO}_{4}^{\prime\prime\prime} + \text{ Na}_{2}\text{O'}$$
(F-1)

$$E_{F} = E_{F}^{\circ} - \frac{2.3RT}{2F} \log \frac{a_{Na_{2}}SO_{4}^{\circ H}a_{Na_{2}}O}{a_{Na_{2}}^{2}O''PSO_{2}^{\circ P}PO_{2}^{1/2}}$$
(F-2)

and upon rearranging

$$E_{F} = \left\{ E_{F}^{\circ} + \frac{2.3RT}{2F} \log \left( a_{Na_{2}0}^{2} P_{SO_{2}}^{\prime \prime \prime} \right) \right\} - \frac{2.3RT}{2F} \log \frac{a_{Na_{2}0}^{\prime}}{P_{O_{2}}^{1/2}} \quad (F-3)$$

where  $a_{Na_2SO_4}^{iii} = 1$  and

$$E_{\rm F}^{\circ} = -\frac{1}{2{\rm F}} \left[ \Delta G_{\rm f}^{\circ}({\rm Na}_2 {\rm SO}_4) - \Delta G_{\rm f}^{\circ}({\rm Na}_2 {\rm O}) - \Delta G_{\rm f}^{\circ}({\rm SO}_2) \right]$$
(F-4)

which is the same as  $E_{C}^{\circ}$ .

Since the reactions in Cells A through F are all consistent, the emfs of the cells are related and can be used to check the internal consistency of the measurements. Some of the relationships are

<sup>Е</sup> А	-	Е <sub>В</sub>	=	ED	(1)
<sup>E</sup> F	-	Е <sub>С</sub>	=	EB	(2)
<sup>E</sup> A	+	Еc	=	EE	(3)
E <sub>D</sub>	+	Е <sub>F</sub>	=	<sup>E</sup> E	(4)

In all cases that have been checked these relationships were always satisfied to within 2 - 3 mV, which is well within the accuracy of measurement. No matter what electrode reactions are postulated, so long as they are consistent for all cells, the above relationships are valid and will be obeyed. Of course, satisfying the above interrelationships in no way confirms the validity of the proposed chemical and electrochemical equilibria.

## Results

Open-circuit potential measurements (OCM) were made using either an Esterline-Angus recorder or a digital voltmeter (Data Precision), each of which have input impedances of 10 megohms. Figures 4 - 8 show how the emf of the various cells changed with time as the gas phase over the molten  $Na_2SO_4$  was changed. The gas compositions utilized are listed in Table I. Figures 9-11 show the effect of additions of  $Na_2O_2$  and  $Na_2S_2O_7$  to the melt when the gas phase was maintained as pure  $O_2$  or Ar (which also contained 20 ppm  $O_2$ ).

Examination of the cell emfs for gases D ("pure" Ar) and E (Ar with 100 ppm  $SO_2$ ) indicate that these gases were very similar in their effect. Gas B ( $SO_2$ )

caused a large sudden change in emf for cells A, B and C while cells D and F exhibited very little change. This result occurs because cells D and F should respond to changes in both  $a_{Na_2O}$  and  $P_{O_2}$ , while cells

A, B and C respond to only one of these parameters. Frequently a fairly large change occurred when the gas flow was first started, with a slow increase or decrease from that extreme value. This response indicates that reactions were taking place that slowly changed the  $a_{Na_20}$  in the salt. Figure 5 shows that

changes in  $P_{0_2}$  in the gas phase caused rapid re-

sponse for cell B. Because of the low solubility of  $0_2$  in Na<sub>2</sub>SO<sub>4</sub>, the rapid equilibration of the Pt electrode contacting the melt does not, however, infer that the bulk melt is so rapidly equilibrated with the gas.

With pure 0<sub>2</sub>, cell B should have had an emf of 0.040 V, and with gas G, 0.033 V. The steady-state values for cell B for these gases differed from the ideally expected values, and repeated measurements of these gases did not give repeatable results. The emf of cell B remained constant after reaching a steadystate value, while cells D and F continued to change over a longer period of time. This indicates that reactions were occurring at the Pt electrode in the

melt which involved  $Na_2^{0}$  (or  $SO_3$ ) rather than  $O_2$ .

When the gas phase was fixed (gas D or F) and additions of  $Na_2O_2$  and  $Na_2S_2O_7$  were made, the cells responded rapidly, followed by a slower variation with time. Again, this indicates a consumption of the addition, probably by corrosion of some ceramic components in the melt.

In Fig. 12, measured values of  $E_F$  obtained during the addition of  $Na_2O_2$  and  $Na_2S_2O_7$  to the melt are plotted as a function of the mol fraction of  $Na_2O$ in the melt after the additions. The addition of  $Na_2S_2O_7$  is considered to consume  $Na_2O$  in accordance with the reaction

$$Na_{2}O + Na_{2}S_{2}O_{7} = 2 Na_{2}SO_{4}$$

and the amount of Na<sub>2</sub>O consumed was thus calculated to get the value of  $N_{Na_2O}$  resulting from the addition of the pyrosulfate. Complete consumption of the added Na<sub>2</sub>S<sub>2</sub>O<sub>7</sub> was assumed. Additions 1, 2 and 3 were of Na<sub>2</sub>O<sub>2</sub> while 4, 5, 6, 7 and 8 were Na<sub>2</sub>S<sub>2</sub>O<sub>7</sub>. A line of expected slope is drawn through the data points and the fit is reasonable for the data points 1 to 5; however, points 6 to 8 deviate sharply from the expected slope. The  $E_F$  values correspond to the steady-state values shown on Figure 11.

## Discussion

As already mentioned, the behavior of cell B in Fig. 9 did not correspond reasonably to known (or possible) values for  $P_{0_2}$  according to Eq.(B-3). After the initial addition of Na<sub>2</sub>0<sub>2</sub>, the indicated  $P_{0_2}$  reach-

ed a value of several atmospheres, and after addition #2, the cell indicated a steady-state of about 3.8 atm. The interpretation of cell B as discussed in Eqs. (B-1) to (B-3) must be questioned, at least when the melt basicity is high. Similar problems were experienced when attempts were made to measure  $P_0$  of gas A.

To avoid this difficulty and be able to check the validity of other proposed cell reactions, the following interpretation is offered. We assume that the manufacturer's analysis of gas G is correct, and that therefore  $P_{0}$  equals 0.76 atm for this gas. Further,

we assume that equilibrium is established in the gas phase between  $SO_2$ ,  $SO_3$  and  $O_2$ , and at the Pt electrode between the gas phase and the salt. The sodium oxide activity of the salt can then be calculated to give  $\log a_{Na_2O} = -12.93$  for gas G. Next, we assume that the proposed equation for  $E_F$  is correct, and we can then calculate  $E_E^O$ ', i.e., the bracketed part of Eq. (F-3).

The result of this calculation gives for the emf of cell F:

$$E_{\rm F} = -1.22 - 0.119 \log \frac{a_{\rm Na_2O'}}{P_{\rm O_2}}$$

The emf of cell E (with gas G) is then used to calculate the term

$$E_A^{o''} \equiv E_A - 0.119 \log \frac{a_{Na_2}SO'_4}{a_{Ag_2}SO'_4}$$

Because the relationship

$$E_{E} = E_{F}^{o'} + E_{A}^{o''}$$

is valid, we get the result

$$E_A = 1.46 + 0.119 \log a'_{Na_20}$$

Then  $E_D$  and  $E_C$  can be calculated

$$E_{\rm D} = 1.42 + 0.119 \log \frac{a'_{\rm Na_2O}}{P_{\rm O_2}^{1/2}}$$

$$E_{C} = -1.26 - 0.119 \log a_{Na_20}$$

Then  $E_F^0$  can be used to calculate the basicity  $a_{Na_20}^{\prime\prime\prime}$  of of the salt inside the mullite tube, which, when assuming  $P_{SO_2}^{\prime\prime\prime} = 1$ , amounts to log  $a_{Na_20}^{\prime\prime\prime} = -13.15$ , log  $P_{SO_3}^{\prime\prime\prime} =$ -3.48 and log  $P_{O_2}^{\prime\prime\prime} = -5.80$ . Finally, the measured emfs for cells F and B are used to calculate log  $\frac{a_{Na_20}^{\prime\prime}}{p_{O_2}^{1/2}}$ 

and 1/2 log  $P_{0_2}$ . The results of these calculations are

shown in Figs. 13-15. The data points fall very close to lines with slope equal to that predicted by the Nernst equations given previously. In fact Figs. 13-15 are demonstrations of the internal consistency of the measurements.

There can be several reasons for the discrepancy between some measured and expected emfs - especially those mentioned for cell B which indicated unreasonably high oxygen pressures. As shown in Fig. 3a, two platinum electrodes were used when working with deep melts. The emf between the two Pt foils should be zero when the salt was equilibrated with the gas phase. This was not the case, however. Even after long times (more than a week), a 10mv difference existed between the electrodes. The foil that was partially immersed in the melt was attacked by the sulfate. Gold is re-latively inert to molten sodium sulfate, and the plat-inum foils and lower parts of the lead wires were substituted with gold foils and wires. The results of these measurements are shown in Table III. Although the two gold foils reached the same potential (in the course of 5-6 days), they failed to indicate correctly the oxygen pressure. For example, the emf given for cell B and gas F in Table III, corresponds to a  $P_{0_2} = 2.7$  atm, which is quite unrealistic.

A possible explanation consistent with this discrepancy is the formation of higher oxides such as peroxide and the superoxide ions in the melt. These oxides have been reported by several investigators,  $^{15,16}$  and are especially stable for basic melts under high oxygen pressures. For cell B, then

$$E_{B} = -\frac{2.3RT}{4F} \log P_{02}(r) + \frac{2.3RT}{4F} \log P_{02}(melt)$$

Since superoxide is the predominant species  $^{10}$  compared to the peroxide

$$Na_2O + \frac{3}{2}O_2 = 2 NaO_2$$
 log K = 2.21

and  $P_{0_2}$  (r) = 0.21 (air), we get

 $E_{B} = 0.128 + 0.0397 \log \frac{a_{Na0}^{2}}{a_{Na_{2}0}}$ 

 $\mathbf{1}_{\text{Og a}_{\text{Na}_20}}$  can be calculated from cell A and log  $\mathbf{a}_{\text{Na0}_2}$ 

from the above equation. The results for gases F and G are shown in Fig. 16. The line drawn through the points has a slope of 0.59, while it should have 0.50 according to the equation above. This calculation only takes into consideration the superoxide and ignores the peroxide, and the agreement is therefore considered satisfactory. In effect, this explanation suggests that in basic melts, especially at high  $P_{0,2}$  an immersed Pt electrode may respond to a redox 2 potential involving the superoxide and peroxide instead of the dissolved molecular oxygen content. In such melts, a PtO<sub>2</sub> film is also observed to form.

There are undoubtedly several possible reactions contributing to the electrode potential of a base Pt metal electrode in  $Na_2SO_4$ .

# Conclusion

The most common electrodes used in molten sulfate research have been investigated and compared and the Nernst equations for the possible electrochemical cells formulated. All of the emfs exhibited the dependences on sodium oxide activity and oxygen as proposed, except the cell B consisting of the zirconia electrode and the platinum electrode. This behavior is rationalized in terms of corrosion of the platinum and formation of higher oxides in the melt. As the anomaly persists when the Pt electrodes are substituted with gold (which is recommended for subsequent work) the most probable explanation is the formation of oxides of sodium.

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		and the second		
G	as	Manufacturer	Composition	-log a <sub>Na2</sub> 0
A	so <sub>2</sub>	Matheson	99.9%	14.00
B	so <sub>2</sub>	Liquid Carbonic	99.8%	13.16
С	so <sub>2</sub>	Matheson	99.9%	14.00
D	Ar		20-50ppm 0 <sub>2</sub>	
Е	$Ar/SO_2$	Matheson	100ppm SO <sub>2</sub>	11.30
F	0,	Cols. Oxygen	99.6%0 <sup>2</sup>	
G	0 <sup>2</sup> /S0 <sub>2</sub> /	N <sub>2</sub> Matheson	76% 0 <sub>2</sub> , 0.1%	12.90
		<b>-</b>	SO <sub>2</sub> bal. N <sub>2</sub>	

Table I Gas compositions and corresponding salt basicity.

Table II Thermodynamic Data

Compound	$AG_{f}^{\circ}$ (1200K)(cal/mole	e) Source
Na <sub>2</sub> SO <sub>4</sub> (1)	-213,612	JANAF <sup>10</sup>
Na <sub>2</sub> 0 (s)	-59,832	11
Na <sub>2</sub> 0 <sub>2</sub> (s)	-60,642	TT
NaO <sub>2</sub> (s)	-23,848	11
S0 <sub>2</sub> (v)	-65,495	11
SO <sub>3</sub> (v)	-62,283	11
Ag <sub>2</sub> SO <sub>4</sub> (1)	-78,736	extrapolated from lata at lower temperature

Gas	EA	Е <sub>В</sub>	<sup>Е</sup> с	<sup>Е</sup> D	EE	Е <sub>F</sub>
C -S02	0.155	-0.326	0.152	0.481	0.306	-0.174
F - 0 <sub>2</sub>	-0.0034	0.066	0.117	-0.100	0.083	0.184
G -SO <sub>2</sub>	,-0.184	0.012	0.372	-0.195	0.185	0.382
02,	Nz					

Table III Emfs (Volts) measured with gold electrodes


Fig. 1

Schematic drawing of experimental setup. The ceramic tubes (electrodes) are lowered into the salt after it is molten.





Fig. 3a Arrangement of the platinum electrodes in the melt when a bulk melt was used.
3b Arrangement of platinum foil on bottom of crucible when a thin salt film was used.



TIME (hr)

Fig. 4 Emf of cell A as function of time the various gases of Table I passed over a thin Na<sub>2</sub>SO<sub>4</sub> film electrolyte.



Fig. 5 Emf of cell B as function of time for the various gases passed over thin  $Na_2SO_4$  film electrolyte.



Fig. 7 Emf of cell D as function of time for the various gases passed over thin  $Na_2SO_4$  film electrolyte.



Fig. 8 Emf of cell F as function of time for the various gases passed over thin  $Na_2'SO_4$  film electrolyte.





Fig. 9 Emf of cell B as function of time with additions of  $Na_2O_2$ . Gas phase is maintained as pure  $O_2$  (gas F).



# TIME (hr)

Fig. 10 Emf of cell B as function of time with additions of  $Na_2O_2$ . Gas phase is maintained as Ar (gas D).



Fig. 11 Emf of cell F as function of time with additions of Na<sub>2</sub>O<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>7</sub>. Gas phase is maintained as pure O<sub>2</sub> (gas F).



Fig. 13 Emf of cell A as function of  $\log a_{Na_20}$ . The full drawn line has the slope predicted by Eq. (A-4).









Fig. 15 Emf of cell D as function of log  $a'_{Na_2O}/P_{O_2}^{\frac{1}{2}}$  calculated from emfs measured with cell F. The full drawn line has the slope predicted by Eq. (D-3).



Fig. 16 Log  $a_{NaO_2}$  plotted as function of log  $a_{Na_2O}$  calculated from  $E_A$  for gases F (pure  $O_2$ ) and G (76%  $O_2$ , 0.1% SO<sub>2</sub>, bal.  $N_2$ ).

# VOLTAMMETRIC STUDIES OF Na<sub>2</sub>O-NaC1 MELTS

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## ABSTRACT

The oxidation of the Na $_0$  in molten NaCl was studied in the presence of oxygen (<10 Torr) at 830 $^{\circ}$ C by cyclic voltammetry. The results indicate the following reaction pathway:

 $2 o^{2} + o_{2} \rightleftharpoons 2 o_{2}^{2-}$   $2 o^{2-} \rightleftharpoons o_{2}^{2-} + 2e^{-}$   $o_{2}^{2-} \rightleftharpoons o_{2} + 2e^{-}$ 

The partial conversion of  $0^{2-}$  to  $0_2^{2-}$  in the melt results in two oxidizable species. Experimental data indicate that superoxide is absent from the Na<sub>2</sub>O-NaCl melts.

In previous studies of the Na<sub>2</sub>O-NaCl system (1), several types of experiments were reported which indicated that oxide ion  $(0_2^-)$  dissolved in molten NaCl is partially oxidezed to peroxide  $(0_2^-)$  and perhaps to superoxide  $(0_2^-)$ . The motivation for this work was the previous finding (2) that  $0^{2^-}$  is oxidized by two distinctly different kinds of reactions in molten nitrates: by molecular  $0_2^-$  in oxygen-containing atmospheres and by the reduction of nitrate to nitrite in the (near) absence of oxygen. Since halide anions were considered difficult to reduce, it was thought likely that  $0^-$  would be stable in NaCl in the absence of  $0_2^-$ . The results of manometric experiments, chemical analyses of quenched melts, and potentiometric studies with  $0^-$  -specific zirconia electrodes gave consistent results. When the atmosphere contained oxygen, Na<sub>2</sub>O-NaCl melts took up  $0_2^-$  reversibly, chemical analysis showed a species which reduces permanganate and the potentiometric experiments indicated that a large fraction of any added Na<sub>2</sub>O disappeared rapidly. These observations are all consistent with substantial conversion of  $0^-$  to  $0_2^-$ , presumably by the reaction  $0^{2^-} + 1/2 \ 0_2 \rightleftharpoons 0_2^{2^-}$ . The experiments did not allow any

conclusions to be drawn about  $0_2^{-1}$  formation, but thermodynamic calculations indicate that its equilibrium concentration is much less than that of  $0_2^{-2}$ .

Results in a low 0, atmosphere were more puzzling. In a helium-filled glove box whose nominal  $0_2$  content was 1-10 ppm, similar chemical and potentiometric studies also indicated peroxide formation, although at a slower rate. None of the several possible explanations examined appeared satisfactory.

The current work was therefore undertaken to (i) determine the number of species to which  $0^{-1}$  transforms and (ii) to shed further light on the remaining unresolved anomalies. Voltammetric techniques had already been used successfully by several workers (3-5) to study oxide species in halide melts and were therefore used in this study.

## Experimental

Apparatus. — The molten salt furnace, temperature controller, and helium-oxygen dry boxes have been previously described (1). High purity gold crucibles were used as containers for the melt.

Current-voltage curves were obtained with a Princeton Applied Research Corporation Model 173 potentiostat/galvanostat. A triangle wave generator (PAR Model 175) was interfaced to the Model 173 to obtain cyclic sweep voltammograms. Fast voltammetric scan rates were recorded with a transient recorder (Biomation Model 802).

Electrodes.—The reference electrode consisted of a silver wire in contact with ~10 mole percent AgCl in NaCl. The reference melt was placed in a mullite tube which was immersed in the melt. The gold container served as the counterelectrode. Since gold is less susceptible to corrosion by the Na<sub>2</sub>O-NaCl melt than is platinum, a gold wire (area ~0.50 cm ) was used as the working electrode.

Reagents. —Reagent grade NaCl was vacuum dried at 500°C before use. Reagent Na<sub>2</sub>O (Alfa Inorganics) (94% Na<sub>2</sub>O by analysis) containing ~2% Na<sub>2</sub>O<sub>2</sub> impurity, and reagent Na<sub>2</sub>O<sub>2</sub> were used without pretreatment. All weighing and transfer operations involving these substances were carried out in the dry box in which the experiments were done.

Procedure. - The temperature of the melt was maintained at

 $830^{\circ} \pm 5^{\circ}$ C. Sodium oxide was added directly to the sodium chloride melt by means of a glass funnel and approximately 5 min were allowed for the oxide to dissolve before electrochemical measurements were made. Na<sub>2</sub>O concentrations were kept as low as possible (<50 mM) in order to minimize corrosion effects on the electrodes and cell container. As will be discussed below, Na<sub>2</sub>O is unstable at high oxygen pressures, resulting in the formation of Na<sub>2</sub>O. Therefore studies were made at oxygen pressures generally below 10 Torr.

## Results and Discussion

Typical voltammograms of the oxidation of Na\_O are shown in Fig.1. The reduction limit occurs at  $\sim -1.3V$  and the oxidation limit occurs at  $\sim +0.3V$  (probably the oxidation of the gold electrode). Two oxidizable species are observed when Na<sub>2</sub>O is added to the melt; the first anodic wave (wave I) occurs at -0.47V vs. the Ag/AgCl reference electrode and the second (wave II) occurs at  $\sim +0.12V$ . Additions of Na<sub>2</sub>O immediately increase the peak current of wave I; therefore this wave is attributed to the oxidation of oxide ions in the melt. Wave II does not immediately increase in peak current with added Na<sub>2</sub>O; however, the peak current does increase with time as shown in<sup>2</sup>Fig. 1, and is believed to be due to the oxidation of peroxide ions formed by the following reaction

 $2 0^{2^{-}} + 0_2 \rightleftharpoons 2 0_2^{2^{-}}$ 

[1]

The decrease in peak current of wave I with time can also be accounted for by reaction [1]. Measurement of this decrease indicated that the oxide concentration decreased in a first order fashion with a half-life of approximately 30 min.

The voltammogram in Fig. 2 was taken 2.3 hr after the first addition of  $Na_2O$  to the melt (at a higher total oxide 2concentration than in Fig. 1). This indicates that the  $O_2$  concentration becomes appreciable when  $Na_2O$  remains in the melt for long periods of time. Loss of oxide ion and peroxide ion due to vaporization and reaction with container, electrodes, etc., also occurs in the melt but is a slow process that takes many hours (1). Attempts were made to enhance the peak current of wave II with additions of  $Na_2O_2$ . The results were the same as for the addition of pure  $Na_2O_2$ . Most likely, solid  $Na_2O_2$  decomposes to  $Na_2O$  before it dissolves in NaCl.

The reversibility of wave I was determined by measuring the separation of its peak and half-peak potential. (E - E ) was \$p\$-p/2\$ a

found to be 120-135 mV at slow scan rates which is in reasonable agreement with the theoretical value of 105 mV for a reversible 2-electron process at  $1103^{\circ}$ K (6). The potential difference between wave I and its corresponding cathodic wave,  $(E_p)_a - (E_p)_c$ , was 125-150 mV, which is also in reasonable agreement with the theoretical value of 105 mV for a reversible 2-electron process (6). The slightly higher experimental values could be attributed to quasi-reversible behavior; however, the higher values are probably due, in part, to uncompensated IR effects in the melt.

The peak potential of a reversible charge transfer should be independent of scan rate. The approximate constancy of peak potential with scan rate, v, for wave I is shown in Table I. The peak potential changes only by ~50 mV for a hundredfold increase in scan rate. The shift in peak potential is probably due, in part, to larger IR drops at fast scan rates.

The second anodic wave (wave II) was not as well defined as the first anodic wave since it appears as a shoulder on the oxidation limit of the electrode. Therefore measurements of the peak potential of wave II were only approximate. Values of  $(E_p - E_{p/2})_a$ ,  $(E_p)_a - (E_p)_c$ , and the constancy of peak potential with scan rate were similar to those of wave I and would suggest a 2-electron process for the oxidation of  $0_2^{2-}$  in the melt.

Based on these results and results reported earlier (1), we postulate the following reaction mechanism

$$2 0^{2^{-}} + 0_2 \rightleftharpoons 2 0_2^{2^{-}}$$
 [2]

$$2 0^{2^{-}} \Longrightarrow 0_{2}^{2^{-}} + 2e^{-}$$
 [3]

$$0_2^{2^-} \rightleftharpoons 0_2 + 2e^-$$
 [4]

Table I. Variation of (E ) and (Ep(2) with scan rate for the oxidation of  $0^{2-}$  in molten NaCl  $\begin{bmatrix} 0^{22} \\ 0 \end{bmatrix}$  = 1.61 X 10<sup>-24</sup>

Scan rate (V(sec)	(E ) (mV) p a (mV)	$\left( E_{p} - E_{mV} \right)^{p/2} a$
0.1	-474	121

0.5	-475	135
1.0	-464	128
5.0	-431	156
10.0	-425	163

Thus in Fig. 2, the first anodic wave (I) represents the oxidation of oxide to peroxide and the second anodic wave (II) represents the oxidation of peroxide to oxygen. On reversing the scan, the first cathodic wave (III) represents the reduction of oxygen and the second cathodic wave (IV) represents the reduction of peroxide.

The theory of cyclic voltammetry for multistep charge transfer systems has been derived and verified by Polcyn and Shain (7). When two electroactive species are reduced or oxidized at sufficiently different potentials ( $\Delta E > 118/n$  mV), the multistep charge transfer reactions can be considered as resulting from separate reactions and will exhibit two separate voltammetric waves. The oxidation potentials for oxide and peroxide differ by several hundred millivolts and appear as uncomplicated charge transfer reactions as previously indicated.

Values of  $i_n \wedge 1/2$  were measured as a function of scan rate to check for possible chemical reactions coupled to the multistep charge transfers. The invariance of  $i \sqrt{3} 1/2$  with scan rate would indicate charge transfers with no chemical complication (6). Our mechanism proposes a chemical reaction, the oxide/peroxide equilibrium (Eq. [2]), coupled to multistep charge transfers, the oxidation of oxide to peroxide to oxygen (Eq. [3] and [4]). However, the equilibrium reaction [2] appears to be a slow process so that essentially no chemical reaction takes place during the time interval of a voltammetric scan (<10 sec). In this case, charge transfer reactions [3] and [4] would occur with no chemical complications. Values of  $i_p/v_1/2$  for the oxidation of oxide (wave I in Fig. 2) at various scan rates are listed in Table II. The times at which the voltammograms were measured with respect to the addition of Na20 to the melt are also given. The initial decrease in  $i_{\rm p}/\upsilon 1/2$  is due to the loss of oxide in the melt. The decrease  $\stackrel{r}{_{\rm D}}$  with time holding  $\nu$  constant is illustrated in Fig. 1. Once in ; the  $\delta xide/peroxide$  equilibrium is established,  $i_p/v^{1/2}$  approaches a constant value within experimental error. Similar results were observed with the oxidation of peroxide (wave II in Fig. 2) except for an initial increase rather than decrease in  $i_{\rm p}/v1/2$  due to the gain of peroxide in the melt. The results indicate that the multistep charge transfer reactions of oxide to peroxide to oxygen proceed with no chemical complications. This interpretation is further supported by the approximate constancy of peak potential

with scan rate for both waves I and II.

Table II. Variation of  $i_p/v 1/2$  with scan rate for the oxidation of  $0^{-1}$  in molten NaCl; before addition,  $[0^{2^{-1}}] = 2.67 \times 10^{-2}$ M; after addition,  $[0^{2^{-1}}] = 4.03 \times 10^{-2}$ M

Soon vata	ip/v1/2	Time elapsed
(V)sec)	v172)	addition (min)
0.5	3.4	9
1.0	3.2	12
2.0	2.9	15
5.0	2.9	20
10.0	3.0	22
20.0	3.0	25
0.5	2.8	57

The presence of only two oxidizable species,  $0^{2-}$  and  $0_2^{2-}$ , would tend to rule out the presence of  $0_2^-$  in the melt. Increasing the  $0_2$  pressure would tend to favor the formation of superoxide in the melt (1). Experiments were carried out in  $0_2$  pressures as high as 60 Torr; however, no additional waves were observed.

According to reaction [2], the formation of peroxide should be minimal at low  $O_2$  pressures. Experiments were carried out in He atmospheres containing less than 1 ppm  $O_2$ . Voltammograms of the oxidation of Na<sub>2</sub>O at this  $O_2$  pressure were similar to those at higher  $O_2$  pressures; however, the decrease in peak current of the first anodic wave was considerably slower than in the case<sub>2</sub>Of higher  $O_2$  pressures. Since  $O_2$  is produced by the oxidation of  $O_2$ , it was impossible to study the formation of  $O_2^{-7}$  at very low  $O_2$ pressures. The second anodic wave would produce  $O_2$  in the vicinity of the electrode in the melt that would eventually react with  $O_2^{-7}$ .

In conclusion, we have shown that when  $Na_2O$  is dissolved in molten NaCl in the presence of oxygen, oxide ions react slowly with oxygen to form peroxide ions. The oxidation of oxide ion at a gold electrode results in two multistep charge transfers, the oxidation of oxide to peroxide followed by the oxidation of peroxide to oxygen.

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Fig. 1. Cyclic voltammograms for the oxidation of  $0^{2^-}$  in molten NaCl.  $[0^{2^-}] = 7.2 \times 10^{-3} M$ , Au working electrode (A  $\approx 0.50 \text{ cm}^2$ ), t = 830°C, 0<sub>2</sub> pressure = 0.3%, scan rate = 0.5 v/sec. Curve A: scan taken 8 minutes after addition of Na<sub>2</sub>O. Curve B: 32 minutes later; Curve C: 59 minutes later.



Fig. 2. Cyclic voltammogram for the oxidation of  $0^2$  in molten NaCl. Cumulative  $[0^{2^-}] = 1.58 \times 10^{-2}$  M, Au working electrode  $(A \approx 0.50 \text{ cm}^2)$ , t = 830°C,  $0_2$  pressure = 0.3%, scan rate = 0.5 v/sec, scan taken 2.3 hours after first addition of Na<sub>2</sub>O.

## THE CATHODIC BEHAVIOR OF SOME FUSED NITRATE SALTS

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# ABSTRACT

The potential of a nickel cathode in contact with molten nitrates,  $E_c$ , was found to be linearly dependent upon the logarithm of the current density,  $\ln i$ , and the absolute temperature, T, under a wide range of conditions,  $-E_c = a + (b_1 + b_2 \ln i)T$ , using calcium metal as the anode in "open-pan" tests. The values of the constant a decreased in the same order as the cation radii: a = 1.81 + 1.23 r;  $a(Rb) \cong a(K^+) > a(Na^+) > a(Li^+)$ . The constants  $b_1$  and  $b_2$  were found to be essentially independent of the cation present. The value of  $b_2$  was found to be consistent with a one electron transfer as the rate determining step. It is postulated that the rate determining electron transfer step for the reduction of nitrate depends upon breakage of the oxygen-nitrogen bond and that this breakage is facilitated by the oxygen being bonded to an acidic metal ion.

## INTRODUCTION

The low melting points and high electrical conductivities of the molten alkali metal nitrates has made them attractive as solvents for other reactants. Studies upon the nitrates themselves have been primarily concerned with the nature and concentration of the acidic and basic species formed from their electrochemical and thermal reactions (1).

At our laboratory, we have been examining the merits of molten nitrates as catholytes for thermal batteries (2) and have recently reported some effects observed concerning calcium as an anode (3). The present study is an outgrowth of the need to examine the cathode under conditions expected for an electrochemical cell having an active metal anode. The only similar galvanostatic study on molten nitrates was that of Jennings who only looked at the overall potential of a large Mg/LiNO<sub>3</sub>-KCl cell at a few temperatures (4).

The primary products from the reduction of dry molten nitrate salts in the absence of silica are nitrite, peroxide, and superoxide. Johnson and Zacharias (5) have shown by chemical analysis that nitrate and peroxide are stable reduction products from molten sodium nitrate, while nitrite and superoxide were the products observed from the reduction of potassium nitrate. In the presence of oxygen, graphite (6) and platinum (7) have been shown to be suitable electrode materials for the reversible oxygen/superoxide reaction

$$0_{2} + e \rightleftharpoons 0_{2} \qquad [1]$$
  
$$E = E_{0_{2}/0_{2}}^{0} + (RT/F) \ln \left\{ [0_{2}]/[0_{2}] \right\} \qquad [2]$$

The value of  $E_{0_2/0_2}^0$  was found to be -0.645 ± 0.005 V vs. Ag/Ag<sup>+</sup> (0.07 m) in an equimolar (Na,K)NO<sub>3</sub> mixture at 500°K.

In the presence of water and oxygen, Zambonin and co-workers (7-10) have shown that the equilibrium

$$20_2^- + H_2^- \rightleftharpoons 20H^- + 1.5 0_2$$
 [3]

lies far to the right, and suggests that the prevalent reaction at the cathode should be

$$0_{2} + 2H_{2}0 + 4e = 40H$$

$$E = E_{0_{2},H_{2}0/0H}^{0} + RT/F \ln [0_{2}]^{\frac{1}{2}}[H_{2}0]^{\frac{1}{2}}[0H]$$
[5]

with a value of  $E_{0_2,H_2O/OH}^0$  of -0.495 V for equimolar (K,Na)NO<sub>3</sub> at  $\sim$ 500°K vs. Ag/Ag<sup>+</sup> (0.07 m).

1

The above reactions are primarily concerned with the "oxygen" electrode reactions that occur at more positive potentials than those observed for the reduction of nitrate. Intermediate to the reduction of superoxide and nitrate is the so called "water wave". Lovering *et al.* (11) have shown that the water wave is absent under certain conditions and proposes that the overall reaction is

 $H_20 + NO_2 + 2e \rightarrow 20H + NO$  [6]

followed by

 $NO^- + NO_3^- \rightarrow 2NO_2^-$ 

By operating at sufficiently high temperatures and current densities, we anticipated that reaction 6 would be minimized. In addition, studies at this laboratory have shown that the water wave is more pronounced on platinum than it is on nickel (12).

[7]

Voltammetric studies on the reduction of nitrate have placed particular emphasis upon the formation of insoluble sodium oxide (or peroxide) as opposed to the more soluble potassium compounds (5, 13). The formation of insoluble oxides rapidly reduce the effective areas of the cathode and consequently cause a shift in potential to more negative values. Voltammetric studies at the higher current densities needed to study nitrate reduction as opposed to the more easily reduced peroxide or superoxide have been consequently hampered by the rapid polarization of the cathode by insoluble "oxides". Examination of the voltammetric studies of Jennings (4) suggested to us that "oxide" polarization might not occur, or would be markedly reduced, by working at higher temperatures than is usually used for cathodic nitrate studies.

Thus our plan of attack was to use a cell configuration similar to that used in a thermal battery, to operate at high enough temperatures to minimize oxide blockage and reduce the concentration of water, and then to compare these results with those at fixed temperatures in a closed system. This approach resulted in what we call "open pan" studies.

#### EXPERIMENTAL

Measurements were made under conditions of varying temperature and constant current upon thin cells that used calcium as the anode. About 0.2 g of the electrolyte was placed in the inverted nickel lid of a 30-ml crucible. Unless otherwise indicated, binder-free fiberglass filters (Gelman type A) were soaked in the molten salt and used as a separator between the electrodes and the nickel lid. Although it was possible to use the nickel lid as one of the electrodes, the measurements in this study used electrodes that were 0.25 inch in diameter (0.3166 sq cm). The nickel cathodes used nickel lead wires, while the calcium anodes used aluminum. Aluminum spot welded to nickel showed a negligible thermal electric effect compared to the measured cell voltages. The back side of the electrodes were coated with Saureisen #1 and baked (under a range of increasing temperatures) so as to ensure a fixed area of contact. The lid was placed on a hot plate while the two electrodes were lowered, side-by-side, about 2 mm from each other, until they were in contact with the molten salt. An L-shaped reference electrode was made from 3-4 mm O.D. soft glass tubing that had been sealed at one end. A pinhole was made in the sealed end by means of a Tesla coil when the tube was under vacuum. All of the material needed for a  $0.1 m \text{ AgNO}_3$  in equimolar potassium, sodium nitrate reference electrode was placed in the bottom portion of the L. Silver wire welded to nickel wire, both of about 0.3 mm diameter, was inserted into the molten electrolyte and the top closed with sealing wax. The conducting tip of the reference electrode was placed in the molten salt close to the cathode.

All cathode voltages,  $E_c$ , were measured with respect to this reference electrode. The anode voltage,  $E_a$ , is calculated with respect to the positive cell voltage, E

 $E_{a} = E_{c} - E$ 

[8]

A 0.3-0.8 mm diameter L-shaped stainless steel-covered thermocouple probe was placed in the test pan and the temperature read to 1°C with a Fluke Model 2165A digital thermometer readout. The cell potential was read with a Fluke Model 8040A multimeter. Cathode reference voltage measurements were made with a digital Princeton Applied Research Model 173/176 Galvanostat.

All of the salts used were reagent grade except for the rubidium nitrate (from Pfaltz and Bauer). The salts were used without further purification except for drying in a vacuum oven overnight at 130°C. Added moisture to potassium nitrate showed little effect upon its voltammetric characteristics. A mixture containing 25 mole percent potassium ions to 75 mole percent lithium ions will be referred to as a formulation. The anions of the formulation were nitrate and up to 25 mole percent chloride. The exact formulation will be identified by the mole percent of chloride.

# RESULTS

Figure 1 shows an example of the variation of the cathode, cell, and anode potentials at varying temperature for a 16% chloride formulation at a current density, i, of 0.1 mA/cm<sup>2</sup>. Except for a hysteresis effect of the cell and anode voltages, the cell potentials measured with increasing temperatures match rather close to those measured with decreasing temperature. Linearity is measured by the statistical linear regression coefficient (LRC). The LRC was calculated using a Texas Instruments Model 59 calculator. The value of LRC lies between -1 and +1 with  $\pm 1$  being a perfect correlation. The measurements are made by starting in the range of 300-400°C, lowering the temperature to near the freezing point of the electrolyte, raising the temperature to near 500°C, and lowering the temperature to past the starting point. At least one-half hr is needed for this sequence. Figure 2 shows examples of individual cathodic curves for the different alkali metal nitrates at 1 mA/cm<sup>2</sup>.

At low (0.1 mA/cm<sup>2</sup>) current densities, and high temperatures, the shape of the cathode curve deviates from linearity as shown in Figure 1. We shall call this a type A deviation. At high current densities and low temperatures, the potential deviates from linearity as shown in Figure 3. We shall call this a type B deviation. Only lithium nitrate or the formulations showed a reproducible type B deviation. At current densities above 20 mA/cm<sup>2</sup>, decending temperatures would often deviate from the ascending values and were excluded from the least squares evaluation. This was particularly true for runs at 100 mA/cm<sup>2</sup>. Figure 4 shows the effect of different current densities upon  $E_c$ , as well as the effect of chloride upon the anode potential.

Least squares lines were fit to the data of E using the absolute temperature as the independent variable. Data in the region of A or B deviations were omitted. An example of the results obtained for a given salt is shown in Table 1. The LRC values indicate that the data are

$i \times 10^3$	·····	<pre>b, volts/°</pre>	Kelvin x 10 <sup>3</sup>	LRC
A/cm <sup>2</sup>	a, volts	original	$ar{b}$ using $ar{a}$	
1	3.25	-2.08	-3.38 ± .09	-0.996
1	2.38	-1.89	-3.46 ± .13	-0.939
1	2.48	-1.59	$-3.50 \pm .05$	-0.990
1	3.84	-2.42	$-3.43 \pm .15$	-0.981
10	3.39	-4.32	$-3.15 \pm .10$	-0.992
10	2.73	-3.21	$-3.09 \pm .07$	-0.961
10	3.00	-3.57	$-3.04 \pm .06$	-0.993
10	1.99	-2.09	$-3.05 \pm .10$	-0.942
20	2.20	-2.34	$-3.00 \pm .08$	-0.907
20	2.55	-2.79	$-2.94 \pm .09$	-0.879

Table 1. Example of Least Squares Fit of  $-E_c$  vs T for Lithium Nitrate  $-E_c = a + bT$ 

		-
a =	2.78	volta

quite linear for a given experiment. The derived a and b values showed, however, sufficient variation so as to make further correlations difficult. There are theoretical arguments that the a values for a given salt should be a constant independent of the current density (12). Using the apriori decision to evaluate data having a current density of 1 mA/cm<sup>2</sup> or higher having absolute LRC values larger than 0.85, mean values of a,  $\bar{a}$ , were calculated for a given salt. The mean value of b was then determined for a given current density

$$-\bar{b} = [\Sigma(E_{a} + \bar{a})T^{-1}]n^{-1}$$
[9]

for the original number of pairs of values, n. The value of n was usually 30 for each run. Table 1 shows examples of the mean values of b calc. using equation 9 and the estimated standard deviation for an individual value. Using a common intercept,  $\bar{a}$ , the data in Table 1 now show the anticipated polarization effect due to an increase in current density. In fact  $\bar{b}$  can now be related to ln i

$$\overline{b} = b_1 + b_2 \ln i \tag{10}$$

Table 2 shows the values of the constants  $b_1$ ,  $b_2$ ,  $\bar{a}$  and the linear regression coefficients for equation 10 for a given salt using current density of 0.1 to 100 mA/cm<sup>2</sup>.

Table 2. Linear Regression Values Relating  $\mathbb{E}_{\mathbf{C}}^{},$  in  $\dot{\imath},$  and T

 $-E_{c} = \overline{a} + (b_{1} + b_{2} \ln i)T$ 

		Intercep	ţ		Temperature C	oefficient	
S	% C1	$\bar{a}$ , $V_{c}$	u	$-b_1 \ge 10^3$ $V/^{\circ}K$	$b_2 \ge 10^3$ V/°K	LRC	R
1	0	2.78 ± 0.69	13	1.99	0.22	-0.96	17
	9	$2.41 \pm 0.60$	2	1.85	0.23	-0.93	10
	12.5	$2.75 \pm 0.43$	7	1.88	0.25	-0.96	7
	16	$2.63 \pm 0.31$	9	2.21	0.19	-0.96	7
	20	$2.79 \pm 0.80$	4	2.38	0.15	-0.97	9
	25	$2.48 \pm 0.38$	7	2.04	0.22	-0.93	8
ined		<b>2.65 ± 0.56</b>	44	2.04	0.21	-0.93	55
	0	<b>2.92</b> ± 0.45	14	1.60	0.21	-0.91	19
	0	$3.61 \pm 0.48$	12	2.15	0.23	-0.95	16
	0	$3.51 \pm 0.61$	7	2.10	0.20	-0.96	6
	0	$4.25 \pm 0.47$	14	3.56	0.17	-0.84	21
					$0.20 \pm .01$		

\* Without fiberglass and with different electrode materials.

Table 3 shows the average values of  $\overline{b}$  for platinum, 302 stainless steel (SS), steel (Fe), and nickel at three different current densities using potassium nitrate as the electrolyte in the absence of fiberglass. The steel electrode results were slightly lower than the other three metals. Most notable was the large quantities of brown discharge from the steel electrode near 500°C.

Table 3. Effect of Different Cathode Materials Upon E for Potassium Nitrate in the Absence of Fiberglass  $^{\rm C}$ 

$$-E_{c} = 4.25 + bT$$

$$-b \ge 10^3 (V/^{\circ}K)$$

$i \ge 10^3$ ,A/cm <sup>2</sup>	Pt	SS*	Fe	Ni
0.1	5.18	5.21	5.15	5.21
1.0	4.82	4.95	4.48	4.66
3.0	4.26	4.34	4.26	4.32

\* Type 302 stainless steel.

## DISCUSSION

The linear relationships observed for both ascending temperature results mixed with descending for  $-E_{\rm C}$  (Figure 1 and Table 1), is evidence that water, calcium ions, and reaction products do not seriously affect the kinetics of the reduction at current densities below 20 mA/cm<sup>2</sup>. It was, in fact, this reproducibility that started us making more use of these open pan tests.

The presence of chloride up to 25 mole percent or 25 mole percent potassium ions makes a negligible dilution effect upon the voltammetric E characteristics of a metal cathode in fused lithium nitrate. Thus the lithium nitrate data were combined with the chloride formulation data in Table 2. Furthermore, the type of metal, of the four examined, makes little difference for the reduction process being examined in this study (Table 3). The negligible effects of chloride upon the cathode kinetics is in marked contrast to its effect upon the anode, (Figure 4).

Although chloride makes little effect upon the cathode, such is not the case for the cations. Using cation radii, r, of 0.68, 0.95,

1.33 and 1.48 Å for Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Rb<sup>+</sup>, respectively,  $\bar{a}$  values can be related by

$\bar{a} = 1.81 + 1.23r$	LRC = 0.96	[11]
$\bar{a} = 4.38 - 1.22/r$	LRC = -0.95	[12]

or

n

The regular relationship between ion size and the  $\bar{a}$  term suggests that the cation plays a role in the reduction reaction. Previous studies have placed emphasis upon the interaction of the cations to form insoluble oxides which in turn shift the equilibrium in favor of reaction products. The data of Figure 3 do indeed agree with lithium ions, for example, forming oxide to the extent that the cathode can become electrically insulated from the molten salt. In addition, we would like to place emphasis upon the possibility of the cation, M', reacting with nitrate prior to bond breakage

$$M^{+} + \bar{}_{0-N-0}^{-} \neq M_{-0-N-0}^{-}$$
[13]

and that the presence of the M-O bond aids in the breakage of the O-N bond

$$M_{-0} - N_{-0} - + e \rightarrow (N0_{2})_{ads} + M0^{-1}$$
 [14]

Potentiometric evidence for the undissociated ion Lio has been reported by Pemberton (14). Thus the effect of the positive shift in the cathode potential observed for the effect of fiberglass in Table 2 can be associated with

$$x + x(SiO_2) + NO_3 \rightarrow \left[ (SiO_2)_x 0 \right]^{-2} + (NO_2)_{ads}$$
 [15]

in two steps similar to equations 13 and 14 where  $xSiO_2$  plays the part of a Lux-Flood acid. The adsorbed  $NO_2$  in equations 14-15 quickly adds an electron to form  $NO_2$ .

The bond breakage in equation 14 is considered to be the slow electron transfer step because of the value of  $b_2$  in equation 10. As is evident in Table 2, all of the nitrates have the same value,  $b_2$ , for the coefficient of  $T \ln i$ , 0.20  $\pm$  .01 x 10<sup>-3</sup> V/°K. Since the coefficient of  $T \ln i$  of the Tafel equation,

$$\frac{RT}{\alpha zF} \ln i = \frac{8.61 \times 10^{-5}}{\alpha z} T \ln i \qquad [16]$$

is 8.61 x  $10^{-5}/\alpha z$  where  $\alpha$  is cathode transfer coefficient and z is the number of electrons transferred in the rate determining step, we can equate the two terms to derive that

$$\alpha z = 8.61 \times 10^{-5} / .20 \times 10^{-3}$$
[17]  
= 0.43

\_

Since  $\alpha$  is usually near the value of 0.5, the results of equation 17 indicate that z is 1 so that a one electron change, as postulated in equation 14, is the rate determining step for the reduction of the nitrate ion.

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Figure 1. Examples of Type A Deviation. 16% Cl<sup>-</sup> formulation at 0.1 mA/cm<sup>2</sup>. LRC of -0.995 for temperatures to 370°C (data below 200°C not included). Solid circle is starting point, circles represent initial descending temperatures, squares indicate ascending temperatures, and triangles represent final descending temperatures.



Figure 2. Example of Individual Measurements of E for four different alkali metal nitrates at 1 mA/cm<sup>2</sup>.



Figure 3. Example of Type B Deviation. Curves A, B, C, and D are representative of current densities of 1, 10, 20, and 30 mA/cm<sup>2</sup>, respectively, for lithium nitrate formulations.



Figure 4. Representative Galvanostatic Curves at Varying Current Densities. Electrolyte for cathodic curves is lithium nitrate or a chloride formulation. Solid lines are cathodic curves of  $\mathcal{E}$  at indicated current densities in mÅ/cm<sup>2</sup>. Dashed lines are anodic curves of  $\mathcal{E}$ : line AA, lithium nitrate at 1 mA/cm<sup>2</sup>; line BB, 12.5 mole % Cl<sup>-</sup> formulation at 0 mA/cm<sup>2</sup>.

## ELECTROCHEMISTRY OF LITHIUM CARBIDE

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## ABSTRACT

EMF measurements and cyclic voltammetry in moltenhalide solutions of lithium carbide are reported. The results suggest that the potential of a carbon electrode in such melts, although fairly stable, is a mixed potential and results from carbide ion discharge as well as lithium underpotential deposition in carbon.

#### INTRODUCTION

This investigation of the electrochemistry of lithium carbide was prompted by apparent lithium-carbon interaction in molten LiCl-KCl eutectic electrolyte, observed during the overdischarge of lithium/ iron-sulfide cells having porous graphite current collectors or  $\text{Li}_2^C_2$  additions in the positive electrode<sup>1</sup>. The discharge of carbide to carbon and the possibility that carbide might be formed by a lithium-carbon interaction made it desirable to investigate the electrochemistry of carbide solutions in molten LiCl-KCl eutectic.

The investigation was carried out in two ways. First, a number of emf measurements were made of cells

Li/LiCl-KCl, Li<sub>2</sub>C<sub>2</sub>(sat)/C(gr) (I)

This cell represents a "formation cell" of Li<sub>2</sub>C<sub>2</sub>. If the carbide is dissociated in Li<sup>+</sup> and C<sub>2</sub><sup>2-</sup> ions and if the electrode reaction

$$c_2^2 \rightleftharpoons 2C + 2e^-$$

takes place reversibly at the carbon electrode, then the emf of cell (I) reflects the standard free energy of formation of  $Li_2C_2$ .

In the second place, a number of cyclic voltammetric measurements were made using a saturated solution of  $\text{Li}_2\text{C}_2$  in LiCl-KC1. The objective was to determine the potential at which  $\text{C}_2^{2^-}$  ions are discharged according to (1).

The experiments described here are considered to be exploratory because the commercially available  $Li_2C_2$  (Alfa Products, Ventron Corp., Beverly, MA 01915) used in this work contained substantial amounts of

(1)

metallic lithium and elemental carbon (together approx. 30 wt%), and a small amount of lithium oxide,  $Li_00$  (2.3 wt%).

#### EXPERIMENTAL

The experimental arrangement was as follows. Commercially available  $\text{Li}_2\text{C}_2$  was dissolved in purified LiCl-KCl (Andersen Physics, Urbana, IL 61801) at temperatures above 660K. Enough Li<sub>2</sub>C<sub>2</sub> was added to ensure that solid Li<sub>2</sub>C<sub>2</sub> would be present even at the highest temperature (850K); the presence of solid Li<sub>2</sub>C<sub>2</sub> on the bottom of the crucible was checked visually by stirring the melt. The solubility of Li<sub>2</sub>C<sub>2</sub> at 440°C was estimated to be 7 wt% (3mol/1).

The working electrode was a 3-mm dia. cylinder of spectrographicgrade graphite, completely submerged in the melt at the end of a tantalum holder. The reference electrode was a lithium-aluminum electrode in the two-phase  $\alpha + \beta$  region of the Li-Al binary (2,3), held by a tantalum wire and contained in a beryllia sheath; the latter allowed communication with the bulk melt through a small hole, to prevent direct contact of suspended Li<sub>2</sub>C<sub>2</sub> particles with the reference electrode.

In preliminary measurements the potential of the Li-Al  $(\alpha + \beta)$  reference electrode was determined with respect to a liquid lithium electrode in LiCl-KCl melt at temperatures between 640 and 850K. The results, shown in Figure 1, indicate an approximate dependence as follows

$$\epsilon(mV vs Li'/Li') = 477 - 0.26T(K)$$
 (2)

The reason for using a lithium-aluminum electrode was the low lithium activity ( $a_{L1}$ = 0.0075 at 700K) thus maintained in the melt. This low activity was desirable to prevent self-discharge of the lithium/carbon cell via the electronic path provided by dissolved lithium metal originating from the commercial-grade Li<sub>2</sub>C<sub>2</sub>. To reduce the initial lithium activity of the melt after addition of Li<sub>2</sub>C<sub>2</sub>, a buffer-electrode containing a large quantity of Li-Al( $\alpha + \beta$ ) was inserted in the melt for several hours prior to immersing the working electrode. It was found that the potentials subsequently measured at the graphite electrode with respect to Li-Al ( $\alpha + \beta$ ) were stable at the mV level over time periods of several hours.

#### RESULTS OF DISCUSSION

The potentials of the graphite electrode, measured in this manner, were fairly reproducible from experiment to experiment  $(\pm 50 \text{ mV})$ ; the values for three series are shown, relative to the potential of liquid lithium, in Figure 2.

These potentials would yield the standard energy of formation of

 ${\rm Li}_2{\rm G}_2$  provided that the reaction (1) occurs reversibly. Values for  $\Delta \ {\rm G}_f^{\ o}$  found in the literature  ${}^{4-6}$  show sizable discrepancies but are generally much less negative than would be suggested by the potentials measured in the present work; the values of the potential corresponding to  $\Delta {\rm G}_f^{\ o}$  values in the literature are included in Figure 2, and various  $\Delta {\rm G}_f^{\ o}$  values are compared in Table I.

	298K	700К	1000K
JANAF <sup>4</sup>	-56.13	-49.90	-44.83
Beskorovainyi <u>et al</u> <sup>5</sup>	-45.46	-23.86	-5.86
Long <sup>6</sup>			-90.0
This work		-109 <sup>a</sup>	

Table I. Values of  $\Delta G_{f}^{o}$  of  $\text{Li}_{2}C_{2}$  (kJ/mol)

a Tentative value owing to uncertainty in the reversibility of cell reaction.

The present data suggest that the free energy of formation of  $Li_2C_2$  is approximately -109 kJ/mol at 700K. However, it is doubtful if reaction (1) is reversible; the poor reproducibility of the potentials measured suggests that a mixed potential may be involved. In any case, the observed potential cannot be ascribed unambiguously to  $Li_2C_2$  formation.

To explore the reversibility of reaction (1) further, a graphite electrode immersed in LiCl-KCl melt containing, or not containing  $\text{Li}_2\text{C}_2$ , was subjected to potential scans. Figure 3 shows a voltammogram obtained at a graphite electrode in LiCl-KCl in the absence of  $\text{Li}_2\text{C}_2$ . The current surge at +  $1V vs \text{Li}^+/\text{Li}^\circ$  is identical to that observed by James<sup>7</sup> at graphite and vitreous carbon in LiCl-KCl eutectic and which he ascribed to underpotential deposition of lithium, e.g., by the formation of intercalation compounds of lithium and, to a much lesser extent, potassium.

Figure 4 was obtained by repeated cyclic scanning upon addition

of a small amount of  $\text{Li}_2C_2$  (enough to give 0.05 M concentration). The scan was in the same direction as in Figure 3. It is evident that the lithium-carbon interaction at + 1 V <u>vs</u> Li<sup>+</sup>/Li<sup>0</sup> is not affected by the presence of Li<sub>2</sub>C<sub>2</sub>, except for an apparent increase in current level upon continued cycling. The latter is evidently caused by the deposition of finely divided carbon at the graphite electrode, resulting from discharge of  $C_2^{2^-}$  ions in the positive branch of the potential scan.

An adherent layer of fine, amorphous carbon is in fact observed to cover the graphite electrode completely upon removal of the latter from the melt after several cycles. It appears, from Figure 4, that this amorphous carbon also participates in the lithium-carbon underpotential deposition reaction, which therefore may not be exclusively of the intercalation type.

The discharge of  $C_2^{2^-}$  ions appears to take place at potentials above + 2.0V vs Li<sup>+</sup>/Li, where a current maximum is observed that decays upon continued cycling, as would be expected if the bulk melt is slowly depleted in Li<sub>2</sub>C<sub>2</sub>. However, the potential of this peak is far higher than that expected from  $\Delta G_f^{0}$  values (Table I). It is also very close to the potential for  $0^{2^-}$  ion discharge in LiCl-KCl<sup>8</sup>; however, the oxide content of the melt (0.13 mol/1) is too low to explain the peaks observed in Figure 4. It appears that the potential of  $C_2^{2^-}$  discharge is shifted strongly in a positive direction by the presence of residual lithium-carbon intercalates or of high Li<sup>+</sup> concentrations near the graphite electrode. The precise reason for this shift is at present not clear.

The small cathodic maximum at  $+ 1.7 \text{ V} vs \text{ Li}^+/\text{Li}^{\circ}$  probably results from reduction of oxygen adsorbed at the increasingly voluminous amorphous carbon deposit. Abrupt potential shifts, as observed at + 1.9 Vin the first few cycles, are commonly observed when electro-active species are occluded by non-electroactive species (e.g., oxide ions by carbon surfaces in molten carbonates<sup>9</sup>); in this case some residual lithium may be responsible for a drop in the reduction wave at + 1.7 Vassigned earlier to adsorbed oxygen.

Although the need for corroboration and extension of these preliminary results is obvious, a tentative explanation of the discrepancy between literature values for  $\Delta G_f^0$  of  $\mathrm{Li}_2 \mathrm{C}_2$  and the observed potentials of cell (I) is here offered. The cell potential of (I) results from a mixed potential at the graphite electrode. This mixed potential is due to the reactions

$$C_2^{2-} \rightarrow 2C + 2e^{-}$$

and

 $Li^+ + xC + e^- \rightarrow LiC_{\downarrow}$ ,

(2)

(3)

Reaction (2) takes place at -0.2V and reaction (3) at potentials near -1.2 to -1.0V vs Li<sup>+</sup>/Li<sup>O</sup>. The potential values shown in Figure 1 suggest that the kinetic and mass transfer resistances (overpotentials) of reactions (2) and (3) are approximately equal.

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<u>Figure 1.</u> Potentials of graphite electrodes in saturated solutions of  $\text{Li}_2\text{C}_2$  in LiCl-KCl eutectic. Dashed lines and square denote potentials predicted from literature values of  $\Delta \text{G}_f^o$  (Li<sub>2</sub>C<sub>2</sub>), Ref. 4-6.



Figure 2. Potential of lithium-aluminum ( $\alpha + \beta$ ) reference electrode with respect to liquid lithium electrode.






<u>Figure 4.</u> Cyclic voltammogram of graphite electrode in LiCl-KCl eutectic saturated with  $\text{Li}_2\text{C}_2$ . The numbers denote successive scans. Scan direction as in Figure 3.

### OXIDE ION TITRATIONS IN MOLTEN NaCL WITH THE ZIRCONIA ELECTRODE

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### Abstract

Stabilized zirconia electrodes can be used to titrate 0<sup>2<sup>-</sup></sup> into and out of molten NaCl. Relations between the oxide activity in the melt and the charge passed through the ceramic have been derived and verified. The technique is applicable to the purification of melts and the determination of oxide solubility products.

### Introduction

Zirconia electrodes stabilized with several percent Ca0, MgO, or Y<sub>2</sub>O<sub>3</sub> are finding increasing use in a variety of applications at high temperatures. All of these depend on the fact that charge transport through this material occurs by migration of oxide  $(0^{2^{-}})$  ions (1). Electrochemical applications may be divided into equilibrium methods in which the stabilized ZrO<sub>2</sub> (SZ) acts as an indicator electrode, and non-equilibrium methods in which a sensible amount of charge is passed through the material.

As indicator electrodes SZ has been used to:

- Measure O<sub>2</sub> partial pressure in gases (2),
  Measure solubility of O<sub>2</sub> in metals (2),
  Measure the dissociation pressures of solid oxides (2),
- (4) Measure the oxide activity in molten salts (3,4,5) and glasses (6).

The transport of O<sup>2<sup>-</sup></sup> through SZ under an applied potential has been used to:

- (1) Operate an oxygen fuel cell (2), (2) Change the  $O_2$  content of gases (7,8),
- (3) Measure the diffusivity of  $O_2$  in metals (9), (4) Titrate  $O_2$  into metals (9).

Most of the applications depend on two properties of SZ: (a) at an interface of the type  $O_2(M)|SZ$ , the potentialdetermining process is

$$1/2 O_2(q) + 2 e \neq 0^2$$
 (in SZ) [1]

where M is an inert metal such as platinum. Studies of such interfaces have shown that the process is readily reversible, at least at temperatures above  $500^{\circ}$  (2). (b) Applications involving the measurement of  $0^{2^{-}}$  activities in molten salts depend on the equilibrium

$$0^{2^{-}} (in SZ) \neq 0^{2^{-}} (melt) \qquad [2]$$

The reversibility of these processes under potentiometric conditions (very small currents) can be regarded as established. However, there seem to have been no studies of what happens in an SZ-molten salt system when one attempts to pass sizeable currents through the SZ. Under such conditions, the SZ electrode can be described by

$$O_2(q)$$
 (Pt) | SZ |  $O^2^-$  in melt 3

for which the electrode reaction is given by the sum of reactions [1] and [2]:

$$O_2(q) (Pt) + 2e \neq 0^2$$
 (in melt) [4]

This process has so far been studied only potentiometrically (3,4,5). The advantages of the SZ electrode over the well known oxygen gas electrode are that (1) the O<sub>2</sub> pressure over the melt can be varied independently of the O<sub>2</sub> pressure inside the SZ tube electrode, and (2) SZ functions as an O<sup>2-</sup>-specific membrane electrode.

These properties should also permit the addition to or removal of  $O^{2^-}$  from melts by reaction [4]. Some preliminary experiments relating to those processes in molten NaCl are reported in this paper.

#### Experimental

All experiments were carried out in a controlled atmosphere glove box (Vacuum Atmospheres Corp.) with moisture and  $CO_2$  content in the ppm range with the  $O_2$  content set ( $O_2$ -He mixtures) for each experiment. NaCl was vacuumdried at 500° for several days. Melts were contained in high purity (99.8%) Al<sub>2</sub>O<sub>3</sub> crucibles. Reference electrodes were Ag|AgCl (10 m/O), NaCl in mullite. Counter electrodes for the electrolyses consisted of heavy Pt wires in a NaClfilled quartz tube with an asbestos-filled pinhole at the bottom. MgO- and  $Y_2O_3$ -stabilized ZrO<sub>2</sub> tubes (Zircoa Corp.) were fit with a large area platinum wire bundle forced into the bottom of the tube covered with fired platinum paste. The tube was left open to the box atmosphere for experiments in  $O_2$ , and connected to an  $O_2$  mainfold sealed through the box wall for experiments in helium. The untreated outside of the tube was immersed in the molten NaCl.

Potentials were measured with high-impedance potentiometers (Orion 801 and PAR 136). Most coulometric titrations were carried out at constant current (Keithley 225 current source), usually at 10 ma, in series with an electronic coulometer (Koslow Model 541). Since most experiments turned out to be rather long, charge passed and emf's measured were recorded automatically at intervals on a Digitem recorder.

#### Results

Some information on the V-I characteristics electrode [3] was obtained by measuring the current as a function of applied voltage against a platinum counter electrode. As can be seen from figure 1, the behavior is non-ohmic above 0.1 V. 0.13V is the 0.C.V. against the Pt counter electrode. The points represent the current one minute after each change of voltage, and fall on the same curve with increasing and decreasing voltage.

In order to explore the application of SZ electrode to coulometric titrations in molten NaCl, the electrode was put in series with a voltage source and the coulometer. Results can be summarized as follows:

1. When the SZ electrode is made positive, current will flow only in the direction consistent with reaction [4] from right to left; when negative, with the reaction from left to right.

2. For current passage in either direction, the current decreases slowly with time at constant voltage.

3. The SZ is highly polarized by the passage of current in either direction so that an electrode through which current has passed cannot be used as an indicator electrode. This polarization is not reversible even after several hours at zero applied voltage.

This last observation necessitated a dual electrolysis and measurement system. Charge was passed through an electrolyzing SZ and a Pt counter electrode, and the resulting  $O^2^-$  activity change in the melt was followed with an SZ measuring electrode vs. an Ag reference electrode. Results for this experiment are shown in figure 2 in which  $0^{2^-}$  was electrolyzed out of the melt which contained no added oxide. The measured potential did not change appreciably until ~100 µequ had been passed through the SZ; for further passage of charge, the slope dE/dQ followed the theoretical RT/2F slope (see below). The duration of this experiment was ~20 hours. A current reversal resulted in an increase of  $0^{2^-}$  in the melt, as indicated by the emf changes, but there again was an "induction period" of several hundred microequivalents before an RT/2F slope was reached.

Somewhat different results were obtained when reagent  $Na_2O$  was added to the melt, the reaction  $Na_2O + 1/2 O_2 - Na_2O_2$  allowed to come to equilibrium, and  $O^2^-$  then electrolyzed out. The result is shown in figure 3. dE/dlnQ is much less than RT/2F until most of the added oxide has been electrolyzed out, and then becomes nearly RT/F. As shown in the Appendix, dE/dlnQ is not expected to equal RT/2F, but a more careful analysis of the data will be required to determine if equation [11] represents the experimental data.

Finally, we show the application of oxide ion coulometric titration to the precipitation of metal ions. Figure 4 shows the titration of Cu(I) dissolved as CuCl in NaCl.

The shape of the curve is typical of potentiometric titrations resulting in the precipitation of an insoluble compound,  $Cu_2O$  in this case. The steepest portion of the curve is close to the expected endpoint. The method is thus applicable to the determination of solubility products of slightly soluble oxides in molten salts.

### Discussion

The results obtained in this work show clearly that  $0^{2^-}$ ions can be titrated into the out of NaCl, and most probably other molten salts as well, through stabilized zirconia electrodes. The method is probably limited to high melting salts since the resistance of the ceramic is otherwise too low for appreciable charge to be passed. Electrolyzing  $0^{2^-}$  out of a melt can be used to purify it of a dissolved oxide. The greatest utility of electrolyzing oxide ions into the melt probably lies in the determination of oxide solubility products. The major unanswered question is why so much charge must be passed through the ceramic before the theoretical response is obtained. One possible explanation is that the solid is depleted in oxide at one interface or the other as a result of kinetic hindrance and that this oxide is first replaced by the electrolysis before the melt composition is affected.

It should also be emphasized that the measuring SZ electrode responds to changes in the  $O^{2^-}$  activity, whereas the electrolyzed SZ passes equivalents. In dilute melts, the activity coefficients are most likely constant and thus activities are proportional to equivalents; but the situation is more complicated for solubility products. The solubility product of an oxide MO is defined as

$$Ksp = a_{M2^+} \cdot a_{O2^-}$$

The activities of the species in molten salts are most commonly defined for a Raoult's law standard state. The activity of  $a_{M2^+}$  is largely determined by the thermodynamics of the MCl<sub>2</sub>-NaCl system, whereas that of  $a_{O2^-}$  is related to the thermodynamics of the Na<sub>2</sub>O-NaCl system. Therefore, the activities of the two species at the stoichiometric endpoint are not necessarily equal. The data in figure 4 show that for Cu<sub>2</sub>O the largest change in emf (and therefore in  $a_{O2^-}$ ) comes near the stoichiometric endpoint.

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## Appendix

The relation between charge passed and the measured emf can be derived as follows:

It is known that in molten NaCl oxide and peroxide ions are in equilibrium. The equilibrium constant for the reaction

$$Na_2O + 1/2 O_2 = Na_2O_2$$
 [1]

is 3.1 at 1100 K (5). At constant  $P_{O_2}$ , the ratio

$$[0_2^2]/[0^2] = K_e P_{0_2}^{1/2} = K'_e$$
 [2]

where the brackets denote mole fractions. Since the electrolysis is slow, it is reasonable to assume that this equilibrium is maintained.

### Case I. Electrolysis of $0^{2^{-}}$ into the melt.

For Q equivalents electrolyzed into the melt, the number of moles  $O^{2^-}$  formed initially is Q/2 and the initial concentration of  $O^{2^-}$  is Q/2n, where n = number of moles solvent, and it is assumed that the  $O^{2^-}$  concentration before electrolysis is negligible. Some fraction of the  $O^{2^-}$  electrolyzed into the melt will form  $O^{2^-}_2$  and therefore

$$[0_2^{2^-}] + [0^{2^-}] = Q/2n$$
 [3]

From [2] and [3]

=

$$\left[0^{2^{-}}\right] = \frac{Q}{2n(K_{e}+1)}$$

For the  $0^2$ -specific SZ electrode

$$E = E^{\circ} - RT/2F \ln [O^{2^{-}}]$$
  
 $E^{\circ} + RT/2F \ln [2n(K_{e}^{+}+1)] - RT/2F \ln Q [4]$ 

]

Since the first two terms are constant,

$$dE/dln \left[O^{2^{-}}\right] = dE/dlnQ = RT/2F \qquad [5]$$

Case II. The melt initially contains a known amount of added Na<sub>2</sub>O which is electrolyzed out. If the added oxide concentration is  $[O^{2^-}]_O$ , then, considering reaction [1] at equilibrium

$$[0^{2^{-}}]_{0}/[0^{2^{-}}] = K'_{e} + 1$$
 [6]

If the equilibrium [1] is maintained during the electrolysis, both  $O^{2^{-}}$  and  $O^{2^{-}}$  must decrease in a ratio fixed by [2]. Let a = decrease in  $[O^{2^{-}}]$ , b = decrease in  $[O^{2^{-}}]$ during electrolysis. Then

$$K_{a} = b/a$$
 [7]

$$a + b = Q/2n \qquad [8]$$

from which

$$a = Q/2n(K_{e} + 1)$$
 [9]

 $\begin{bmatrix} 0^{2} \end{bmatrix}$  during the electrolysis is then obtained from [6] and [9]

$$[0^{2^{-}}] = \frac{[0^{2^{-}}]_{0} - Q/2n}{(K'_{0} + 1)}$$
[10]

$$E = E^{\circ} - RT/2F \ln \left[O^{2^{-}}\right] = \left[E^{\circ} + RT/2F \ln (K_{e} + 1)\right]$$
$$- RT/2F \ln \left(\left[O^{2^{-}}\right]_{O} - \frac{Q}{2n}\right)$$
$$= E^{\circ} + RT/2F \ln \left[\frac{(K_{e} + 1)}{\left[O^{2^{-}}\right]_{O} - Q/2n}\right]$$
[11]

and dE/dlnQ does not equal RT/2F since  $[O^{2^{--}}]_{O}$  is not negligible compared to Q/2n.



Fig. 1 Current - voltage characteristics of electrode [3].  $P_{O_2}$  (inside SZ) = 1 atm. Helium atmosphere above melt.



<sup>4</sup> Fig. 2 Electrolysis of  $0^{2^-}$  out of reagent NaCl at 830°C. Current = 10 ma, 20% 0<sub>2</sub> above melt.







Fig. 4 Coulométric titration of Cu(I) in a CuCl-NaCl melt with  $O^{2^-}$ .



### ELECTRODE POLARIZATION STUDIES IN MOLTEN

#### Na<sub>2</sub>CO<sub>2</sub> IN REDUCING ENVIRONMENTS

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### Abstract

An electrode comprised of a carbon dioxide/carbon monoxide mixture bubbled over platinum immersed in molten sodium carbonate within a closed-end sheath of commercial-purity alumina was found to be ohmic, with an apparent sheath resistivity of the order of 1 M ohm cm at 1000°C, and to respond in a Nernstian manner to variation in the  $P_{C0}$  and  $P_{C02}$  values. This electrode permits independent control of cell and reference environments and, by virtue of cationic transport within the alumina sheath, is insensitive to anionic electrolyte variations. Electrode polarization data for Ni 200 in molten sodium carbonate under reducing environments are reported; these data are matched to an empirical function via computer modelling.

#### I. Introduction

Hot corrosion has been a major concern with respect to materials serving at high temperature in alkali salt environments. In such corrosion processes metal degradation is accelerated by attack on the passive oxide layer normally present. This attack, also known as salt-induced accelerated oxidation, may occur on contact of a structural metal with a molten salt, either by deposition of the volatile salt or by immerision.

Serious problems have occured in the gas turbine engines 1,2,3and in high-temperature fuel cell systems 4,5, with the potential of causing catastrophic failure. Similar material limitations are projected in the design of reactors for coal conversion processes 6,7,8. Material degradation in coal conversion is manifested in metal oxidation by the low-oxygen gas phase and by hot corrosion processes at sites where metal is in contact with molten salts 9,10. Such salts may condense from the gas phase in cooler regions of a gasifier system or be a deliberate constituent of the system as in the molten sodium carbonate gasifier 11. There have been, in general, three complementary lines of approach re understanding of hot corrosion phenomena:

1) Establishment of the thermodynamic regimes in which hot corrosion in particular systems may occur,

2) Development of effective means of protection, and

3) Employment of specimen polarization from which kinetic parameters determining corrosion rate may be obtained. First two approaches have contributed to understanding and to minimizing hot corrosion processes<sup>12,13</sup>; however, the last approach s a necessary prelude leading to more detailed knowledge about controlling the hot corrosion process and, of course, has enjoyed success in predicting the behavior of aqueous corrosion systems<sup>14</sup>.

Electrochemical studies on metal/molten salt systems have been conducted to evaluate corrosion processes at high temperature<sup>1</sup>, but hot corrosion in a reducing environment has not been studied extensively. The reducing nature of the environment, which may allow metal degradation by constituents other than oxygen, is an important aspect of this study since the typical gasifier environment is dominated by CO and H<sub>2</sub>, with CO<sub>2</sub> and H<sub>2</sub>O being present in lesser quantities, together with other agressive species such as H<sub>2</sub>S.

This paper will present two aspects pertaining to polarization in molten sodium carbonate in reducing environments.:

1) Establishment of a reference electrode which will permit monitoring of hot corrosion processes occuring in the vicinity of  $1000^{\circ}$ C regardless of variation in the corroding environments in the cell, and

2) Polarization curve-fitting by computer modelling.

#### 1) Reference Electrode in Hot Corrosion Systems

Reference electrodes employed in the high-temperature electrochemistry have been discussed in the literature<sup>16</sup>,17. A major difficulty involved in the development of a reference electrode for use in molten salt systems is the corrosive nature of fused salts to the component materials. To minimize the effects of corrosion products on the reference electrode potential a reference electrolyte separated from the cell electrolyte has generally been used. Ionic conduction occurs via a restricted channel of the molten electrolyte<sup>18</sup>,19,20 or via a solid state process<sup>17</sup>,21,22 which facilitates the transport of cations, anions, or oxygen ion vacancies as charge carriers. In either case a "liquid junction" potential difference may arise; this has been discussed in some detail elsewhere<sup>17</sup>. The liquid junction potential is minimal if (a) conduction between the two electrolytes occurs via oppositely charged species whose transport number is  $\geq$  0.5, or (b) conduction occurs via one or more species whose activity is the same in the two electrolytes.

The use of electrode polarization to study corrosion behavior in molten salt systems requires the availability of a reference electrode that 1) is not degraded by such electrolytes, 2) permits control of the atmosphere of the cell, and 3) is not itself affected by variation in the cell atmosphere. The use of a molten conducting path restricts use of the cell in that it precludes or renders difficult use of different pressures in the reference and test compartments, while glasses and porcelains offer very poor resistance to the attack of basic salts such as sodium carbonate. A Y203-doped Zr02 has been utilized as a reference electrolyte container for polarization studies in molten salt systems<sup>3</sup>. The transference number of oxide ion in this material is essentially unity. This clearly minimizes the liquid junction potential only to the extent that the oxide ion activity is the same in both the cell and the reference electrolytes. The present authors found the  $\mathtt{Y}_2\mathtt{0}_3\text{-}$ doped ZrO2 to become severely degraded after long term exposure to molten sodium carbonate (50-100 hours at 1000°C).

The present study was designed to test the behavior of recrystallized alumina as a container for a  $CO/CO_2$  reference electrode for use in molten sodium carbonate. This gas mixture, at a fixed total pressure, yields a fixed value of P<sub>CO2</sub> needed to establish the oxide activity in the electrolyte via the

$$Na_{2}^{+}CO_{3}^{-} \neq Na_{2}^{+}O_{-}^{-} + CO_{2}(g)$$
 (1)

while control of the  ${\rm P}_{\rm CO}$  value as well fixes the expected value of the potential for the half cell reaction

$$2e^{-} + 2CO_{2}(g) \stackrel{2}{\downarrow} CO(g) + CO_{3}^{-}$$
 (2)

This electrode was enclosed in a closed-end tube of recrystallized alumina. Reported conductivity values for alumina range widely<sup>23</sup>, from  $10^{-4}$  to  $10^{-10}$  ohm<sup>-1</sup>cm<sup>-1</sup> at  $1000^{\circ}$ C. The alumina used in this study was of 99.8% purity and approximately 97% dense.\* A typical analysis is shown in Table I. Conduction at other than very high

#### Table I

Typical Chemical Analysis of McDanel Type 998 Alumina

 $Al_2O_3 SiO_2 MgO Na_2O CaO Fe_2O_3 Ga_2O_3 TiO_2 MnO ZrO_2 K_2O$ 99.8 .070 .050 .005 .030 .025 .009 .004 .001 - -

\*Type 998 alumina, McDanel Refractory Porcelain Co., 510 Ninth Avenue, Beaver Falls, Pennsylvania 15010 temperatures is presumed due to impurity cations, with sodium and calcium dominating due to the very basic character of their oxides. Conductivity due to a particular ion,  $\sigma_i$ , may be directly related to the ionic diffusivity,  $D_i$ , through equation (3),

$$\sigma_{i} = n_{i} z_{i}^{2} e^{2} D_{i} / kT \qquad (3)$$

in which kT has its usual significance,  $z_1e$  is the charge on the ion, and  $n_1$  is its concentration. Although diffusivity data also show considerable scatter, high temperature data for Al diffusion and 0 diffusion in polycrystalling alumina generally extrapolate to values of the order of 10  $^{-1}$  cm<sup>2</sup>/sec at 1000°C<sup>24</sup>. The data of 0ishi and Kingery<sup>25</sup> suggest a reduction in the activation energy for these processes below approximately 1400°C, however, which would lead to somewhat higher values. In contrast, the data of Frischat<sup>24,26</sup> for Na diffusion in commercial purity alumina, 95% dense 11 cm<sup>2</sup>/sec at 1000°C, and suggest a similar value for Ca diffusion. Assuming this value for both Na and Ca and further assuming that  $z_{Na} = 1$ ,  $z_{Ca} = 2$ , and  $\sigma = \sigma_{Na} + \sigma_{Ca}$ , using the values of Table I a conductivity of 4 x 10<sup>-9</sup> ohm<sup>-1</sup> cm<sup>-1</sup> is obtained for Type 998 alumina at 1000°C. The cell configuration planned for this study has an electrode geometric factor of approximately 66 cm, giving an effective electrode conductance of 0.27 x 10<sup>-6</sup> ohm<sup>-1</sup>. The resistance of a two-electrode cell, is, thus, predicted to be of the order of 7.4 M ohm, well within the range of conventional instrumentation.

Thus, commercial purity alumina as a reference electrode container for basic salts offers cationic conduction, eliminating or minimizing the liquid junction potential, and acceptable conductance, as well as resistance to dissolution.

#### 2) Electrode Polarization and Computer Modelling

The viability of electrode polarization as means for investigating corrosion phenomena in molten salts has been demonstrated  $^{3,21}$ . As this technique is customarily practiced, a current is impressed upon an electrode fashioned from the metal under study (the working electrode) using a second, inert electrode (the counter electrode). The potential of the working electrode relative to the electrolyte is measured to within an additive constant using a third (reference) electrode and a high impedance potential-measuring device.

Rate equations of cathodic polarization for a corroding system generally expressed as  $^{14}\,$ 

$$i = i_0 e^{-v/b} c$$
 (4)

for activation polarization; as

$$i = i_{sat} (1 - e^{v/b}c)$$
 (5)

for concentration polarization; and as

$$i = v/R_{c}$$
(6)

for resistance polarization; where i is current density, i.e., corrosion rate,  $i_0$  is 'exchange current density',  $i_{sat}$  is saturation current density, v is over-potential, and  $b_c$  Tafel slope for the cathodic reaction, and  $R_c$  is the applicable cell resistance. Rate equations of anodic polarization for a corroding system can be expressed in the same manner. The net current passed by the electrode experiencing, for example, one anodic and two cathodic reactions is calculated as

$$i = i_a - i_{c1} - i_{c2}$$
 (7)

where  $i_a$ ,  $i_{c1}$  and  $i_{c2}$  are the components of current which are responsible for one anodic and two cathodic branches. Establishment of the electrode polarization curve for a hot corrosion system is schematically illustrated in Fig. 1.

The interpretation of semilogarithmic electrode polarization curves is especially difficult when there are competing electrode reactions or when there is no clear-cut region of Tafel behavior<sup>14,27, <sup>28</sup>. Under these circumstances graphical analysis of polarization curves may be impossible and statistical analysis difficult due to the nonlinearity of the current-voltage relationship and the number of empirical parameters needed for a system involving several reactions. However, it can be reasonably well interpreted through a computer graphics interactive program without the pitfalls, complexity, and expense of developing and operating the nonlinear regression procedure necessary to a statistical analysis. A procedure for this computer modelling was reported elsewhere in detail<sup>29</sup>.</sup>

The current due to a single cathodic reaction experiencing combined activation, concentration, and resistance polarization may be written  $^{14}$ 

$$i_{c} = (1 - i_{c}/i_{sc})^{RT/nFb}c \cdot e^{-(v-v_{c}^{\circ})/b}c \cdot e^{(-i_{c}c_{c}^{R}c_{c}/b_{c})}$$
 (8)

where v is the potential of the electrode (relative to a suitable reference electrode);  $i_c$  is the current due to this electrode process; R, T, and F are the usual constants; n is the number of charges on the ion whose limiting diffusion rate is responsible for the concentration polarization;  $i_{sc}$  is the limiting diffusion current; 2.303b<sub>c</sub> is the Tafel slope; R<sub>c</sub> is the applicable cell resistance; and

 $V_{c}^{0/b}$  may be written

$$c^{o} = v^{o}/b_{c}$$

e

where  $i^{0}$  is the 'exchange current' and  $v^{0}$ , the 'rest potential'. A single empirical constant is chosen to represent the exchange current and rest potential because those parameters have significance only if the reverse electrode reaction makes a significant contribution to the total cell current. Similarly, the current due to a single anodic reaction experiencing activation, concentration, and resistance polarization may be written

$$i_a = (1 - \frac{i_a/i_{sa}}{a})^{RT/nFb}a \cdot e^{(v-v_a^o)/b}a \cdot e^{-i_aRa/b}a$$
 (10)

(9)

The net current passed by the electrode can be determined by the use of Equation 7.

#### II. Experimental Procedures

#### 1) Reference Electrode

The reference electrode studied was comprised of a 20 mil (0.0508 cm) platinum wire immersed in molten sodium carbonate (Fisher Certified ACS) contained in a McDanel Type 998 alumina closed-end tube. The wire entered the electrolyte through a small diameter (1/4" (0.635 cm) or 1/8" (0.318 cm) 0.D.) alumina tube, through which a preset mixture of carbon monoxide and carbon dioxide was introduced at a flow rate of approximately 25 ml/min. Within the electrode compartment, the wire was shaped into a helix to increase the exposed electrode area. The external alumina sheath was 1/2 in. outside diameter (1.27 cm), with 1/16 in. wall thickness (0.159 cm) and was immersed in the cell to a depth of about 3 cm. The cell electrolyte was also molten sodium carbonate and was contained in an alumina The cell was housed in a vertical retort heated by a glow crucible. bar furnace with a proportioning solid state controller. Cell temperature was measured directly by an alumina-sheathed Pt-10% Rh/Pt thermocouple immersed in the electrolyte; no discernible temperature variation occured.

Gas mixtures were derived through appropriate mixing of bottled CO (Matheson G.P. purity), CO<sub>2</sub> (Norwich medical grade), and a nominal 95% CO/5% CO<sub>2</sub> mixture (Matheson certified mixture 95.2% CO/4.8% CO<sub>2</sub>). Individual and total flow rates were determined with rotameter flow gauges. Initial drying of the electrolyte was accomplished by heating of the cell slowly under vacuum to test temperature. Equilibrium hydroxide activities have been computed for this system and for low inlet moisture contents are not sufficiently high to significantly alter the carbonate activity in the melt.<sup>30</sup>

The current-voltage characteristic of the reference electrode was determined by impressing a potential from an external dc power supply between two ostensibly identical reference electrodes and measuring the resulting current with a zero resistance ammeter. The emf developed by the cell was monitored by a Keithley Model #616 electrometer, and recorded by a Varian Model #G-1000 recorder. During the emf measurement the mullite retort was grounded to eliminate inductive pick-up by the wire leads in the cell.

#### 2) Electrode Polarization

The polarization cell contained three electrodes; a Pt-counter electrode, a working electrode (the specimen), and a Pt reference electrode contained in a recrystallized alumina tube developed in this study. All were immersed in molten sodium carbonate. The cell was contained in a mullite retort in a vertical furnace as explained The specimen was polarized by impressing current both anodiabove. cally and cathodically. The degree of polarization was measured as the specimen potential with respect to the reference electrode, while the rate of the electrode reaction was measured as the cell current. Polarization was started after steady-state rest potential of the specimen was obtained. Current readout and potential control were provided by a Wenking Potentiostat Model No. 68TS3 with an attached Wenking Stepping Motor Scanning Potentiometer Model No. 69. A Hewlett Packard Model No. 7030A X-Y recorder and a Hewlett Packard Model No. 7563A logarithmic converter served to record cell current and specimen potential on a semi-logarithmic plot.

#### 3) Computer Modelling.

Curve fitting was accomplished through a series of programs written in Fortran and PL/1, run via the Conversational Monitor System (CMS) component of an IBM Virtual Machine Facility/370. Input and output, including graphical output, were accomplished with a Tektronix 4006-1 graphics terminal which, in this case, operates as a remote terminal, communicating with the University of Connecticut Computer Center via the telephone line and an acoustic coupler. All programs necessary to the process are stored on disk and are readily accessed through simple commands.

#### III. Results and Discussion

#### 1) Reference Electrode

A typical curve for the current-voltage characteristic of the reference electrode, using the nominal 95% CO/5% CO $_2$  mixture at both

electrodes at 1000°C, is shown in Figure 2. Simple ohmic behavior was seen in all cases with observed cell resistance values falling in the range of 0.0282 to 0.0353 M ohm, the variation apparently reflecting differences in the immersed electrode area from one experiment to the next. Using a geometric factor of 66 ohm per electrode, the apparent sheath resistivity is  $\simeq 1$  M ohm-cm. The cell resistance was smaller than the predicted value by a factor of approximately 200. This is attributed to one or more of the following reasons: 1) A substantial increase in the Na<sub>2</sub>O concentration within the alumina due to contact with the molten sodium carbonate, 2) A change in the activation energy for Na transport with temperature, rendering invalid extrapolation of Frischat's data, or 3) A simple manifestation of the tremendous variation in the reported values for diffusivity of various species and for conduction in alumina, presumably attributable to variations in method of preparation, impurity content, and/or measurement technique.

Nernstian response of the reference electrode was evaluated by maintaining the same cell configuration of two identical reference electrodes, but diluting the flow of the nominal 95% CO/5% mixture through one of the electrodes by admixing CO or CO<sub>2</sub>. The range of  $P_{CO}/P_{CO_2}$  employed was 0.11 <  $P_{CO}/P_{CO_2}$  < 103, with  $P_{CO} + P_{CO_2}$  l atm. Assuming only a negligible effect of this dilution upon the carbonate activity, the potential of this cell is expressed by

$$E = E_{o} + \frac{RT}{2F} \ln \frac{(P_{CO_{2}}^{2})r(P_{CO})w}{(P_{CO_{2}}^{2})w(P_{CO})r}$$
(12)

where E is the measured cell potential; E°, the standard cell potential; and the subscript r and w refer to the reference (constant) electrode and working (variable) electrode; respectively. The standard cell potential is ideally zero, but non-zero values were observed when tacitly identical gas mixtures were passed through both electrodes. The magnitude of these values was typically in the range of 5 to 40 mv, with occasional larger values, and was reasonably consistent for a given pair of electrodes. This is within the range of error attributable to the rotometer gauges, since, for the worst case, the possible error in volumetric flow rate determination was  $\simeq 20\%$ ; the cummulative errors for this case yield a maximum uncertainty in electrode potential of  $\simeq 20$  mv. For the purpose of evaluating Nernstian response of these electrodes, an effective  $E^\circ$ was measured at the start of each series of experiments and subtracted from the subsequently measured potential values. Figure 3 shows such values of  $(E-E^{\circ})_{meas}$  compared with  $(E-E^{\circ})_{calc}$ ; Nernstian behavior is clearly demonstrated.

An additional study was performed to compare the behavior of this reference electrode to a low resistance reference electrode during an electrode polarization experiment. In this study, three electrodes were involved: The reference electrode, which was either the electrode described or a similar electrode in which a 92% ZrO2 -8% Y<sub>2</sub>O<sub>3</sub> crucible (resistivity 10 ohm cm) was substituted for the Type 998 alumina tube, a nickel (Ni 200) working electrode, and a platinum counter electrode. Although the thermodynamic state of the electrolytes was not fixed thereby, reproducible conditions were established by bubbling oxygen through the reference and cell electrolytes. Figure 4 shows anodic and cathodic polarization curves obtained at 1000°C. Similar behavior is evidenced with both reference electrodes. Taking into account the expected difference in rest potential (zero current) of the nickel as measured against the different; reference electrodes, the discrepancy between the curves representing the different reference electrodes is comparable to that between curves representing different scans with the same electrode. During prolonged cathodic polarization under a CO rich atmosphere, a slight blackening of these electrodes was observed due to the presence of cathodically reduced carbon. This is discussed in detail by Boruka<sup>19</sup>.

It is clear that the Pt, CO<sub>2</sub>/CO Na<sub>2</sub>CO<sub>3</sub> electrode contained in commercial purity alumina fulfills the requirements of a reference electrode for molten sodium carbonate systems, and, very likely, for other basic electrolyte systems operating at temperatures near or exceeding 1000°C. The alumina is readily obtained, is not degraded by basic electrolytes, and has an acceptable resistivity. The electrode is Nernstian and permits separate control of the cell and reference environment. Conduction through the alumina is presumed to be by sodium and calcium ions; exchange of calcium for sodium ion at the alumina/electrolyte interfaces will permit this without requiring calcium in the electrolytes or postulating an electrodic reaction at these interfaces. The cation of the electrolyte need not to be restricted to sodium provided such an exchange is feasible. In cell in which the cell electrolyte and the reference electrolyte possess similar cation activities, no liquid junction potential is expected; if these activities are substantially different, a liquid junction will exist, but will be constant unless such activities are altered by environmental control or the electrode reactions. Such alteration is unlikely in alkali metal salts, where these reactions primarily involve anions.

#### 2) Electrode Polarization and Computer Modelling

Electrode polarization study of various candidate metals for coal gasifier structural components is presently in progress. The curves shown in Fig. 5 are typical results for Ni 200 polarized at 1000°C in two different reducing environments: Curve #1, in 4.8%  $CO_2/95.2\%$  CO; and curve #2, in 5.8%  $H_2S/94.2\%$  H2. The electrode potential was measured with respect to a reference electrode developed in this study; however, the reference gas composition was

38.2% CO/61.8% CO<sub>2</sub> since this composition defines a convenient thermodynamic potential scale<sup>19</sup>. Rest potentials of -27 mv and +103 mv were observed for curve #1 and #2, respectively. The rest potential became stable about 5-7 hours after the gas environments were introduced at operating temperature. The cathodic branch of curve #1 has only one component, probably cathodic reduction of CO<sub>2</sub> by

while the cathodic branch of curve #2 has two components, the first hydrogen reduction

$$2H^+ + 2e^- \stackrel{\rightarrow}{\leftarrow} H_2$$

and the other reduction. The anodic curves in both cases show distinct branches representing different reactions, and show a pseudo-passive state. Such passive behavior has, to date, not been included in our computer program.

An example illustrative of computer modelling is shown in Fig. 6. A sample of Ni 200 was polarized in molten oxygen-saturated sodium carbonate at  $1000^{\circ}$ C. The dotted line represents experimental data, while the solid line represents the curve calculated by computer modelling. This curve has one anodic component and two cathodic components. In the oxygen environment the anodic curve shows no pseudo-passive state, seen in reducing environments. The first cathodic component is presumed to be oxygen reduction and the second component,  $CO_3^{-1}$  reduction. The most appropriate values found for the empirical constants are listed in Table 2.

### Table 2

#### Values of Empirical Constants

i sa2	= 360	ma/cm <sup>2</sup>	i scl	=	7	ma/cm <sup>2</sup>
isc2	= 105	ma/cm <sup>2</sup>	<sup>b</sup> a2	R	100	mv
<sup>b</sup> c1	= 140	mv	<sup>b</sup> c2	=	20	mv
v <sub>a2</sub> o	= -210	mv	v <sub>cl</sub>	=	50	mv
v <sub>c2</sub>	= -500	mv	Ra	=	1.	ō ohm
R <sub>c</sub> .	= 1.5	ohm				

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Figure 1: Schematic illustration of establishing the kinetic expression for a "hot corrosion" system.



Figure 3: Demonstration of Nernstian behavior of the aluminasheathed electrode. 0, 0. and 0 represent different electrode pairs. Data for 0 and 0 taken at 928°C; 0, at 957°C.



Figure 2: Current-voltage dependence of cell comprised of two alumina-sheathed reference electrodes.



Figure 4: Anodic and cathodic polarization behavior of Ni 200 measured against alumina-sheathed and  $Y_2O_3$ -doped ZrO<sub>2</sub> electrodes.



Figure 5: Anodic and cathodic polarization curves for Ni 200 in a molten sodium carbonate at 1000° in reducing environments. Curve #1 in 4.8%  $CO_2/95.2\%$  CO, and curve #2 in 5.8%  $H_2S/94.2\%$   $H_2$ .



Figure 6: Experimental polarization curve (dotted line) with calculated curve (solid line) using constants in Table 2, by computer modelling.

### THE HOT CORROSION OF METALS BY MOLTEN SALTS

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## ABSTRACT

Some theoretical mechanisms for the hot corrosion attack of metals and alloys under thin fused salt films are discussed. The chemical fluxing (dissolution) of the protective oxide on a pure metal is proposed to occur wherever the gradient in the oxide solubility in the salt at the oxide/salt interface is negative, such that a reprecipitation of dissolved oxide occurs. In turn, the oxide solubility gradient is established by the nature and site of the electrochemical reduction step which always generates local basicity. The interrelation of the basicity gradient in the melt to the oxide solubility map decides the occurrence of continuing hot corrosion. In the hot corrosion of alloys, the possibility of a synergistic coupling of the dissolution for the several oxides of the components can result depending upon the specific details of the oxide solubility plots and the local basicity as established by the site of the cathodic reduction step.

### Introduction

Alloys experience accelerated corrosion attack upon exposure at elevated temperatures to an oxidizing gas when a thin film of fused salt coats the surface. Corrosion problems related to the attack of metals by molten nitrates, carbonates, hydroxides, sulfates, coal ash, etc. are well known and very important to the functioning of many engineering systems. In the operation of aircraft gas turbines near and over the ocean, a fused Na SO -NaCl film from an injested sea-salt aerosol may coat the hardware and lead to accelerated oxidation of the turbine alloys. In this corrosion environment, the oxidant gas contains the products of fuel combustion including SO and excess 0. In this paper, some novel theoretical mechanisms and criteria for the hot corrosion of metals and alloys in Na SO are presented. These mechanistic proposals, however, 2 should find general applicability in the analysis of other metal/salt/oxidant corrosion reactions.

A chemical mechanism(s) of hot corrosion has been previously described in terms of an acid-base dissolution of the protective oxide film  $(A1_0, or Cr_0)$  on a high -temperature alloy or coating. Other authors have conducted electrochemical studies of metals submerged in deep sulfate melts to establish anodic and cathodic pelarization curves. However, a generalized theory which integrates the chemical and electrochemical phenomena for corrosion beneath a thin salt film has not been proposed, nor have previous experiments been properly designed to evaluate the details of a mechanism for hot corrosion. The presentation of such a generalized mechanistic theory and suggested experiments is the purpose of the present paper.

A considerable insight into the mechanism of accelerated oxidation beneath a thin fused salt film can be won from the literature on aqueous solution corrosion at ambient temperature. The geometry of hot corrosion (thin film electrolyte coating) closely resembles that for aqueous "atmospheric corrosion" where the electrochemistry and the rate-limiting step have been analyzed by Mansfeld and Kenkel<sup>15,16</sup>. However, considerable differences with respect to ease of an electron transfer step and the rate of dissolved gas transport must be expected. Both for aqueous solutions and for fused Na<sub>2</sub>SO<sub>4</sub> the thermodynamic stabilities of phases are graphically illustrated as a function of redox potential and an acid-base parameter by Pourbaix diagrams. In Figs. 1 and 2, Pourbaix-type phase stability plots are presented for the Na-A1-S-O and Na-Cr-S-O systems for those conditions where Na<sub>2</sub>SO<sub>4</sub> is the stable phase in the Na-S-O system. The ordinate of log  $P_{0,2}$  could be related to an electrode potential if a proper reference electrode to indicate log  $P_{0}$  were available. The basicity of the melt is described <sup>2</sup> in terms of the thermodynamic activity of sodium oxide,  $a_{Na_20}$ , relative to pure sodium oxide. The -log  $a_{Na_20}$  abscissa of the Pourbaix-type plot could also be considered an electrode potential, if a proper reference electrode were available to indicate log  $a_{Na_20}$ . Such an electrode would be equivalent to a pH electrode in aqueous solutions. Unfortunately, the convention accepted for Pourbaix diagrams in fused salt systems plots the abscissa as -log  $a_{Na_20}$ , with high basicity at the left and low basicity at the fight-opposite to the convention for aqueous solution diagrams.

From Pourbaix diagrams such as Figs. 1 and 2, within the respective fields of Al\_0 and Cr\_0 stability, the solid oxides exhibit a basic <sup>3</sup> and acid solubility in the  $Na_2S0_4$  melt, which in principle, could be plotted for known values of the activity coefficients for the solute ions, according to the reactions:

ions, according to the reactions:  $A1_20_3 \neq 2 A1^{3+} + 3 0^{2-}$  acid dissolution (1a)  $A1_20_3 + 0^{2-} \neq 2 A10_2^-$  basic dissolution (1b)  $Cr_20_3 \neq 2 Cr^{3+} + 3 0^{2-}$  acid dissolution (1c)  $Cr_20_3 + 2 0^{2-} + 3/2 0_2^{-2} Cr0_4^{2-}$  basic dissolution(1d) Alternatively, lacking a prior knowledge for the solute activity coefficients, or wishing to test the validity of Eqs. (1a-d), one can establish experimentally the solubility of the oxides in Na<sub>2</sub>S0<sub>4</sub> as functions of P<sub>0</sub> and <sup>a</sup>Na<sub>2</sub>0.

Stroud and Rapp<sup>17</sup> developed an electrochemical electrode to measure the sodium oxide activity in Na<sub>2</sub>SO<sub>4</sub> melts equilibrated at given oxygen pressures. From Na<sub>2</sub>SO<sub>4</sub> solutions equilibrated with excess  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> or Cr<sub>2</sub>O<sub>3</sub>, samples were taken and analyzed to establish the solubilities of these oxides as a function of a at fixed P<sub>0</sub> at 1200K. Superimposed plots for Al<sub>2</sub>O<sub>3</sub><sup>20</sup>solubility<sup>2</sup> at P<sub>0</sub> = 10<sup>-4</sup> and 1 atm are given as Fig. 3. Based on the slopes of the solubility lines, the acidic

dissolution reactions (1a) and (1c) were substantiated. If solid NaAlO<sub>2</sub> did not form on Al<sub>2</sub>O<sub>3</sub> for log  $a_{Na_2O}$  -8.3, then Eq. (1b) is valid. The basic dissolution of Cr<sub>2</sub>O<sub>3</sub> at P<sub>O2</sub> = 10<sup>-4</sup> atm was consistent with Eq. (1d), but this basic solubility of Cr<sub>2</sub>O<sub>3</sub> decreased with increasing P<sub>O2</sub>, which cannot yet be explained. Further experiments are in progress to substantiate the values for the solubilities of Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> in Na<sub>2</sub>SO<sub>4</sub> at 1200K.

For the purposes of present paper, we do not need to assume that the data of Fig. 3 are exactly correct; rather we only want to admit that in general the solubility curve (s) for any given oxide must resemble those of Fig. 3, with specific slopes for the acidic and basic solutes which are decided by the stoichiometric coefficients in the dissolution reactions. Of course, the solubility curves for some oxides may be complicated be the presence of more than two important solutes. For the discussion to follow, the solutes. For the discussion to follow, the solutes of Eqs. (la-d) and the general form of the solubility curves of Fig. 3 are accepted as correct.

An Acid-Base Fluxing Mechanism For Hot Corrosion of a Pure Metal

As a criterion for the continued (stable) hot corrosion of a pure metal, we propose that the gradient at the oxide/ salt interface in the solubility of the protective oxide (as acid or basic solute species) is negative, i.e.,

$$\frac{d[\text{oxide solubility}]}{dx} = 0 < 0$$
(2)

By this criterion, as illustrated schematically in Fig. 4, the continuous reprecipitation of the oxide in the salt film away from the oxide/salt interface is expected to permit local equilibrium between the oxide and salt throughout the salt film.

The concentration gradient criterion of Eq. (2) may be considered as an empirical condition for dissolution and reprecipitation in the salt. However, in an isothermal system, the concentration gradient would not serve as the driving force for the transport of the soluble ionic species because no gradient in the chemical potential of the oxide would exist in a salt film in local equilibrium with the oxide throughout. In general, the diffusion flux of the oxide, MO, can be expressed according to a linear law as follows:

$$j_{MO} = -L_{11} \frac{d\mu_{MO}}{dx} - L_{12} \frac{d\mu_{Na_2}O}{dx} - L_{13} \frac{d\mu_{Na_2}SO_4}{dx} - \frac{L_{10}}{T} \frac{dT}{dx}$$
(3)

where  $\mu$ , is the chemical potential of the component and  $L_{ik}$  is the transport coefficient. When oxide is reprecipitated in the salt,  $\mu_{MO}$  becomes uniform if local equilibrium is assumed. Then, in an isothermal system, the first term of the r.h.s. of Eq. (3) would be zero, as would the fourth term, while the third term should be negligible small. But the second term of the r.h.s. of Eq. (3) would not be zero so long as the basicity gradient and the cross-term  $L_{12}$  were not zero.

The only other means for the transport of the soluble ionic species is local convection set up by density differences in the salt film. The Stokes sinking of the heavier oxide precipitates might in this case contribute to convective transport.

Because a reprecipitated oxide cannot form as a continuous protective layer, a voluminous, porous oxide pro-duct interspersed with salt is expected; this morphology is indeed representative of hot corrosion products. This model illustrated schematically in Fig. 4 may be considered as an empirical criterion which assumes local equilibrium at the oxide/salt interface and throughout the salt film. The oc-currence of oxide reprecipitation in the salt film is common with the acid-base fluxing mechanism proposed by Goebel and Pettit<sup>18</sup>, but these authors assumed that basic fluxing arose from a chemical reaction to form sulfides (sulfidation) in the metal. Indeed, the reduction of the sulfate ion to form sulfide would release oxide ions at the oxide/salt interface in excess of those required for the growth of the oxide scale, and basic fluxing should occur. Later, acid fluxing of the scale was described by Goebel  $etal^3$  as arising from the removal of oxide ions in the salt upon the formation of basic complexes by other metallic components in the metal, e.g., formation of  $MoO_A^{2-}$  following the oxidation of Mo in the alloy.

In the present acid-base fluxing model for a pure metal, we propose that the gradient in the solubility of the protective oxide (as given by Fig. 3, for example) in the salt film is established by the local variation of sodium oxide activity, and perhaps  $P_0$ , across the salt film. In turn, these conditions are 2 established principally by the basicity necessarily generated at the site of the electrochemical reduction reaction, as well as the chemical interaction between the oxidant and the salt. As in any electrochemical process, the open-circuit half-cell potential  $E_0$  for each possible reduction reaction is expressed as:

 $E_0 = E_0^{\circ} - \frac{RT}{nF} \ln [\frac{a_{red}}{e_{oxid}}]$ (3)

for the half-cell reduction reaction

oxidized species+ n e  $\rightarrow$  reduced species where  $E_0^O$  is the standard open-circuit half-cell potential for the reduction reaction. A tentative, standard electrochemical reduction series for Na<sub>2</sub>SO<sub>4</sub> at 1200K is proposed as Table I. Quantitative values<sup>2</sup> for the redox reactions of Table I have not been determined, and indeed, a standard reference electrode has not been decided. Perhaps<sub>19</sub> a Au/ 0<sub>2</sub>-SO<sub>3</sub> (1:2) electrode, as suggested by Rahmel<sup>19</sup> would represent<sup>2</sup> a suitable standard reference electrode (equivalent to standard hydrogen electrode), with the Ag/10 mole % Ag<sub>2</sub>SO<sub>4</sub> : Na SO<sub>4</sub> electrode serving as the equivalent of

the calomel electrode in aqueous solutions.

According to Table I, the effects of melt basicity, oxidation potential of melt, the gaseous environment, and the presence of transition metal ions are all important in deciding the predominant reduction reaction, as is also the case in aqueous solution corrosion. In a highly basic melt (perhaps,  $a_{Na_20} > 10^{-4}$ ) reduction reactions a and b should

be favored. In a highly acid melt (perhaps  $a_{Na_20} < 10^{-15}$ ), reduction reaction c would be favored, at least for a salt film thin enough to support the necessary molecular S0, and S0, countertransport. As illustrated in Fig. 5a, oxygen reduction by reaction d would be favored only for reasonably neutral, thin films of Na<sub>2</sub>S0<sub>4</sub>, as will be

discussed later. If the metal or alloy should provide dissolved transition metal ions to a highly oxidized melt, then the reactions e-g could predominate, and should introduce a very important shift in the site of the reduction reaction to the salt/gas interface, as shown in Fig.5b.

For dilute  $M^{2+}$  and  $M^{3+}$  concentrations, counterdiffusion of these species would be required. But if the total concentration of the mixed valence transition metal ions were sufficiently high, then electronic exchanges between these ions  $(M_{*}^{2+} + M^{3+} \rightarrow M_{*}^{3+} + M^{2+})$  could introduce a more rapid transport by electronic conduction through the melt. Electronic conduction was established for SiO<sub>2</sub>-CaO-FeO-Fe<sub>2</sub>O<sub>3</sub> slags at high temperatures by Engell and Vygen<sup>20</sup>.

If all these reactions with higher  $E_0^{\circ}$  exhibit a lower E because of concentration polarization according to Eq.

(3), then the sulfate anion itself can be reduced according a sequence of reduction reactions such as h-k, although the details of these reactions have not been specifically established. The reduction of the sulfate anion is obviously favored for deep, reasonably neutral melts, especially at the start of a reaction before the transition metal ions become available. Because of the general availability of sulfate anions, reduction of the anion would certainly not be limited by a slow arrival flux to the oxide/metal interface. The reduction of the sulfate anion could lead to such high local levels of sulfur activity that the formation of metal sulfides could occur; frequently, hot corrosion is associated with simultaneous sulfidation. However, when sulfidation is viewed as the result of only one of the possible reduction reactions, hot corrosion is not necessarily tied to sulfidation.

The other half of the electrochemical hot corrosion mechanism, the oxidation half-cell reaction is the oxidation of the metal at the metal/scale interface. As revealed by the Pourbaix thermodynamic diagrams, most metals could not exist in local equilibrium in contact with  $Na_2SO_4$ , so gen-

erally, an intervening electronically-conducting oxide film is expected. The oxidation of the metal at the metal/oxide interface with the ensuing transport of cations plus electrons to the oxide/salt interface would equal the rate of the electrochemical reduction reaction. A time-independent rate of oxide dissolution at the oxide/salt interface with an ensuing oxide reprecipitation would lead to the maintainance of a constant steady-state oxide thickness and constant steady-state reaction kinetics as is frequently found in hot corrosion. An exactly analogous model exists for the coupling of scale growth and scale evaporation in metal/gas reactions<sup>21,22</sup>. Then for "linear" hot corrosion kinetics at steady-state, if the interfacial reactions can be reasonably assumed to satisfy local equilibrium, the corrosion rate would be controlled by the diffusion of cations through the oxide in series with diffusion of reactants and products of the electrochemical reduction reaction through the salt film.

Let us return to an integration of the electrochemical reduction reaction into the hot corrosion criterion of Eq. (2) as illustrated in Fig. 4. Each electrochemical reduction reaction of Table I introduces increased local basicity at the reduction site. As illustrated in Fig. 5a, the reduction reaction would usually be expected to occur at the oxide/salt interface, but as shown in Fig. 5b, the presence of mixed valence transition metals could allow the reduction step to occur at the salt/gas interface. In either case, the site of the reduction reaction would be expected to be the most basic local condition in the salt film.

Figure 6 illustrates a schematic oxide solubility plot with superposition of four different sets of relative basicities at the salt/gas interface II and at the oxide/salt interface I which would set up and support continued hot corrosion of a pure metal according to the model outlined here. In each case, the condition of Eq. (2) as illustraed in Fig. 4 is satisfied. Of course, for some oxides, the solubility of the oxide ( $Cr_2O_3$ , for example) also depends upon  $P_{O_2}$  so that a three-dimensional diagram would be more suitable.

According to cases A and C of Fig. 6, the basicity gradient in the salt film is opposite in direction, but then the mode of oxide dissolution is also opposite. For case B, one would expect continued hot corrosion whenever the local basicities at interfaces I and II straddle the minimum. In general, one would expect that the value for the basicity at the oxide/gas interface would be fixed approximately by the value of  $P_{SO_3}$  in the ambient atmosphere, unless the salt

basicity were somehow otherwise established by the detailed mode of continuing salt deposition. If the relative basicities at the interfaces I and II for cases A and C of Fig. 6 were reversed, then the hot corrosion criterion of Eq. (2) would not be met, and one would expect the entire salt film to saturate with the oxide consistent with the basicity at interface I after which time accelerated hot corrosion should stop. Nickel coated with a film of  $Na_2SO_4$  and exposed to air experiences transient accelerated hot corrosion<sup>18</sup>.

To test this dissolution model for the hot corrosion of a pure metal, a knowledge of the oxide solubility as a function of the  $P_{0_2}$  and basicity (log  $a_{Na_20}$ ) must be known and

experimental determination of  $P_{0_2}$  and basicity at both the

oxide/salt and the salt/gas interfaces are required. The latter determinations have not been previously made for hot corrosion beneath thin fused salt films.

In Fig. 7, a novel experimental arrangement is introduced for electrochemical studies of the hot corrosion of metals beneath thin fused salt films. The provision of two monitoring electrodes, a  $2rO_2$ -CaO oxygen sensor and a mul-

lite-electrolyte probe with fixed  $P_{SO_3}$  and  $P_{O_2}$ , provides

the means to measure both  $P_{0_2}$  and  $P_{SO_3}$  (or a  $Na_20$ ) at both

the corroding metal specimen and at a submerged Au electrode. The calibration and comparison of the various electrodes in fused  $Na_2SO_4$  at 1200K are described in detail by Watt, et al <sup>23</sup> in another paper of this symposium. At this point, it should suffice to reiterate that the zirconia probe can indicate the oxygen activity at both the corroding metal surface and at the gold electrode, which should enjoy an equilibrium with the gas phase, i.e., represent the salt/gas interface. Further the  $Ag/Ag_2SO_4$  or  $Pt/SO_2$ ,

 $O_2$  electrode in a mullite electrolyte tube each respond to the ratio a  $Na_2O'PO_2^{1/2}$ , so that combined with the reading

of the zirconia probe, the local basicity at the corroding metal and at the gas/salt interface (Au electrode) can be established. These are exactly the measurements required to test the mechanism and criterion for hot corrosion outlined here. Such measurements have been completed for several metals in several gaseous ambients and will be reported shortly.

The experimental arrangement of Fig. 7 further provides the novel possibility for anodic and cathodic polarization studies beneath a thin layer of fused salt. In such studies, either gold or the  $ZrO_2$  or the mullite probe could be used as the reference electrode with the corroding metal as the working electrode, and a gold electrode as the counter electrode. Because the solubility of the oxide film on the working electrode may depend upon both  $PO_2$  and  $a_{Na_2}O$ , two

probes are again required to independently track these parameters at the corroding metal (working electrode) surface. The past use of a  $Ag/Ag_2SO_4$  electrode as the sole reference electrode in polarization studies in deep melts fixes only

the ratio  $a_{Na_20}/P_{0_2}^{1/2}$  at the oxide or metal/salt interface, and this control may be inadequate to specify or know the local solubility.

As a further use of the arrangement of Fig. 7, a freely corroding specimen can be shorted through a high-impedance microammeter to an immersed gold electrode to form a galvanic couple. As applied by Mansfeld and Kenkel<sup>15,16</sup> to study atmospheric corrosion under aqueous thin films, the galvanic current can represent exactly the corrosion current when transport through the electrolyte film constitutes the rate limiting step. Preliminary electrochemical thin film polarization and galvanic coupling studies have been completed and will be reported shortly.

Mansfeld and Kenkel<sup>15,16</sup> have shown that the kinetics of atmospheric corrosion are limited by the diffusion of molecular oxygen through the thin aqueous surface film. From recent measurements of the solubility<sup>24</sup> and diffusivity<sup>25</sup> of molecular oxygen in molten  $Na_2SO_4$ , a Fick's first law calculation can be made to test the rate of arrival of oxygen for the cathodic reduction reaction in rapid hot corrosion. For a density of  $Na_2SO_4$  of 2.5gm/cm<sup>3</sup>, a thin film of 0.5 mg/cm<sup>2</sup> would amount to a thickness **S** of 2 x 10<sup>-4</sup> cm. The maximum arrival flux of molecular oxygen from P<sub>O2</sub> = 1 atm is given by

 $J_{0_2}$  (moles  $0_2/cm^2 sec$ ) =  $D_{0_2} \frac{C_{0_2}}{\delta}$ 

where the solubility  $C_0$  equals about 3 x 10<sup>-7</sup> moles  $O_2/cm^3$  at 1000°C and the diffusivity about 5 x 10<sup>-5</sup> cm<sup>2</sup>/sec. Upon substitution into the preceeding equation, with one mole  $O_2$  weighing 3.2 x 10<sup>4</sup> mg, a maximum oxygen flux of 2.4 x 10<sup>-3</sup> mg/cm<sup>2</sup> sec is calculated. This value can be compared with the very fast rate of oxygen gain reported in Fig. 2 of Goebel and Pettit<sup>18</sup> upon the hot corrosion of pure Ni in pure  $O_2$  under 0.5 mg/cm<sup>2</sup> of Na<sub>2</sub>SO<sub>4</sub> at 1000°C. These kinetics approximated a gravimetric rate of 1.7 x  $10^{-2}$  mg/cm<sup>2</sup>-sec, a factor of seven greater than the calculated maximum oxygen flux. Several conclusions are

obvious: 1) in rapid hot corrosion, the arrival of oxygen may be inadequate to supply the cathodic reduction of oxygen, and 2) for hot corrosion experimentation in deep (crucible) melts, oxygen reduction cannot represent the cathodic step. Understandably, in the experiment of Goebel and Pettit, <sup>18</sup> nickel sulfide was observed as a corrosion product from the reduction of the sulfate anion. Finally, the hot corrosion of metals beneath a thin fused salt film and the atmospheric corrosion of metals beneath aqueous films do not generally share the same rate limiting step (transport-limited oxygen reduction).

Finally, subsequent to the mechanism and criterion for continued hot corrosion of a pure metal proposed here, one might inquire about the behavior expected for the hot corrosion of a binary A-B solid solution alloy. Unlike some of the variable-composition, amorphous corrosion products formed in aqueous solutions, at elevated temperatures, the products usually are crystalline and frequently exhitit little mutual solubility. Thus, the adherent corrosion products in fused salt corrosion might be represented by AO and BO, each of which would exhibit solubility curves similar to those shown in Fig. 3 for  $Cr_2O_3$  and  $Al_2O_3$ . These solubilities would depend upon  $a_{Na_2O}$  and perhaps upon  $P_{O_2}$ . The two solubility curves would naturally exhibit some lateral and vertical displacements relative to each other. One may consider Fig. 3 as illustrative for the superposition of two solubility curves.

In highly acidic (low  $a_{Na_20}$ ) salts, the AO and BO oxides would each exhibit acidic dissolution which would provide oxide ions as a soluble product of each oxide. Under this condition, i.e., for interfacial values of  $a_{Na_20}$  to the

right of each solubility minimum, the previously proposed criterion for a pure metal could be applied to each oxide separately. However, in an environment which would fix the  $a_{\rm Na_20}$  value at the oxide/salt interface at a value between

the two minima, the oxide with its minimum on the right would exhibit basic dissolution upon complexing with oxide ions, while the other oxide would experience acidic dissolution to release soluble oxide ions. Under this condition, the combination of an acidic and a basic dissolution, rapid synergistic attack (AO + BO  $\rightarrow$  AO<sub>2</sub><sup>2-</sup> + B<sup>2+</sup>) would be expected. Obviously, a knowledge of solubility curves forms the basis

for testing and avoiding this condition. But further, the experimental assembly of Fig. 7 is required to establish the independent values of  $a_{Na_20}^{0}$  and  $P_{0_2}^{0}$  at the oxide/salt interface.

When the electrochemical probes indicate that the oxide/ salt interface lies to the left (is more basic) than either of the minima of the solubility curves, then each oxide should exhibit basic dissolution without rapid synergistic attack. The previously suggested criterion would then be individually applied for each product oxide.

In conclusion, we suggest here that accelerated hot corrosion corresponds to a rapid dissolution and reprecipitation of an oxide film, a process supported by a negative gradient in the solubility of the oxide across the salt film. The local values for oxide solubility should be established by an increased basicity necessarily introduced at the site of the electrochemical reduction reaction. A novel experimental arrangement is proposed to test these ideas by independent measurements of  $a_{Na_20}$  and

 $P_0$  locally in thin fused salt films. A model is suggested for the occurrence of rapid synergistic hot corrosion of a binary alloy.

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Table I. Electrochemical	Tentative (Qualitative) Standa: L Reduction Series for $Na_2SO_4$ at	rd t 1200K
0 <sup>-</sup> 2 (superoxide)	+ $1e \rightarrow 0^{2-}_2$ (peroxide)	a
0 <sup>2-</sup> (peroxide)	+ 2e $\rightarrow$ 20 <sup>2-</sup> (oxide ions)	Ъ
S0 <sub>3</sub> (g)	+ 2e $\rightarrow$ S0 <sub>2</sub> (g) + 0 <sup>2-</sup>	с
1/2 0 <sub>2</sub> (g)	+ 2e $\rightarrow$ 0 <sup>2-</sup>	d
Fe <sup>3+</sup>	$+ e \rightarrow Fe^{2+}$	e
Co <sup>3+</sup>	+ e $\rightarrow$ Co <sup>2+</sup>	f
Ni <sup>3+</sup>	+ e $\rightarrow$ Ni <sup>2+</sup>	g
so <sup>2-</sup>	$+2e \rightarrow S0_{3}^{2-} + 0^{2-}$	h
50 <sup>2</sup> -	$+2e \rightarrow S0_2^{2-} + 0^{2-}$	i
s02 <sup>-</sup>	$+2e \rightarrow S +20^{2-}$	j
S	+2e $\rightarrow$ S <sup>2-</sup>	k
Ni <sup>2+</sup>	+2e → Ni	1
Co <sup>2+</sup>	+2e → Co	m
Fe <sup>2+</sup>	+2e → Fe	n
Cr <sup>3+</sup>	+3e → Cr	ο
A1 <sup>3+</sup>	+3e → A1	g
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Fig. 1 Thermodynamic Phase Stabilities in the Na-Al-S-0 System at 1200K



Fig. 2 Thermodynamic Phase Stabilities in the Na-Cr-S-0 System at 1200K



Fig. 3 Solubilities of  ${\rm Al}_2{}^0{}_3$  and  ${\rm Cr}_2{}^0{}_3$  in Molten  ${\rm Na}_2{}^{\rm SO}{}_4$  at 1200K







Fig. 5 Cathodic Reduction of Molecular Oxygen

 (a.) for a high permeability of 0<sub>2</sub> in thin salt film
 (b.) for high concentrations and diffusivities of M<sup>2+</sup> and M<sup>3+</sup>
 or else for electronic conduction in the salt film.



Fig. 6 Cases of Continuous Hot Corrosion of a Pure Metal (I is the oxide/salt interface, and II is the salt/gas interface)



Fig. 7 Schematic Diagram of Cell Assembly to Measure Na $_2^{\rm O}$  Activity and P $_{\rm O}$  both at the Metal/Salt Interface and in the Fused  $^2Salt$  During Hot Corrosion

# WETTING AND WICKING PROPERTIES OF SOME CARBON SURFACES IN MOLTEN SULFUR AND POLYSULFIDES

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#### ABSTRACT

The present communication reports a study of the wetting properties at moderately high temperatures ( $\sim$  350°C) using a modified wicking technique. Both the detachment technique and a standing wick technique were adapted for studies in this temperature range. Preferential wetting of bare carbon surfaces by molten sulfur is confirmed through the adhesion tension ratios, and the thereby derived contact angles. The wettability appears approximately 10 times greater than with molten polysulfides. The effect of various metal oxide deposits on such properties was investigated and, specifically, the wettability of alumina-treated carbon surfaces by molten polysulfides. A technique for coating the carbon surfaces with metal oxide deposits of good adherence is reported. Some results are reported for the polysulfide transport properties of such treated carbons. There is a need to examine carefully the morphology of such surface deposited oxides.

#### Introduction

In the present communication we report an investigation of the wetting properties of molten sulfur and polysulfides at Na/S cell operating temperatures ( $350^{\circ}$ C). Inspection of the phase diagram for sulfur/polysulfides in Figure 1 is useful in defining some aspects of the task, viz: temperature range, composition range, and the choice of Na<sub>2</sub>S<sub>4</sub> and sulfur as model liquids for the present studies. In the "Sulfur Electrode" concept of this battery some form of carbon/ graphite is used as current collector - generally in the form of a yarn or "felt". One form of this, as a felt matrix, is illustrated in Figure 2.

During the charge cycle, the oxidation of the polysulfides results in the formation of sulfur as a second phase. Since this reaction takes place on the conducting surfaces, such as the carbon fibers, an insulating barrier of sulfur is established. In the charge cycle, the mixing of reactants and the removal of the insulating

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sulfur layer are major factors in determining reaction time, and therefore, mass transport is a very important consideration.

It is observed that despite elimination of container corrosion, the utilization of sulfur appears limited to less than 100% capacity and that this appears mainly due to a failure to recharge fully in the two-phase composition range (of the polysulfide/sulfur phase diagram). Effective capacity losses up to 50% apparently are not uncommon over extended periods of cell operation (e.g., after  $\sim$  100 discharge-charge cycles).

One theory, advanced to explain the poor rechargeability, links this observation to the relative wetting properties of sulfur and the polysulfides on the carbon surface. Information on the wetting properties of molten sulfur and polysulfides for carbon surfaces has followed largely from cyclic voltammetry and related techniques in studies of the processes occurring during the charge-discharge cycling of the sulfur electrode in Na/S cells.<sup>1-5</sup>

Such aspects led us to the studies reported herewith, namely the wettability of some carbons in contact with molten sulfur and polysulfides at cell operating temperatures, i.e., 350°C.

Some recent studies of contact angle measurements  $^{4,6-9}$  for molten salts systems are listed in Table 1 for reference here. The difficulties of such work with Na polysulfides are compounded by the great flammability and hydroscopicity of this salt system, and the opacity of the molten state, i.e., virtually black in color. An alternate to the direct observations of contact angle is to observe the extent of capillary penetration by wicking, i.e., the substrate is dipped into the liquid and the wetting properties are observed by the liquid rise in the porous "wick". Some of the investigations  $^{10-13}$  that proved informative are listed in Table 2. The former two are informative, particularly relative to the theory of wetting applied to such fibrous systems; Yamamoto proposed a "dynamic technique", as illustrated in Figure 3 for wetting measurements. A Mettler digital type-balance is used to observe the weight gain (with time) as a measure of the wetting. Both Yamamoto and Chwastiak proposed the use of a tube to confine the bundle of fibers to a well defined geometry for the wicking studies.

Our interest in the present work was to gain insight on the relative wetting properties of these two fluids for various carbon surfaces, and to investigate these with modified carbon surfaces, e.g., metal oxide deposits. The preparation of a series of treated carbon surfaces was undertaken and is reported, together with the results of a series of wicking measurements with molten sulfur and polysulfides.

### Experimental

Polysulfides: Na<sub>2</sub>S<sub>4</sub> (Alfa-Ventron) was used both "as received" and after

toluene-extraction. Last traces of toluene were removed at  $\sim 150\,^{\circ}\text{C}$  and  $10^{-2}$  Torr dynamic vacuum. In the latter step small amounts of sulfur sublimed (identified by mpt. and Raman spectra); we attribute this to the small but finite sulfur pressures reported for polysulfides  $^{14}$  rather than trace impurities. Sulfur (Fisher, reagent grade) was used in the limited series of sulfur wetting measurements. It was used "as received", except for pre-drying (85°C,  $10^{-4}$  Torr dynamic vacuum). All transfers were effected in dry N2 atmosphere.

<u>Carbons</u>: Electrographitic Rod (Arco Speer Grade 580) and WDF Graphite Felt (Union Carbide Corp.) were used for the wettability measurements. The pore size distributions, gained from Hg intrusion porosimetry, are summarized in Table 3 and Figure 4 together with the results for massive graphite (block) and vitreous carbon (foam) for comparision. Prior to the wetting measurements, the carbons were acid washed, and baked-out at reduced pressures and elevated temperature ( $\sim$  500°C,  $10^{-3}$ –  $10^{-5}$  Torr dynamic vacuum).

Metal Oxide Deposits on Carbons: The decomposition of metal nitrates<sup>15-20</sup> to the oxides, e.g., for a divalent salt:

 $M(NO_3)_2 \rightarrow MO + 2NO_2 + \frac{1}{2}O_2$ (1)

offers a method for the deposition of a variety of oxides on carbon surfaces. The procedure adopted for the surface treatment of the carbons is summarized in Table 4. Some of the details are:

- aqueous soak: The carbon specimens are immersed in aqueous solutions of metal nitrates; the soaking period is extended for a time sufficient for penetration of the porous carbons.
- (ii) nitrate decomposition: The water is removed from the soaked carbons at reduced pressures and moderate temperatures (25°-150°C), and the temperature is increased with the specimens under dynamic vacuum until the nitrate decomposition is complete (i.e., no further evolution of nitrogen oxides). The temperature range for this step must be determined for each metal nitrate; for aluminum nitrate it was in the range of 450°-600°C.
- (iii) thermal "bake-out": The temperature of the carbon specimens is further increased under reduced pressures to well above the nitrate decomposition temperatures, and the specimens are "baked-out", e.g., in the present work,  $10^{-5}$  Torr,  $\sim 900^{\circ}-1000^{\circ}C$ .

The weight of the sample on completion of this procedure was noted to gain the amount of the metal oxide thus deposited. The adherence of the deposit was tested after the bake-out, using aliquots with an ultra-sonic adhesion test.<sup>21</sup>

The surfaces were characterized by scanning electron microscopy (SEM)

and X-ray fluorescence. Some illustrative results for a series of alumina deposits on WDF graphite felts are in Figure 5. The porosity of such treated surfaces was found to decrease approx. 20% relative to the untreated carbons (Hg intrusion porosimetry). For a series of alumina coated samples the nature of the surface deposit was analyzed by atomic absorption spectroscopy; the results are summarized in Table 5. The agreement with the weight analysis, (based on complete decomposition of the nitrate to alumina) provides support for this procedure as a method for the deposition of metal oxides on carbon surfaces.

Wetting Measurements: The capillary penetration technique was adapted for the present measurements as follows. For small carbon samples ( $\sim$  5 cm length), the experimental assembly is illustrated in Figure 6A. The under-the-pan suspension and analytical balance ensures a vertical alignment for the wicking sample and provides a sensitive detection for the contact of the wick and wicking fluid as the crucible is raised. The temperature gradient in the hot zone at 350°C was  ${\rm ^{0}20^{\circ}}$ in the arrangement illustrated. With molten polysulfides (i.e., Na<sub>2</sub>S<sub>4</sub>) no difficulties were encountered due to vapor transport/condensation on the sample suspension, and the observed weight change correlated well with the amount "wicked". Owing to the high sulfur vapor pressures and consequent recondensation on the suspension, this procedure was modified with molten sulfur. For the latter, the amounts wicked were gained after the sample had been removed from the assembly. To extend the measurements to longer wicks (e.g., 25-30 cm lengths), a second arrangement as illustrated in Figure 6B was used in which the wicking chamber was a sealed long-necked round-bottom flask. The sulfur (or polysulfide) was loaded through a side-arm near the lower part of the wick to minimize .

contact prior to the wicking measurements. Loading the wicking chamber was under a dry Argon atmosphere. The chamber was next evacuated to 0.5 Torr and sealed off with a torch. The chamber was vertically positioned in a larger furnace already at the wicking temperatures. The temperature flat zone was  $\pm 4^{\circ}$  at 350°C over a 32 cm length. The amounts of polysulfide wicked, in this series of measurements, were gained by sectioning the wick for weight analysis, using a soaking technique to leach out the water soluble polysulfide.

The wicking studies undertaken were as follows: (i) wettability studies of carbon surfaces (bare), with molten polysulfides and molten sulfur; (ii) an exploratory series of wettability studies, using a variety of metal oxide deposits on carbon surfaces (in trace amounts), (iii) wettability studies, with increasing amounts of metal oxide surface deposits, and (iv) some measurements of wettability for carbon surfaces prepared with incompletely decomposed nitrates. The nitrates of cobalt, iron (III), silver, nickel, aluminum, and mixtures (e.g., Co, Al; Ni, Al; Ag, Al; and Fe, Al) were used in the exploratory series at soak solution concentrations from 0.1-2M; for the later follow-up series, the studies were largely limited to alumina-treated surfaces.

### Results and Discussion

The results of the wetting measurements with molten polysulfide and molten sulfur and carbon surfaces, the influence of added metal oxides on these surfaces, and the further studies with alumina treated carbon substrates are discussed in that order.

Carbon Surfaces: Using the electrographitic carbon (rod) a series of wetting measurements with both molten polysulfide (Na2S4) and molten sulfur, at 350°C were undertaken to investigate the preferential sulfur wettability of such surfaces. The results of this series of measurements are in Table 6, and the appearance of the specimens in Figure 7. It is apparent that the carbon surfaces are readily wetted by molten sulfur, and that, at 350°C, molten polysulfides are relatively non-wetting. With WDF graphite felts wicks, it was observed that sulfur wicked virtually over the complete specimen length (5 cm); by contrast, the polysulfide, as shown in Figure 7, was found not to wick to any appreciable extent. It is seen that a polysulfide residue "clings" to the porous system; this surface excess was removed mechanically with care prior to the weight analysis (Table 3). Nevertheless, an uncertainty is imposed on the quantitative nature of the results since it is very difficult to discriminate between a very small capillary rise and the liquid that may cling to the porous substrate (for molten polysulfides). It is of interest, nevertheless, to examine the results from viewpoints of adhesion tension and contact angle.

The adhesion tension, defined as  $\gamma \cos \phi$ , has been used as a measure of the wettability of a substrate surface.<sup>22</sup> Here  $\phi$  is the contact angle and  $\gamma$ , the interfacial (surface) tension. The adhesion tension may be calculated from a knowledge of the equilibrium height, h<sub>e</sub> and the classical capillary rise equation, viz:

$$\gamma \cos \phi = \rho g r / 2 \tag{2}$$

where r is the average pore radius, and  $\rho$  and g are as defined conventionally. Correspondingly, the volume of liquid wicked at equilibrium would be  $v_e = N\pi r^2 k h_e'$  where N is the number of capillaries, and k, the tortuosity factor for the wicking substrate. The equilibrium weight would be  $w_e = \rho v_e$ . Comparing the results for two fluids (sulfur, s; polysulfide, ps) and the same wicking material, it follows that the adhesion tensions ratio is given, simply, by:

$$\frac{(\gamma \cos \phi)}{(\gamma \cos \phi)_{\text{DS}}} = \frac{(w_{\text{e}})_{\text{S}}}{(w_{\text{e}})_{\text{DS}}} = \frac{(h_{\text{e}}\rho)_{\text{S}}}{(h_{\text{e}}\rho)_{\text{DS}}}$$
(3)

and that either measurements of the equilibrium weights or equilibrium heights may be used. In the present work the observed results (Table 6) may be taken as equilibrium wicking results; the measurements were under vapor saturated atmospheres,  $^{23,24}$  and little, if any, evaporation would

be expected from the liquid contents for the felts. The data in Table 6 show a factor of 10 difference in the weights of liquid wicked. From the adhesion tension criterion, the wettability of the carbon surface at  $350^{\circ}$ C by molten sulfur would appear as much as 10 times greater than by the molten polysulfide.

Provisional results for the contact angles, by direct observations, have been reported by Ludwig.<sup>4</sup> Under a helium atmosphere and short-time measurements, the observed values of  $\phi$  were 20°-30° and 100°, respectively for molten sulfur and polysulfide at 318°C, on graphite surfaces. Taking 25° as a probable value for molten sulfur, and values of the surface tensions for molten sulfur<sup>25</sup> and polysulfide<sup>26</sup> as 46 and 128 dyn cm<sup>-1</sup> (at 350°C) respectively, it follows from eq. 3 and the present wicking data (Table 6), that a value of 91° is predicted for  $\phi_{\rm PS}$ , i.e., the molten polysulfide is thus predicted to be non-wetting on bare carbon surfaces.

The difficulties of the present technique in discriminating between a very small capillary rise (for  $\phi$  slightly less than 90°), and the liquid residue that may cling to the wick (for  $\phi$  slightly greater than 90°) should be noted relative to the preceding calculations of adhesion tensions and contact angles. The significant result is the observation that porous carbon is much more wettable by molten sulfur than by molten polysulfide. The observations of preferential wetting of carbon graphite surfaces by molten sulfur, from cyclic voltammetry and related measurements,  $^{1-5}$  and contact angle measurements,  $^4$  are clearly supported by the preceding observations at 350°C.

Metal oxides: The effects of various metal oxides deposited on both electrographitic carbon rod and the WDF graphite felt were investigated with the small wicking assembly (5 cm length wicks). The amount retained by the wick (after 30 to 60 minute contact with the molten polysulfide) relative to the amount wicked by the untreated (bare) carbon wick provides a measure of the changes in adhesion tensions. With the exception of two metal oxides, aluminum and cobalt, the various metal oxides did not markedly improve the wettability of the carbon surfaces by molten polysulfides. Some of the results for the cobalt oxide and alumina treated surfaces are in Table 7. The amount wicked is given both as weight, and wt% (relative to the wick weights prior to the measurements). A quantitative comparison of the relative effectiveness of the various metal oxides is thus shown. It is clear that alumina (either through the thermal decomposition of the nitrate, or as hydrosol of a dispersable form of alumina, i.e., Dispal) markedly promotes the wettability of the carbon surfaces by molten polysulfides. Inspection of these specimens after the measurements showed that the polysulfide had penetrated the full 5 cm length of the felt wicks. By contrast, the bare felts showed virtually no penetration; the amount "wicked" on the bare carbons (Table 7) can be accounted for as the polysulfide retained as a pendant drop after wick detachment from the molten polysulfide.

To investigate the polysulfide transport properties of aluminatreated graphite surfaces, a series of felt wicks were prepared from increasingly more concentrated soak solutions (4 to 40 wt%  $Al(NO_3)_3$ . 9H20). Because of the increasingly larger alumina loadings, the resiliency of the felt matrix is largely lost; the ultrasonic tests for adherence, however, indicated that approx. 90% of the surface deposited alumina was adherent at the higher felt loadings. Inspection of the surface morphologies (see for e.g., Fig. 5) showed dendritic deposits, with increasing build-ups at fiber intersections as the alumina loadings were increased. The polysulfide transported as a function of wick length was gained quantitatively by weight analysis of the felts sectioned into aliquots after each measurement. The results for the limiting felt loadings ("wicked" to equilibrium conditions) are summarized in Table 9. The equilibrium heights attained for the two alumina treated felts were, respectively, 4 and 5 cm. for the felts loaded with the 4.43 and 40 wt% nitrate soak solutions; inspection of the amounts wicked, shows that the polysulfide transport is almost in the ratio of the soak concentrations, i.e., approximately a nine-fold increase.

There appears a need to examine carefully the morphology of such surface deposited oxides; the possible role of water-related species in conferring enhanced wettability should also be examined. Some studies of the thermal transformation of aluminum salts are summarized in Table 9. Thermal decomposition to amorphous alumina seems complete at 600°C, and at somewhat lower temperatures, transformations to a basic salt and/or "impure" amorphous alumina are to be expected. Lower temperatures would lead to markedly different surface deposits, and rehydration [possibly to AlO(OH)] has been reported.

In the present work the preparation of a series of loaded felts with 350°C as the terminal temperature was undertaken. Samples of these felts (prior to wicking measurements) were found to have strong tendencies to rehydrate, e.g., a continuing weight gain was observed. With further heating under dynamic vacuum (500°C,  $10^{-5}$  Torr), both H<sub>2</sub>O and nitrogen oxides were evolved.

Very marked wicking of polysulfides is observed if the thermal decomposition is restricted to temperatures of  $\sim 350^{\circ}$ C. For example, with a 20 wt% soak solution, a wicking height of 10 cm was observed after 4 hrs, and this had increased to 25 cm after 100 hrs (350°C).

The very effective transport properties of the  $350\,^{\circ}\text{C}$  aluminatreated felt surfaces may be undoubtedly attributed, in part, to the trace amounts of H<sub>2</sub>O inherent with the surface deposits, and the consequent species from the following chemical reactions with molten polysulfides. However, the possibility of the alumina also being in a more "reactive" morphology for polysulfide transport e.g., boehmite, is not ruled out.

In Summary:

Both the detachment technique and a standing wick technique have been adapted for studies at moderately high temperatures. The wettability of bare carbon surfaces by molten sulfur appears approximately 10 times greater than by molten polysulfides.

A technique for surface oxide deposition on such graphitic surfaces, with good adherence, is reported.

Some metal oxides, and most notably alumina, on the graphite fibers seem to confer effective transport properties for the molten polysulfides.

There is a need to examine carefully the morphology of such surface deposited oxides.

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Table 1. Recent Contact Angle Studies: Molten Salt Systems

Ref.	4	9	7	80	8	6
Gas Environment	argon; He	argon; Cl <sub>2</sub>	argon; CO	various	various	N2
Substrate	graphite	graphite	graphite	BN; MgO; ZrO; ss	Ni; NiO; ss	beta-alumina
Molten System	Na polysulfides	MgCl <sub>2</sub> , CaCl <sub>2</sub> , molten Mg	NaF, ZrF <sub>4</sub> , ZrO <sub>2</sub>	LiC1-KC1 electrolyte	molten carbonate electrolytes	Na polysulfides





Fig. 2. Graphite Felt [300X, showing yarn-like matrix].

Table 2. Some Studies of Capillary Penetration of Fibrous Materials

	Ref.	10	11	12	13
CTRIDING STRIET	Substrates	filter paper	various metal sinters	carbon yarns (fiber bundles)	carbon fibers (fiber bundles)
10	Liquid Systems	var. organic fluids	water; freons	var, organic fluids and water	epoxy resins



Table 3. Porosity and Pore Spectra for Various Carbons

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e Distribution	est dia. Dia. range for crons) 90% pore space	005 0.02 - 30	004 0.02 - 1.30	005 0.01 - 0.05	003 0.004 - 0.10
Pore Size	a. Smalle (mic	0.0	0.0	0.0	×.0
	Median di (microns	3.5	0.8	0.02	0.006
	Porosity E	24.25\$	13.62\$	11.64%	17.77\$
	Sample	A*	8	U	D

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\* A: Graphite Block; B: Electrographitic Rod; C: Graphite Fig. 3. Schematic of assembly for dynamic wetting measurements as used in studies of graphite wetting by epoxy fluids.



Fig. 4. Comparison of porosity of four carbons by Hg intrusion porosimetry. A: Graphite block; B: Electro-graphite Rod; C: Graphite Felt; D: Vitreous carbon foam.

Felt; D: Vitreous Carbon Foam

Table 4. Outline of the "ASBOT" Procedure for Coating Graphites

5. Thermal bake-out (859°C; vacuo)<sup>‡</sup> Nitrate decomposition (600°C; vacuo)  $[M(NO_3)_2 \rightarrow MD + 2NO_2 + \frac{1}{2}O_2]$ Acid decomposition (600°C; vacuo)<sup>‡</sup> Aqueous nitrate soak (25°C) Acid soak (50% V/V  $HNO_{\tau}$ ) 

tsample weighed for ∆w data





b



с



d

#### Fig. 5. Alumina-Treated Graphite Felts -SEM Photomicrographs

a) Moderately loaded felt (4.43 w/o  $\Lambda 1 (NO_3)_3 \cdot 9H_2O$  soak solution); 5000X

- b) Heavily loaded felt (8.27 w/o Al(NO\_3)\_3  $^{\circ}9\mathrm{H}_2\mathrm{O}$  soak solution); 2000X
- c) Moderately loaded felt; intersection of two fibers; 5000X
- d) Heavily loaded felt; intersection of two fibers; 5000X



Α



Fig.6 Experimental assemblies for wetting/wicking studies of various graphites in contact with molten polysulfides and sulfur.

Table 5. Characterization of the Coated Carbon Surfaces

Soak Solution	Sample Weight	Aluminu	n Content
Al (NO <sub>3</sub> ) 3.9H <sub>2</sub> O	(after bake-out)	<b>Predicted<sup>a</sup></b>	Found <sup>b</sup>
(wt. percent)	(wt. percent)	(wt. pe	srcent)
0.92	1.26	0.67	0.78±.05
1.74	1.84	0.97	1.04±.005
4.43	6.72	3.56	4.88±.05
9.27	12.49	6.61	4.60±.05

1

(a) from wt. gain, assuming surface deposit to be Al203 (b) from Atomic Absorption Spectroscopic Analyses Table 6. Molten Sulfur and Polysulfide Wicking at 350°C

	Amo	unt Wicke	P	Penetrati	on Limits
Wicking (min.)	> <u>6</u>	v (cm <sup>3</sup> )	- (j)	pore dia. (µm)	v/v* (percent)
Molten Na <sub>2</sub> S <sub>4</sub>					
30	0.008	0.0044	0.43	1.9	154
60	0.005	0.0027	0.35	2.8	111
06	0.005	0.0027	0.22	1.7	184
120	1	•	0.55	ı	
	_	_	_	_	
Molten Sulfur					
40	0.0084	0.0050	1.2	0.34	60%
60	0.0065	0.0039	6.0	0.29	62%
06	0.006	0.0040	1.0	0.48	578
300	0.0070	0.0042		0.34	618
V* - porous vo	lume in 1	ength (h)	penetz	ated	

Table 7. Molten Polysulfide Wicking of Graphite Felts

Treatment	Wicking C	onditions	Amount	Wicked
(WDF felt)	T (°C)	t(min.)	Ē	wte
1. bare	350°	30	0.1212	123*
2. bare	350°	60	0.1105	107*
3. Al (NO <sub>3</sub> ) <sub>3</sub>	350°	60	4.2953	, , ,
4. Dispal	350°	60	3.0860	1090
5. Co (NO <sub>3</sub> ) 2	350°	60	0.3926	290

bare felt: the polysulfide was attached as a pendant drop the felt matrix was completely penetrated, i.e., 100% "wicked"

Table 8. Molten Polysulfide Transport by

Alumina-Treated Graphite Felts

	Total	ļ	50°C
(8		ŝ	6 3
5	(em	4	hrs
cked	e		560
ide Wid	t surfe	3 - 4	ricked :
Polysulf	bove mel	2 - 3	soak; w
of	e a		te*
ount	stand	- 3	nitre
An	đ	-	ţ,
			£
		0 - 1	4

0.2989 0.2822 0.0093 0.0051 0.0023 0.0000

40 wt% nitrate\* soak; wicked 150 hrs @ 350°C

2.4322

0.0894

0.2161

0.5373

0.6331

0.9563

\* Al  $(NO_3)_3 \cdot 9H_2 O$  and ASBOT'ed



Fig. 7. Wettability of Carbon Surfaces at 350°C with molten sulfur and molten polysulfide.

Bare electrographitic carbon (rod) contacted with (a) molten sulfur and (b) with molten polysulfide. The close up shows a "non-wetting" globule of molten polysulfide (after solidification). Bare WDF felt wicks, after contacted with molten sulfur and polysulfide at 350°C are shown in (c) and (d), respectively.



Table 9. Thermally Induced Transformations

 Parravano et. al. (1926)
 Yakovkin et. al. (1935)

 Kalinina et. al. (1957)
 Funaki et. al. (1959)
 Nikolic et. al. (1960)

### STABILITY OF CERAMICS IN MOLTEN ALKALI CARBONATES

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Chemical and structural stability of ceramic materials in molten alkali carbonates is critically evaluated. The materials showing acceptable stability include nickel oxide, cobalt oxide, high density alumina and alkali aluminates. Among the alkali aluminates, lithium aluminate in various high surface area forms has been extensively employed as a support material in molten carbonate fuel cells. A detailed discussion of the stability of lithium aluminate under various conditions is presented.

Molten alkali carbonates ( $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ and their binary and ternary mixtures) offer a wide range of physicochemical and kinetic characteristics desirable for electrolytes and reaction media. Melting points of the alkali carbonates can be varied from 400°C for the ternary eutectic to 900°C for K<sub>2</sub>CO<sub>3</sub>. Other properties such as viscosity, electrical conductivity and gas solubility can also be varied by suitably changing the compositions of the mixtures [1]. A list of some of the applications, temperature range of the application, mixtures employed, and pertinent references is presented in Table 1.

# TABLE 1. APPLICATION OF MOLTEN CARBONATES

Application	Temperature Range, °C	Carbonate Mixture	References
Fuel Cell	600- 700	Binary and Ternary	1,2
Thermal Energy Storage	400- 600	Binary and Ternary	3
Coal Gasification	800-1000	$Na_2 CO_3$	4,5
Desulfurization of Gases	400- 500	Ternary	6

Stability of ceramics is of interest in molten carbonate systems because these materials can be used as constituents of various components in these systems. For example, various types of ceramic electrolyte support materials in the form of fine powder and/or fibers have been employed in molten carbonate fuel cells [1]. The support material holds the electrolyte by capillarity and provides a 'paste-like' separator between the electrodes. Additions of ceramics have also been suggested for providing a sintering resistance to porous metal electrodes in the molten carbonate fuel cell environments [7]. Also, the ceramic materials in the form of coatings or bulk can be used as materials of construction for reaction vessels [8]. Ceramics have also been suggested as volume-change-control additives in thermal energy storage applications employing carbonate salts [3].

The behavior of ceramics in contact with the molten carbonates is strongly influenced by

- Composition of the melt, including minor impurities, and moisture content
- b. Surrounding gas environment, especially  $CO_2$ ,  $H_2O$ ,  $SO_2$ ,  $Cl_2$
- c. Physical form of the ceramic material, such as powder, fibrous, porous disks, coatings or bulk solid
- d. Operating potential and temperature

The available information should therefore be applied with a careful consideration of these factors. A critical evaluation of the available data on chemical and structural stability of various ceramic materials is presented in this paper. For convenience, the ceramic materials are grouped as

- a. Single oxides
- b. Mixed oxides, and
- c. Other non-oxide ceramics

Since lithium aluminate has been used extensively as an inert material in the molten carbonate systems, a detailed discussion of the stability of this material is also included.

# 1. Single Oxides

#### 1.1 Oxides of Alkaline-Earth Metals (MgO, CaO)

The MgO in the form of sintered porous discs [9, 10] or a fine powder [11, 12] has been employed as a support material in the molten carbonate fuel cells. Janz and Coworkers [13, 14], using a simple thermodynamic analysis, predicted that pure MgO should be 'practically' inert against  $\text{Li}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$  in the temperature range of 750 to 1000°C. Tseung and Tantram [10], however, observed laminar faults in sintered MgO diaphragms in the presence of carbonates. These faults may have been caused, at least partly, by a dissolution of impurities from the diaphragm, but MgO itself may not be as stable as predicted from the simple thermodynamic calculations. Van Velden [15] showed that MgO has a significant solubility in alkali carbonate melts in the presence of CO<sub>2</sub>:

$$MqO(s) + CO_2(q) \rightarrow Mq^{++}(melt) + CO_3^{-}(melt)$$
(1)

In the ternary melt at 1 atm  $CO_2$  they experimentally measured a 5 mol% molten MgCO<sub>3</sub> at 550°C and a 1 mol% at 700°C. At higher temperatures and larger Li contents, the stability of MgCO<sub>3</sub> (melt) decreases. In addition to Reaction 1, water vapor equilibrium may also affect the solubility of MgO:

. .

. .

$$MgO(s) + H_2O(g) \rightarrow Mg^{++}(melt) + 2 OH^{-}(melt)$$
(2)

Because of the solubility problems, the use of MgO as a support material was discontinued [1].

The behaviour of CaO is similar to that of MgO, i.e., it also shows a finite solubility in the presence of  $CO_2$ . Flood, <u>et al</u>. [16] investigated the solubility of CaO in single alkali carbonate melts at temperatures above 900°C. The solubility at a given temperature increased in the order of  $\text{Li}_2\text{CO}_3 < \text{Na}_2\text{CO}_3 < \text{K}_2\text{CO}_3$ . At 1 atm CO<sub>2</sub> and 1000°C, the CaCO<sub>3</sub> solubility was estimated to be 27, 37 and 50 mol% respectively in single Li-, Na- and K- carbonate melts. The solubility at lower CO<sub>2</sub> levels, is however, expected to be proportion-ately lower.

### 1.2 Oxides of Nickel, Cobalt and Iron

Nickel, cobalt and iron remain stable in a metallic form under a reducing gas environment, such as that encountered on the anode side of the molten carbonate fuel cells [1]. In the oxidizing environment, or at higher (more positive) potentials, oxides of these metals are formed. These oxides are very stable in the molten carbonate environment. In fact, NiO having surface areas of 0.1 to 1 m<sup>2</sup>/g has been used as a stable cathode in the molten carbonate fuel cells [1]. It is interesting to note that when the oxide is formed in the presence of  $\text{Li}_2\text{CO}_3$ , Li atom enters into the structure of NiO ( $\text{Li}_\delta\text{Ni}_{1-\delta}$ O) and imparts semiconductor properties [17]. The electronic conductivity of such lithiated-nickel oxides is several orders of magnitude greater than that of pure NiO. The experience with the oxides of cobalt and iron has been limited. An iron oxide cathode has been used by SRI [18] in a direct-carbon molten carbonate fuel cell.

# 1.3 Silica and Quartz

Silica and quartz in direct contact with molten carbonates react readily to form silicates. In the apparatus where a transparent jacket or window is required in a noncontact application, such as in the carbonate vapor environment, quartz may be used for a short period. Eventually, however, the carbonate vapor tends to react with the surface of quartz and the quartz becomes nontransparent.

#### 1.4 Lead Oxide

Lead oxide is one of the few materials that show nonwetting contact angles with carbonate melts. Davis and Kinnibrugh [19] experimented with this material in an attempt to find an analogous material to Teflon used at lower temperatures for aqueous media. The lead oxide showed high contact angles (nonwetting) initially, but after several hours, the contact angles approached zero, indicating some reaction with the carbonates.

# 1.5 Oxides of Zirconium, Titanium and Chromium

Oxides of these metals form mixed oxides with the carbonates. For example [20]

$$ZrO_2 + Li_2CO_3 + Li_2ZrO_3 + CO_2$$
(3)

The chemical equilibrium depends on the activity of  $CO_2$ . Broers and Van Ballegoy [21] suggested small additions of  $ZrO_2$  to the carbonate electrolyte to provide a buffer capacity with regard to  $CO_2$ .

Titanium oxide has been investigated by IGT [22] in a powder form, but was found unsuitable as an electrolyte support material.

Chromium oxide  $(Cr_2O_3)$  protective layer is generally formed on 300 and 400-series stainless steels. In the presence of carbonates, however, Grantham and Coworkers [23] observed no presence of  $Cr_2O_3$  film during their examination using X-ray diffraction, X-ray fluorescence, and emission spectrographic techniques. Instead they found a LiCrO<sub>2</sub> (predominantly the hexagonal structure) film on the stainless steels. This indicates that LiCrO<sub>2</sub> is a stable material in the presence of carbonates. Even if Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> are present in the melt, the film was found to be primarily LiCrO<sub>2</sub>.

# 1.6 Aluminum Oxide

Alumina has been used extensively as a corrosion resistant material in the presence of carbonates. High density, high purity fused-cast or slip-cast  $\alpha$ - alumina is corrosion resistant at temperatures up to 1200°C. (Grantham and Ferry [23]). Low density or amorphous alumina is not corrosion resistant. Alumina with numerous voids or impurities (particularly silica) is disintegrated by the carbonate melts. Grantham and Ferry [23] noted that the external crystal structures of the cast alumina bricks is more corrosion resistant than the internal structure. Therefore, care must be exercised in using these bricks.

To ensure the minimum reaction of the bulk-form alumina with the carbonates, a 'pretreatment' of the alumina with an appropriate carbonate melt is recommended. This pretreatment results in formation of an alkali aluminate that is lower in density as compared with alumina. Thus, for example,

# $1 \text{ cc } Al_2O_3 \rightarrow l_2^{\frac{1}{2}} \text{ to } 2 \text{ cc } LiAlO_2$

Thus, even if the alumina surface is somewhat porous, or contains some cracks, these cracks are likely to be filled because of the increase in volume after the pretreatment. Thus a passive film of alkali aluminate formed on the surface of  $Al_2O_3$  appears to be the factor responsible for the excellent stability of bulk-form  $Al_2O_3$ . Interestingly, even aluminum metal hardware has been used in the molten alkali carbonate environment at temperatures up to 600°C [22], in spite of the fact that aluminum melts at 660°C. Again, the protecting layer of  $Al_2O_3$ , subsequently converted to an alkali aluminate may be credited for this stability.

Alumina in a powder form, however, reacts readily with alkali carbonates to form corresponding alkali aluminates. Among the various forms of alumina,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is found to be the most reactive and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> the least [38].

# 2. Mixed Oxides

# 2.1 Titanates and Zirconates

Mixed oxides of  $\text{TiO}_2$  and  $\text{ZrO}_2$  with alkali carbonates are likely to be stable in the carbonate environment, however their stability is dependent on gas environment as noted in Section 1.5.

Potassium hexatitanate  $(K_2 \text{Ti}_6 O_{13})$ , manufactured in a fibrous form, has been used extensively as a separator material in alkali environment at low temperatures. In the molten carbonates, however, this material reacts with carbonates and forms rounded particles, possibly potassium metatitanate.

Calcium titanate ( $CaTiO_3$ ) is expected to be thermodynamically unstable in a carbonate environment [24].

Lithium zirconate may be stable in the carbonate environment, but its stability has not been fully investigated.

### 2.2 Silicates

Alkali silicates are also soluble in carbonates, as is the case with silica. Russian investigators [25] studied the possibility of using lithium aluminosilicates as inert support materials for carbonate electrolytes. These materials showed cationic conductivity and lower specific resistance than the oxides discussed earlier. The aluminosilicate/carbonate electrolyte also had good mechanical properties. However, the aluminosilicates reacted with the carbonate, as shown from the lowering of melting point of the carbonate phase. Thus, silicates appear unsuitable as inert material in a carbonate environment.

# 2.3 Aluminates

Magnesium aluminate (MgAl<sub>2</sub>O<sub>4</sub>) spinel and magnesia-rich spinel (Mg<sub>1+x</sub>Al<sub>2</sub>O<sub>4</sub>) both are expected to be thermodynamically stable in a carbonate environment [24]. The experiments at General Electric, however, with a high surface area powder ( $\sim$ 20 m<sup>2</sup>/g) showed a degradation of MgAl<sub>2</sub>O<sub>4</sub> to LiAlO<sub>2</sub> by the reaction [26] -

$$MgAl_2O_4 + Li_2CO_3 \rightarrow MgO + 2 LiAlO_2 + CO_2\uparrow.$$
(4)

Calcium aluminate is also a possible candidate material, however, no data on its stability is available.

Alkali aluminates show a good stability in a carbonate environment, as will be discussed in greater detail in Section 4.

# 2.4 Perovskites

Perovskites (e.g., LaCrO<sub>3</sub>) have been employed as stable materials at 800 to 1000°C in solid oxide fuel cells. These materials show significant electrical conductivity and are also likely to be stable in carbonate environment, especially in H<sub>2</sub>S-containing environment, and thus these materials appear promising as sulfur tolerant anode materials [26]. Stability of these materials needs to be examined in more detail.

# 3. Other Nonoxide Ceramics

Boron nitride,  $B_3N$ , has been employed as a separator material for high temperature Li/S batteries, where it is used as a matrix. The material has been investigated as a wet-proofing agent [19] in a carbonate system, but its wetproofing capabilities are destroyed above 400°C in contact with the carbonates [27].

Titanium carbide, TiC, is expected to be unstable from thermodynamic considerations because it will form an oxide in the presence of carbonates [24].

Tungsten carbide, WC, often used as an electrode material in various fuel cell systems, may be stable in a carbonate environment and may also be tolerant to  $H_2S$ -containing gases [28]. The stability data are, however, not available.

# 4. Alkali Aluminates

Alkali aluminates, particularly the meta aluminates  $(\text{LiAlO}_2, \text{NaAlO}_2, \text{ and KAlO}_2)$ , show a remarkable chemical stability in alkali carbonate melts. As stated in Section 1, the formation of these aluminates is responsible for passivation of bulk  $\text{Al}_2\text{O}_3$  in the presence of carbonates. Because of their stability, the aluminates have been commonly used in the molten carbonate fuel cells as high surface area inert support materials for electrolyte matrices. As a support material, the aluminates not only have to be chemically stable, but their structural characteristics, i.e., particle shape and size, should also be stable. For optimum mechanical

properties of the matrix, a needle-like shape of the inert particles is desirable [29, 30]. These aspects are discussed below.

# 4.1 <u>Chemical Stability of Alkali-Metal Aluminates in</u> Carbonates

Broers and Van Ballegoy [21] presented thermodynamic data for aluminates and determined phase diagrams for stability regions of various alkali aluminates with respect to carbonate composition. From their work, the following important points are summarized.

The formation reaction of alkali aluminates (using  $\alpha\text{-Al}_2\text{O}_3)$  ,

$$Al_2O_3 + M_2CO_3 \rightarrow 2 MAlO_2 + CO_2^{\uparrow}$$
(5)

at 725°C has a  $\Delta G$  of -54.5 kJ/mol for LiAlO<sub>2</sub> and -14.7 kJ/mol for NaAlO<sub>2</sub> and KAlO<sub>2</sub>. Because of the considerably lower free energy, the formation of LiAlO<sub>2</sub> is favored relative to NaAlO<sub>2</sub> and/or KAlO<sub>2</sub>. Therefore, LiAlO<sub>2</sub> is stable over a wide range of carbonate compositions. The rate of Reaction 4 increases with increasing Al<sub>2</sub>O<sub>3</sub> surface area. Chemical activity of a given Al<sub>2</sub>O<sub>3</sub> phase also affects  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> being the least active,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 'amorphous' Al<sub>2</sub>O<sub>3</sub> have greater activity, in the order stated.

By assuming that the activity of individual carbonates in a mixture of alkali carbonates is equal to their ionic fraction, they derived equilibrium composition curves  $\phi(T)$ for a coexistence of the corresponding aluminates (Figure 1). The liquidus curve f(T) intersects the equilibrium curve  $\phi$ (T) at an invariant point T<sub>c</sub>. It can be seen in Figure 1A and 1B that in the  $Li_2CO_3$  - containing binaries,  $LiAlO_2$  is the stable phase for Li<sub>2</sub>CO<sub>3</sub> contents greater than 20 to 25%. A similar conclusion was also reached for the ternary carbonate system. Note that the equilibrium curves were derived without a specific reference to different crystal phases (See Section 4.2) of the meta aluminates, or to other possible aluminates [31, 41]. The equilibrium curves should therefore be verified for specific situations by considering all the likely phases and compositions of the aluminates.

A limited solid solubility among mixed aluminates was found, i.e., in a mixed carbonate melt, one alkali aluminate may contain small amounts of other alkalies in its crystal lattice. For example, in a  $\text{Li}_2\text{CO}_3-\text{K}_2\text{CO}_3$  binary, a saturated solid solution composition of  $\text{Li}_{0.94}$  K<sub>0.06</sub> AlO<sub>2</sub> is likely [21]. Such solid solutions, have also been qualitatively verified by X-ray diffraction measurements.

## 4.2 Phase and Structural Stability of LiAlO2

The meta-lithium aluminate (LiAlO<sub>2</sub>) exists in three different allotropic forms\*:

- 1.  $\alpha$ -LiAlO<sub>2</sub> The structure of this phase as determined by Marezio and Remeika [32] is a hexagonal and of the space group R3m. It is isostructural with NaHF<sub>2</sub>, which can be described as a distorted NaCl structure elongated along a threefold axis. The cations are octahedrally coordinated. The lattic parameters are: a = 2.800 Ű and c = 14.216 Ű, with an X-ray density of 3.401 g/cm<sup>3</sup>.
- 2.  $\beta$ -LiAlO<sub>2</sub> This phase has a monoclinic structure with lattice parameters: a = 8.147 Ű, c = 6.303 Ű and  $\beta$  = 93.18°, as determined by Chang and Margrave [33]. Their IR spectra studies indicated that Al ions are in both tetrahedral and octahedral coordination. The space group for this phase was not determined. The density as determined from the X-ray data is 2.59 g/cm<sup>3</sup>.
- 3.  $\gamma$ -LiAlO<sub>2</sub> This phase has a tetragonal structure with lattice parameters: a = 5.169 A° and c = 6.268 A°, space group P41212 and density 2.615 g/cm<sup>3</sup> [34]  $\gamma$ -LiAlO<sub>2</sub> is piezoelectric [35].

Marezio and Remeika [32, 35] pointed out that like any other  $LiMO_2$  compounds, where M can be B, Al, Ga, In, or Tl (Group III elements),  $\gamma$ -LiAlO<sub>2</sub> (lower cationic coordination) can be converted to  $\alpha$ -LiAlO<sub>2</sub> (higher cationic coordination) under high temperature and pressure. On the other hand,  $\alpha$ -LiAlO<sub>2</sub> transforms easily to  $\gamma$ -LiAlO<sub>2</sub> by heating at 600°C under normal pressure. They considered  $\gamma$ -LiAlO<sub>2</sub> stable and  $\alpha$ -LiAlO<sub>2</sub> metastable at low temperatures and normal pressures.

Chang and Margrave [33] synthesized  $\beta$ -LiAlO<sub>2</sub> from a mixture of Li<sub>2</sub>O<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> at 18 kbars pressure and 370°C. They also found that the same mixture produced  $\alpha$ -LiAlO<sub>2</sub> at 25 kbars and 530°C. However, they could not form  $\gamma$ -LiAlO<sub>2</sub> by heating either  $\alpha$ -LiAlO<sub>2</sub> or  $\beta$ -LiAlO<sub>2</sub> at 710°C, as was observed by Marezio and Remeika [35], and they suggested this process may be slow.

The alpha to gamma phase transformation in LiAlO2 at

<sup>\*</sup> Caution must be exercised regarding the nomenclature of various LiAlO<sub>2</sub> forms, as different investigators use different designations. In this paper we will follow the nomenclature as described in this text.

elevated temperatures was also observed by other investigators [22, 36, 37]. This process is irreversible at normal pressure, and the reverse reaction can only be achieved by applying pressure or by grinding followed by heating [38]. At much higher temperatures ( $\sim$ 1300°C), LiAlO<sub>2</sub> transforms [38] to LiAl<sub>5</sub>O<sub>8</sub>. Recently Stork and Pott [37] have reported a decomposition LiAlO<sub>2</sub> to LiAl<sub>5</sub>O<sub>8</sub> at temperatures as low as 800°C.

Thus, starting with  $\alpha$ -LiAlO<sub>2</sub>, transformation to  $\gamma$ -LiAlO<sub>2</sub> occurs at about 600°C, and further heating above 1300°C promotes partial decomposition forming LiAl<sub>5</sub>O<sub>8</sub>. Upon cooling, however,  $\gamma$ -LiAlO<sub>2</sub> retains its structure at room temperature. More recently, Mason and Van Drunen [39] have investigated the stability and formation of  $\beta$ -LiAlO<sub>2</sub> in various carbonate and gas environments.

A recent systematic study of the phase transformations in a carbonate environment has been carried out at Argonne National Laboratory [40]. The major conclusions are -

- 1. The presence of  $\text{Li}_2\text{CO}_3$  either in the eutectic mixture or as a solid decreased the temperature at which either  $\alpha$ -LiAlO<sub>2</sub> or  $\beta$ -LiAlO<sub>2</sub> transformed into  $\gamma$ -LiAlO<sub>2</sub> (from 925°C to 700°C).
- 2. The gas environment also had an effect on the time and temperature required for transformation:  $\alpha$ -LiAlO<sub>2</sub> transformed more readily than  $\beta$ -LiAlO<sub>2</sub> in both air and H<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O gas, but in pure CO<sub>2</sub> both transformations occur more slowly.

An approximate phase stability diagram based on the best judgment of all the available data is presented in Figure 2. A more accurate thermodynamic phase stability diagram considering the gas environment, particularly  $CO_2/H_2O$  ratio, melt composition, is needed to optimize the electrolyte support.

Structural stability (particle shape and size) is equally, or perhaps more important.  $\alpha$ -LiAlO<sub>2</sub> is generally produced as a high surface area (20 to 80 m<sup>2</sup>/g) fine powder.  $\beta$ -LiAlO<sub>2</sub> exhibits a lath habit with L/D ratios of 2 to 10.  $\gamma$ -LiAlO<sub>2</sub> is produced as a bipyramid. For an electrolyte matrix with optimum mechanical and retention properties, a mixture of these structures may be desired.

A study of the structural changes in various forms of  $LiAlO_2$  has also been reported by Argonne National Laboratory [40]. The following conclusions have been derived from their work.

- 1. The growth of the particles was quite rapid in air, slower in  $CO_2$ .
- 2. The particle growth was slower in solid state than in molten carbonates.
- 3. The rod-shaped  $\beta$ -LiAlO<sub>2</sub> converted to low surface area bipyramids if heated at 700°C.

#### 5. Summary

The behavior of ceramics in contact with the molten carbonates is strongly influenced by various factors, including melt composition, operating conditions and the physical form of a ceramic material. The available data should therefore be utilized with caution. Generally, in the low surface area or bulk solid forms, high density alumina, alkali aluminates, and zirconia are stable in the carbonate environment. On the other hand, silica, silicates, alumino silicates, magnesium aluminate, calcium oxide and magnesium oxide are found to be In the high surface area forms, nickel oxide and unstable. cobalt oxide show an excellent stability in oxidizing environments. High surface area alkali aluminates, particularly lithium aluminate, are promising nonconductive materials in oxidizing and reducing environments. Additional systematic study of alkali aluminate stability is required.

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Figure 1. Liquidus curves f(T) for binary carbonate systems and semiempirical equilibrium composition curves  $\phi(T)$  at the coexistence of corresponding aluminates [21]



Figure 2. Approximate lithium aluminate phase stability

### THERMOSONIMETRY IN FUSED SALTS

Ъy

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### ABSTRACT

Three binary systems; NaCl-CsCl, CsCl-BaCl<sub>2</sub> and LiCl-AlCl<sub>3</sub>, have been chosen to test if Thermosonimetry (TS) could be used in phase-diagram studies of salt systems. In the TS technique the sample is heated at a constant rate and the sonic radiation from the sample is recorded. Whenever a change of phase takes place, an increase in the sonic activity is observed. One of the advantages of thermosonimetry is that compared to the slow diffusion of heat to the sample surface and subsequent pick-up by a thermocouple or calorimeter, the propagation of information is practically instantaneous and given by the sound velocity. The TS results compare well with DTA measurements in the LiCl-AlCl<sub>3</sub> system and with the known phase-diagrams of the binary systems NaCl-CsCl and CsCl-BaCl<sub>2</sub>. Some noise, however, is observed above and in the liquidus region in the LiCl-AlCl<sub>3</sub> system.

#### INTRODUCTION

The present preliminary work intends to show the potensiality of thermosonimetry in phase-diagram studies. This technique is newly developed (1), and has not previously been used to study phase-diagrams. Certain applications have already been demonstrated within the field of phase transitions, decompositions of chemical compounds and minerals and thermomechanical fracturing. In this technique one measures the sonic activity from the process in question. The technique resembles "acoustic emission spectroscopy", the main difference being that the transformations causing the sonic emission are activated thermally. The background TS-activity in the absence of a physical process involving say some change of phase, is so low that the TS signal from the physical process can be clearly identified. When liquids are present, however, reactions between the liquid and container material evaporation/condensation processes or liquid creeping on the container walls may create thermal noise which will disturb this simple picture. It is therefore of importance when investigating the usefulness of this technique in systems containing fused salts to cheque the influence of these disturbances on the TS signal.
#### EXPERIMENTAL

All salts were dried carefully before use. Anhydrous  $AlCl_3$  was distilled at  $200^{\circ}C$  three to four times in a closed evacuated quartz tube to get rid of oxide impurities. The pure hygroscopic salts and their mixtures were transferred to the quartz stethoscopes in a drybox with less than 5 ppm of water. The stethoscope-salt-container was then evacuated and sealed. Before use the salts were fused, mixed and then quenched by dipping the stethoscope in water. Fig. 1 shows the seismically mounted quartz stethoscope resting on the piezoelectric cell for conversion of the induced vibrations in the stethoscope. The electric signals from the piezoelectric cell are then processed for recording or storage. In this system the TS activity can be monitored by recording:

1. The mean signal amplitude

2. The number of sonic bursty per second (Cps)

3. The frequency of the sonic ratiation.

This flexibility allows us to study different aspects of the process giving rise to sonic activity. The measurements were run with nominal heating rates of 5, 10 and  $20^{\circ}$ C per minute. The TS activity was recorded as a function of temperature over the range  $25^{\circ}$ C to  $750^{\circ}$ C. The reference temperature provided by the thermocouple (Fig. 1) was later calibrated against the alpha-beta quartz transition at  $573^{\circ}$ C.

#### RESULTS AND DISCUSSION

#### The NaCl-CsCl system

500°C. Fig. 2 shows the thermosonigram obtained from the mixture 15 mol% NaCl - 85 mol% CsCl (2). The  $\beta \rightarrow \alpha$  transition, eutectic temperature and liquidus line can clearly be seen. When the first liquid is formed, the rearrangements of the atoms in the crystals create strong sonic emission which is picked up by the stethoscope, and when the eutectic composition is reached the TS activity decreases since one solid phase is gone. Dissolution of CsCl still takes place and creates a fairly strong sonic emission which reaches a final maximum at the liquidus temperature. An increase in the surface to volume ratio will increase the rate with which the dissolution reaction takes place, and an increase in the sonic emission might be the result when the last crystals dissolve. We are not, however, ready to give a quantitative and definite explanation of this increase in sonic activity at the liquidus temperature before more experimental information on this effect is available.

#### The CsC1-BaCl<sub>2</sub> system

In the CsCl-BaCl<sub>2</sub> binary, which has been studied by thermoanalysis (3), two compounds exist (see Fig. 3). One, Cs<sub>2</sub>BaCl<sub>4</sub>, melts congruently at 588°C and the other, CsBaCl<sub>3</sub>, melts incongruently at 600°C. The system has two eutectic temperatures at 543°C and 582°C. In Fig. 3 the thermosonigram is shown. The interpretation of the experimental results is somewhat questionable. The eutectic and liquidus temperatures are clearly seen, and we think that the strong sonic activity at 622°C is due to the peritectic reaction. To correlate further the sonic data with the reported phase-diagram we have plotted the sonic transition temperatures as a function of the rate of temperature rise. On extrapolating to zero rate (isothermal heating) we find the data given in Fig. 4. The liquidus temperature coinside with the reported phase-diagram and the peritectic and eutectic temperatures are somewhat higher than those obtained by thermoanalysis.

# The LiC1-A1C13 system

Five different compositions: 10, 20, 30, 40 and 46 mol%  $AlCl_3$  were investigated, and since the LiCl-AlCl<sub>3</sub> phase diagram is not known, the TS data are compared with preliminary DTA curves obtained on cooling (4). The DTA cooling curves show extensive supercooling and the liquidus temperatures estimated from these data are therefore tentatively only.

In Figs. 5-8 TS results are shown for a melt containing 10 mol% AlCl3. The TS curves show a strong sonic activity around 600°C which drops of abruptly just above 600°C. This reduction in activity indicates that the liquidusline is reached. Just above this temperature a final increase in the TS activity is observed. The intensity of this peak, however, is smaller than that of the main peak when the heating rate is high  $(5^{\circ}C/min \text{ and } 10^{\circ}C/min)$ , but greater when the heating rate is low  $(2^{\circ}C/min)$ . We tend to believe that the last peaks are representative for the melting at the liquidus temperature. In Fig. 8 the isothermal melting point for the 10/90 melt is found to be 598°C. This agrees very well with the DTA data which gives  $T_f = 596°C$ . At higher contents of AlCl<sub>3</sub> it was difficult to obtain reproducible thermosonigrams. The most reliable results are presented in Figs.9-12. It is a reasonable agreement between the TS data around the liquidustemperature and the DTA data for the 20/80 and 30/70 melts. In Fig.11, however, strong sonic activity is observed at temperatures far above the liquidus temperature. For the 46/54 melt it was not possible to obtain a DTA signal on cooling (4). The TS data shown in Fig. 12 indicate a melting temperature below 390°C. This is in agreement with a calculation of the liquidus temperature based on vapour pressure data giving  $360^{\circ}C$  (5).

On the basis of the present preliminary results it may be concluded that thermosonimetry seems to be a promising method for phase diagram studies. The very strong sonic activity which occurs at phase transitions may give additional informations to data obtained through more conventional methods.

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Fig. 3. Thermosonigram of the mixture 40 mol% (CsCl)<sub>2</sub> -60 mol% BaCl<sub>2</sub>. Heating rate: 10<sup>o</sup>C/min. Fig. 4. Temperature of sonic trasitions at the eutectic, peritectic and liquidus as function of heating rate in the



609°C (peritectic)

599°C(eutectic)

211

640

620

600





Fig. 5. Sonic activity as function Fig. 6. Sonic activity as function of temperature. Heating rate: 2<sup>o</sup>C/min. System: AlC1<sub>3</sub>/LiC1 = 10/90.





Fig. 7. Sonic activity as function Fig. 8. Temperature of ionic tranof temperature. Heating rate: 10°C/min. System:  $A1C1_3/LiC1 = 10/90$ .



sitions as function of heating rate in the 10/90AlCl<sub>3</sub>/LiC1 mixture.





of temperature. Heating rate: 20°C/min. System:  $A1C1_{3}/LiC1 = 20/80$ .









of temperature. Heating rate: 20<sup>o</sup>C/min. System: AlCl<sub>3</sub>/LiCl = 46/54.

# ELECTROCHEMICAL STUDIES IN A ROOM TEMPERATURE MOLTEN SALT

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#### ABSTRACT

A new, low temperature molten salt, N-(n-butylpyridinium) chloride (BPC) -aluminum chloride has been investigated as a solvent. The system, represented as  $R^+Alcl_{4}^-$ , has a dominant solvolysis,  $2 \ Alcl_{4}^- \neq Al_2Cl_7^-$ + Cl<sup>-</sup>, and the 1:1 AlCl\_3:BPC is liquid at  $27^{\circ}C$ . The solvolysis constant has been determined as  $3.8 \times 10^{-13}$ (mole fraction) at  $30^{\circ}C$ . Marked variation in acid-base properties results from addition of BPC or AlCl<sub>3</sub> to the 1:1 system. The oxidation of a number of polynuclear aromatic hydrocarbons has been studied. In a number of cases, the radical cation formed during the first oxidation step is stable to cyclic voltammetric measurements. Acid-base interactions of the hydrocarbons with the solvent, as indicated by reversible, melt compositiondependent color changes, are noted.

As part of our continuing investigation into the chemistry and electrochemistry of aluminum halide based molten salts (1,2) we had, several years ago, initiated work on the electrochemistry of certain organic compounds in the sodium chloride-aluminum chloride melt at 175°C. While we had demonstrated that certain compounds were both stable in these systems and possessed interesting electrochemistry, it was nevertheless not a tractable system for a great deal of organic electrochemistry which, at least in principle, might be carried out in such systems (3). In search for lower temperature melts, which would still be aluminum halide based, we found that Hurley and Wier, in the early 1950's, had carried out work in aluminum chloride-ethylpyridinium bromide (EPB) melts which, at a mole ratio of 2 AlCl<sub>3</sub> to 1 EPB was a liquid at room temperature and furthermore, could be employed as a solvent for a variety of inorganic ion reactions as well as for aluminum deposition (4). We have carried out a certain amount of electrochemical and photochemical studies in this melt, taking advantage of its anhydrous nature and low melting point (5,6,7). However, our main interest has been in investigations of solute chemistry in the aluminum halide based melts which show acid-base dependent behavior, and, for such behavior to manifest itself, it is necessary to work in an aluminum halide system where the ratio of  $AlX_3$  to halide salt is variable about the 1:1 mole ratio.

Aluminum chloride based melts, with a chloride salt, RCl, may be indicated as  $AlCl_3:RCl$  (1:1 mole ratio) and may appropriately be represented as  $R^+AlCl_4^-$  where  $R^+$  may be an alkali metal cation or, as will be shown, an organic cation. The solvolysis equilibrium which dominates the acid-base chemistry of the solute, may be written as

$$2 \text{ A1C1}_{\mu} \rightarrow \text{A1}_{2}\text{C1}_{7} \rightarrow \text{C1}_{7}$$

Most work in these systems to date has involved the NaCl:AlCl<sub>3</sub> system where, at  $175^{\circ}$ C, the equilibrium constant for the solvolysis reaction 1 is 1.06 x  $10^{-7}$  on the mole fraction scale. For this melt the equilibria of reaction 1 is not sufficient to describe the overall system behavior, as determined from the potential variation of an Al electrode in the melt with melt composition. (0.98:1 < AlCl<sub>3</sub>:NaCl < 2:1). Equilibria such as

AlCl<sub>4</sub><sup>-</sup> + AlCl<sub>3</sub> 
$$\neq$$
 Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> (2)  
Al<sub>2</sub>Cl<sub>6</sub>  $\neq$  2 AlCl<sub>3</sub> (3)

must be considered and, in addition, changes in the apparent activity coefficient of  $AlCl_4$  were employed to "fit" the curve generated when the potential of an Al electrode in the melt was measured versus an arbitrary reference — usually an Al electrode in a NaCl saturated melt — as a function of melt acidity. A titration curve (E vs. mole ratio of  $AlCl_3$ :RCl) similar to that generated by a strong acid-strong base titration in aqueous solution results from such an experiment. The Al electrode may be considered to respond to Cl<sup>-</sup> activity in basic melt according to:

$$A1C1_{\mu}^{-} + 3 e^{-} \neq A1 + 4 C1^{-}$$
 (4)

which, when expressed as the potential of a concentration cell with negligible liquid junction may be written as

$$\Delta E = \frac{RT}{3F} \ln \left[ \frac{A1C1_{+}^{-}}{A1C1_{+}^{-}} \right]_{0}^{1} + \frac{4RT}{3F} \ln \left[ \frac{C1_{-}^{-}}{C1_{-}^{-}} \right]_{1}^{2}$$
(5)

or, in acidic melt,

$$4 \text{ Al}_2 \text{Cl}_7^- + 3 \text{ e}^- \neq 7 \text{ Al} + 7 \text{ Al} \text{Cl}_{\mu}^-$$
 (6)

which leads to an analogous expression to (5):

$$E = \frac{4RT}{3F} \ln \left[ \frac{[A_{12}C_{17}^{-}]}{[A_{12}C_{17}^{-}]} \right]_{2}^{1} + \frac{7RT}{3F} \ln \left[ \frac{[A_{12}C_{14}^{-}]}{[A_{12}C_{14}^{-}]} \right]_{1}^{2}$$
(7)

It is thus apparent that the 2  $AlCl_3:1$  EPB melt described above, although liquid at room temperature, did not possess the potential for varying the acidity of the system, since it was not liquid about the 1:1 mole ratio at low temperatures. Recently, however, we found that the system N-(n-butylpyridinium) chloride (BPC) -  $AlCl_3$ , at a mole ratio of 1:1, was liquid at  $27^{\circ}$ C and, in fact, could readily be handled at  $40^{\circ}$ C over the range 1:1.33<AlCl<sub>3</sub>:BPC<2:1 (8). BPC is readily prepared from the direct reaction of n-butyl chloride and pyridine; extensive purification is required to obtain a suitable salt for melt preparation (8).

Raman spectra on the AlCl<sub>3</sub>:BPC melt at  $40^{\circ}$ C at various mole ratios of AlCl<sub>3</sub> to BPC revealed bands essentially identical to those found previously by other workers for both NaCl:AlCl<sub>3</sub> and KCl:AlCl<sub>3</sub> melts at various mole ratios, indicating the predominant species were as in these other, higher temperature melts (9,10,11). However, integrated intensities at two different mole ratios of AlCl<sub>3</sub> to BPC for the most intense bands assigned to AlCl<sub>4</sub><sup>-</sup> and Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> suggested that reaction 2 above was markedly to the right compared to the NaCl:AlCl<sub>3</sub> system. This has since been verified by other work (12).

A number of polynuclear aromatics were studied in this melt as a function of melt acidity. Initially, the ferrocene-ferrocinium ion, which has seen extensive use as a probe species in nonaqueous systems, was examined (8). Cyclic voltammetry indicated a reversible, one electron transfer process, with no dependence on melt acidity being manifested by the oxidation potential, which was 0.24 V vs an Al reference in the 2:1 AlCl<sub>3</sub>:BPC melt. The initial  $E_{p/2}$  potential for the first oxidation step of the hydrocarbons studied<sup>2</sup> is presented in Table I. Anthracene showed behavior rather similar to that presented in acetonitrile (13-16); two oxidation steps were observed, the first to the radical cation, the second to the dication which undergoes rapid followup chemistry. Cyclic voltammetric studies indicated the radical cation was much more stable in the molten salt than in acetonitrile. This is manifested by the appearance, at low sweep rates on the reverse scan, of the reduction of the radical cation formed during the first oxidation step. At scan rates of the order of 500 mV/sec, the reaction appears to be reversible. All potential values listed in Table I were independent of melt acidity at sweep rate up to 5 V/sec. The first six hydrocarbons listed in Table I showed evidence of significant radical cation stability, although benzo(e)pyrene and pyrene showed evidence of product adsorption at the glassy carbon electrode employed. No reduction of the radical cations of the last six aromatics listed in Table I was found at sweep rates up to 10 V/sec. If the  $E_{p/2}$  values obtained were plotted against the ionization potential for obtained were plotted against the ionization potential for first electron removed, a linear plot was found, indicating minimal differences in the solvation energy between the parent hydrocarbon and the radical cation.

For reasons at this time unknown, those hydrocarbons with  $E_{p/2}$  of less than 1.4V were spontaneously oxidized in the most acidic<sup>p/2</sup> melts. The mechanism, or oxidant, is not known. In melts of mole ratios AlCl<sub>3</sub>:BPC less than 1.2:1, no oxidation was observed.

$E_{p/2}$ Values for First Oxidation of	Aromatic	Hydrocarbons
Compounds	E <sub>p/2</sub> ,	volts vs Al
Benzo(a)pyrene 9,10 Diphenylanthracene Pyrene Anthracene Benzo(e)pyrene Hexamethylbenzene Pentamethylbenzene Napthalene Phenanthrene Durene Biphenyl Mesitylene		$ \begin{array}{r} 1.03\\ 1.02\\ 1.09\\ 1.16\\ 1.20\\ 1.36\\ 1.53\\ 1.58\\ 1.59\\ 1.59\\ 1.73\\ 1.75 \end{array} $

TABLE I

It was observed, however, that even in melts where no oxidation was found, color changes were noted when the hydrocarbons were added to acid melts in which no spontaneous oxidation took place. These changes were reversible upon making the melt basic. While the absorption spectra of a number of melts containing the hydrocarbons were recorded, no quantitative work in terms of the determination of extinction coefficients was performed. The reversibility of the color changes with melt composition strongly suggests an acid-base dependent equilibrium between the acid species in the melt and the hydrocarbon. While somewhat speculative, it is our view that these represent the formation of  $\sigma$ -complexes, (17,18) which are formed by an equilibrium of the sort given in reaction 8.



Comparison between the  $\lambda_{max}$  values for the spectrum of the colored species formed in the max melt with those reported for the related aromatic carbonium ion in HF and HF-BF<sub>3</sub> leads to reasonable agreement except for phenanthrene and biphenyl (19). Even here an argument may be advanced that the lack of agreement indicates a steric hindrance related to the size of the acid moiety, written in reaction 8 above as AlCl<sub>3</sub>, compared to the proton.

The solvolysis equilibrium, reaction 1 above, has been determined from potentiometric titration and has a value of  $3.8 \times 10^{-13}$  at  $30^{\circ}$ C (12). The data for the titration curve may be fit completely by the equilibrium represented by equation 1, and does not require the additional equilibria, reactions 2 and 3, as is the case in the NaCl: AlCl<sub>3</sub> system. Further support to the evidence cited above from Raman for the increase in reaction 2 to the right is found in the fact that, at  $175^{\circ}C$ , the 2:1 AlCl<sub>3</sub>:BPC melt — which is marginally stable at this temperature — does not appear to have anywhere near the vapor pressure of AlCl<sub>3</sub> above it compared to the 2:1 AlCl<sub>3</sub>:NaCl melt at the same temperature.

This leads us to suspect that the chemistry of a variety of solutes, particularly organics, may in fact be drastically different than in the NaCl:AlCl<sub>3</sub> system, where the  $Al_2Cl_6$  (or AlCl<sub>3</sub>) activity is considerably greater. Preliminary experiments have already verified this expectation (20).

Various properties of these, and related systems have been measured, and  ${}^{1}\text{H}$  and  ${}^{13}\text{C}$  NMR have been performed on the solvent (21,22). In addition, metal ion redox couples have been studied by King, Hussey and co-workers, and the behavior of Ni(II) in the melt has been investigated (23,24,25).

These solvents appear to represent unique and unexplored systems in which it is anticipated much new, novel and hopefully useful chemistry and electrochemistry can be carried out.

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# ELECTROCHEMICAL STUDIES OF TRANSITION METALS IN MOLTEN ALUMINUM CHLORIDE-N-METHYLPYRIDINIUM CHLORIDE

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# Abstract

Copper(II) dissolved readily in aluminum chloride-N-methylpyridinium chloride (67-33 mol %) melt and underwent two reduction steps. The first reduction step, Cu(II) +  $e^- \leftarrow$  Cu(I) ( $E^0$  = 1.85V vs Al) was reversible at both glassy carbon and tungsten electrodes. The diffusion coefficient for the ·Cu(II) species was 2.9 x  $10^{-7}$  cm<sup>2</sup>/sec. The second reduction step,  $Cu(I) + e \leftarrow Cu (E^{O} = 0.78V \text{ vs Al})$ , was controlled by rate of nucleation in the initial phase of deposit formation on platinum, tungsten, and glassy carbon electrodes. Potentiostatic current-time transients for copper deposition on the latter two electrodes were found to obey the criteria for instantaneous three dimensional nucleation followed by hemispherical growth of the nuclei. The equilibrium constant for the reaction  $Cu(II) + Cu \leftarrow Cu(I)$  was appreciably larger than observed for this reaction in acidic, inorganic chloroaluminate melts.

Iron(III) chloride also was soluble in the melt, but FeCl<sub>3</sub> - melt solutions slowly decomposed. The proximity of the Fe(III)/Fe(II) standard potential ( $E^{\circ} = 2.05 v_{\circ}$  Al) to the anodic limit of the melt at ca.2.2V suggested that the instability of the solutions resulted from slow oxidation of the melt by Fe(III). The Fe(III) +  $e \neq$  Fe(II) electrode reaction was found to be quasireversible at glassy carbon and tungsten electrodes. The standard heterogeneous rate constant,  $k_s$ , and cathodic transfer coefficient,  $\alpha$ , for this electrode reaction were determined with a glassy carbon rotating disc electrode (GC-RDE). The diffusion coefficient for the Fe(III) species was found to be 3.5 x  $10^{-7}$  cm<sup>2</sup>/sec. It was not possible to study deposition of iron onto glassy carbon or tungsten electrodes since overpotentials cathodic of aluminum deposition (0.0V vs Al) were required to initiate nucleation.

# INTRODUCTION

Recently, investigations of the ionic conductivity and physical properties of aluminum chloride-N-alkylpyridinium halide molten salts were completed in this laboratory (1). This study has generated interest in the use of these liquids, particularly the 67-33 mol% compositions which are liquid at room temperature, as electrolytes for secondary batteries, solvents for metallurgical separations, and media for electrodepositing various metals. Practical application of these unique molten salts for these purposes depends upon knowledge of the electrochemical behavior of metal solutes in them.

The distribution of chloroaluminate species with melt composition in aluminum chloride-N-alkylpyridinium chloride melts appears to differ considerably from that of inorganic chloroaluminate melts. Raman spectral studies of aluminum chloride-N-(*n*-butyl)pyridinium chloride revealed that the 67-33 mol% composition of this melt may consist almost entirely of  $Al_2Cl_7^-$  (2). This is in contrast to high temperature inorganic chloroaluminate melts, e.g.,  $AlCl_3$ -KCl (67-33 mol %), which have been shown to contain  $AlCl_4^-$ ,  $Al_2Cl_7^-$ , and  $Al_2Cl_6$  (3).

The Cu(II)/Cu(I) and Cu(I)/Cu couples have been studied previously in the ternary  $AlCl_3-NaCl-KCl$  (66-20-14 mol%) melt at 135°C (4) and in the equimolar region of the  $AlCl_3-NaCl$  melt at 175°C (5). The electrochemistry of the Fe(III)/Fe(II) couple has also been studied in the latter melt system (5). However, voltammetric data for these couples in acidic ( $AlCl_3$  rich) regions of these melts were not reported. In this paper the electrochemical behavior of the Cu(II)/Cu(I), Cu(I)/Cu, and Fe(III)/Fe(II) electrode processes in the aluminum chloride-Nmethylpyridinium chloride (67-33 mol %) melt are reported and compared, when possible to results previously obtained in inorganic chloroaluminate melts. Techniques used for this investigation were stationary and rotating disc electrode voltammetry, chronoamperometry, controlled potential coulometry, and potentiometry.

#### EXPERIMENTAL

Apparatus - The cells used for voltammetry, chronoamperometry, and controlled potential coulometry, the electrochemical instrumentation, and the dry atmosphere system were described in a previous publication (6). A glassy carbon working electrode, geometrical area = 0.22cm<sup>2</sup>, was constructed according to the procedure given by Phillips et al.(7). A tungsten disc working electrode was prepared by sealing a 3.2 mm tungsten rod (Alfa-Ventron Corp., m5N5; t4N) in a 4mm i.d. canary glass tube, slicing off the end, and polishing the exposed surface successively with 600 grit silicon carbide paper, 320 mesh Carborundum powder (Fisher Scientific Co.), and finally with Type B alumina (Fisher Scientific Co.). The geometrical area of the tungsten electrode was 0.080 cm<sup>2</sup>. Working electrodes for copper deposition studies consisted of either the tungsten disc, the glassy carbon disc, or a platinum wire (Englehard Industries, Inc.) of 0.4 cm<sup>2</sup> geometrical area. Potentials reported in this study were measured with reference to an aluminum electrode in pure melt. Resistence compensation was applied during cyclic voltammetric measurements according to instructions given in the instrument manual supplied by the manufacturer. Only 1% of the total signal was fed back. This represented a resistance drop of approximately 80  $\Omega$  between the working and reference electrodes.

Reagents - Synthesis of N-methylpyridinium chloride as well as preperation, purification, and physical properties of the 67-33 mol % aluminum chloride-N-methylpyridinium chloride melt appear in another publication (1). Copper(II) chloride (Great Western Inorganics, 99.999%) was obtained and used without further purification. Copper(I) chloride (Baker "Analyzed Reagent", J. T. Baker Chemical Co.) was obtained and found to contain substantial amounts of Cu(II). Coulometric analysis revealed 33.9% by weight copper(II) chloride in the Cu(I) stock. This material was not subjected to pretreatment; however, when it was used appropriate corrections for the presence of Cu(II) were made. Copper foil, 0.13 mm thick, (99.9%, J. T. Baker Chemical Co.) was immersed briefly in aqueous HNO<sub>3</sub>, rinsed thoroughly with triply distilled water, and dried with absolute ethanol prior to use. Iron(III) chloride (Matheson, Coleman, and Bell, anhydrous reagent, sublimed) and iron(II) chloride (Ventron Corp., anhydrous) were used as received.

Neutron Activation Analysis Samples - Samples of copper were deposited onto tungsten sheets by controlled potential electrolysis from melt containing Cu(II). The deposit covered sheets were removed from the drybox and washed free of melt with distilled water. The deposits were scraped from the sheets with a spatula, washed repeatedly by suspension in distilled water followed by centrifugation, dried and weighed, and dissolved in concentrated nitric acid (Baker "Analyzed Reagent") prior to activation.

# RESULTS AND DISCUSSION

Copper(II) - Introduction of copper(II) chloride into the (67-33 mol %) aluminum chloride-M-methylpyridinium chloride melt resulted in a bright yellow solution. This is in contrast to the green color of Cu(II) solutions in the ternary AlCl<sub>3</sub>-NaCl-KCl (66-20-14 mol %) melt at 135°C which Anders and Plambeck (4) observed and attributed to Cu(II) solvated by chloride. Based on the presence of  $Al_2Cl_7$  as the sole solvating species in the melt used for the present study, this color difference must reflect participation of  $Al_2Cl_7$  ions in the solvation of Cu(II) rather than chloride. In agreement with the results of Boxall *et al*. (5) in AlCl<sub>3</sub>-NaCl melt no solubility problems were encountered in the present melt and solutions 50mM in Cu(II) were prepared readily. Solutions of Cu(II) were stored in the drybox for several months with no visual or electrochemical evidence for decomposition.

Polarograms constructed from current-time transients which illustrate the reduction of Cu(II) at glassy carbon and tungsten electrodes are shown in Figs. 1 and 2 respectively. The first reduction wave in these polarograms was well defined with both electrodes and gave linear log  $[(\dot{a}_{\rm d} - \dot{a})/\dot{a}]$  vs E plots. A value of n = 1.0 was calculated from the slopes of both plots, indicating that the waves were due to the reversible reduction of Cu(II) to Cu(I). Controlled potential coulometric reduction of Cu(II) to Cu(I) at 1.5 V gave n = 0.98 confirming this. The dependence of the polarographic diffusion current for this wave on the Cu(II) concentration is shown in Fig. 3. A slight positive deviation of the diffusion current at low Cu(II) concentrations was evident and was attributed to a weak adsorption of the reactant. Similar positive deviation in the diffusion current at low Cu(II) concentrations was observed with a tungsten electrode. However, voltametric behavior indicative of weak adsorption (8) was not obtained at scan rates of up to 5V/sec. The exact cause of the increased diffusion currents at low Cu(II) concentration could not be determined. The second wave in the polarograms (Figs. 1 and 2) was attributed to reduction of Cu(I) to the metal since a tungsten electrode polarized to 0.4 V became coated with a deposit of finely divided copper metal. The Cu(I) reduction process will be discussed in more detail in the next section.

Cyclic voltammograms of the melt background at a glassy carbon electrode and of Cu(II) at glassy carbon and tungsten electrodes are shown in Fig. 4. The reduction peak at 1.83V and oxidation peak at 1.89V in the latter two voltammograms illustrate the solution red-ox behavior of the Cu(II)/Cu(I) couple. Cyclic voltammetric data obtained for this reaction at a glassy carbon electrode in a 7.36mM Cu(II) solution at 30°C are presented in Table I. Examination of this table reveals that at low scan rates  $E_p^{a}-E_p^{c}$  and  $E_p^{c}-E_z$  approach theoretical values of 0.060V and -0.029V expected for a one electron reversible process at 30°C. At faster scan rates these values increased suggesting that the Cu(II)/Cu(I) electrode reaction might be quasireversible. However, values of  $i_{\rm L}/\omega^2$  obtained with a glassy carbon rotating disc electrode were constant with rotation rate at potentials corresponding to the ascending portion of the polarographic wave for Cu(II) reduction (Fig. 1) over a range of rotation rates of from 105 to 419 rad/sec. The voltammetric current function,  $i_p C/v^{\frac{1}{2}}$  was constant and  $i_p a^{\prime}/i_p C$  was 1.0 indicating that the Cu(II)/Cu(I) couple was not complicated by homogeneous kinetic processes in the range of scan rates employed.

The results obtained in this study for the Cu(II)/Cu(I) electrode process differ from those reported by Boxall *et al.* (5) in chloride rich AlCl<sub>3</sub>-NaCl at 175°C. These workers found the electrode process to be dependent on Cu(I) concentration in their melt which they attributed to the low solubility of CuCl<sub>2</sub> (*ca.* 5mM). In addition, they report the Cu(II)/Cu(I) couple to be reversible at CuCl concentrations less than 5mM (although  $E_p^{-a}-E_p^{-c}$  was 20% larger than theoretical) but obscured by Cl<sub>2</sub> evolution at CuCl concentrations below 2mM). In contrast, Cu(II)/Cu(I) electrochemistry is relatively straightforward and independent of concentration in the low temperature melt employed in the present study. The lack of excess chloride ion also permits greater anodic voltammetric excursion, particularly at glassy carbon electrodes.

Potentiostatic rotating disc electrode experiments were used to obtain diffusion coefficients for Cu(II) as a function of temperature. Figure 5 shows plots of  $i_{\rm L} vs \ \omega^2$  constructed from rotating disc data

at 1.6 V which span a temperature range of 30 to 70°C and a rotation rate of 105 to 419 rad/sec. Diffusion coefficients for Cu(II) calculated from these plots using the Levich equation obeyed the expression

$$\log v = \frac{-1242}{T} -2.375$$
 [1]

The diffusion coefficient for Cu(II) calculated from Eq. [1] at 25°C was  $2.9 \times 10^{-7}$  cm<sup>2</sup>/sec and compared well with published values of the diffusion coefficients of iron dimine complexes in aluminum chloride-N-ethylpyridinium bromide (67-33 mol %) at 25°C (10). The activation energy for the diffusion of Cu(II) was estimated from Eq. [1] to be 5.7 kcal/mol. This value is very close to that measured for Nb(V) in chloride rich AlCl<sub>3</sub>-NaCl (11).

v (V/sec)	Ер (V)	E <sup>a</sup> - E <sup>c</sup> (V)	$E_{p}^{c} - E_{z}$ (V)	$i_{p}^{C}/\sqrt{2}$ ((mA sec <sup>2</sup> )/ $\sqrt{2}$ )	i <sup>a</sup> /i <sup>c*</sup>
0.010	1.823	0.067	-0.030	2.3	1.00
0.020	1.825	0.065	-0.031	2.3	1.01
0.050	1.822	0.069	-0.029	2.3	1.03
0.100	1.819	0.074	-0.029	2.3	1.04
0.200	1.817	0.078	-0.029	2.3	1.05
0.500	1.825	0.097	-0.043	2.3	1.07
1.000	0.820	0.104	-0.036	2.2	1.10

Table I. Voltammetric Data for the Reduction of Cu(II)

Calculated using Nicholson's empirical procedure (9).

Copper(1) - Cu(I) was added to the melt most conveniently by polarizing a copper foil electrode. Polarization of the foil 0.50 V anodically from its rest potential gave an initial current of 0.3 mA/cm<sup>2</sup>. Solutions of Cu(I) in the melt produced in this fashion were colorless and stable indefinitely, provided precautions were taken to avoid exposing the melt to oxygen. After prolonged exposure to a dry atmosphere containing oxygen, Cu(I) solutions became faintly yellow, suggesting the formation of Cu(II). As a precaution only freshly prepared, colorless Cu(I) solutions were used in this work. Cu(I) solutions obtained by exhaustive coulometric reduction of Cu(II) at 1.0 V were also colorless. Voltammetric waves for the Cu(I)/Cu couple are also evident in Fig. 4. At the tungsten electrode the voltammogram was of the form expected for deposition and stripping of an insoluble substance. The behavior observed at the glassy carbon electrode was different than at the tungsten electrode in that current hysteresis was observed anodic of the deposition peak at 0.16V and the stripping peak was broad and poorly defined. This hysteresis persisted during the scan until a potential sufficient to reoxidize the deposit was reached. As the scan rate was increased the broad stripping peak began to exhibit shoulders, suggesting that it was a composite of several stripping peaks. In addition, deposition peaks at both tungsten and glassy carbon shifted cathodically with scan speed. The shifts were 0.10V and 0.18V per order of magnitude increase in scan speed, respectively.

Further indication that the reduction of Cu(I) was markedly dependent on the nature of the electrode material is shown by comparison of the second wave in Figs. 1 and 2. Current-time transients for data points on the ascending portion of the second waves in these figures exhibited maxima both for glassy carbon and tungsten electrodes. However, a diffusion current was obtained with the tungsten electrode at potentials cathodic of 0.57V. No diffusion current, as would be evidenced by constant values of  $it^{\frac{1}{2}}$  with decreasing potential, was obtained at a glassy carbon electrode prior to the increase in background current at about 0.2V. When the polarogram in Fig. 1 was constructed from current-time data at longer times, a wave with a diffusion limited plateau was observed just anodic of the increase in background current at 0.2V. This wave shifted anodically with an increase in the time at which the data were taken from the current-time curves. This shift was about 0.015V per second increase in time. The wave for Cu(I) reduction at a tungsten electrode (Fig. 2) was not shifted appreciably when constructed from current-time data at longer times.

The maxima observed in current-time curves and the rapid cathodic shift of the reduction peak potential with increasing voltammetric scan rate were reported in a number of previous studies of metal deposition from molten salts (6, 12, 13). These observations indicate that the initial phase of deposit formation is controlled by rate of nucleation.

To study further the influence of different electrode materials on the rate of nucleation during copper metal deposition, current-time transients were measured at glassy carbon, tungsten, and platinum electrodes in a 9.14mM Cu(I) solution (Figs. 6, 7, and 8). Examination of Fig. 6 shows that considerable overpotential was required to induce nucleation and growth on glassy carbon. Both the slope of the ascending portions of the current-time curve and the time delay of the current maxima were dependent on the applied potential. Values of the current and time taken from the rising portion of the current-time transients were fit best by a plot of i vs  $t^2$  (Fig. 9) while the descending portions of the transients exhibited the usual  $1/t^2$  decay. Similar results were obtained with the tungsten electrode (Fig. 7), but a smaller overpotential was required to initiate copper metal deposition. The ascending portions of the current-time transients were again proportional to  $t^{\frac{1}{2}}$  (Fig. 10). An increase in Cu(I) concentration resulted in a decrease in the overpotential required to induce nucleation at both glassy carbon and tungsten electrodes. This was most evident during cyclic voltammetric scans. For example, at the tungsten electrode at a scan rate of 0.020V/sec in a 9.14mM Cu(I) solution the copper deposition peak occurred at 0.448V while at the same scan rate in a 24.6mM Cu(I) solution this peak was observed at 0.575V. Nucleation of copper metal on platinum (Fig. 8) was much faster than observed on the other two electrodes. In fact, the narrow potential range in which nucleation phenomena could be observed at this electrode precluded detailed analysis of the ascending portion of current-time curves with equipment available for this study. Deposition of copper metal onto platinum proceeded readily at 0.5V and a smooth adherent deposit was produced. The absence of prolonged nucleation and the relative ease with which copper was plated onto platinum may be due in part to the fact that both copper and platinum metal have similar crystal structures. The platinum electrode was thus a less foreign substrate for deposition than were glassy carbon or tungsten.

The copper deposition process on both glassy carbon and tungsten obeyed the criteria of Hills *et al.* (12) for instantaneous three dimensional nucleation followed by hemispherical growth of the nuclei. Similar results were reported by Rolland and Mamantov (13) for deposition of aluminum on glassy carbon from slightly acidic AlCl<sub>3</sub>-NaCl melts at 175°C. Boxal *et al.* (5) reported a small nucleation peak on chronopotentiograms obtained during Cu(I) reduction at a tungsten electrode in the equimolar AlCl<sub>3</sub>-NaCl melt, but gave no further details.

Codeposition of Aluminum with Copper - The increase in current beginning around 0.2V (which can be seen in Fig. 2) indicated that another component of the melt was undergoing reduction. This merited investigation since the wave at 0.2V was absent from melts which did not contain Cu(II) or Cu(I). The background current for both polarograms was  $2 \times 10^{-6}$  A or less in this region. To gain insight into the process occurring during this reduction, copper metal was deposited from a Cu(I) solution onto separate tungsten sheets at 0.4V and 0.1V until the sheets were uniformly coated with thick deposits. The sheet polarized at 0.4V was covered with a finely divided deposit of reddish metallic copper which appeared to be of high quality, while the sheet polarized at 0.1V was covered with a dark brown deposit. Identical deposits were obtained on glassy carbon electrodes at these potentials, although the deposition process was initiated more slowly. Neutron activation analysis of the dark brown deposit indicated that the deposit contained about 25 mol % (The deposit did not contain detectable quantities of chloaluminum. The deposit obtained at 0.4V did not contain detectable quanrine.) tities of either aluminum or chlorine. Thus, it was concluded that the reduction wave occurring at potentials cathodic of 0.2V was due to codeposition of aluminum with copper.

Standard Potentials - Data for construction of a Cu(II)/Cu(I) Nernst plot were obtained by pipetting together solutions of Cu(II) and Cu(I) prepared by dissolving CuCl<sub>2</sub> and CuCl individually in two otherwise identical melts. A Nernst plot for the Cu(II)/Cu(I) couple constructed from this data and corrected for Cu(II) contamination of the Cu(I) solution is shown in Fig. 11. The standard potential for the Cu(II)/Cu(I) couple was determined from least squares treatment of the data shown in Fig. 11 and is given in Table II. The standard potential value for the Cu(II)/Cu(I) couple is in good agreement with values of  $E_k$  (1.86V) estimated polarographically (Figs. 1 and 2) and corrected for the cell resistance.

F٥ Reaction Slope of Nernst Plot (V) Molar Molal  $Cu(II) + e^{-4} \leftarrow Cu(I)$ 1.851 ± 0.000 1.851 ± 0.000  $0.0597 \pm 0.0003$  $Cu(I) + e^{- \stackrel{2}{\leftarrow}} Cu$ 0.777 ± 0.001 0.787 ± 0.001  $0.0600 \pm 0.0005$  $Fe(III) + e^{-2} + Fe(II) 2.045 \pm 0.000$  $2.045 \pm 0.000$  $0.0647 \pm 0.0008$ 

A Cu(I)/Cu Nernst plot on a molar basis (Fig. 12) was constructed using data obtained by coulometric generation of Cu(I) at a copper foil electrode. The Cu(I)/Cu standard potential determined from least squares treatment of the data shown in Fig. 12 appears in Table II, as does a value of the molal standard potential for this couple. Data in Table II were used to calculate the value of  $5.0 \times 10^{17}$  for the Cu(II) + Cu  $\leftarrow$  equilibrium constant on a molal basis. This value is about three orders of magnitude larger than the value reported for this reaction in the ternary AlCl3-NaCl-KCl (66-20-14 mol %) melt (4). However, the value of  $\Delta E^{\circ}$  calculated in the present study is almost identical in magnitude to the value reported previously (4). The larger equilibrium constant observed in the present study indicates that the acidic, low temperature chloroaluminate melts tend to stabilize low oxidation state species even more strongly than inorganic chloroaluminate melts of similar composition. This enhanced stability appears to originate primarily from the decreased temperature at which these molten salts may be employed.

A Nernst plot for the Fe(III)/Fe(II) couple is shown in Fig. 13. Data for this plot, given in Table II, were obtained by coulometric oxidation of a solution containing Fe(II) at a potential of 2.10V.

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Table II. Standard Potential Data at 30.0 ± 0.1°C

The data were corrected for the effect of background current due to slight oxidation of the melt.

Iton(111) - Iron(III) chloride dissolved readily in the melt to give a yellow-orange solution. The rest potential of a glassy carbon or tungsten indicator electrode in a 13.9 mM solution of Fe(III) was 2.11V. The rest potential could be observed to decrease and the color of the solution to fade over a period of several days. The anodic limit of the pure melt was established with linear sweep voltametry at a glassy carbon electrode to be ca. 2.2V. The proximity of the Fe(III) solution rest potential to the anodic limit of the melt suggested that the instability of the solution resulted from slow oxidation of the melt by Fe(III). Only freshly prepared Fe(III) solutions were used in this study.

Iron(II) chloride was soluble in the melt and gave a clear to faintly salmon colored solution. Deposition of iron from solutions containing Fe(II) was accompanied by nucleation as previously observed during copper deposition. However, in this case overpotentials cathodic of aluminum deposition (0.0V) were required to initiate nucleation on glassy carbon or tungsten electrodes. For this reason, the electrochemical behavior of Fe(II) was not considered further.

Cyclic voltammograms for the reduction of Fe(III) at glassy carbon and tungsten electrodes are shown in Figs. 14 and 15. As the scan rate was increased, an increase in  $E_p^a - E_p^c$  was noted and the waves became more drawn out. At very slow scan rates,  $E_p^a - E_p^c$  began to approach values expected for a one electron reversible process. Voltammetric behavior of this type has been attributed to a quasireversible charge transfer process (14). An estimate of the standard potential for the Fe(III)/Fe(II) couple, obtained from the average of  $E_p^a$  and  $E_p^c$ , was 2.06V. This value was in good agreement with that determined from the Nernst plot (see above).

Galus and Adams (15) describe a RDE technique attributed to Levich (16) which can be employed to estimate rate constants for the Fe(III)/Fe(II) system. This technique requires that only Fe(III) be present. Using their procedure, the heterogeneous rate constant for the reduction of an oxidized species,  $k_{\rm f}$ , is calculated from the intercepts of  $1/i \ vs \ 1/\omega^2$  plots according to Eq. 2

$$\frac{1}{i} = \frac{1}{n F k_F C_O^{b}} + \frac{1.61 v^{1/6}}{n F v^{2/3} C_O^{b}} \frac{1}{w^{\frac{1}{2}}}$$
[2]

The method is applicable provided that the electrode reaction is first order and that measurements are made at large overpotential (15). The standard heterogeneous rate constant,  $k_{\rm c}$ , and cathodic transfer

coefficient  $\alpha$ , can be determined from a plot of E vs ln  $k_{f}$  as indicated by Eq. 3 if the standard potential is known.

$$k_{f} = k_{s} \exp\left(\frac{-\alpha \ n \ F \ E}{RT}\right)$$
[3]

This technique was ideally suited to the present investigation since the anodic limit of the melt precluded a rigorous study of Fe(II) oxidation in our melt system.

An i vs E curve for the reduction of Fe(III) obtained at constant rotation rate with a glassy carbon electrode is shown in Fig. 16. To exclude possible interferences from melt decomposition, data for this and subsequent curves were not taken at potentials anodic of 2.10V. In addition, concentrations of Fe(III) were kept high, *i.e.*, equal to or greater than  $10^{-2}$ M, to ensure that the observed current accurately represented the current resulting from Fe(III) reduction. Plots of i vs  $w^{i_2}$  constructed from data measured at selected potentials on both the ascending and plateau portions of the i vs E wave are shown in Fig. 17. In this figure, the current can be observed to transition from charge transfer control (2.00V) to mass transport control (1.00V), confirming the quasireversible nature of the Fe(III)/Fe(II) electrode reaction.

Figure 18 shows plots of  $1/i vs 1/w^2$  as a function of applied potential. These plots were linear indicating that the Fe(III)/Fe(II) electrode reaction was first order (17). Similar results have been obtained for this electrode reaction in aqueous solution (15, 18, 19). Diffusion coefficients were calculated from the slopes of  $1/i vs 1/w^2$  plots constructed with data taken at potentials corresponding to the plateau of the i vs E wave. The average value of the diffusion coefficient, obtained at Fe(III) concentrations of 10.6, 13.7, and 13.9mW with the kinematic viscosity of the melt taken as 0.1263 cm<sup>2</sup>/sec (1), is  $3.5 \times 10^{-7}$  cm<sup>2</sup>/sec. This value compared well with the Cu(II) diffusion coefficient.

Potential dependent values of  $k_{\rm f}$  were determined from the intercepts of  $1/i \ vs \ 1/\omega^{\frac{1}{2}}$  plots constructed at potentials corresponding to the ascending portion of the polarographic wave. A plot of ln  $k_{\rm f} vs E$  for these data is shown in Fig. 19. The standard heterogeneous rate constant,  $k_{\rm g}$ , for the Fe(III) reduction process at 30.0°C was determined from the intercept of this plot at the standard potential. The cathodic transfer coefficient,  $\alpha$ , was calculated from the slope of the plot according to Eq. 3. Both values, determined with a glassy carbon rotating disc electrode (GC-RDE), are given in Table III.

For comparative purposes,  $k_{\rm S}$  was estimated for Fe(III) reduction using a method which was more or less independent of the rotating disc electrode technique. Values of  $k_{\rm S}$  were determined from the increase in  $E_{\rm P}^{\rm a} - E_{\rm P}^{\rm C}$  with increase in scan rate using cyclic voltammetry according to the procedure described by Nicholson (14). Estimates of  $k_{\rm S}$  determined in this fashion at glassy carbon (GC) and tungsten (W) electrodes are given in Table III. The good agreement found between GC-RDE and GC determined values of  $k_{\rm g}$  was not anticipated, because it was necessary to begin cyclic voltammetric sweeps at potentials well into the melt decomposition region in order to obtain reproducible values of  $E_{\rm p}{}^{\rm a} - E_{\rm p}{}^{\rm c}$  at each scan rate.

Table III. Kinetic Data for the Fe(III)/Fe(II) System at 30°C



Comparison of  $k_{\rm S}$  for Fe(III) reduction at glassy carbon and tungsten electrodes reveals that  $k_{\rm S}$  for Fe(III) reduction at a tungsten electrode is only 38% of the value obtained at glassy carbon. However, a fundamental comparison of the difference in  $k_{\rm S}$  is not warranted since there may be gross differences in the electrode surface areas due to blockage, etc.

It is also difficult to make rigorous comparisons between  $k_{\rm S}$  for Fe(III) reduction in aqueous solutions and that measured in the molten salt used in the present study owing to the fundamental differences in the media and the slight temperature difference (30°C vs 25°C). None-theless, for the sake of a qualitative comparison selected values of  $k_{\rm S}$  for the Fe(III)/Fe(II) electrode reaction and  $\alpha$  determined in aqueous media at various electrodes are reported in Table IV. On a qualitative basis, the value of  $k_{\rm S}$  and  $\alpha$  appear to agree well with values previously reported.

Electrolyte	Electrode	k <sub>s</sub> (cm/sec)	α	Ref.
1M H <sub>2</sub> SO <sub>4</sub>	Pt	$4.3 \times 10^{-3}$	0.46	(15)
1M H <sub>2</sub> SO <sub>4</sub>	C-paste	$5.4 \times 10^{-5}$	- "	(15)
9M LiCl-O.1M HCl	C-paste	$2.2 \times 10^{-4}$	_	(15)
1M HClO4	Pt	$9.0 \times 10^{-3}$	0.50	(18)
1M H <sub>2</sub> SO <sub>4</sub>	Au	$1.0 \times 10^{-4}$	-	(20)
ALC13-MPC*	GC	$1.6 \times 10^{-4}$	0.38 This	s work (30°C)

Table IV. Comparison of Kinetic Data for the Fe(III)/Fe(II) System.

\*AlCl<sub>3</sub>-N-methylpyridinium chloride (67-33 mol%)

# LIST OF SYMBOLS

c <sup>b</sup>	Concentration of oxidized material in bulk melt (mol/cm <sup>3</sup> )
D	Diffusion coefficient (cm <sup>2</sup> /sec)
E	Potential (V)
EO	Standard electrode potential (V)
E <sub>1/2</sub>	Polarographic half-wave potential (V)
$E_p^a, E_p^c$	Anodic and cathodic peak potentials (V)
F	Faraday Constant
i	Current (A)
id	Polarographic diffusion current (A)
$i_{\rm L}$	Rotating disc electrode limiting current (A)
ip <sup>a</sup> , ip <sup>c</sup>	Anodic and cathodic voltammetric peak currents (A)
k <sub>f</sub>	Hetereogeneous forward rate constant (cm/sec)
k <sub>s</sub>	Standard hetereogeneous rate constant (cm/sec)
М	Molarity (mol/liter)
n	Number of electrons in charge transfer step
R	Cell resistance ( $\Omega$ ); Gas constant
t	Time (sec)
т	Temperature (K)
α	Transfer coefficient
ν	Sweep rate (V/sec)
ω	Rotation rate (rad/sec)

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Fig. 1 Polarogram constructed from current-time transients for the reduction of Cu(II) at a glassy carbon electrode at 30°C. Cu(II) concentration was 25.4 mM; current was measured at 3 sec.



Fig. 3 Dependence of the polarographic diffusion current at a glassy carbon electrode on the Cu(II) concentration at 30°C.



Fig. 2 Polarogram constructed from current-time transients for the reduction of Cu(II) at a tungsten electrode at 30°C. Cu(II) concentration was 25.4 mM; current was measured at 3 sec.



Fig. 4 Cyclic voltammograms at 30°C; A. melt background at a glassy carbon electrode, sweep rate was 0.050V/sec, B. Cu(II) at a glassy carbon electrode, Cu(II) concentration was 13.2 mM, sweep rate was 0.020V/sec, C. Cu(II) at a tungsten electrode, Cu(II) concentration was 9.52 mM, sweep rate was 0.020V/sec.



Fig. 5 Variations of the limiting current at a glassy carbon rotating disc electrode with square root of the rotation rate as a function of temperature. Potential was 1.6 V; Cu(II) concentration was  $9.52 \text{ mM}, \bigcirc 30^{\circ}\text{C}, \bigoplus 40^{\circ}\text{C},$  $\square 50^{\circ}\text{C}, \bigoplus 60^{\circ}\text{C}, \triangle 70^{\circ}\text{C}.$ 



Fig. 7 Current-time transients for Cu(I) reduction at a tungsten electrode at 30°C. Cu(I) concentration was 9.14 mM.



Fig. 6 Current-time transients for Cu(I) reduction at a glassy carbon electrode at 30°C. Cu(I)concentration was 9.14 mM.



Fig. 8 Current-time transients for Cu(I) reduction at a platinum electrode at 30°C. Cu(I) concentration was 9.14 mM.



Fig. 9 Plot of the current from the ascending portion of the transients in Fig. 6 vs square root of time;  $\bigcirc$  0.15 V,  $\bigcirc$  0.25 V.



Fig. 11 Nernst plot for the Cu(II)/Cu(I) couple.



Fig. 10 Plot of the current from the ascending portion of the transients in Fig. 7 vs square root of time;  $\bigcirc$  0.50 V,  $\bigcirc$  0.55 V.



Fig. 12 Nernst plot for the Cu(I)/Cu couple. Cu(I) concentration was in units of molarity.







Fig. 15 Cyclic voltammogram of the Fe(III)/Fe(II) couple at a tungsten electrode at 30.0°C. Sweep rate was 0.002 V/sec.







Fig. 16 Current-potential curve for the reduction of Fe(III) at a glassy carbon rotating disc electrode at 30.0°C. Fe(III) concentration was 13.9 mM; rotation rate was 209 rad/sec.





Fig. 17 Plot of the current versus the square root of the rotation rate for the reduction of Fe(III) at a glassy carbon electrode at 30.0°C. Fe(III) concentration was 13.9 mM; O 1.00 V, 1.80 V, 1.90 V, 1.97 V, and  $\Delta$  2.00V.







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## SPECTROELECTROCHEMISTRY IN MELTS: APPLICATIONS TO MOLTEN CHLOROALUMINATES

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#### ABSTRACT

Spectroelectrochemistry is an effective approach to studies of redox chemistry in solutions. We have recently initiated UV-visible spectroelectrochemical studies in molten chloroaluminates (AlCl<sub>3</sub>-NaCl mixtures) using a silicon vidicon rapid-scan spectrometer. Electrodes made from glassy carbon foam and metal grids are used in optically transparent thin layer cells. The solute species of interest are the oxidation products of sulfur and some of the Group IVB-VIB transition metal ions. In this paper the apparatus and the initial results are described.

#### INTRODUCTION

The use of spectroelectrochemistry as a tool for studying redox chemistry in solutions has developed rapidly over the last several years (1). This technique yields simultaneous spectral and electrochemical information useful in the elucidation of mechanisms of redox reactions. By using appropriate experimental designs, short-lived intermediate species, which may be undetectable electrochemically, can be studied.

The transmission mode spectroelectrochemical experiment involves the use of an optically transparent electrode (OTE), i.e. an electrode which is transparent in the spectral region of interest. Radiation of the desired wavelengths is passed through the solution and the OTE where a portion is absorbed by the solute species. The attenuated radiation is then measured to give a spectrum. Spectroelectrochemistry most commonly involves the UV-visible-IR spectral regions, but it has been applied to ESR, NMR and mass spectrometry as well (1).

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We are currently developing UV-visible spectroelectrochemical techniques for studying redox systems in molten chloroaluminates (mixtures of AlCl<sub>3</sub> and alkali halides). Solute chemistry in these melts is quite dependent on the melt acidity (2-4). The acid-base properties of the chloroaluminate melts near the 1:1 AlCl<sub>3</sub>-NaCl mole ratio can be described by the equilibrium (5-9)

$$2 \text{ A1C1}_{4} = \text{A1}_{2}\text{C1}_{7} + \text{C1}_{7}$$

AlCl<sub>4</sub><sup>-</sup> is the predominant anion in the equimolar AlCl<sub>3</sub>-NaCl melt. As the acidity is increased, Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> becomes more abundant (5-9).

To date we have examined by spectroelectrochemistry the reduction of niobium (V) and the oxidation of sulfur in chloroaluminate melts. The use of OTE's to study species in melts spectroelectrochemically has not been reported previously.

#### **EXPERIMENTAL**

A block diagram of the spectrometer/data acquisition system used to carry out spectroelectrochemical experiments is shown in Figure 1. The spectrometer is a silicon-vidicon based rapid-scan spectrometer (RSS) which is controlled by the PDP-8/I minicomputer. To obtain an absorption spectrum of a sample, white light is passed through the sample and into a polychromator where it is dispersed by a grating. A 400 nm wide segment of this spectrum is directed across the face of the vidicon detector, where it is read as light intensity vs. wavelength by an electron beam. The sweep frequency of this beam can be adjusted so that spectra may be acquired at time intervals varying from 10 msec to 5 sec. Since the spectrometer operates in a single-beam mode, a 100% transmission spectrum (with no sample in the beam) is also acquired and the absorbance spectrum is calculated using the computer. Spectra are stored either on disk or cassette tape. An absorption spectrum can be viewed either on a CRT display, or displayed on an X-Y recorder. A potentiostat is also interfaced to the system; this makes it possible to synchronize the start of spectral data acquisition with the initiation of the electrochemical experiment as well as to simultaneously acquire and store both spectral and electrochemical data. A more detailed description of the spectrometer and the computer interface system is available (10).

A typical cell used to carry out molten salt spectroelectrochemical experiments is illustrated in Figure 2. The optically transparent electrode consists of a piece of porous glassy carbon (11), a platinum screen or a tungsten grid. The OTE is inserted into the quartz cuvette, the pathlength of which ranges from 0.25 mm to 2.00 mm, and the OTE assembly is held in place by a Cajon vacuum fitting. The counter electrode is a platinum foil electrode and the reference electrode is an aluminum wire in a separate fritted compartment. Other electrodes, not shown for clarity, include a platinum or tungsten wire working electrode for cyclic voltanmetry, and an extra platinum foil electrode. The melt is added via a filling tube (not shown) in the top of the cell which is then sealed under vacuum. The cell is mounted in a suspension assembly by means of the support ring, and this assembly is then lowered into an optical furnace. The furnace consists of a glass tube wrapped with a nichrome heating element, and contains two quartz windows through which spectra are taken. The furnace temperature is controlled by using a variable voltage transformer. A tungsten lamp and a xenon arc lamp serve as light sources.

# SPECTROELECTROCHEMICAL STUDY OF THE REDUCTION OF NIOBIUM (V)

The redox chemistry of transition metals in Groups IVB-VIB in chloroaluminate melts is unusual because of the tendency to form metal clusters in which the metal exists in an unusually low oxidation state (2,4,12-14). The electrochemical reduction of Nb(V) in both acidic (mole % AlCl<sub>3</sub> > 50) and basic (mole % AlCl<sub>3</sub> < 50) chloroaluminates has been previously reported (4). Potentiometric and spectroscopic studies of Nb(V) in AlCl<sub>3</sub> VCl relations have a spectroscopic studies of Nb(V) in AlCl<sub>3</sub> VCl relations have a spectroscopic studies of Nb(V) in AlCl<sub>3</sub> VCl relations have a spectroscopic studies of Nb(V) in AlCl<sub>3</sub> VCl relations have a spectroscopic studies of Nb(V) in AlCl<sub>3</sub> VCl relations have a spectroscopic studies of Nb(V) in AlCl<sub>3</sub> VCl relations have a spectroscopic studies of Nb(V) in AlCl<sub>3</sub> VCl relations have a spectroscopic studies of Nb(V) in AlCl<sub>3</sub> VCl relations have a spectroscopic studies of Nb(V) in AlCl<sub>3</sub> VCl relations have a spectroscopic studies of Nb(V) in AlCl<sub>3</sub> VCl relations have a spectroscopic studies have a spec of Nb(V) in AlCl<sub>3</sub>-KCl melts have also been performed (15). In basic melts the first step of the reduction of the bright-yellow Nb(V) results in the formation of purple Nb(IV). The spectroelectrochemistry of this reduction was studied at a Pt screen OTE in a NaCl-saturated (basic) melt at 225°C. Figure 3 illustrates the spectra obtained during the course of the reduction. At t = 0 sec, an absorption band at 300 nm due to Nb(V) is observed. Following a potential step to the diffusion plateau of the first reduction wave, two new absorption bands appear at 275 nm and ~350 nm. Previous spectra of Nb(IV) obtained in this melt (14), in solid phase (16), and in another solvent (17) show bands near 285 nm and 325 nm, plus other lower wavelength bands. The reported band positions vary by as much as 10-15 nm. Figure 4 shows a thin-layer coulogram of this reduction calculated from chronoamperometric data obtained simultaneously with spectral data. The charge value obtained from this curve yields an n-value of 0.99, thus confirming a simple electrochemical reduction.

In acidic melts, the reduction of Nb(V) proceeds through an ECE mechanism to produce a Nb(III) species (4) as shown below:

 $Nb(V) + e \implies Nb(IV)$   $2 Nb(IV) \implies Nb_2^{8+}$   $Nb_2^{8+} + 2e \implies Nb_2^{6+}$ 

This reduction was studied spectroelectrochemically in an acidic melt  $(AlCl_3-NaCl 63-37 \text{ mole })$  at 225°C, and the resulting spectra are shown in Figure 5. The Nb(V) band at 300 nm disappears as the reduction is carried out, and no new bands are observed. The slight increase

in absorbance seen at the longer wavelengths is probably due to the formation of a precipitate containing Nb(III) (14). Because this precipitate apparently was deposited on the screen OTE, it could be reoxidized completely to Nb(V), as indicated by the reappearance of the band at 300 nm. Thin-layer coulometry carried out simultaneously with spectral acquisition gave an n-value of 2.2.

#### · SPECTROELECTROCHEMICAL STUDY OF SULFUR OXIDATION

The electrochemistry of sulfur in molten chloroaluminates is of considerable importance to the development of a molten salt battery using a sodium anode and positive oxidation states of sulfur as the cathode (18,19); it has been investigated in both basic and acidic melts (20-22). Because sulfur can be oxidized to higher oxidation states in acidic melts, its chemistry in these melts is of greater importance to the battery work. In acidic AlCl<sub>3</sub>-NaCl melts sulfur is oxidized in three steps, the final product being S(IV) as indicated by voltammetry and controlled-potential coulometry (22). Both Raman (23) and potentiometric (24,25) studies have indicated that S(IV) is present as  $SCl_3^+$ .

We are using spectroelectrochemistry to study further the mechanism of the oxidation of sulfur in acidic chloroaluminates. By oxidizing elemental sulfur in the melt to S(IV), at least five intermediate oxidation states can be produced (24,25). Several of these species have characteristic absorption maxima which can be used to ascertain the species present as a function of the potential applied to the OTE.

Elemental sulfur was dissolved in an acidic chloroaluminate melt (AlCl<sub>3</sub>-NaCl 63-37 mole %); this solution was studied spectroelectrochemically at platinum and carbon OTE's at 225°C. Thin-layer coulometry was carried out on the first oxidation wave by holding the potential of a Pt OTE at + 1.65V. N-values ranging from 0.14 to 0.16 were obtained. These results agree with those obtained through exhaustive bulk coulometry (22). An n-value of 0.125 would correspond to the formation of  $S_{16}^{2+}$  (or  $S_8^+$ ), while an n-value of 0.25 would indicate formation of  $S_8^{2+}$ . The intermediate value suggests that a mixture of these species is formed. The spectra shown in Figure 6, obtained at a carbon OTE, substantiate this supposition. As the oxidation takes place, three absorption bands appear approximately simultaneously at 16600 cm<sup>-1</sup> (600 nm), 13700 cm<sup>-1</sup> (730 nm) and 10200 cm<sup>-1</sup> (980 nm). The latter two bands achieve a maximum absorbance after about four minutes and begin to decrease as the first band continues to increase. This can be seen clearly from the absorbance-time profiles illustrated in Figure 7. According to previously published work (24,25), the 600 nm band is attributed to  $S_8^{2+}$  and the 730 nm and 980 nm bands are due to  $S_{16}^{2+}$ . This first oxidation step then produces a mixture of  $S_{16}^{2+}$  (or  $S_8^+$ ) and  $S_8^{2+}$ . Marassi et al. (22) have proposed mechanisms involving chemical reactions which could account for these results.
The spectra shown in Figure 8 were obtained by stepping the potential of the carbon OTE from 1.65V (plateau of the first wave) to 1,85V (just past the plateau of the second wave). The band at  $13700 \text{ cm}^{-1}$ , due to  $S_{16}^{2+}$  (or  $S_8^+$ ) immediately vanishes while the band at 16600 cm<sup>-1</sup>  $(S_8^{2+})$  initially increases. This band then slowly disappears as  $S_8^{2+}$ is oxidized to S(I). In a similar experiment carried out at a Pt screen OTE, but recording spectral data at shorter wavelengths, bands at ca. 26300 cm<sup>-1</sup> (380 nm) and  $\sim$  31000 cm<sup>-1</sup> (323 nm) appeared as the oxidation proceeded. At least one and perhaps both of these bands can be attributed to the formation of S(I) (as S<sub>2</sub><sup>2+</sup>) (25). The third sulfur oxidation wave is not very interesting for spectroelectrochemical study because the S(IV) product does not exhibit any absorption in the visible region (25).

#### CONCLUSION

We have demonstrated that spectroelectrochemistry can be carried out successfully in melts using optically transparent electrodes. The correlation of the spectral data with the electrochemical results has proven very helpful in determining what species are formed during the reduction or oxidation, thereby yielding insight into the mechanisms of the electrochemical processes in melts.

#### ACKNOWLEDGEMENTS

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Figure 2. Typical spectroelectrochemical cell used in the molten salt studies. The reference electrode is isolated from the bulk melt by a porous ceramic frit



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Figure 3. Spectra obtained during the reduction of Nb(V) in the NaCI-saturated chloroaluminate melt. Potential stepped from 1.5V to 1.0V vs. the Al(III)/Al reference electrode in the NaCI-saturated melt. OTE: Pt screen. Pathlength: 0.25 mm Conc. Nb(V): 0.0015 molal



Figure 4. Charge vs. time plot for the thin-layer coulometric reduction of Nb(V) in the NaCi-saturated chloroaluminate melt. Potential stepped from 1.5V to 0.9V vs. the Al(III)/Al reference electrode in the NaCi-saturated melt. OTE: Pt screen

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Figure 5. Spectra obtained during the reduction of Nb(V) in AlCl<sub>3</sub> – NaCl (63-37 mole %) melt. Potential stepped from 1.5V to 0.9V vs. the Al(III)/Al reference electrode in the 63-37 melt. OTE: Pt screen. Pathlength: 0.25 mm Conc. Nb(V): 0.0036 molal



Figure 6. Spectra obtained during the oxidation of sulfur at a glassy carbon OTE in the AICl<sub>3</sub> - NaCl (63-37 mole %) melt. Potential stepped from 1.3V to 1.65 V vs. the AI(111)/AI reference electrode in the 63-37 melt. Conc. S: 0.013 molal



Figure 7. Absorbance vs. time plots for the three absorbance bands shown in Figure 6. Pathlength: 2.0 mm



Figure 8. Spectra obtained during the oxidation of sulfur at a glassy carbon OTE in the AlCl<sub>3</sub> – NaCl (63-37 mole %) melt. Potential stepped from 1.65 V to 1.85V vs. the Al(III)/Al reference electrode in the 63-37 melt. Conc. S: 0.013 molal

# ELECTRODE POTENTIALS, ELECTRONIC SPECTRA AND OXIDATION STATE STABILITIES

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# ABSTRACT

E.m.f. series and the electronic spectra of transition metal ions, particularly  $Co^{2+}$  and  $Ni^{2+}$ , permit one to draw conclusions concerning the structure of molten salt solvents and the oxidation state stabilities of metal compounds dissolved in them. A few electrode potential measurements, current-voltage scans and color comparisons enable one to characterize a new solvent well.

In order to carry out a variety of chemical experiments involving a new molten salt solvent it is advisable to collect together certain basic facts, either by extrapolation or interpolation from literature data or by actual measurements. We have found it useful to know the density of the solvent but not the conductivity, the surface tension, at least approximately, because capillary action can be useful in making salt bridges, the thermal properties only qualitatively, but the phase equilibria of the components in some detail.

The affinity of many molten salts for water is well known so that sundry attempts at removing the last traces of moisture from the components and then the mixture should be a matter of course for several types of measurement, particularly those of a voltammetric nature or involving reducing agents. In many cases water and its reaction products will show up in a voltammetric scan of the solvent using moderately inert cathode materials and it will also give rise to heavy metal hydroxide precipitates; especially of Fe<sup>3+</sup>; however water may not interfere obviously with electrode potential measurements above the 10<sup>-fm</sup> level or with the formation of clear solutions of many transition metal salts.

These last observations mean that voltammetry can be used to determine the purity of the solvent and, with the assistance of coulometry and surface and solution analysis, to determine the solvent oxidation and reduction products at a given purity level. E.m.f. measurements on the right systems-not those with potentials near the solvent limits-and electronic spectral studies of structure-sensitive ions such as  $Co^{2+}$  and  $Ni^{2+}$  should not be affected unduly by the solvent purity but should give some idea of the complexing ability and coordination preference of the solvent.

Table 1 lists the differences between the electrode potentials of certain couples in a variety of solvents [1]. The number 0.210 in the second column is the e.m.f. in volts of the  $cell^{(2)}$ :

Co/Co(II) in NaCl-CaCl<sub>2</sub> // Ag(I) in NaCl-CaCl<sub>2</sub>/Ag

with equal metal ion concentrations in mole fractions. The cell reaction is

 $Co + 2Aq(I) \rightarrow 2Aq + Co(II)$ 

The number is forthcoming from a concentration cell experiment and the Nernst plots appear in Figure 1. Careful perusal of the Table shows that

- (a) the cobalt potential is close or positive to the
- silver potential in thiocyanate and chloroaluminate; (b) the cobalt potential is 0.2 to 0.3 v negative to the silver potential in alkali chlorides;
- (c) the cobalt potential is very (0.7-1.1 v) negative to
- the silver potential in oxygenated solvents; the nickel and Cu(II)/Cu(0) potentials closely follow (d) the cobalt potential;
- (e) the Cu(I)/Cu(0) potential follows the silver potential except in thiocyanate, metaphosphate and hydroxide.

From these observations we conclude that Cu(I) is especially stable in CNS<sup>-</sup>, PO<sub>3</sub><sup>-</sup> and OH<sup>-</sup> melts, that Ag(I) and Cu(I) are moderately stable in Cl<sup>-</sup> melts but not very stable in H<sub>2</sub>O and CO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> melts and that Co(II), Ni(II) and Cu(II) behave similarly in all the systems.

In Figure 2 we reproduce (3) the electronic spectrum of Co(II) in A. water; D. a chloride melt; C. a nitrate melt and B. a sulfate melt. The colors of these solutions are pink, blue, purple and purple respectively, reflecting the spectral shapes. The intensities of the absorption bands also follow the colors: the blue being the strongest and the pink the weakest. These spectra have been associated with octahedral coordination of Co(II) in water (the pale pink case), tetrahedral coordination in chloride (the deep blue case) and dodecahedral coordination in sulfate and nitrate (the purple cases). When  $CoCl_2$  was dissolved in NaCl-CaCl<sub>2</sub><sup>(2)</sup>, the resulting solution was deep blue and almost identical in appearance to CoCl2 in LiCl-KCl; on the other hand a Co(II) solution generated coulometrically in  $Li_2Co_3-Na_2CO_3$  was purple<sup>(4)</sup>. It is safe to conclude that the symmetries about Co(II) in NaCl-CaCl2 and Li2Co3-Na2CO3 are  $T_d$  and  $D_{2d}$  respectively.

In Figure 3 we reproduce (3) the electronic spectrum of Ni(II) in D. CsCl C. LiCl B. LiCl-KCl and A. a sulfate melt. The first solvent gives rise to regular tetrahedral coordination of Ni(II); the second

and third to mixtures of distorted tetrahedral and distorted octahedral chromophores with the octahedral one more prevalent in B than C; the sulfate gives rise to a similarly distorted octahedral chromophore. The complex NiCl<sub>4</sub><sup>2-</sup>, made from LiCl or KCl and NiCl<sub>2</sub> in dimethyl sulfone (5) is blue, the solution of NiCl<sub>2</sub> in LiCl-KCl is violet and the solution of NiSO<sub>4</sub> in the sulfate melt is red-brown. The ion Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> is octahedral but imparts a green color to solutions, while many Ni(II) salts are yellow in the solid state and contain octahedral Ni(II). When NiCl<sub>2</sub> was dissolved in NaCl-CaCl<sub>2</sub><sup>(2)</sup> the resulting solution was purple, decidedly more red than the LiCl-KCl solution indicating that the Na<sup>+</sup> and Ca<sup>2+</sup> polarized the would-be NiCl<sub>4</sub><sup>2-</sup> complex sufficiently to produce more distorted tetrahedral chromophores than Li<sup>+</sup> and K<sup>+</sup> in combination. A solution of Ni(II) in Li<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> was red-brown<sup>(4)</sup> like the sulfate solution and presumably contained similar-shaped species.

Everyone is familiar with the pale blue  $Cu(H_2O)6^{2+}$  ion and should not be surprised to learn that Cu(II) in a sulfate melt is pale green like the product of atmospheric copper corrosion. In chloride melts, however, a deep golden color arises from the charge transfer as well as ligand field bands of  $CuCl_4^{2-(6)}$ .

Thus, to get some idea of the coordination possibilities and hence the structure of a molten salt solvent, it may be sufficient to observe the colors of dilute solutions of Co(II), Ni(II) and Cu(II)in it. To get an impression of the e.m.f. series it is necessary to determine the Co-Ag standard potential difference and perhaps the Ag-Cu standard potential difference (in some systems, e.g. sulfate, the nickel potential is not available).

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Potential in V. vs. Ag(I)-Ag(0) reference

Fig. 1 Nernst plots for A Co(II)-Co(0) and B Ag(I)-Ag(0) in NaCl-CaCl<sub>2</sub> at 524 °C.





Figure 3 Spectrum of Ni<sup>2+</sup>

ω

B in Licl - Kcl





ω







# MIXED ALKALI EFFECT IN HYDRATE MELTS

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Electrical conductivities, densities and glass transition temperatures have been measured as a function of composition in the hydrate melt systems X NaNO3 - $(0.2 - X) MNO_3 - 0.8 Ca (NO_3)_2 \cdot 4.09 H_2O$ for M = K and Tl. Unlike mixed monovalent cation fused salts and network oxide glasses and melts, in the experimental range of -5 to 70°C no minima were observed in the isotherms of equivalent conductance  $\Lambda$  for the Na/K hydrate melts and weak minima (~3%) only at the lowest temperature for the Na/Tl hydrate melts. А review of data and theories currently in the literature leads to the conclusion that a strong mixed alkali effect, i.e., minimum in the  $\Lambda$  isotherm, should be observed only if the time scale for rearrangement of the local liquid structure is very long compared to the time scale for local ionic transport. This condition is not met by the hydrate melts in the experimental temperature range. It should however, be met at lower temperatures, and extrapolation of the data indicates that the hydrate melt  $\Lambda$  isotherms will develop appreciable minima at such lower temperatures.

#### I. INTRODUCTION

The "mixed alkali effect" refers to deviations from additivity in isotherms of various properties as a function of composition as one alkali is replaced for another in a glass or melt, e.g., the system  $(1 - X)Na_2O - X K_2O - 3SiO_2$ , where  $0 \le X \le 1$  and the compositions refer to numbers of moles. The term "mixed alkali effect" should more properly be "mixed monovalent cation effect", since the phenomena of interest are also observed in systems containing non-inert gas configuration monovalent cations such as Ag<sup>+</sup> or Tl<sup>+</sup>. However, in the present

paper we shall defer to the more common usage and use the more restrictive term.

A number of comprehensive reviews of the mixed alkali effect in network oxide glasses and melts have been pub-lished in recent years 1-6. In general it is found that there is no mixed alkali effect for equilibrium thermodynamic properties. E.g., molar volumes, elastic moduli, heat capacities, etc., are either linear functions of composition in mixed alkali systems, or there are small deviations from additivity no larger than those encountered in typical non-mixed alkali systems. Also in mixed alkali glasses there are no changes with composition in IR vibrational frequencies due to cation motions, and Raman vibrational frequencies due to network motions vary linearly with composition<sup>6</sup>. On the other hand, a very pronounced mixed alkali effect is observed for properties related to ionic transport. This is illustrated in Fig. 1 by the very deep minima in isotherms of electrical conductivity  $\sigma$  versus composition for the system (1 - X) Na<sub>2</sub>O - XK<sub>2</sub>O -  $3SiO_2$  7. There is some question as to whether a mixed alkali effect can be said to occur for properties related to the rearrangement of the overall liquid structure, e.g., shear viscosity  $\eta$  and glass transition temperature  $T_q$ . Mixed network oxide glass viscosity and  ${\rm T_g}$  isotherms generally show minima at intermediate compositions, but Shelby4 has noted that these deviations from additivity are no larger than those typically observed in non-mixed alkali systems. In addition Moynihan and co-workers <sup>8,9</sup> have noted that linear composition dependence of the parameters of the VTF equation for the temperature dependence of shear viscosities of liquids can lead to moderately non-linear viscosity isotherms for systems which would ordinarily be expected to form fairly ideal solutions. Likewise Moynihan et al.<sup>10</sup> found that in mixed alkali glasses the parameters characterizing non-linearity and the distribution of relaxation times in structural relaxation are composition invariant.

In the present paper we present the results of an investigation to determine whether a mixed alkali effect could be detected in monovalent cation nitrate - calcium nitrate tetrahydrate melts. The properties measured were electrical conductivity, density and glass transition temperature.

#### **II. EXPERIMENTAL PROCEDURE**

The systems investigated were of molar composition

X NaNO<sub>3</sub> -  $(0.2 - X)MNO_3 - 0.8$  Ca $(NO_3)_2 \cdot 4.09$  H<sub>2</sub>O with  $0 \le X \le 0.2$  and M = K or Tl. Compositions studied corresponded to X = 0.0, 0.1 and 0.2.

Reagent grade chemicals were used to prepare the melts. The exact  $H_2O/Ca(NO_3)_2$  molar ratio in the calcium nitrate tetrahydrate was  $4.090 \pm 0.007$ , as determined by vacuum dehydration of three samples. The melts were prepared by weighing the components into a container, which was then tightly capped to prevent water loss and heated to 50°C in a water bath to melt the calcium nitrate tetrahydrate. Agitation at 50°C with a magnetic stirrer caused the monovalent cation nitrates to dissolve in the molten calcium nitrate tetrahydrate.

During measurement of conductivity and density  $\rho$  the samples were thermostatted in a water bath equipped with a refrigeration unit. Bath temperatures were determined to a precision of  $\pm$  0.02°C using a calibrated Hg-in-glass thermometer for density measurements and a calibrated Pt resistance thermometer for conductivity measurements. Densities were determined to an accuracy of 0.1% over the range 0 to 70°C with a dilatometer. Glass transition temperatures at a heating rate of 8°C/min were measured by DTA to an accuracy of  $\pm$  0.5°C using the procedure of Angell and Sare<sup>11</sup>.

Electrical conductivities were measured over the range -5 to 70°C using a dipping cell with the electrodes separated by a length of glass capillary. The cell was calibrated with 0.1 demal KCl solution and had a cell constant of 51.28 cm<sup>-1</sup>. Conductances were measured to an accuracy of 0.1% with a Wayne-Kerr B221 admittance bridge over the frequency range 0.35 to 5 kHz. Over this frequency range the measured conductances increased by about 0.5% at the highest temperatures and by only 0.1% at the lowest temperatures, showing that there were no substantial contributions to the measured conductances from electrode polarization. The conductivities reported below were calculated using the values measured at 1 kHz.

### III. RESULTS

Densities were linear functions of temperature within experimental error and are presented in Table I in the form of least squares fits to the equation

$$p(q/cm^3) = a - bT(^{\circ}C)$$
(1)

Also given in Table I are equivalent weights E and equivalent volumes  $V_e$  at 20°C. Within experimental error the equivalent volumes are linear functions of composition.

Table 1	I. P a f 4	Parameters for density equation, equivalent weights, and equivalent volumes at 20°C for X NaNO <sub>3</sub> - $(0.2 - X)MNO_3 - 0.8 Ca(NO_3)_2 \cdot 4.09 H_2O$ melts.							
M		x	<u>a</u>	<u>10<sup>4</sup>b</u>	<u>E(g/eq)</u> V	e (cm <sup>3</sup> /eq)			
-	0	. 2	1.797	9.3	115.1	64.7			
K	0	.1	1.792	8.8	116.0	65.4			
K	0	.0	1.797	8.7	116.9	65.7			
Tl	0	.1	1.930	9.4	125.2	65.5			
Tl	0	.0	2.064	10.0	135.3	66.2			

In Fig. 2 the temperature dependence of the electrical conductivity  $\sigma_0$  for one of the melts is shown in the form of an Arrhenius plot. Arrhenius plots for the other melts were quite similar in appearance. The non-Arrhenius temperature dependence, i.e., curvature of the plot in Fig. 2, is typical for highly concentrated aqueous solutions in this temperature range. The isothermal dependence of the conductivity on melt composition is shown in Fig. 3. Our  $\sigma_0$  values for the 0.2 KNO<sub>3</sub> - 0.8 Ca(NO<sub>3</sub>)<sub>2</sub> · 4.09 H<sub>2</sub>O melt are in good agreement with those interpolated from the results of Angell<sup>12</sup>, taking into account the likelihood of small differences in the water contents of the melts in the two studies and the strong dependence of  $\sigma_0$  on water content in this concentration range <sup>13-15</sup>.

Equivalent conductances for the melts were calculated from the expression

$$\Lambda = \sigma_0 E / \rho \tag{2}$$

In the temperature range of this study the temperature dependence of  $\Lambda$  for hydrate melts can be well described by the so-called VTF equation  $^{8}, ^{12}-16$ 

$$\ln \Lambda (cm^2/\Omega eq) = A - \frac{1}{2} \ln T(K) - B/(T(K) - T_0)$$
(3)

where A, B and T are adjustable parameters. The equivalent conductance data for the melts were fitted to Eq. (3) to the nearest 1K in T using a procedure described previously<sup>16</sup>. The best fit parameters are given in Table II. In each case the VTF equation fits the data within a few tenths of a percent. The experimental glass transition temperatures are given in the last column of Table II.

Tal	ole I	I. Bes tra MN(	st fit v ansitior $D_3 = 0.8$	/TF equat: n temperat 3 Ca(NO <sub>3</sub> )	ion param cures for 2 • 4.09	eters and g X NaNO <sub>3</sub> - H <sub>2</sub> O melts.	lass (0.2 - X)
	M	x	A	B	<u> </u>	Std. Dev. $\ln \Lambda$	<u>т<sub>д</sub> (к)</u>
	-	0.2	8.355	633.4	203	0.004	217.2
	К	0.1	8.314	625.1	203	0.004	215.5
	K	0.0	8.342	632.7	202	0.003	216.1
	Tl	0.1	8.226	608.7	203	0.003	216.4
	Tl	0.0	8.248	611.8	201	0.002	214.4

The B and T values in Table II are about the same as those reported in previous studies<sup>8</sup>,12,14-16 in this temperature range for melts containing substantial amounts of calcium nitrate tetrahydrate. The T parameter may be interpreted theoretically as the temperature at which the free volume<sup>17</sup> or configurational entropy<sup>18</sup> of the melt vanishes. T<sub>g</sub> is the temperature at which the shear viscosity reaches about  $10^{11}$ P for concentrated aqueous solutions<sup>19</sup>. The ratio T<sub>g</sub>/T<sub>o</sub> for the systems studied here is constant within experimental error and equal to about 1.07. Roughly constant values of T<sub>g</sub>/T<sub>o</sub> of about this magnitude have been observed for other ionic liquids in which T<sub>o</sub> has been extracted form data in a temperature range corresponding to the few orders of magnitude in shear viscosity above the highly fluid lower limit of around  $10^{-2}$ P for liquids<sup>8</sup>,14,20-24. This is the range in which free volume or configurational entropy theories of transport seem to give the best correlations with other liquid properties.

Comparing Fig. 1 and 3, it appears that the X NaNO3 -

 $(0.2 - X)MNO_3 - 0.8 Ca(NO_3)_2 \cdot 4.09 H_2O$  hydrate melts do not exhibit a mixed alkall effect in the temperature range studied here. That is, the logarithmic  $\sigma_0$  isotherms in Fig. 3 do not show perceptible negative deviations from linearity.

A somewhat more sensitive indicator of the electrical mixed alkali effect is the deviation from additivity of the  $\sigma_0$  or  $\Lambda$  isotherms on a linear scale. This may be characterized by the ratio r defined either as

$$\mathbf{r}_{\sigma} = \sigma_{o, add} / \sigma_{o} \tag{4a}$$

or as

$$\mathbf{r}_{\Lambda} = \Lambda_{\mathrm{add}} / \Lambda \tag{4b}$$

taken at the composition of maximum deviation from additivity, where  $\sigma_0$  and  $\Lambda_{add}$  are the conductivity or equivalent conductance predicted on the basis of mole fractionweighted additivity of the  $\sigma_0$ 's or  $\Lambda$ 's of the two single alkali systems. (r and r are generally not greatly different).

In Table III are given values of  $r_{\Lambda}$  calculated from the parameters of Table II at the temperature extremes (-5 and 70°C) of this study for the hydrate melts. In view of experimental uncertainties, the best accuracy that can be claimed for  $r_{\Lambda}$  is about  $\pm$  0.01. Hence in terms of  $r_{\Lambda}$  only the Na/Tl hydrate melt at the lowest experimental temperature shows a mixed alkali effect ( $r_{\Lambda} > 1$ ), and this barely outside experimental uncertainty.

The equivalent conductance activation enthalpy  $\Delta H^*$  can be calculated from the VTF equation parameters of Table II:

$$\Delta H^* \equiv -Rdln \, \Lambda/d(1/T) = RBT^2/(T - T_0)^2 - RT/2$$
(5)

where R is the ideal gas constant. In the experimental temperature range the  $\Delta H^*$  values for the hydrate melts are all very similar at a given temperature and range from 6.9-7.2 kcal/mol at 70°C to 19.2-21.1 kcal/mol at -5°C. In the last column of Table III are tabulated the deviations of activation enthalpy from additivity as a function of composition:

$$\delta \Delta H^* = \Delta H_{0,5}^* - 0.5 \ (\Delta H_0^* + \Delta H_1^*) \tag{6}$$

where the subscripts refer to the monovalent cation fraction, e.g., M/(M + Na), of one of the monovalent cations.

Table III.	$r_{\Lambda}$ and $\delta \Delta H^*$ X NaNO <sub>3</sub> - (0 H <sub>2</sub> O melts. are extrapol temperature	as a function of .2 - X)MNO <sub>3</sub> - 0. Entries in rows ated beyond the range.	temperature for $8Ca(NO_3)_2 \cdot 4.09$ marked with an * experimental
M	<u>T(°C)</u>	<u>r</u> Λ	δ∆H*(kcal/mol)
К	70	0.99	0.0
	-5	0.99	0.0
	-20*	1.01	0.2
	-40*	1.18	1.4
Tl	70	1.01	-0.1
	-5	1.03	0.1
	-20*	1.11	0.5
	-40*	1.88	2.7

In the experimental temperature range the  $\Delta H\star$  values are additive functions of composition within experimental error.

# IV. DISCUSSION

# A. Experimental Manifestations and Theories of the Mixed Alkali Effect

To attempt to account for the lack of an appreciable mixed alkali effect in electrical conductivity of the hydrate melts, we begin with a more complete summary of experimental observations on mixed alkali system electrical transport properties and theories for this behavior. In this section references will be given only for points which are not covered adequately in the general review papers<sup>1-3</sup>,<sup>5</sup>.

The following are the experimental characteristics of the electrical transport mixed alkali effect:

1. For vitreous substances the mixed alkali effect (i.e., r>1) is observed both in glasses and liquids and in network oxide and fused salt systems. r can vary from very large values  $(r_{\sigma}$  = 2.6 x 10^4 at 50°C in Fig. 1) to values close to unity  $(r_{\Lambda}$  = 1.04 for molten Na/KNO<sub>3</sub> at 350°C<sup>25</sup> and 1.14 for molten Na/TINO<sub>3</sub> at 310°C<sup>26</sup>) to nearly unity within experimental error for the hydrate melts studied here.

2.  $\Delta H^*$ , the conductivity activation enthalpy, exhibits positive deviations from additivity as a function of composition, i.e.,  $\delta \Delta H^* > 0$ . This has the effect of making r increase with decreasing temperature (cf. Figs. 1 and 4). For the hydrate melts in the experimental temperature range  $\delta \Delta H^* = 0$ .

3. Other conditions being the same, r increases with an increase in difference in the alkali ion radii.

4. The source of the mixed alkali effect on electrical conductivity in terms of the individual monovalent ion mobilities is that the mobilities exhibit different composition dependences. Usually there is a crossover composition for the mobility isotherms, such that at the composition extremes the monovalent cation present in higher concentration possesses the higher mobility<sup>27,28</sup>.

5. For a given system the magnitude of the mixed alkali effect shows a complicated dependence on overall monovalent cation concentration. At a given temperature there always seems to be a concentration below which the mixed alkali effect is absent (or at least indetectably small). This is shown in Fig. 4 in which isotherms of resistivity  $\rho_0$  (=  $1/\sigma_0$ ) are plotted for three compositions for Y(Na<sub>2</sub>O + K<sub>2</sub>O) - (1 - Y)B<sub>2</sub>O<sub>3</sub> melts<sup>29</sup>. At 1000°C no mixed alkali effect, i.e., no deviation from additivity in the  $\rho_0$  isotherms, is observable for any of the compositions. By 850°C, however, the 20 and 28 mol % alkali melts exhibit a mixed alkali effect, i.e., a maximum in the  $\rho_0$  isotherms, but no mixed alkali effect is yet discernible in the 12 mol % alkali melt. For the borate melts of Fig. 4  $r_{\sigma}$  at a given temperature increases with increasing total alkali concentration. At high alkali concentrations, however, this trend may be reversed. This is shown in Fig. 5 for Y(Na<sub>2</sub>O + K<sub>2</sub>O) - (1 - Y)SiO<sub>2</sub> melts<sup>30</sup> for which  $r_{\sigma}$  decreases with increasing alkali concentration.

Numerous explanations have been proposed for the

mixed alkali effect on electrical transport properties. Some of these have now been shown experimentally to be incorrect, e.g., the theory that the mixed alkali effect is due to phase separation. The remaining theories, all of which have at least some drawbacks, may be classified into two general categories-cationic interaction theories and structural/mechanistic theories.

The cationic interaction theories are typified by those proposed by Moynihan and Laity<sup>27,28</sup>, Mazurin<sup>31</sup> and Hendrickson and Bray<sup>32</sup>. In general they suggest that partial replacement of one monovalent cation by a second leads to some sort of attractive interaction among the cations or, in the extreme, to the formation of associated cationic complexes. This in turn causes a relative reduction in the average ionic mobilities. While such interactions may account for moderate deviations from additivity in the  $\sigma_0$  or  $\Lambda$  isotherms, they cannot explain the extreme sort of behavior typified by Fig. 1. In this case the initial replacement of a small amount of K<sub>2</sub>O by Na<sub>2</sub>O in the K<sub>2</sub>O - 3SiO<sub>2</sub> glass causes such a rapid drop in  $\sigma_0$  at 50°C that one would have to assume that each Na<sup>+</sup> ion complexed and completely immobilized some 40 K<sup>+</sup> ions<sup>33</sup>.

An example of a structural/mechanistic explanation of the mixed alkali effect is that of Stevels<sup>34</sup>. He assumes that a variety of monovalent ion sites exist in a glass or liquid. When the glass or liquid contains a mixture of monovalent ions, each kind of ion preferentially occupies sites which are energetically most favorable for it. Presumably these most favored sites are different for different types of ions. Thus mixing of the monovalent ions leads to a net reduction in the number of ions loosely bonded to the network. If these are responsible for the measured electrical conductivity, then mixing of the monovalent ions leads to a relative reduction in  $\sigma_0$ . Evidence in favor of this last point of view is to be found in the recent papers of Ravaine and Soquet<sup>35</sup> and of Tomozawa<sup>36</sup>, who suggest that network oxide glasses are weak electrolytes and that electrical conductivity is due to the transport of a relatively small number of mobile, i.e., loosely bound, ions.

Whatever the correct explanation for the mixed alkali effect, it seems inevitable that it must predict that the effect will eventually decrease and disappear as the total concentration of monovalent cations decreases. As the average distance between cations increases, any intercationic interactions must become progressively weaker and any correlations among the interactions of the cations with the structure must vanish.

## B. Importance of the Relative Rates of Ionic Transport and Structural Rearrangement

A condition required by all of the structural/mechanistic theories for the mixed alkali effect, which is usually left unstated, is that the structure of the medium be fixed or, more precisely, that the time scale for rearrangement of the local structure be long compared to that required for the local diffusion of monovalent cations from site to site. If this condition is not met, to use Stevels' theory<sup>34</sup> as an example, the character of the sites occupied by the various ions will change constantly on the time scale of average occupancy, so that the notion of preferential occupancy of different types of sites by different ions becomes meaningless.

A good figure of merit for the relative time scales of local structural rearrangement and ion transport is the ratio  $^{37}$ 

$$<\tau_{s}>/<\tau_{\sigma}> = (\eta/G_{\omega})/(\varepsilon_{c}\varepsilon_{\omega}/\sigma_{c})$$
 (7)

 $<\tau_{\rm S}>$  is the mean relaxation time at constant strain for disappearance of a shear stress via viscous flow, and  $G_{\infty}$  the solid-like (i.e., limiting high frequency) shear modulus of the melt or glass.  $<\tau_{\rm O}>$  is the mean relaxation time at constant polarization for disappearance of an electric field within the material via the ionic transport process,  $\epsilon_{\rm O}($  = 8.854 x 10<sup>-14</sup> F/cm) the permittivity of free space, and  $\epsilon_{\infty}$  the limiting high frequency dielectric constant. Typical values for ionic melts and glasses of  $G_{\infty}$  and  $\epsilon_{\infty}$  are respectively  $\sim$  10<sup>11</sup> dyne/cm<sup>2</sup> and  $\sim$ 6, so that

 $\langle \tau_{s} \rangle / \langle \tau_{\sigma} \rangle \sim 20 \eta \sigma_{o}$  (8)

with  $\eta$  in P and  $\sigma_{0}$  in ohm<sup>-1</sup> cm<sup>-1</sup>.

In Fig. 6 are shown logarithmic plots of  $\langle \tau_g \rangle / \langle \tau_\sigma \rangle$ versus  $\eta$  for a number of ionic melts. The data for LiCl  $\cdot$  5.77 H<sub>2</sub>O and 0.4 Ca(NO<sub>3</sub>)<sub>2</sub> - 0.6 KNO<sub>3</sub> are from previous publications<sup>19</sup>, 37. For Ca(NO<sub>3</sub>)<sub>2</sub>  $\cdot$  8H<sub>2</sub>O we have plotted the longitudinal stress to electric field relaxation time ratio  $\langle \tau_L \rangle / \langle \tau_\sigma \rangle$ <sup>38</sup>; this should differ very little from  $\langle \tau_g \rangle / \langle \tau_\sigma \rangle$ . The  $\langle \tau_g \rangle / \langle \tau_\sigma \rangle$  ratios for the network oxide melts were calculated via Eq. (7) using measured values of  $\eta$  and  $\sigma_{o}$  and estimated values of G<sub> $\infty$ </sub> and  $\epsilon_{\infty}$ , taken all from the data compilations of Mazurin et al.<sup>39</sup>, except for the  $\sigma_0$  values at high  $\eta$  for 0.2 Na<sub>2</sub>O - 0.8 SiO<sub>2</sub>, which were taken from the paper of Kaneko and Isard<sup>40</sup>. The main uncertainties in Fig. 6 arise from the estimation of G<sub>{\pi}</sub> and  $\epsilon_{\infty}$  for the low viscosity melts; this may lead to errors of at most a factor of 2 in the <\tau\_s>/ <\tau\_{\sigma} < \tau\_{\sigma} > / <\tau\_{\sigma} > <

The first thing to note about the plots of Fig. 6 is that at low viscosities and high temperatures the  $\langle \tau_{\rm g} \rangle / \langle \tau_{\sigma} \rangle$  ratios for all systems approach unity. This is in fact predicted from the approximate validity of the Stokes-Einstein equation (which relates  $\eta$  to ionic diffusion coefficient D) and the Nernst-Einstein equation (which relates  $\sigma_{\rm O}$  to D) for high temperature ionic melts<sup>28</sup>. Combining these two expressions with Eq. (7) one gets

$$\langle \tau_{s} \rangle / \langle \tau_{\sigma} \rangle = N_{A} Z^{2} e^{2} C_{M} / 3 \pi d \varepsilon_{o} \varepsilon_{\infty} G_{\infty}$$
 (9)

where N<sub>A</sub> is Avogadros number, Z the ionic charge in units of the electronic charge e, C<sub>M</sub> the ionic concentration, and d the ionic diameter. Using typical values of C<sub>M</sub> = 20 mol/L for ionic melts (cf. Table IV), z = 1, d = 0.2nm,  $\varepsilon_{\infty} = 6$  and G<sub>s</sub> = 10<sup>11</sup> dyne/cm<sup>2</sup>, one obtains via Eq. (9) the value  $\langle \tau_{g} \rangle / \langle \tau_{g} \rangle = 0.3$ , i.e., of the order of unity.

With decreasing temperature and increasing viscosity  $<\tau_{\rm S}>/<\tau_{\sigma}>$  increases and, in the case of the network oxide melts and the anhydrous fused salt, reaches extremely large values in the vicinity of the glass transition  $(\eta ~ 10^{11} - 10^{13} {\rm P})$ . This increase in  $<\tau_{\rm S}>/<\tau_{\sigma}>$  at high viscosities is due to the failure of the Stokes-Einstein equation, since it is known that the Nernst-Einstein equation is approximately valid for alkali ions in network oxide glasses in and below the glass transition region  $^{41}$ .

In view of all the foregoing, we suggest the following with regard to the causes and/or conditions for the mixed alkali effect on electrical transport properties. Monovalent cationic interactions may give rise to relatively small mixed alkali effects, i.e., r values slightly larger than unity, such as those observed in fused salts at high fluidities where  $\langle \tau_s \rangle \langle \tau_\sigma \rangle \cong 1$ . Such cationic interactions depend strongly on interionic distance and should decrease rapidly in magnitude, along with the magnitude of the mixed alkali effect, with decreasing monovalent cation concentration. For large mixed alkali effects of the magnitude of those in Figs. 1, 4 and 5 to be observed the condition must be met that

 $<\tau_{\rm S}>/<\tau_{\rm G}> \gg 1$ , i.e., that the melt structure remain fixed on the time scale of the local diffusive steps of the monovalent cations. This condition allows structural/mechanistic effects to come into play. Probably structural/ mechanistic effects do not depend as strongly on interionic distance as do the monovalent cation interactions.

In Table IV we have listed the viscosity ranges of the sodium ion melts of Fig. 6 corresponding to the temperature ranges of the conductivity data of Figs. 3-5. Correlations between the magnitude of the mixed alkali effect, i.e., of r, and the value of  $\langle \tau_{\rm S} \rangle / \langle \tau_{\rm O} \rangle$  are immediately apparent. For the 12 mol% alkali borate melt of Fig. 4  $\langle \tau_{\rm S} \rangle / \langle \tau_{\rm O} \rangle$  is small (between about 4 and 8) from 1000 to 850°C and no mixed alkali effect

Table IV. Temperature and viscosity ranges and alkali ion concentrations for sodium ion melts with conductivity data shown in Figs. 3-5.

Syste	em	T	(°C)	<u>)</u>	100	<b>ց ղ (</b>	<u>(P)</u>	<u>C_M (mo</u>	1/L)
0.2 1 4.09	$MaNO_3 - 0.8 Ca(NO_3)_2 \cdot H_2^0$	-5	to	70	-0.5	to	2.0	1.7	7
0.12	$Na_2O - 0.88 B_2O_3$	850	to	1000	0.5	to	1.3	6.3	3
0.20	$Na_2O - 0.80 B_2O_3$	800	to	1000	0.3	to	1.8	11.9	5
0.28	$Na_2O - 0.72 B_2O_3$	800	to	1000	-0.3	to	1.5	16.9	9
0.2 1	Na <sub>2</sub> 0 - 0.8 SiO <sub>2</sub>	(	900		4	4.6		15.3	1
0.3 1	Na <sub>2</sub> 0 - 0.7 SiO <sub>2</sub>	(	900			3.9		22.8	8
0.4 1	Na <sub>2</sub> 0 - 0.6 SiO <sub>2</sub>	9	900		:	3.2		30.4	4

is observed in this temperature range. For the 20 and 28 mol% alkali borate melts  $\langle \tau_{\rm S} \rangle \langle \tau_{\rm T} \rangle$  varies respectively from about 5 to 30 and from about 6 to 40 in the range 1000 to 800°C. No mixed alkali effect is observed at the higher temperature where  $\langle \tau_{\rm S} \rangle \langle \tau_{\rm T} \rangle$  is small. At the lower temperatures, where  $\langle \tau_{\rm S} \rangle \langle \tau_{\rm T} \rangle$  becomes substantially larger however, a pronounced mixed alkali effect is observed. For the alkali silicate melt data of Fig. 5 at

900°C  $<\tau_{\rm S}>/<\tau_{\sigma}>$  is about 5 x 10<sup>4</sup>, 2 x 10<sup>4</sup> and 0.8 x 10<sup>4</sup> for the respective compositions 20, 30 and 40 mol % alkali;  $<\tau_{\rm S}>/<\tau_{\sigma}>$  decreases in the same order as the  $r_{\sigma}$  values obtained from Fig. 5.

### C. Mixed Alkali Effect in Hydrate Melts

The absence or smallness of the mixed alkali effect in the X NaNO<sub>3</sub> -  $(0.2 - X)MNO_3$  - 0.8 Ca(NO<sub>3</sub>)<sub>2</sub> · 4.09 H<sub>2</sub>O melts in the temperature range studied here is probably due to a number of reasons. First, the total alkali concentration  $C_M$  in the hydrate melts is considerably smaller than in the other systems discussed here, as shown in Table IV. This concentration is small enough probably to make any cationic interaction contributions to the mixed alkali effect negligible. Second, from the data for the two hydrate melts given in Fig. 6 and the estimated viscosity data for the present systems in Table IV,  ${<}\tau_{{\bf S}}{>}/{<}\tau_{\sigma}{>}$  is close to unity for this system in the experimental temperature range. Third, judging from reducible cation  $(Ag^+, T1^+ \text{ and } Cd^{+2})$  diffusion coefficients in a Ca(NO<sub>3</sub>)<sub>2</sub> · 4.09 H<sub>2</sub>O melt in the range 15 to  $60^{\circ}C^{42}$ , the Ca<sup>+2</sup> and alkali ions in this temperature range have comparable electrical mobility-charge products. This means that in the present experiments we are attmepting to observe an effect on  $\sigma_0$  due to the mixing of monovalent cations against a background due to the other ions which contributes at least 80% of the total  $\sigma_0$ . Note that the second and third reasons are not unrelated. At lower temperatures  $\langle \tau_s \rangle / \langle \tau_\sigma \rangle$  for these melts should gradually become considerably larger than unity. When this occurs some species in the system must become immobile relative to the monovalent cations. In silicate or borate systems the immobile part is the silicate or borate network. In the hydrate melts the immobile part would be presumably some sort of network formed at low temperature from the hydrated divalent cations and the anions.

We predict, consequently, that at temperatures somewhat below those investigated here these hydrate melts should begin to show an appreciable mixed alkali effect. To provide a rough test of this prediction we have listed in Table III  $r_{\Lambda}$  and  $\delta \Delta H^*$  at -20 and -40°C extrapolated from experimental data using Eqs. (3) and (5) and the parameters of Table II. There is some danger in doing this, since it is known<sup>5</sup> that extrapolation of data to lower 'temperatures using the VTF equation invariably leads to underestimates of  $\Lambda$  and overestimates of  $\Lambda H^*$ . However for each of the hydrate melts should respectively all be of the same sign, the errors in  $r_{\Lambda}$  and  $_{\delta\Delta}H^{\star},$  which measure properties of the melts relative to one another, should be considerably smaller than the errors in the  $\Lambda$  or  $\Delta H^*$  values themselves.

The extrapolated r\_{\Lambda} ( > 1) and  $\delta \Delta \texttt{H*}$  ( > 0) values for the hydrate melts do indeed indicate that at lower temperatures these systems will exhibit appreciable mixed alkali effects. Confidence in this conclusion is enhanced by these observations. 1) The results show the expected trend of increase in  $r_\Lambda$  with decreasing T. 2) That  $r_\Lambda$  is greater for the Na/Tl hydrate melt than for the Na/K hydrate melt in the extrapolated region agrees with the same trend in the experimental region, although the latter result is close to the limits of experimental uncertainty. 3) In the anhydrous alkali nitrate melts  $r_{\Lambda}$  is also larger for the Na/Tl system than for the Na/K system<sup>25,26</sup>.

In the near future we intend to check experimentally whether these hydrate melts do exhibit appreciable mixed alkali effects at low temperatures and high viscosities. If indeed they do, mixed alkali nitrate - divalent cation nitrate systems, which are good glass formers over wide composition ranges in the form of both hydrate melts and anhydrous fused salts, may prove valuable low temperature model systems for unravelling the combined dependence of the mixed alkali effect on concentration and  $\langle \tau_{c} \rangle / \langle \tau_{\sigma} \rangle$ ratio.

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Figure 1. Electrical conductivity isotherms for  $(1 - X)Na_2O - XK_2O - 3SiO_2$  glass.



Figure 2. Arrhenius plot of electrical conductivity of 0.2 KNO<sub>3</sub> - 0.8 Ca(NO<sub>3</sub>)<sub>2</sub> · 4.09 H<sub>2</sub>O melt.



Figure 3. Electrical conductivity isotherms for X NaNO<sub>3</sub> -  $(0.2 - X)MNO_3 - 0.8 Ca(NO_3)_2$ 4.09 H<sub>2</sub>O melts.  $\bigcirc M = K^3$ ,  $\bigtriangleup M = T1$ .



Figure 4. Electrical resistivity isotherms for  $Y(Na_2O + K_2O) - (1 - Y)B_2O_3$  melts.



Figure 5. Electrical conductivity isotherms at 900°C for  $Y(Na_2O + K_2O) - (1 - Y)SiO_2$  melts.



Figure 6. Ratio of shear or longitudinal stress relaxation time to electric field relaxation time versus shear viscosity for ionic liquids.

COMPOSITION AND TEMPERATURE DEPENDENCE OF CONDUCTIVITY OF MOLTEN CADMIUM NITRATE TETRAHYDRATE + ALKALI METAL NITRATE MIXTURES

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Conductivity of molten  $Cd(NO_3)_{2}$ ,  $4H_{2}O + MNO_3$ (M = Li, Na, K, Rb, Cs) mixtures have been measured as a function of temperature and composition. The results indicate the existence of hydration-dehydration phenomena in the system containing LiNO\_3. Temperaturedependence of conductivity have been interpreted in terms of VTF equation and environmental relaxation model of liquid transport. The low values of  $\checkmark v^*/v_m$  indicate that random distribution of free volume is apparently not obtained. The exponential electrical relaxation and the linear plots T ln ( $1/A \ G_{\infty} \land$ ) <u>vs</u> ( $1 + \epsilon^2$ )<sup>3</sup>/2 exhibit the applicability of the environmental relaxation model to describe the temperature dependence of conductivity.

## INTRODUCTION

It has been recognised from the solubility, spectral and transport (1-17) measurements in concentrated aqueous solutions of divalent cations as calcium, cadmium, magnesium etc. containing 4-6 moles of water per mole of cation that water is retained, almost exclusively, by the dipositive cations forming species of the type  $M(H_20)^{2+}$ . This confers upon these solutions essentially the Same properties as expected theoretically from the "hard sphere" cations of same charge/radius ratio. For this reason these have been considered (1) as analogue of molten anhydrous salts. Also, because of their low liquidus temperature, good solvent properties, high conductivity and strong supercooling and glass forming tendencies at some compositions, such solutions are of intrinsic chemical and possibly future applied interest. Braunstein et al. (8) studied the association equilibria, vapour pressure and diffusion coefficients in molten  $NH_ANO_3.2H_O$  and  $Ca(NO_3).4H_O$  and used the quasi-lattice model to interpret data on ion-association. Angell (1-3) Moynihan (4-6) and others (13-17) have carried out extensive investigations of mass and transport porperties in molten hydrated salts and over a limited range of temperature, have interpreted the transport behaviour of the data in terms of VIF equation (18) based on free volume (19) and configurational entropy (20) models of liquid transport. Recently, Tweer, Simmon and Macedo (21-22) developed the environmental relaxation model which has enabled interpretation of the temperature-dependence of transport properties over a wider temperature range.

In this paper, the effect of addition of alkali metal (Li, Na, K, Rb, Cs) nitrates on the conductivity of molten cadmium nitrate tetrahydrate, over a wide temperature and composition range, has been examined with a view to establish some correlation between the adjustable parameters of liquid transport models and the composition of the system.

## EXPERIMENTAL

Cadmium nitrate tetrahydrate was of Analar (BDH) grade. Water of hydration, determined volumetrically using EDTA, was found to be 4.0±0.01. Lithium, sodium potassium, rubidium and cesium nitrates, also Analar (BDH) or equivalent purity, were heated at about 120°C to constant mass and stored over anhydrous magnesium perchlorate until used. Mixtures were prepared individually by fusing the requisite amounts of the salts in an inert atmosphere, filtering through sintered glass tube (Porosity G-3) under nitrogen pressure and matured by keeping it at  $50-60^{\circ}$ C for few hours. A single capillary, dip type conductivity cell with platinised platinum electrodes was employed. Cell constants were determined using 0.10 and 1.00 KCl solution at  $25^{\circ}$ C using the conductivity data of Jones and and Prendergast (23); re-determination after 5-6 runs showed no appreciable change in the cell constant. A liquid paraffin bath (capacity <u>c</u> 20 lit) was used as thermostat. Melt temperature was controlled and measured with a precision of  $\pm 0.05^{\circ}$ C. Solution resistence was measured with a Beckman conductivity

bridge (model RC-18A), based on Wien's bridge principle, provided with a Wagner earth and a CRT null detecter. It was operated at 1kHz. A parallel combination of resistance (R) and capacitance (C) was used in the measuring arm<sup>P</sup> and the resistances of ratio arms of the bridge were matched. Considering the cell impedance as a series combination of a resistance (R) and a capacitance (C), it follows from ac theory that at balance point,

$$R_{s} = \frac{R_{p}}{1 + (R_{D}C_{p} 2\pi f)^{2}}$$

where f is the frequency of ac signal in Hz. The conductivity data were least-square fitted into the equation

$$\times = A + B(T - 300) + C(T - 300)^{2}$$

using IBM 360/44 data processing system. Coefficients A, B and C, characteristic of composition, are given in Table I.

## RESULTS AND DISCUSSION

Conductivity data of molten Cadmium nitrate tetrahydrate + alkali metal nitrate mixtures at various compositions were obtained in the temperature range 290 to 365 K. Typical trend in the variation of conductivity at 348.2 K with the mole fraction of alkali metal nitrates is shown in Fig.1. The conductivity of the mixtures increases with the addition of sodium, potassium, rubidium and cesium nitrates which is consistent with the notion that addition of smaller and mobile ion will increase the conductive power of the medium. On the other hand, addition of Lithium nitrate lowers the conductivity of cadmium nitrate tetrahydrate. This may be interpreted considering preferential hydration of Li<sup>+</sup> ions because of its high charge/radius ratio, as follows,

$$Cd(H_20)_4^{2+} + Li^+ \longrightarrow Cd(H_20)_{4-x}^{2+} + Li(H_20)_x^+$$

This would lead to lowering of the mobility of Li<sup>T</sup> ions because of its increased size and mass due to hydration and hence a decrease in the conductivity, as observed.  $Ca(NO_3)_2.4H_2O$  + LiNO<sub>3</sub> system also showed a

similar behaviour but in addition there was a minima at about 25 mole % of LiNO<sub>3</sub> (also Fig.1); it was considered to arise due to the existance of hydrationdehydration equilibrium. A continuous decrease in the present case indicates the absence of such an equilibrium. Also,  $Cd^{2+}$  ions are more covalent than  $Ca^{2+}$  ions and thus the cation-dipole binding energy will also be smaller in former case.

Pronounced curvature in the  $\log_X vs T^{-1}$  plots (not shown) show the inadequancy of Arrhenius equation in describing the temperature-dependence of conductivity. At a given composition, Arrhenius coefficients, calculated from equation 1 and other mathematical  $\times$ -T expressions using,  $E_x = R( \partial \ln \times / \partial (1/T))$ , (Table 1) increase with the lowering of temperature. At a given temperature, except for LiNO<sub>3</sub>,  $E_x$  decrease with the addition of monovalent nitrate which appear justified in view of lower restricting potential for the more mobile monovalent cations replacing Cd(H<sub>2</sub>0)<sup>2+</sup><sub>4</sub> ions. The anomalous behaviour of Li<sup>+</sup> is consistent with the preferential hydration (wide supra).

Non-Arrhenian behaviour of transport properties has frequently been interpreted the terms of a 3-parameter VTF equation,

$$\Lambda = A T^{-\frac{1}{2}} \exp\left(-\frac{B}{T-T_0}\right)$$
(3)

based on the free volume model (19) and the cooperative rearrangement theory (20). The equivalent conductivities ( $\Lambda$ ) were calculated using density data earlier reported and parameters of equation 3 were evaluated by iteration method. Angell (1) has correlated  $E_x$ 's to a parameter T<sub>0</sub>, the <u>ideal glass-transition temperature</u>, through the expression

$$E_{corr} = E_{\kappa} + \frac{1}{2}RT + \alpha RT^{2} = BR \left[\frac{T}{T - T_{o}}\right]^{-}$$
(4)

where  $\prec$  is the coefficient of expansion of the melt at temperature T, R the gas constant, and B an empirical constant. For all the mixtures,  $\prec$  was approximated to that for molten cadmium nitrate tetrahydrate at  $T/T_m = 1.1$  (4.75 x  $10^{-4} \text{ deg}^{-1}$ ). E<sub>corr</sub> - temperature data were least square fitted into a linear equation. Computed T<sub>o</sub>, and constants A and B at various compositions are given in Table II. Variation of T with mole fraction of monovalent nitrate and mean cationic potential is shown in Fig.2. To values for Cd \NO\_3)\_2.4H\_2O + (Na, K, Rb, Cs NO\_3 system investigated in the present study are in qualitative accord with the expectations that the average cation field strength ( $\sum n_i z_i/r_i$ ) in these mixtures rises in a nearly linear manner, when Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup> with  $z_i/r_i$  values of 1.05, 0.75, 0.68, 0.60 are added to the melt of hydrated salt, Cd(NO\_3)\_2.4H\_2O ( $z_i/r_i$  for Cd(H<sub>2</sub>O)<sup>\*</sup><sub>4</sub> = 0.535). A slight decreasing trend in T<sub>o</sub> with the addition of Li<sup>+</sup> inspite of high charge to radius ratio (1.67) would consistent only if Li<sup>+</sup> is assumed to be enlarged by hydration. If the effective size of the hydrated Li<sup>+</sup> is taken as 3.38 Å ( $= r_{Li^+} + 2r_{H_2O}$ ), its

charge to radius ratio comes to 0.295. The addition of Li to Cd(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O melt would cause a decrease of  $\Sigma n_i z_i / r_i$  and hence T<sub>o</sub> as observed. When T<sub>o</sub> <u>vs</u>  $\Sigma n_i z_i / r_i$  plots are extrapolated to a hypothetical state of zero cation field strength, the value 120 ± 20 K for T<sub>o</sub> is comparable with the glass transition temperature value of about 100K for molecular liquids.

There is no systematic variation in the preexponential term (A) in this study. Cohen and Turnbull's model suggest a direct dependence of A on particle size and an inverse dependence on the square root of particle mass. In ionic molten systems the jump distance would have to include the diameters of cations and anions since an ion must cross the first co-ordination shell of oppositely charged ions to reach its new equilibrium position. This would lead the pre-exponential constant to be insenstive to particle radii and depend only on relative ionic masses. Thus the addition of lighter cations, to molten hydrated cadmium nitrate, should result in a systematic increase in A over the entire composition range. An almost constant values of A for the systems would require a more appropriate formulation to describe it.

The near-constant values of B, for a given system, is consistent with the Cohen and Turnbull's "hard sphere" model, in which

$$B = \frac{\gamma v^*}{\alpha v_m}$$

A being the mean expansion coefficient of the melt over the temperature range  $T_n$  to T and  $\gamma_7$  a geometric

$$r_{Cd}(H_{2}^{0})_{4}^{2+} = r_{H_{2}^{0}} + r_{Cd}^{2+} + r_{H_{2}^{0}}$$
factor to correct for the overlap of free volume  $(V_{f})$  in the calculation of the probability of occurence of a critical void  $(V^{\#})$ . Since  $\ll$  varied only by about 2% in the composition range studied, B would be, more and less, independent of compositions, as observed.

However the values of  $\gamma v^* / v_{\mu}$  calculated from B are low compared with those predicted from Cohen and Turnbull's model. This might be due to the higher probability of a diffusing particle finding a suitable void as expected from a purely random distribution of free volume. These observations are similar to those of Angell (1-3) for molten anhydrous salts and a similar argument can be given for this. However, relatively lower value of  $\gamma v^* / v_{\mu}$  in the systems containing Na and K nitrate are unaccountable and may be considered to arise from the covalent character of Cd<sup>2+</sup> ions.

Recently measurements on several oxides and nitrates glasses at temperatures in the vicinity of of glass-transition (25,31) and also the negative pressure dependence of glass-transition temperatures in LiOAc.10H\_O (32) have created doubts about the applicability of the free volume model. The environmental relaxation model (EMR) of Tweer <u>et al.</u> successfully predicts the Arrhenius behaviour at high and low (relative to T<sub>o</sub>) temperature extremes and an intermediate region of varying activation energy. In this model distribution of relaxation times or activation energies is related to some order parameter controlling the size of microstructure in the local environments. A semiempirical mathematical relation containing five adjustable parameters of the type,

 $\ln Y = \ln (G_{oc} A) + \frac{\hat{E}}{RT} + \frac{1}{2} - \frac{C_o}{RT} \left[ \frac{1}{1 + \epsilon^2} \right]^{3/2}$ where  $\epsilon = \epsilon_o \left[ \frac{T}{T_o} - 1 \right]^n$ 

was developed assuming the distribution of relaxation times to be log-Gaussian and that of energies to be Gaussian; the change in the width of distributions is proportional to the change in the distribution of local environments of the flow species in the material.

To find out the applicability of the ERM model, the equivalent conductivity-temperature data were fitted into the equation -3.3/2

$$-\ln \Lambda = \ln(G_{\infty} A) + \frac{\hat{E}}{RT} + \frac{1}{2} \frac{C_{o}}{RT} \left[ \frac{T_{o}^{4}}{T_{o}^{4} + \epsilon_{o}^{2} (T - T_{o})^{4}} \right]^{3/2}$$

by iteration method using IBM 360/44 data processing system. The value of  $\boldsymbol{\xi}$  which relates the size of microstructure ( $\boldsymbol{\lambda}$ ) to that of range of interaction (r) was found to be in between 1.0 to 5.6 which suggest that  $\mathbf{r} \approx \boldsymbol{\lambda}$ , a characteristic of non-Arrhenius behaviour. The value of T corresponds to that evaluated from free volume model. The linearity of plots between -T log (A  $G_{\infty} \wedge$ ) and (1 +  $\boldsymbol{\epsilon}^2$ )<sup>3/2</sup> (Fig.3) exhibit the applicability of the environmental relaxation model.

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	Table I.	LEAST SQUARE MNO <sub>3</sub> system.	EQUATIONS	OF THE CO	NDUCTIVITY	0F Cd(NO <sub>3</sub> ) <sub>2</sub> •4H <sub>2</sub> 0 +
	Temn.Ranne	-	X = A -	+ B(T-300)	+ C(T-300) <sup>2</sup>	, 5cm -1
MN03	(1, K)	A.10 <sup>2</sup> 6	3 <b>.</b> 10 <sup>3</sup>	c.10 <sup>5</sup>	se.10 <sup>3</sup>	Activation Energy (k J mole <sup>-1</sup> )
			<sup>9NO3</sup> = LiNC	2		
0.00	300-365 305-365	1.3475 0.7822	0.5559 7.2369	1.1165 1.2494	0.41	39.34-22.73 46.37-25.72
0.413	300-365	0.5834	0.4267	0.9873	0.25	52.48-26.70
J.524	340-365	1.2217 (	0.7725	0.8250	0.45	58.28-26.70
			MNO <sub>3</sub> = NaN(	_ <mark>.</mark>	•	
0.153	300-365	0.9058	0.7624	0.9533	0.13	38.50-22.18
J <b>.</b> 302	305-365	1.2197	0.7853	0.9183	0.18	52 <b>.</b> 85 <b>-</b> 24 <b>.</b> 90
			MNO <sub>3</sub> = KNO.	MI	,	
0.201	290-365	0.9538	0.7193	1.0069	0.13	59.67-23.31
9.291 201	290 <b>-</b> 365	0.9656	0.7214	1.0006	0.31	63 <b>.</b> 74 <b>-</b> 23 <b>.</b> 02
1.563	z90 <b>-</b> 365	0.8313	U• (492 D•6886	1.2052	0.91	59.30-24.18
			MNO <sub>3</sub> = RbN(	3		
0.072	300-355	1.2661	0.7095	0.8934	0.19	41.96-22.56
0.133	300-355	1.3129	0.7217	0.8856	0.16	41.17-22.35
J.373	285-355	1.2694	0.7053	1.0559	0.32	58.47-23.47
	•••		MNO3 = CsN(	3		
0.113	295-355	1.3188	0.7010	0.9347	0.22	44.36-22.67
J.287	295-355	1.2860	0.6871	0.9328	0.19	44.52-22.79

Table II. Parameters of VTF equation for conductivity data of Cd(NO\_3)\_2.4H\_2O +  $$\rm MNO_3$  syatem

, r , v		<b>√</b> = AT <sup>-</sup> <sup>2</sup>	<sup>†</sup> exp(-B/(	τ-τ <sub>0</sub> ) )	Ecor	<sub>cr</sub> = BR(T/(T-T <sub>0</sub> )) <sup>2</sup>
<b>L</b> "i'i'' A	А		80	TO	,  œ	т <sub>о</sub>
				MNO <sub>3</sub> = L:	i NO <sub>3</sub>	
0.538 4016 605.	4016 605.	605.	S	185.5	605.6	188.5
0.917 4048 664,	4048 664,	664,	o	207.2	663.4	205 <b>.</b> 2
<b>1.004</b> 4152 631,	4152 631,	631,	'n	<b>1</b> 93。2	631 <b>。</b> 6	190.2
1.133 4050 645.	4050 645.	645.	ы	190.7	645.3	188.4
				MNO <sub>3</sub> = N	aNO <sub>3</sub>	
0.617 4050 469.5	4050 469 <b>.</b> 5	469°5		205.0	468.7	206.5
0.693 4080 468.8	4080 468.8	468.8		220 <b>.</b> 5	467。4	224,5
				MNO <sub>3</sub> = KI	۲0 <sub>3</sub>	
0.581 4080 288.5	4080 288.5	288 <b>。</b> 5		230 <b>.</b> 5	284.5	230.4
0.600 4040 378.6	4040 378.6	378.6		226。4	376 <b>。</b> 0	226 <b>.</b> 5
0.621 4132 343.5	4132 343.5	343°5		226.2	343.4	226 <b>.</b> 4
0.648 4120 301.6	4120 301.6	301.6	_	232.5	301.8	232.2
				MNO <sub>3</sub> = RI	5N03	
0.544 4050 607.8	4050 607.8	607.8		188.0	608 <b>,</b> 5	187.5
0.553 4027 622.5	4027 622.5	622.5		189。2	622.5	189.0
0.567 4020 620.8	4020 620.8	620.8		192.0	620.6	<b>1</b> 91 <b>.</b> 4
0.588 4048 628.2	4048 628.2	628.2		194.5	628 <b>.</b> 5	193.6
				$MND_3 = C_3$	s NO <sub>3</sub>	
0.537 4008 620.2	4008 620.2	620.2		187°0	620.5	186.8
0.541 4020 628.5	4020 628.5	628 <b>.</b> 5		187°5	628 <b>.</b> 5	186.8
0.547 4004 640.2	4004 640.2	640.2	~.	188 <b>.</b> 5	640.5	187.6
0.552 4032 620.	4032 620.	620.	ى د	188 <b>。</b> 6	620.8	188.6



Figure 1. Conductivity( $\kappa$ ) <u>vs</u> mole fration of MND<sub>3</sub>(X) isotherms of Cd(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O + MNO<sub>3</sub> systems.at 348.2 K. M for  $\bullet$ ,Li; O,Na;  $\blacktriangle$ ,K;  $\bullet$ ,Rb;  $\checkmark$ ,Cs. Dotted line represent the data of Ca(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O + LiNO<sub>3</sub>; Y-axis for this is on RH5.



Figure 2. Parameters of VTF equation vs mole fration
of MNG<sub>3</sub> for Cd(NG<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>0 + MNO<sub>3</sub> systems. ●,Li;
▼,Na; ●,K; ○,Rb; ▲,Cs.



Figure 3. Plots of  $-T \ln(AG_{\sim} \Lambda) \underline{vs} (1/(1 + \epsilon^2))^{3/2}$ for  $Cd(NO_3)_2 \cdot 4H_2O + MNO_3$  systems. X-axis scale(I) for 1,2,3,4,5; (II),6,7,8,9; (III),10,11,12,13,14; (IV), 15,16,17,18. Y-axis scale(I) for 1,3,6,9,12,16,18; (II).4,8,10,11,14,17; (III),2,5,7,13,15.

ELECTROCHEMISTRY OF URANYL ION IN MELTS AND AQUEOUS SOLUTION

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# INTRODUCTION

Species which undergo complex electrochemical reductions have been studied in hydrated melts, but studies comparing their reductions in hydrated melts and aqueous solutions are uncommon. We have recently studied (1) the reduction of uranyl ion in fused calcium nitrate tetrahydrate. The present paper presents a parallel study in aqueous media and compares the aqueous results with those obtained in the hydrated melt.

A hydrated melt has a known water content and ionic content, but the activity of hydrogen ion in it is not expressible on the aqueous pH scale without ad hoc assumptions. The electroreduction of aqueous uranyl ion, like many complex reductions, involves protons and is therefore pH dependent; its reduction process in hydrated melts should be similar to those of buffered or unbuffered aqueous solutions containing high concentrations of the ions of the melt salt.

When calcium nitrate tetrahydrate is diluted to an arbitrary concentration of 0.5 mol/litre, the resulting solution has a pH of  $3.65 \pm 0.05$ ; the variation arises from different batches and sources of salt. The studies were therefore carried out in three solutions: unbuffered aqueous 0.5 M Ca(NO<sub>3</sub>)<sub>2</sub>, and aqueous 0.5 M Ca(NO<sub>3</sub>)2 buffered at pH 3.63 or 4.63 with acetate. These solutions at 25°C are compared with molten calcium nitrate tetrahydrate at 55°C. The temperature difference is unavoidable, because comparison with the extensive aqueous work at 25°C is necessary. The most significant difference in solvent arises

\*On leave of absence from Department of Chemistry, Ramjas College, University of Delhi, Delhi-110007 (INDIA). from the change in ratio of  $H_2O$  to Ca<sup>++</sup> from about 110:1 (aqueous) to 4:1 (melt), with concomitant major changes in structure and viscosity.

The reduction of U(VI) was selected because it has been extensively studied in aqueous media by different electrochemical methods; most of these studies have been carried out in acidic (HClO<sub>4</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>) media. In sufficiently acidic solution, the generally accepted reduction mechanism (2) is that the uranyl cation is reduced in a one-electron step and that the resulting U(V) species disproportionates, regenerating U(VI). The disproportionation rate has been found to be first order in H<sup>+</sup> concentration according to the following scheme:

(E)  $UO_2^{2+} + e^- \neq UO_2^+$ 

(C) 
$$UO_2^+ + H^+ \neq UO_2 H^{2+}$$

(D)  $UO_2^+ + UO_2H^{2+} \neq UO_2^{2+} + UO_2H^+$ 

(E)

 $UO_2H^{2+} + e^- \ddagger UO_2H^+$ , followed by other reactions to yield stable forms of U(IV)

These steps following the initial reduction of U(VI) to U(V) are all strongly pH-dependent and the final outcome may be U (V) complexes or even precipitation of U(IV) as  $UO_2(s)$  on the electrode surface, depending upon the pH. Reaction of the electrochemically produced U(V) or U(IV) with components of the solution (such as nitrate ion in the present case) is also possible.

In less acidic solutions the disproportionation of U(V) does not take place (3). Since the present solutions are weakly acidic, directly relevant studies are few (3,4).

# EXPERIMENTAL

The electrochemical cell was a Princeton Applied Research (P.A.R.) Model 9300-9301 polarographic cell employed in a three electrode configuration. The working electrode was either a P.A.R. Model 9323 hanging mercury drop electrode (HMDE) or a dropping mercury electrode (DME) in conjunction with a P.A.R. Model 172A mercury drop timer. These electrodes were set up using triply distilled mercury (Englehard). For the HMDE, a fresh mercury drop of constant known area  $(0.0176 \text{ or } 0.0349 \text{ cm}^2)$  was taken for each observation. The auxiliary electrode was a large platinum flag. A commercial saturated calomel reference electrode (SCE), Corning 47600, was used; aqueous potentials are with reference to this SCE. Potentials in the tetrahydrate melt are with reference to Ag(I), 0.31 mmol/litre/Ag (s) in the same melt.

The polarographic behaviour was studied using a P.A.R. Model 174A polarographic analyzer. The chronopotentiometric potential-time curves and the chronoamperometric currenttime curves were obtained with a P.A.R. Model 173 potentiostat/ galvanostat. The cyclic voltammetry was performed with this potentiostat/galvanostat coupled to a P.A.R. Model 175 universal programmer. The polarograms, current-time curves, some of the potential-time traces, and the cyclic voltammograms at slow scan rates (< 1 V/S) were recorded with an x-y and x-t recorder (Houston Instrument Type 2000). The cyclic voltammograms at higher scan rates and the chronopotentiograms were photographed from the screen of a Tektronix Model 535A oscilloscope. All values of the polarographic currents were corrected for the residual current of the base electrolyte. The pH of the unbuffered aqueous 0.5 molar solutions were measured and found to be  $3.65 \pm 0.05$  depending on the batch

of Ca(NO<sub>3</sub>) $_{2}$ ·4H<sub>2</sub>O employed; buffered solutions were either pH 3.63 or 4.63.

Before electrolysis, all solutions were purged with purified nitrogen for at least 15 minutes and blanketed with it during the run. Analytical reagent grade uranyl nitrate and calcium nitrate tetrahydrate (BDH AnalaR), acetic acid, and sodium acetate were used without further purification. The aqueous experiments were all carried out at 25°C, the tetrahydrate melt experiments at 55.0  $\pm$  0.1°C. Further details of the tetrahydrate melt experiments have been given elsewhere (1).

RESULTS AND DISCUSSION

# Polarography

Polarograms of aqueous uranyl solutions (Fig. 1) show two reduction waves. In all solutions the first wave is a reversible one-electron process, as it is in the melt, as shown by Heyrovsky-Ilkovic plots. The values of the half-wave potential are: unbuffered aqueous,  $-0.180 \pm 0.005$  V; pH 3.63 buffer,  $-0.254 \pm 0.005$  V; pH 4.63 buffer,  $-0.323 \pm 0.005$ V; melt (silver reference),  $-0.475 \pm 0.005$ V. The plateau height is directly proportional to uranyl concentration.

In unbuffered aqueous solutions, a second wave is observed near -1.0 V, while in buffered aqueous solutions the wave is absent. In the melt (Fig. 2) a wave is observed at -0.67 V in addition to a wave near -1.0 V. In melt and in aqueous solutions, the i-t curves for individual drops do not follow simple diffusion-controlled behavior, although diffusion-controlled behavior is observed in the final part of drop life.

#### Chronopotentiometry

The potential-time curves in unbuffered solution (Fig. 3)

show one sharp transition with quarter-time potential  $E_{\tau/4}$ of -0.175 ± 0.010 V, in agreement with the polarographic half-wave potential. The Sand plot of  $\tau^{1/2}$  against the reciprocal of the current density for this process was a straight line passing through the origin. This indicates that under the conditions of these measurements the mass transport is diffusion controlled and linear diffusion theory is an adequate approximation to diffusion towards a HMDE. The Karaoglanoff plot of E vs. log  $(\tau^{1/2} - t^{1/2})/t^{1/2}$ was likewise a straight line of slope 0.061 V which is in reasonable agreement with the theoretical value of 0.059 V for a reversible, single-electron, reduction process at 25°C where the product of the electrode reaction is soluble. For a reversible process (5), the polarographic half-wave potential,  $E_{1/2}$ , is equal to  $E_{\tau/4}$  whereas for the reoxidation process after the current reversal, it should correspond to the potential at time 0.222  $\tau$ '. For the first transition, in the present case, both  ${\rm E}^{}_{\tau/4}$  and the potential at 0.222  $\tau^{*}$ were found to be the same as  $E_{1/2}$ , regardless of the time at which the current was reversed, further confirming the reversibility of this step.

Chronopotentiometry with current reversal was carried out by reversing the current at various points in the E-t curve, i.e. towards the end of the first transition, at the rising portion after the first transition and after the appearance of the peak where the second process commences (Fig. 3 A,B,C). When the direction of the electrolysis current was reversed even at some time after the peak, the electrode potential immediately dropped to a value corresponding to the first reduction process. The value of the *first* forward to reverse transition times,  $\tau_f/\tau_r$ , was found to be approximately three in all cases and independent of the length of time beyond  $\tau_f$ . These observations imply that the

product of the second electrode reaction cannot be reoxidized and that the product of the first process is being regenerated, perhaps catalytically, during the second reduction step.

These results, which are remarkably similar to those obtained in the melt (Fig. 4), indicate that the process observed at -1.0 V in the unbuffered aqueous solution is similar to that observed at -0.67 V in the hydrated melt.

#### Chronoamperometry

The reduction of uranyl ions at the HMDE was studied using potential-step chronoamperometry; the curves obtained in unbuffered solution are presented in Fig. 5. The shape of the I-t curves was normal for applied potentials corresponding to the first reduction step, up to -0.92 V. The curves show maxima for applied potentials in the range -0.94 to -1.12 V corresponding to the second electrode process, but are of normal shape at more negative potentials. After the initial capacitive current decay, the current increases and then slowly decreases after reaching a maximum. The position and intensity of the maxima depend upon the potential step applied. The height of the maximum increases and it appears after shorter times as the applied potential is made more cathodic. No maxima in the I-t curves are observed at applied potentials more cathodic than -1.12 V. At such negative potentials, it may be that the maxima appear at such a short time interval that it is not possible to detect them on the pen recorded transients and only the usual diffusion controlled curves, in which I is proportional to  $t^{-1/2}$ , are observed.

When the potential step applied corresponds to a value on the diffusion plateau, the current-time transient should show the proportionality of the current to  $t^{-1/2}$ . This

indicates the absence of hydrolysis of  $UO_2^{2+}$  in buffered or unbuffered weakly acidic 0.5 *M* Ca(NO<sub>3</sub>)<sub>2</sub>.

Collat and Lingane (6) have shown that U(VI) or U(V) is reduced, perhaps to U(III), at a potential of -1.1 V vs. SCE in aqueous KCl at pH 2-3. In the absence of uranium, nitrate ion is not reduced at this potential; the reduction of nitrate occurs at potentials about 0.2 V more negative than the half-wave potential (-1.58 V) for the hydrogen ion wave. But during the uranium-catalyzed reduction of nitrate the nitrate ion is reduced by a lower oxidation state of uranium at the electrode surface, this uranium being reoxidized to U(V) which is rapidly re-reduced to produce a catalytic cycle. The reduction of nitrate removes hydrogen ions, and nitrate is chiefly reduced to hydroxylamine in the presence of uranyl ion, the electron/proton ratio being approximately unity.

This catalytic reduction of nitrate is probably

(E) 
$$UO_2^+ + 3H^+ + e^- + UOH^{3+} + H_2O$$

(C) 
$$6UOH^{3+} + NO_3^- + 4H_2O \neq 6UO_2^+ + NH_2OH + 11H^+$$

giving a net reaction of

 $6e^{-} + NO_{3}^{-} + 7H^{+} \rightarrow NH_{2}OH + 2H_{2}O$ 

and an electron/proton ratio of 6/7, in reasonable agreement with the values near unity obtained coulometrically (6). Reduction of  $UO_2^+$  to  $U^{3+}$  rather than  $UOH^{3+}$  would give the same net result. The reduction of nitrate in the absence of the uranium catalyst proceeds (6) by a different route, the products being a mixture of nitrite and nitrous acid.

The catalytic reaction of this pH is simple and not complicated by insolubility of  $UO_2$ , which precipitates in more basic solutions (4), or by the more complex behavior observed in highly acidic solutions.

It is easier to interpret the chronoamperometric curves by integration rather than directly because the separation of the different processes can then be achieved. The integrated area (7) from t = 0 to t = 16 sec is plotted in Fig. 6. This length of time was necessary in order to include the peak of D, Fig. 5, but even such a long time does not permit inclusion of the peak of C so that the point at -0.94 V on Fig. 6 is anomalously low. The contribution of doublelayer charging on this time scale is negligible but the coulombs due to the first reduction of  $UO_2^{2+}$  are not. Since, however, this process is reversible this charge can be calculated by integration of the Cottrell equation, which vields Q =  $2nFC(Dt/\pi)^{1/2}$ . Using the experimental values of 16 sec, 1.006 mmol/litre, 1 electron/ion, and appropriate values of the fundamental constants, Q is an insensitive function only of the diffusion coefficient of uranyl ion. The diffusion coefficient obtained in this and other work is  $7.7 \times 10^{-6} \text{ cm}^2/\text{sec}$ , which yields 1.22 mcoul/cm<sup>2</sup> for charge due to the  $UO_2^{2+}$  reduction to  $UO_2^+$ . This value, plotted as a solid horizontal line in Fig. 6, is in excellent agreement with the coulombs observed for the first wave. For the second wave even a value of three times this, plotted as a broken line in Fig. 6, cannot describe the coulometry of this process which then cannot be  $UO_2^{2+} \rightarrow U(III)$ . Indeed, it cannot be limited by diffusion of  $UO_2^{2+}$  at all and thus must correspond to the catalytic reduction of nitrate, whose concentration is sufficiently great that the observed coulombs can be passed without exceeding the limit imposed by mass transport.

# Cyclic Voltammetry

Cyclic voltammetry was used in all media, and a fuller discussion will be published elsewhere. Briefly, in aqueous

solution the first process near -0.2 V is a one-electron reversible process but that at slow scan speeds or with a potential range beyond -0.5 V additional cathodic processes appear and the anodic peak of the first process becomes severely distorted; in the melt, this distortion is always present.

#### CONCLUSION

The electroreduction of uranyl ion is a complex pHdependent process in aqueous nitrate solution. Experimental observations made in aqueous 0.5 M Ca(NO<sub>3</sub>)<sub>2</sub> are remarkably similar to those in calcium nitrate tetrahydrate melt, in which there is an additional complication due to UO<sub>2</sub> precipitation (1). The reduction of UO<sub>2</sub><sup>2+</sup> in the hydrated nitrate melt is dissimilar to its reduction in anhydrous nitrate melts in which UO<sub>2</sub> is reoxidized to uranyl ion.

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Figure 1. Polarograms of Reduction of Uranyl Ion in Aqueous Solution. Curve A, unbuffered, pH 3.65; Curve B, acetate buffer, pH 4.63; Curve C, acetate buffer, pH 3.63. 0.5 M Ca(NO<sub>3</sub>)<sub>2</sub>, maximum current, controlled drop time 2 s, uranyl concentration 1.00 mmol/litre (A,B), 0.70 mmol/litre (C).



Figure 2. Polarogram of Reduction of Uranyl Ion in Calcium Nitrate Tetrahydrate Melt. Temperature, 55°C; uranyl concentration 1.97 mmol/litre, maximum current, controlled drop time 2 s.



Figure 3. Chronopotentiograms Obtained on Reduction of  $UO_2^{2+}$ in Unbuffered Solution. Curve A, current reversed on first plateau; B, current reversed on rising portion following first plateau; C, current reversed on second plateau at time 1.81 seconds. Concentration of  $UO_2^{2+}$ , 1.006 mmol/litre; current density 0.285 mA/cm<sup>2</sup> both forward and reverse.



Figure 4. Chronopotentiograms Obtained on Reduction of  $UO_2^{2+}$ in Calcium Nitrate Tetrahydrate Melt. Curve A, current reversed on first plateau; B, current reversed on rising portion following first plateau; C, current reversed on second plateau at time 4.33 sec. Concentration of  $UO_2^{2+}$ , 1.975 mmol/litre; current density 0.0570 mA/cm<sup>2</sup> both forward and reverse; temperature 55°C.



TIME, sec

Figure 5. Typical Chronoamperometric Curves of Uranyl Ion Reduction in Aqueous Unbuffered 0.5 M Ca(NO<sub>3</sub>)<sub>2</sub>. Concentration of UO<sub>2</sub><sup>2+</sup>, 1.006 mmol/litre. Potential steps applied (from 0.0 V): A, -0.90 V; B, -0.92 V; C, -0.94 V; D, -0.96 V; E, -0.98 V; F, -1.00 V; G, -1.02 V; H, -1.04 V; I, -1.06 V; J, -1.08 V; K, -1.10 V; L, -1.12 V; M, -1.14 V; N, -1.20 V. Curve K, as J, possesses peak distinguishable from initial rise while curves L, M, and N do not. Current scales: curves A-G, 0.5  $\mu$ A/division, curves H-J, 1.0  $\mu$ A/div; curves K-N, 2.5  $\mu$ A/div. Curves arbitrarily displaced on time axis. Area of HMDE, 0.0176 cm<sup>2</sup>.



Figure 6.

5. Chronoamperometric Charge in Aqueous Solution. Curves integrated to 16.0 sec; concentration of  $\mathrm{UO}_2^{2+}$ , 1.006 mmol/litre; electrode area 0.0176 cm<sup>2</sup>. Circles correspond to experimental points in unbuffered solution. Curve A is obtained in buffered solution of pH 3.63 and B in buffered solution of pH 4.63. For explanation of horizontal lines see text.

# THE INITIAL HYDRATION OF IONS IN MOLTEN NITRATES

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#### ABSTRACT

The electrochemical consequences of adding small amounts of water (0-3.36 molal) on the transport and electrode kinetics of tracer metal ions (especially Ni<sup>2+</sup>) dissolved in molten  $LiNO_3$ -KNO<sub>3</sub> at 145°C have been investigated using d.c., pulse and fast linear sweep polarographic methods at mercury electrodes. An initial and sharp anodic half-wave potential shift at low water concentrations for Ni<sup>2+</sup> ions is interpreted in terms of dramatic coordination changes associated with rupture of bidentate nitrate linkages. It is thought that this accounts for apparent changes in the polarographic reversibility. Results obtained for Pb<sup>2+</sup> and Tl<sup>+</sup> solutes support these interpretations. A warning is sound to molten salt workers concerning the purity and dryness of their solvents.

Water is perhaps the most ubiquitous and certainly the most important contaminant in molten salts. Its relatively high solubility at elevated temperatures surprised earlier workers who often believed that they were dealing with truly anhydrous solvents. More recently, and as we shall now show, the presence of traces of water in melts may be rather worrying.

In this work we aimed to discover just how ions become hydrated when anhydrous melts are titrated with water and what effects such changes might have on ion transport and electrode processes. The region we have primarily been interested in lies towards the top of Braunstein's water-melt diagram<sup>1</sup>. We chose to use Ni<sup>2+</sup> tracer ions to monitor kinetic and transport changes because this small, highly polarising ion has proved particularly sensitive to water content in aqueous media<sup>2</sup>. We employed d.c. and pulse polarographic methods at mercury electrodes in eutectic LiN03-KNO3 at 145°C to follow the Ni<sup>2+</sup>/Ni<sup>0</sup> (Hg) reduction, again because there was a good range of previous data available for comparison.

In some earlier work, we had found that that the polarographically determined diffusion coefficient for Ni<sup>2+</sup> in molten, eutectic LiNO<sub>3</sub>-NaNO<sub>3</sub>-KNO<sub>3</sub> at  $\sim$  145°C was rather slower than expected on the basis of its small ionic radius (0.69 Å) and by comparison with other divalent cations. At that time, we rationalized this in terms of the presence of large, stable nitrato-nickel<sup>II</sup> complexes. These were later confirmed spectroscopically<sup>8-10</sup>. We also drew attention to the relatively anodic reduction half-wave potential,  $E_2^1$ , for Ni<sup>2+</sup> ions as

compared with aqueous solution behaviour and relative to other divalent cations. The polarographic wave was also close to reversibility.

Later<sup>11-13</sup> we turned our attention to the reduction of cations in aqueous melts. When we titrated a solution of  $Cd^{2+}$  ions dissolved in molten  $Ca(NO_3)_2 \cdot 4H_2O$  + 56 mole % KNO<sub>3</sub> at 50°C with water, the polarographic wave was shifted cathodically, as shown in Figure 1. It was considered <sup>11</sup> that this reflected the normal, stepwise displacement of contacting nitrate ions<sup>14</sup> present in the inner coordination sphere of the cadmium ions. In contrast, Ni<sup>2+</sup> ions were reduced beyond the intervening cathodic reduction of nitrate ions in molten Ca(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O at 50°C and the polarographic wave could not be resolved<sup>12</sup>. Neverthe-less, the Ni<sup>2+</sup>/Ni<sup>°</sup> (Hg) reduction wave was discernable<sup>2</sup> in the aqueous melts Ca(NO3)2·4H20 + 46 mole % KNO3, in LiNO3·3H2O and in Ca (NO3)2· 4D20, in each case as quite irreversible polarograms close to the nitrate reduction wave. We concluded that the (interesting) initial hydration processes were already essentially complete in these media and that the substitution by aquo-ligands had proceeded well towards the familiar hexaquonickelate<sup>II</sup> species. Surprisingly, however, in  $CaCl_2 \cdot 6H_2O$  and  $MgCl_2 \cdot 6H_2O$  aqueous melts<sup>12</sup> at 35°C and 115°C, Ni<sup>2+</sup> polarographic waves were reversible and occurred close to the theoretical standard potential, as in anhydrous nitrate melts. Clearly coordination by chloride ions is sufficient to remove kinetic restrictions in the reduction mechanism<sup>2,15</sup>. Notwithstanding, the yellow-green solutions in the Ca<sup>2+</sup>-containing melt and the blue solutions in the Mg<sup>2+</sup> - containing melt evidence different states for the Ni<sup>2+</sup>; some spectroscopic data is available for these systems<sup>12,16</sup>.

More recently<sup>17</sup> we have titrated solutions of Ni<sup>2+</sup> ions in anhydrous LiN0<sub>3</sub>-KNO<sub>3</sub> eutectic melts at 145<sup>o</sup>C with water. Unlike other workers, we employed anhydrous Ni<sup>II</sup>NO<sub>3</sub> solute<sup>†</sup> prepared from liquid N<sub>2</sub>O<sub>5</sub>. At the lowest concentrations of water (0-3.10<sup>-2</sup> m.) an equilibration technique using standard water vapours at fixed temperatures was used; residual water vapour pressures were monitored by Baratron equipment. At higher water concentrations,  $(2 \cdot 10^{-1} - 3 \cdot 36 \text{ m.})$ , direct injection into a closed cell was employed, via a microlitre syringe and septum. Henry's Law could be adopted for calculating the concentration of dissolved water, on the basis that it forms regular solutions with the melt<sup>18</sup>.

The polarographic wave for Ni<sup>2+</sup> was initially (<  $4.5.10^{-3}$  m. H<sub>2</sub>O) shifted in the ANODIC direction, as shown in Figure 2. Not only was this E<sub>1</sub> shift,  $\sim 40$  mV, entirely reproducible, but it was also dramatically sharp in the first portion. This effect should worry all molten salt workers who have not rigorously dried their solvents, or those who have used hydrated solutes.

<sup>T</sup>prepared by B. O. Field at City University, London.

At these lowest water contents, there is little apparent change in the overall size of the diffusing species or its interaction with the bulk solution or electrode, since the limiting currents, which are always diffusion-controlled, vary little. Certainly, density changes<sup>19</sup> account wholly for such increase in the diffusion current as is observed. Thus, water may be presumed to behave as a regular ligand in this concentration regime.

A closer inspection of the polarographic wave shape confirmed<sup>4</sup> that the reduction was not completely reversible in the anhydrous medium. At water concentrations corresponding to the maximum anodic  $E_1$  shift, however, the wave became completely reversible ( $\alpha$  n<sub>a</sub> = 2). At higher water concentrations, polarographic reduction waves for Ni<sup>2+</sup> ions reverted to increasingly irreversible character, eventually approaching aqueous melt behaviour. A consequence of these changes is that the specific rate constant, fully corrected for density changes and  $E_1$  shifts (to which we refer k<sub>s</sub> values), gradually increases with increasing water concentration. This sharply contrasts with a previous report<sup>5</sup> which studied the reaction by the a.c. impedance method. The lack of availability of density data at that time, as well as those author's apparent unawareness<sup>5</sup> of  $E_1$  changes may partly account for these discrepancies. Nonetheless, it is difficult to reconcile the large difference between their value of k<sub>s</sub> and ours, as shown in the Table of selected data:-

#### TABLE

Selected polarographic data for the  $\text{Ni}^{2^+}/\text{Ni}^{\circ}$  (Hg) reduction in molten LiN0<sub>3</sub>-KNO<sub>3</sub> eutectic at 145<sup>°</sup>C, containing 8.35 x 10<sup>-4</sup> m. Ni<sup>2+</sup>, at the d.m.e. (m.t. = 4.8 mg.).

C <sub>H20</sub> molal	E <sub>1</sub> , mV (Åg/Ag (I) 10- <sup>3</sup> m)	∆E <u>1</u> mV	$i_d^{max.}_{\mu A}$	$\begin{array}{c} D \times 10^6 \\ cm^2 \cdot s^{-1} \end{array}$	αn a	$k_s \times 10^3$ cm.s
0	-560	-	1.86	0.225	1.8(3)	1.0
2•25.10 <sup>-3</sup>	-540	+ 20	1.86	0.225	1.9(1)	1.1
4.5.10 <sup>-3</sup>	-521	+ 39	1.86	0.225	2.0	1.1
9•0.10 <sup>-3</sup>	-525	+ 35	1.87	0.225	2.0	1,.1
1•8.10 <sup>-2</sup>	-530	+ 30	1.87	0.225	1,9(6)	1.1
0.45	-576	- 16	1.94	0.25	1.7(9)	1.1
1.32	-640	- 80	2.04	0.30	1.6(5)	1.2
2.16	-686	-126	2.13	0.35	1.5(2)	1.2
3.36	-709	-149	2.34	0.46	1.3(5)	1.4

the previous value<sup>5</sup> of  $k_s$  having been given as  $\sim 5.10^{-3}$  cm.s.<sup>-1</sup> (anhydrous melt),  $\sim 2.2.10^{-3}$  cm.s.<sup>-1</sup> (mole fraction water = 0.5).

At higher concentrations,  $(2.10^{-1} - 3.36 \text{ m})$ , the  $\text{E}_{1}$  for Ni<sup>2+</sup> shifts in the cathodic direction as shown in the Table. In this region, it would appear that the more stable less labile aquonickelate<sup>II</sup> complexes are being formed according to a normal stepwise replacement equilibrium. The larger variation in the limiting currents follows the considerable modification of the melt density, and viscosity. After correcting for these factors, however, the value of the diffusion coefficient is only twice as fast as in the anhydrous melt - a consequence of the smaller effective radius<sup>-1</sup> of the water molecule compared to the nitrate anion which, respectively, coordinate the Ni<sup>2+</sup> ion. The small inflection in the diffusion coefficient at 2m.H<sub>2</sub>O, corresponding to  $\sim \frac{1}{2}$  mole H<sub>2</sub>O/mole Li<sup>+</sup> may be a real effect, perhaps due to some reorganization in the bulk melt structure?

Focussing on possible reasons for the initial anodic E1 shift in the Ni<sup>2+</sup> polarographic wave, there can be no doubt that more stable species, involving substitution by water ligands, are formed in this region. Any explanation must, therefore, be framed in terms of kinetic, rather than thermodynamic arguments. Hence, the acceleration of the reaction rate in the presence of traces of water must not only be superimposed upon, but must overwhelm an apparently small cathodic shift in E1, required on thermodynamic grounds. An alternative approach might consider an enhancement of lability, a bulk homogeneous phenomenon, of a newly substituted Ni<sup>2+</sup> species, leading to an easier reaction pathway. All such explanations will be based on radical changes in the coordination of the Ni<sup>2+</sup> ion, therefore, although a subsequent paper<sup>2</sup> will discuss yet further interpretations. Some explanations for the anodic E<sub>1</sub> shift can summarily be dismissed. In separate experiments we titratedboth the main cell compartment, as well as the reference electrode compartment, with appropriate amounts of water. Since this had no apparent effect on the sign and magnitude of the measured half-wave potentials, it seems that liquid junction potential variations are not pertinent. Neither, at very low water contents, are bulk structure changes in the melt implicated, since a wealth of evidence<sup>18</sup> suggests that water is an "ideal" solute under these conditions. Although adducts between complex ions and  $N_2O_5$  are documented, we believe our nickel nitrate sample to be quite pure. However, any residual N205 would be converted to nitric acid by water, that the presence of HNO3 has no measurable effect on the and we know rate of Ni<sup>2+</sup> reduction in nitrate melts.

In order to determine to what extent the nature of the solution species influenced the reduction kinetics during titration with water, we further examined the polarographic behaviour of both  $Pb^{2+}$  and  $T1^+$  in the LiNO<sub>3</sub>-KNO<sub>3</sub> melt. Divalent lead ions are relative large, weak-field ions of low polarising power and being non-transition metal ions exhibit fairly simple, weakly complexing ability. Quite large

( $\circ$  lm.) concentrations of water were required to effect only small cathodic E1 shifts in the Pb<sup>2+</sup>/Pb<sup>0</sup> (Hg) reduction wave: no variation was observed at low water levels. A typical polarogram for Pb<sup>2+</sup> is compared with that for Ni<sup>2+</sup> and Tl<sup>+</sup> in Figure 3. At concentrations of Tl<sup>+</sup> > 10<sup>-5</sup> m., the characteristic adsorption maximum was evident in the polarographic wave. We used this phenomenon as a direct probe of the interfacial region during similar water titration experiments. It was hoped to detect any variations in surface-controlled processes when water was introduced, in this way. However, there appeared to be no variation with water concentration of the ratio of ip/id, where ip = current at maximum, <sup>1</sup>d = post-maximum limiting current, typically 1.2 at CT1<sup>+</sup> = 1.95 x 10<sup>-9</sup> m. [N.B. Use of the ratio of currents avoided the need for density/viscosity corrections during a titration, on the assumption that both processes were approximately similarly influenced by these factors.] This evidence, as well as that from directly measured double-layer capacitances<sup>21</sup>, suggest that small amounts of water present in the nitrate melt do not specifically interact with electrode processes via an adsorption or any other type of mechanism.

Thus, on the basis of all the above evidence, we prefer to interpret our results in terms of dramatic initial changes in the coordination of Ni<sup>2+</sup> ions consequent upon the addition of traces of water to the anhydrous nitrate melt. Moreover, the ensuing electrochemical phenomena appear to be kinetically based. Notwithstanding, it is interesting to speculate on the nature of a possible substitution mechanism. Spectroscopic evidence convincingly favours the presence of hidentate nitrate linkages in the anhydrous melt. These bonds are extremely susceptible to water, and it seems reasonable to assume. therefore, that ring opening will be the first step in the hydration displacement equilibrium. This may lead to a sharp entropy decrease due to an "inverse" chelate effect. The complex would be destabilized, perhaps with a consequent "trans effect" which might then influence further substitution kinetics as well as labilising some nitrate ligands remaining. This could constitute the major contribution to the anodic shift in the polarographic half-wave potential and the increase in reversibility observed at the lowest water concentration regime, where the molal ratio of water : nickel is already  $\sim$  5:1. The favourable enthalpy term resulting from the relief of steric ring-strain by disruption of bidentate nitrate bonds is presumably a relatively small effect, although the increase in the important translational entropy term at ring scission must offset the effect of increase in ligand number i.e. loss of an H20 particle from the system. The situation is obviously complicated with many competing factors, hence a further spectroscopy study might usefully parallel future electrochemical investigations now planned.

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# THE CHEMISTRY OF THE ROCKGAS PROCESS FOR COAL GASIFICATION

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#### ABSTRACT

In the Rockgas process, coal is gasified with air or with oxygen and steam within a Na<sub>2</sub>CO<sub>3</sub>-containing melt. The gasification reaction takes place at about  $1800^{\circ}$ F and at a pressure of 1 to 30 atm. The sulfur and ash of the coal are retained in the melt. Gasification experiments were performed on different types of coal ranging from low-rank lignite to high-rank anthracite. The composition of the product gas at steady state was, in general, in good agreement with that calculated from carbon, hydrogen, and oxygen balances and assuming the water gas shift reaction attained thermodynamic equilibrium. The times for the product gas heating value and the carbon content of the melt to reach steady state decreased as the coal rank decreased. Evidence is presented that the primary gasification step is the conversion of carbon to CO<sub>2</sub>. The secondary step is the reduction of CO<sub>2</sub> to CO by the carbon in the melt.

### I. INTRODUCTION

The U.S. has adequate coal reserves to supply our national energy needs over the next several hundred years. However, the pollution problems associated with the release of sulfur oxides, nitrogen oxides, and particulates into the atmosphere have severely limited our use of coal and compelled us to consume other, more valuable and less abundant, sources of energy. The utilization of our coal reserves in a manner which does not add to the existing pollution problem is therefore, of utmost importance in the interest of convervation of more valuable natual resources in the national economy. Gasification of coal and generation of clean fuel gas offers one of the most promising approaches to our utilization of this fuel. It has been assigned a high-priority in the U.S. Energy Development Program. Several of the coal gasification processes presently under development are now at the initial pilot plant operation stage. One of these processes is the Rockwell International Molten Salt Coal Gasification Process (Rockgas Process). In this process, the coal is gasified at a temperature of about 1800°F and at pressures up to 30 atm by reaction with air in a highly turbulent mixture of molten sodium carbonate containing sodium sulfide, ash, and unreacted carbonaceous material. Sulfur and ash of the coal are retained in the melt, a small stream of which is continuously circulated through a process system for regeneration of the sodium carbonate, removal of the ash, and recovery of elemental sulfur.

In this paper, emphasis is placed on discussion of the chemistry taking place in the gasifier. A description of the coal gasification concept is given first. This is followed by a discussion of some of the bench-scale gasification tests.

# II. CONCEPT OF THE ROCKGAS COAL GASIFICATION PROCESS

In the Rockgas process, the fuel is gasified at a temperature of about 1800°F and at pressures up to 30 atm (depending upon the specific requirements of the process) by reaction with air within a highly turbulent mixture of molten sodium carbonate containing sodium sulfide, ash, and unreacted carbon. The concept is shown in Figure 1. The oxidation is catalyzed by the presence of the sulfur compounds in the melt. The sulfur and ash of the coal are retained in the melt, a sidestream of which is circulated continuously through a process sys-tem for regeneration of the carbonate, removal of the ash, and recovery of elemental sulfur. The fuel gas that is produced carries, as sensible heat, a major fraction of the heat released in the molten salt gasifier and has an effective heating value of approximately 150 Btu/scf (low-Btu gas). When steam and oxygen are substituted for air, the elimination of nitrogen produces a higher quality gas with an effective heating value of approximately 300 Btu/scf (medium-Btu gas). Following removal of entrained particulates, the gas can be used as a clean nonpolluting fuel gas for either utility power generation or industrial heat applications.

A steady-state concentration of ash and sulfur in the melt is maintained by the continuous withdrawal of melt from the gasifier and return of regenerated sodium carbonate to the gasifier. In order to carry out this process, the melt is quenched with water and processed in an aqueous regeneration system which removes the ash and sulfur compounds retained in the melt and returns the regenerated sodium carbonate back to the molten salt gasifier. A simplified flowsheet of the process, including the regeneration system, is shown in Figure 2. The ash is filtered out and disposed of in a conventional manner. Th The sulfur compounds are converted into hydrogen sulfide by carbonation and steam stripping of the aqueous solution, and the hydrogen sulfide thus released is, in turn, converted into elemental sulfur in a Claus The sodium carbonate is regenerated as sodium bicarbonate which plant. is filtered out the of solution and then calcined to yield sodium car-The regenerated sodium carbonate and the makeup required to bonate. replace the small amount of salt lost in the process are returned to

the molten salt gasifier. The regeneration process is based on technology presently in existence in the sodium-based sulfite pulp and paper industry.

# III. EXPERIMENTAL SECTION

# A. COALS GASIFIED

The coals gasified were Honghei anthracite, Daidoo medium-volatile bituminous coal, Miike high-volatile bituminous coal, Kentucky No. 9 high-volatile bituminuous coal, and a Texas lignite. The coals are listed in order of decreasing rank with the anthracite having the highest rank. The first three coals were supplied by Electric Power Development Corporation of Japan, the Kentucky No. 9 coal was supplied by the Kentucky Coal Association, and the lignite was supplied by Phillips Petroleum Company.

The proximate and ultimate analyses of the coals are listed in Table 1.

	Honghei Anthracite	Daidoo Medium- Volatile Bituminous	Miike High- Volatile Bituminous	Kentucky No. 9 High- Volatile Bituminous	Texas Lignite
Proximate Analysis (wt %)				e e	
Moisture	2.78	2.26	0.85	6.18	32.46
Matter	4.92	30.36	38.71	35.31	28.70
Carbon Ash	87.51 4.79	56.53 10.85	37.69 22.75	43.17 15.34	25.50 13.34
Ultimate Analysis (wt %)					
Moisture Carbon Hydrogen Nitrogen Oxygen* Sulfur Ash	2.78 85.27 3.21 0.81 1.97 0.67 4.79	2.26 71.85 4.60 0.78 8.59 1.07 10 85	0.85 62.26 4.95 0.82 5.60 2.77 22 75	6.18 62.19 4.29 1.31 6.43 4.26 15.34	32.46 35.34 2.52 0.96 14.85 0.53 13.34

# TABLE 1 ANALYSIS OF COALS TESTED

\*By difference
# B. BENCH-SCALE MOLTEN SALT GASIFIER

A schematic of the bench-scale molten salt gasifier is shown in Figure 3. Approximately 12 lb of molten salt are contained in a 6-in. ID and 36-in. high alumina tube placed in a Type 321 stainless steel retainer vessel. This stainless steel vessel, in turn, is contained in a 8-in. ID, four-heating-zone Marshall furnace. The four heating zones are each 8 in. in height, and the temperature of each zone is controlled by a silicon-controlled rectifier. Furance and reactor temperatures are recorded by a 12-point Barber-Colman chart recorder.

The coal ground in a hand-turned burr mill is metered into the 1/2-in. ID central tube of the injector by a screw feeder. Rotation of the screw feeder is provided by a 0 to 400 rpm Eberback Corporation Con-Torque stirrer motor. The coal is mixed in the injector with the air being used for gasification, and this coal-air mixture passes downward through the center tube of the injector and emerges into the 1-1/2-in. ID alumina feed tube. This alumina feed tube is adjusted so that its tip is  $\circ 1/2$ -in. above the bottom of the 6-in.-diameter alumina reactor tube. Thus, the coal-air mixture is forced to pass downward through the feed tube, outward at its bottom end, and then upward through  $\circ 6$  in. of salt in the annulus between the 1-1/2-in. and the 6-in. alumina tubes.

# C. RESULTS

# 1. Product Gas Composition From Gasification With Air

The test conditions for the gasification tests for all the coals except Kentucky No. 9 are listed in Table 2 which gives the melt temperature, the air and coal feed rates, the air/coal ratio, and the percent theoretical air. The last value is the percent of the amount of air which is required to oxidize the coal completely to  $CO_2$  and H<sub>2</sub>O. The air/coal ratios and thus the percent theoretical air were chosen to give a good quality product gas from a heating value point of view. The steady-state composition and the higher heating value (HHV)\* of the product gas obtained from the four coals are shown in Table 3. In each case, a good quality (>120 Btu/scf) low-Btu product gas was obtained. The product gas compositions were calculated on the basis of the carbon, hydrogen, and oxygen mass balance and assuming thermodynamic equilibrium for the water-gas shift reaction

$$CO + H_2O \neq CO_2 + H_2.$$
 ...(1)

To perform the mass balance, the coal analytical data shown in Table 1 were expressed in terms of an empirical formula,  $C_{c}H_{b}O_{c}$ . The results

\*The higher heating values include the heat of condensation of steam to liquid water.

t rank	Ratio Percent b) Theoretical Air	45.3	44.2	32.4	n Class 1, 1-1 is higher	ION		Liqnite		Observed Calculated	24.3 22.2	15.4 19.4	I.7 0.9*	0.2 0.0*	10.9 11.3	44.6 46.2		,	149.2 143.6
JF DIFFEREN	Air/Coal   (scf/11	66.7	56.4	37.7 19.0	number. Iı	VS COMPOSIT	ike	'olatile	SNOUL	Calculated	33.4	17.7	0.1*	0.0*	0.0	49.5			164.2
TH COALS C	Feed Rate (1b/h)	1.67	1.97	2.95 5.06	the group	PRODUCT GA	ĻΜ	High-V	Bltu	0bserved	31.4	14.7	0.3	0.0	4.3	49.5			151.1
N TESTS WI	Rate Coal				llowed by	ABLE 3 ALCULATED	0	Volatile	Inous	Calculatec	26.2	11.0	0.1*	0.0*	4.1	58.6			120.0
<b>SIFICATIO</b>	Air Feed F (scfm	1.85	1.85	1.85 1.60	number fo	TI VED AND CI	Daid	Medium-	BITUM	0bserved (	28.7	6°.	0.0	0.0	4.8	57.3			122.7
ONS FOR GA	Melt Tempera- ture (oF)	1791	1773	1740 1781	STM class	N OF OBSER		cite		alculated	28.9	8.0	0.1*	0.0*	2.6	60.4			120.3
ST CONDITI	Rank Number*	te 1-2	ous 2-2 ile	2-5 4-1	hows the A	COMPARISC		Anthra		Observed C	29.9	9.3	0.3	0.0	2.9	58.6			129.0
TE	Coal	Honghei Anthraci Daidoo Medium-	Volatile Bitumin Miike High-Volat	Bituminous Texas Lignite	*The rank number s than 1-2, etc.				1		8	H2	CH4	C2H6	C02	No	Hīgher Heating	Value	(Btu/scf)

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\*Arbitrarily assumed values

TABLE 2

are shown in Table 3.\* The agreement between the observed and calculated values is, in general, quite good.

In general, the heating value of the product gas increases as the percent theoretical air decreases. This can be seen in Table 1, where in the case of anthracite and medium volatile bituminous coals, a product gas resulted with an HHV of about 125 Btu/scf at about 45%theoretical air, and the high-volatile bituminous and lignite coals resulted in a product gas with an HHV of about 150 Btu/scf at about 32% theoretical air. However, there are practical lower limits as to the percent theoretical air which should be used. If the percent theoretical air is too low, there will not be sufficient oxygen to gasify all the carbon and the carbon content of the melt will become excessive. This is most pronounced with high rank coals such as anthracite. In addition, if the percent theoretical air is too low there will be insufficient heat released to the melt to sustain the operating temperature. This is most pronounced in the low rank coals such as lignite which contain a considerable amount of combined oxygen and moisture. Thus, there is a practical limit to the heating value that can be obtained for the product gas.

No sulfur-containing gases (detection limit = 10 ppm) were detected in the product gas. Any  $H_2S$  formed during gasification reacts with the melt as follows:

$$H_{2}S + Na_{2}CO_{3} + Na_{2}S + H_{2}O + CO_{2}$$
. ...(2)

The  $NO_X$  concentrations in the product gas were 30 to 40 ppm. These relatively low values are expected since at these low temperatures for gasification little  $NO_X$  is formed as a result of fixation of nitrogen by oxygen.

# 2. Gasification of Coal With Oxygen and Steam

Tests were carried out in which Kentucky No. 9 coal was gasified with oxygen and steam. The steam serves as a source of hydrogen and moderates the exothermic reaction with oxygen to control the temperature of the molten salt. Typical test conditions and results are shown in Table 4. As expected, the heating value of the product gas is much higher when steam-oxygen is used than when air is used since the product gas is now not diluted with nitrogen. Again, the results agreed quite well with those predicted on the basis of mass balances and thermodynamic equilibria of the water-gas shift. In these tests, H<sub>2</sub>S emissions were observed (100 to 200 ppm). This is due to the much higher water content of the product gas which slightly reversed reaction (2).

<sup>\*</sup>In these calculations, the methane composition in the product gas was arbitrarily assumed to be 0.1% in all cases, except lignite where it was assumed to be 0.9%

	Test	Cond	itions		
Coal (1b/h) Oxygen (1b/h) Steam (1b/h)	7.70 4.26 0.93	Oxyg Stea Temp	gen/Coal am /Coal perature	(1b/1b) (1b/1b) (ºF)	0.55 0.12 1720
	Gas (vol	Compos %, dry	sition y basis)		
C0 H2 CH <sub>4</sub> C <sub>2</sub> H <sub>6</sub>	55. 33. 2. 0.	5 1 0 4	C02 N2 02	8.2 0.6 0.2	

TABLE 4 GASIFICATION OF KENTUCKY NO. 9 COAL WITH OXYGEN AND STEAM

Higher Heating Value (Btu/scf) = 313

Nevertheless, even in this case 98 to 99% of the sulfur in the coal remained in the melt.

# 3. Effect of Other Variables on the Product Gas Obtained From Gasification of Coal With Air

Extensive testing was performed on Kentucky No. 9 bituminous coal. These tests included the study of the effect of the air/coal ratio, melt temperature, and coal particle size.

The effect of air/coal ratio on the higher heating value of the product gas was studied. As expected, the heating value of the product gas increased as the air/coal ratio decreased. For example, the higher heating values of the product gas were 36, 118, 138, and 151 Btu/scf at 77, 55, 44, and 39 scf of air per pound of coal, respectively. As explained earlier, there is a practical limit to the heating value of the product gas. The practical limit for this coal is probably about 140 Btu/scf.

The effect of melt temperature ( $1600 \text{ vs } 1800^{\circ}\text{F}$ ) on the product gas composition was quite small, just as in the case of oxygen-steam gasification. This is not surprising since the temperature effect of the water-gas shift reaction is small. Increasing the coal particle size from 275 to 950 microns had little or no effect on the product gas composition. However, the increase in coal particle size resulted in less bed expansion and in fewer carbon particles in the off-gas.

# 4. Kinetics of Coal Gasification

A certain amount of time was required for the heating value of the gas to reach a high value (e.g., >100 Btu/scf); this time was different for coals of different rank. A plot of product gas heating value vs cumulative run time is shown for the four coals in Figure 4. It can be seen that the time for the product gas to reach a high value (100 Btu/scf) decreased with decreasing coal rank. In the case of anthracite and the medium-volatile bituminous coal, the times were about 2 h and 1/2 h, respectively. The product gases of the lignite and the high-volatile bituminous coals both had initial heating values in excess of 100 Btu/scf with the lignite initially producing somewhat richer gas than the high-volatile bituminous coal. During the early stages of an experiment when the product gas heating value was increasing, it was found that the CO<sub>2</sub> concentration was initially very high and continued to decrease while the CO concentration was very low and continued to increase. It was also found that the carbon content of the melt increased with time. This effect is shown for the case of anthracite in Figure 5. This suggests that conversion of carbon to CO<sub>2</sub> is the primary step; reduction of CO<sub>2</sub> to CO by carbon in the melt is a secondary step.

Primary Step $C + U_0 \rightarrow UU_0$ (3)	),(3)	$C + 0_2 \rightarrow C0_2$	Primary Step
---	-------	----------------------------	--------------

Secondary Step 
$$CO_2 + C \rightarrow 2CO$$
 . ...(4)

The steady-state carbon contents of the melt are shown for the four coals in Table 5. The steady-state carbon content for lignite is only 0.3 wt % in contrast to 12% for anthracite. Thus, the lower the rank of the coal being gasified, the more reactive the carbon and the less free carbon in the bed necessary to promote CO production; hence, the time required to achieve steady state is shorter with lower rank coal.

### TABLE 5

STEADY-STATE	CARBON	CONTENT	0F	MFLT	
STERET STREET	0/11/00/1	OONTENT	0.	11661	

Coal	Rank Number*	Steady-State Carbon Content of Melt (wt %)
Lignite	4-1	0.3
High-Volatile Bituminous Coal	2-5	2.4
Medium-Volatile Bituminous Coal	2-2	3.6
Anthracite	1-2	12.0

\*The rank number shows the ASTM class number followed by the group number. In Class I, 1-1 is higher rank than 1-2, etc.



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### DEVELOPMENT OF SULFUR-TOLERANT COMPONENTS FOR THE MOLTEN CARBONATE FUEL CELL

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# ABSTRACT

The sulfur tolerance of candidate anode and anode current collector materials for the molten carbonate fuel cell were evaluated in an electrochemical half-cell using both steady-state and transient potentiostatic techniques. H<sub>2</sub>S was introduced into the fuel at concentrations of 50 and 1000 ppm. At the higher sulfur concentration using low-Btu fuel, both nickel and cobalt were observed to undergo a negative shift in their open-circuit potentials, and high anodic and cathodic currents were observed compared with clean fuels. Kinetic currents measured using the transient potentiostatic technique were not greatly affected by 50 ppm H<sub>2</sub>S introduced into the fuel. However at higher sulfur concentrations, higher kinetic currents were observed, indicating a probable sulfidation reaction. Of the new anode materials evaluated Mg<sub>0.05</sub>La<sub>0.95</sub>CrO<sub>3</sub> and TiC showed good stability in the anodic region. With the former material, exchange current densities in low-Btu fuel were calculated to be  $\simeq$  11 mA/cm<sup>2</sup> at 650°C, lower values than found for either nickel or cobalt anodes under similar conditions.

Of the anode current collector materials evaluated, high stabilities were found for 410 and 310 stainless steels. The implications and relevance of these results on fuel cell performance is discussed here.

### INTRODUCTION

The essential components which comprise the molten carbonate fuel cell are a porous anode and a porous nickel oxide cathode, which are separated by an ionically conducting molten carbonate mixture supported on a lithium aluminate matrix, both components together being commonly referred to as the tile. To date, these fuel cell components have shown good electrochemical performance and corrosion stability under cell operating conditions over several thousand hours in the absence of sulfur-containing species in the fuel and oxidant. However, commercialization of this system for electric utility power plants will dictate that the fuel cell will operate on fuel oils in the short term and on the products of coal gasification in the longer term, all of which can be expected to contain sulfur. Two general approaches can be followed towards solution of the sulfur problem in the molten carbonate fuel cell: The first approach is to completely remove the sulfur contaminants from the fuel cell before entry into the fuel cell anode. The second approach is to determine the sulfur tolerance of currently used cell components. Then, when degradation in cell performance and materials stability becomes evident, the next step is to identify, characterize, and develop sulfur-tolerant components that show acceptable long-term electrochemical performance under defined sulfur concentrations within the overall system. It is the second of these two approaches which will be discussed here. Previous literature(1) has indicated that the catalytic activity of nickel may be poisoned because of the  $H_2S$  chemisorption at the temperatures present in the molten carbonate fuel cell ( $\simeq 650$ °C), which may result in the formation of nickel sulfide(1) at the porous nickel anode, possibly resulting in a loss of structural integrity and electrocatalytic activity(2,3).

No work has been reported on the corrosion of nickel by sulfide or sulfate while in the presence of molten carbonate under those conditions present in the molten carbonate fuel cell. Most work reported to date has focused on nickel in contact with various sulfurcontaining gases. For example, the corrosion rate of nickel either in pure SO<sub>2</sub> or in SO<sub>2</sub>/O<sub>2</sub> mixtures has shown parabolic gravimetric kinetics, which can result in the growth of external NiO and internal Ni<sub>3</sub>S<sub>2</sub> scales and at temperatures above 645°C the Ni<sub>3</sub>S<sub>2</sub> in contact with nickel becoming liquid. There has been some evidence for the growth of an inner Ni<sub>3</sub>S<sub>2</sub> layer within nickel(4) via diffusion of SO<sub>2</sub> through open chaunels or crevices in the initial oxide layer. The overall rate of this process is probably diffusion of nickel through the Ni<sub>3</sub>S<sub>2</sub> phase in the nickel oxide matrix.

Large-scale molten carbonate fuel cells will require the implementation of a catalytic burner between the anode outlet and the cathode inlet for  $CO_2$  management for the maintainence of the desired electrochemical process. This requirement will introduce sulfur to the cathode originating from the anode inlet which, under the oxidizing conditions present there, will occur as  $SO_2$  and can be expected to readily absorb into the molten carbonate mixture present both at the porous nickel oxide cathode and within the tile by the equilibrium reaction -

 $M_2CO_3 + SO_2 + 1/2 O_2 \rightarrow M_2SO_4 + CO_2$ 

which can be expected to strongly favor the formation of the alkali metal sulfate. The concentration of sulfur species at the anode may possibly be influenced by electrochemical transport of sulfur species (initially present as sulfate) from the sulfur-contaminated cathode and may well have an impact on the long-term stability of the anode.

The emphasis of the work reported here is on electrochemical halfcell measurements on presently used anode and anode current collector materials with both clean and sulfur-containing fuels. By this means, the effect of such sulfur-containing species on their chemical stability and electrode kinetics can be evaluated. The initial selection of candidate sulfur-tolerant components for the molten carbonate fuel cell included materials which had previously shown evidence of extended stability when used in applications such as methanation catalysis, positive electrode current collector components of high-temperature metal/sulfur batteries and interconnect materials used in solidoxide fuel cells. The latter materials, which included Mg<sub>0.05</sub>La<sub>0.95</sub>CrO<sub>3</sub>, were of particular interest because they had shown previous high stability to both oxidizing and reducing conditions in the hightemperature solid oxide fuel cell. These materials were initially subjected to preliminary corrosion testing by simulating those chemical conditions expected in the anode environment of the system. Materials evaluated as sulfur-tolerant anodes in the electrochemical half-cell have included nickel, cobalt, CoMo, CoW, WC, TiC, Mg<sub>0.05</sub> La<sub>0.95</sub> CrO<sub>3</sub>,  $Cr_2O_3$  (doped with TiO<sub>2</sub>), and NbN. Materials for the anode current collector have included hastelloys, kanthal, 400 and 300 stainless steels, and iron aluminum manganese and iron aluminum molybdenum alloys. The relative stabilities of these materials at the anode and anode current collectors for the molten carbonate fuel cell and a comparison of the electrocatalytic behavior of the candidate anodes selected will be discussed.

### EXPERIMENTAL

The initial corrosion screening of selected candidates was performed by partially immersing in a lithium/potassium carbonate mixture at 650 °C contained in ceramic boats within an alumina tube, through which was equilibrated on different occasions both clean and sulfur-containing fuel gas.

Materials for the anode and anode current collectors were obtained from commercial sources (Materials Research Corporation, Orangeburg, New York and CERAC, Inc., Milwaukee, Wisconsin). All electrochemical measurements were performed in a half-cell system. The working electrodes were attached to an alumina-sheathed current collector fabricated from 316 stainless steel wire. For nickel and cobalt, however, the current collectors were made from nickel and cobalt, respectively. A gold wire bubbled with 33.3%  $O_2$ -66.7%  $CO_2$  inside an alumina tube served as a reference electrode. The gold was in contact with the melt via a small hole (0.015-inch diameter) at the bottom of the tube. All measurements were performed in electrolyte of composition 62 mole percent Li<sub>2</sub>CO<sub>3</sub>-38 mole percent K<sub>2</sub>CO<sub>3</sub> at 650°C. The counter electrode used in this work consisted of Palau of nominal composition 80% Au, 20% Pd, which proved to have a higher sulfur tolerance than a pure gold counter electrode, the usual material used by us when clean fuels are used in electrochemical half-cell work. Fuels with a predetermined high-sulfur content or pure  $H_2S$  were mixed into the primary fuel after the humidification step at the rate required to achieve the desired sulfur content. Experimental observations in this work indicated some apparent sensitivity of the open-circuit potential obtained at both nickel and cobalt electrodes to the presence of  $H_2S$  introduced into the fuel gas. At concentrations of 50 ppm and below, such variations in the open-circuit potential were found to be somewhat erratic and were not completely reproducible. Apart from some variations in the open-circuit potential, steady-state polarization curves for clean fuel and fuel containing 50 ppm H<sub>2</sub>S were of almost identical slope, indicating little evidence of electrode poisoning. Polarization data were performed in both low- and high-Btu fuels corresponding to the respective compositions 21.4%  $\rm H_2$ , 17.7% CO, 9.2% CO\_2, 1.1% CH\_4, 45%  $\rm N_2$ , 5.6%  $\rm H_20;$  and 68.1%  $\rm H_2$ , 23.4% CO, 3.39% CO\_2, and 5.03%  $\rm H_20.$  Emphasis on this work was placed, however, on the low-Btu fuels corresponding to coal gasification.

The potential of the working electrode was controlled by a Wenking-Model 66TSI potentiostat. Steady-state currents were recorded on a Hewlett-Packard 7046A X-Y recorder. To eliminate errors caused by mass-transfer effects, transient potentiostatic techniques were employed using a Wenking ST72 potentiostat. This instrument has a risetime of about 7  $\mu$ s when a step voltage is applied. A Tacussel type GSTP2B pulse-sweep generator was used to control this potentiostat with the output voltage being monitored with a Fluke Type 8020A digital voltmeter. Signals from the transient techniques were displayed and photographed on a Tektronix Type 547 oscilloscope. The recordings were performed with a pinderg Hevi-Duty BPC Type 59344 temperature control was used to heat the half-cell. The temperature of the melt was monitored with an alumina-sheathed chromel-alumel thermocouple.

# RESULTS AND DISCUSSION

To determine the effect of sulfur-containing fuels on the electrochemical performance of nickel and cobalt anodes, both steady-state and potential-step type measurements were performed in an electrochemical half-cell. Steady-state techniques were used to identify the enhanced currents caused by anodic sulfidation reactions and changes that may occur in the open-circuit potential as a result of such reactions. Figures 1 and 2 compare steady-state polarization curves for nickel and cobalt anodes in low-Btu fuel with and without 50 ppm  $H_2S$ . In both cases, introduction of sulfur as  $H_2S$  into the fuel was observed to perturb the open-circuit potential.

In the case of nickel (Figure 1) the shift was 15 mV positive of the initial -1154 mV open-circuit potential, whereas in the case of cobalt (Figure 2), the shift was very slightly in the cathodic direction by around 7 mV. Other than these minor shifts in the open-circuit potential, the current voltage characteristics are very similar in each case.

In the fuel cell, sulfur can be expected to enter the cathode as  $SO_2$  where it will form sulfate. It would then be available for migration to the anode, where it could be reduced to sulfide species under the reducing conditions present. This could result in locally high accumulations of sulfide in the proximity of the anode. Consequently, H<sub>2</sub>S introduced at concentrations of around 50 ppm with low-Btu fuel in the half-cell may not simulate the local high-sulfur content that may occur in the real fuel cell. This was probably responsible for the erratic open-circuit potential readings obtained at both nickel and cobalt anodes, which may be speculated to be either a mixed potential effect caused by the formation of possible metal sulfide species on such anodes or due to some subtle changes in the fuel composition from one measurement to another.

The effect of higher sulfur concentrations on both the opencircuit potential and electrochemistry of nickel and cobalt anodes was evaluated using H<sub>2</sub>S concentrations of approximately 1000 ppm. Steadystate polarization data on nickel and cobalt anodes in low-Btu fuel containing around 1000 ppm  $H_2S$  gave significantly enhanced anodic currents compared to clean fuel or that containing 50 ppm  $H_2S$ . Upon removal from the half-cell, evidence of extensive sulfidation on each of these electrodes was observed as shown in Figure 3. In each case, the open-circuit potential was observed to be shifted to more negative values, possibly indicating a mixed-potential effect caused by the fuel oxidation reaction and the presence of metal sulfide on the anode surface. For nickel at 650°C (in low-Btu fuel), the open-circuit potential was shifted from -1154 to -1185 mV and for cobalt the shift was -1160 mV to -1200 mV. Clearly, neither of these two anode materials can be expected to be stable at such high-sulfur levels.

Potential step techniques were used to compare electrode kinetics in clean and sulfur-containing fuel. With the electrochemical conditions present in the half-cell, the rate of the overall electrochemical reaction was found to be dependent upon not only fuel bubbling rate, but also on the voltage sweep rate used. Such observations indicated diffusion or mixed control. To assess the impact of introducing sulfur species into the electrolyte from the fuel, it was of interest therefore to compare the electrode kinetics for both nickel and cobalt with clean and sulfur-containing fuels to indicate if any electrocatalytic poisoning effects occurred by the introduction of such sulfur impurities. Transient potentiostatic measurements(5,6) were performed for the separation of kinetic data under the probable mixed control condition present in the half-cell. This technique involved applying a voltage step to the nickel or cobalt working electrode and recording the current as a function of time. Under such conditions of mixed or diffusion control, the assumption was made that at time zero, only activation control will be present, that is, sufficient supply of electroactive species will be present together with minimal reaction products, so that any mass transfer effects will be minimized. Figure 4 shows a typical oscillogram for nickel with and without 50 ppm  $H_2S$  in low-Btu fuel. The kinetic current i(0) was obtained by extrapolating currents between 0.8 and 1.2 ms to time zero. Here, the exchange current density calculated from the i(0) value was found to be around 25 mA/cm<sup>2</sup> in both cases, indicating that such low levels of sulfur (50 ppm  $H_2S$ ) appear to have little effect upon the electrode kinetics for fuel oxidation, in essential agreement with the steadystate data.

A series of progressively more anodic and cathodic potential steps were applied to both nickel and cobalt in fuel with and without 50 ppm  $H_2S$  introduced into low-Btu fuel at 650°C. The respective activation polarization curves for these two anodes are shown in Figures 5 and 6, where they are compared with such data obtained using clean fuel. As was indicated earlier, 50 ppm H<sub>2</sub>S does not appear to drastically poison the electrode kinetics for either the anodic or cathodic processes, although some small lowering in electrode activity does become apparent at higher applied overpotentials. Upon introduction of 50 ppm  $H_2S$ , the exchange current density was observed to become slightly lower, reducing from 26 to 25 mA/cm<sup>2</sup>, and from 19.5 to 18.5 mA/cm<sup>2</sup>, respectively, for nickel and cobalt, although such small variations in kinetic data can be considered to be well within the experimental error of this work. When potential step techniques are performed on these anode materials in fuel containing 1000 ppm H<sub>2</sub>S anodic and cathodic currents appear to be dominated by the sulfidation reaction.

On the basis of this data, when high sulfide concentrations build up in the proximity of the anode, either directly from sulfurcontaining fuel or indirectly from  $SO_2$  introduced into the cathode, neither nickel or cobalt appear to be viable candidates. Considerable incentive exits to identify potentially sulfur-tolerant anode materials for this fuel cell system.

Preliminary corrosion results for selected sulfur-tolerant candidate anodes are shown in Table 1. Materials which showed apparent stability in this corrosion test were then subjected to steady-state potentiostatic polarization evaluation in the electrochemical halfcell. These results are summarized in Table 2 where open-circuit potentials and anodic currents at 50 mV overpotential are compared.

Apart from nickel and cobalt anodes, which have already been discussed, highest stabilities were found for  $Mg_{0.05}La_{0.95}CrO_3$  and TiC.

Figure 7 compares steady-state polarization data on  $Mg_{0.05}La_{0.95}CrO_3$ in low-Btu fuel with and without 50 ppm H<sub>2</sub>S. No shift in the opencircuit potential was observed, and current voltage characteristics were very similar in both cases, particularly in the anodic region. Introduction of fuel containing 1000 ppm of H<sub>2</sub>S did not shift the open-circuit potential to negative values as observed with nickel and cobalt anodes. Examination of this material afterwards indicated no surface corrosion even after prolonged anodic potentiostatting.

Figure 8 compares activation data performed on this material using the potential step technique with that obtained for nickel. For  $Mg_{0.05}La_{0.95}CrO_3$  exchange current densities of around 8 mA/cm<sup>2</sup> were obtained in low-Btu fuel. Although considerably faster kinetics can be observed with the nickel anode, the exchange current density at the  $Mg_{0.05}La_{0.95}CrO_3$  electrode is still rapid enough to expect mass transfer control for the fuel oxidation process.

Consequently from the kinetic data and apparently high-sulfur tolerance of  $Mg_{0.05}La_{0.95}CrO_3$ , this material is an interesting candidate for a sulfur-tolerant anode. However, comparison of steady-state potentiostatic data obtained with  $Mg_{0.05}La_{0.95}CrO_3$  and nickel in clean electrolyte showed lower currents for the chromite. Because both electrodes exhibited rapid electrode kinetics, the smaller currents observed with  $Mg_{0.05}La_{0.95}CrO_3$  in comparison with nickel may be due either to more local hinderance by the diffusion of reaction products away from the electrode surface or caused by differences in the electrolyte stirring rates in the two experiments.

Steady-state polarization measurements have been respectively performed on TiC,  $Cr_2O_3$  (1 mole percent of TiO<sub>2</sub>), WCo (W - 75.7%, Co - 24.3%), nichrome (80% Ni, 20% Cr), and NiAl all in the lithium/ potassium carbonate electrolyte at 650°C in low-Btu fuel. Upon examination of all of these materials, evidence of surface corrosion became evident. Candidate anode current collector materials were subjected to an initial screening conversion test as described previously for the selected anodes. The materials selected, together with the corrosion results, are shown in Table 3. From these results, good corrosion stability was found for 446 and 310 stainless steels, together with Uniloy. More promising materials were subjected to steady-state potentiostatic evaluation. Figure 9 shows the steadystate current voltage characteristics obtained with 446 stainless steel. The results of such potentiostatic testing for the selected anode current collector materials are summarized in Table 4. Materials were anodically potentiostatted at 75 mV in low-Btu fuel with and without  $H_2S$  and the currents recorded as a function of time. A decay in current with time was taken as indicative of surface oxide formation as shown in Figure 10 for 446 stainless steel. Of those materials evaluated, high stabilities were found for 410 and 310 stainless steels. Open-circuit potentials found for the stainless

steels in low-Btu fuel were fairly close to those expected; nevertheless some of the other candidates that readily corroded showed somewhat more cathodic potentials.

### CONCLUSION

At low-sulfur concentrations ( $\pm$  50 ppm) the electrode kinetics for fuel oxidation on both nickel and cobalt anodes do not appear to be poisoned. At high-sulfur concentrations ( $\pm$  1000 ppm) shifts in the open-circuit potential of both these materials occurred together with evidence of sulfidation.

Promising anode materials which may show long-term sulfur tolerance include  $Mg_{0.05}La_{0.95}CrO_3$  and TiC. However, their long-term performance as porous sintered anodes has yet to be evaluated. Anode current collectors showing high stability have been found to include 410 and 310 stainless steels.

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Table 1. CORROSION RESULTS FOR CANDIDATE ANODE MATERIALS

Comments		Completely corroded.	Completely corroded.	Completely corroded.												Completely corroded.	Completely corroded.	Completely corroded.	Completely corroded.			Sample broken.		Completely corroded.	Completely corroded.		Completely corroded.	Completely corroded.	Completely corroded.	•		Completely corroded.	Completely corroded.	Completely corroded.	Cample broken
Total Weight Change, %	- 3.3	1	ł	ł	- 1.0	-24.7	+10.1	+ 0.1	+ 0.7	- 1.1	-32.4	-27.8	-53.2	6.0 -	-48.5		1		!	+13.7	+ 0.3	+ 7.0	-44.7	ł	ł	+ 3.5	1	1	1	+25.9	+ 0.9	1	I	!	-27.0
Period in H <sub>2</sub> S (274 ppm), hr	1301	1122	432	none	1051	187	1051	1051	1080	1080	1080	1554	432	1554	432	648	648	648	1122	1122	1122	1122	1122	1122	474	474	474	474	474	474	474	474	474	648	648
Total Exposure to Low-Btu Fuel, hr	1588	1122	432	168	1506	355	1506	1506	1343	1343	1080	1554	432	1554	432	648	648	648	1122	1122	1122	1122	1122	1122	474	474	474	474	474	474	474	474	474	648	648
Composition, %	WC-10; C0-90	TaC	TIB2	ZrC	TIC	VC	NbN	Mg 0.05La 0.95CrO3	TiO <sub>2</sub> (Ta-doped)	T102 (Nb-doped)	Mo-90; T1-10	Co-64.8; Mo-35.2	Co-38.1; Mo-61.9	Nickel	Fe-90.0 Cr-9.0; Mo-1.0	Cr-30.6; Co-69.4	Co-49; 51-W	Co-24.3; 75.7-W	Co-63.0; Cr-30.0; Mo-7.0	Co-22.1; Cr-77.9	Cobalt	$Cr_2O_3(1 mole TiO_2)$	Tungsten	Molybdenum	FeB	N1-50; Co-50	CoPS	WS <sub>2</sub>	CoP <sub>3</sub>	N1-50; A1-50	CoAs <sub>2</sub>	MoS <sub>2</sub>	Cr <sub>3</sub> Co <sub>2</sub>	WC	MnS

	Clean	Fuel	Fuel with	50 ppm H <sub>2</sub> S	
Composition, %	Open Circuit Potential, mV	Current i (at 50 mV from rest potential) mA/cm <sup>2</sup>	Open Circuit Potential, mV	Current 1 (at 50 mV from rest potential) mA/cm <sup>2</sup>	Comments
≿z03-99; T102-1 Hackel-S0; Cobalt-50 Nungsten Carbide	-1032 -1138 -1368	0.122 0.383 2.918	-1102 1305	0.202 1.134	Electroúe badly cracked. Trace of Current very noisy. Indicates corrosion;
lungsten Cobalt	-1402	2.299			not run cathodically. Electrode Corroded;
ltanium Carbide 18 0.05La0.95CrO3	-1142* -1130	0.166* 0.040		0.167 0.041	NOE FUN IN $H_2S$ .
11-50; A1-50 102 (Ta doped)	-1160	0.918	-1106**	0.157**	Electrode corroded; not run 1n H <sub>2</sub> S.
102 (Nb doped) iickel iickal	-1154	0.114 0.250	-1134** -1141 -1185**	0.105** 0.193 17 51**	Very large cathodic current.
obalt obalt	-1158	0.304	-1163 1201 <b>*</b> *	0.304 8 4.7 **	
lobium Nitride	-1104	0.493	1011		Indicates corrosion;
hromium-77.9; Cobalt-22.1 :0482	-1290 -1136	0.0 0.32			not run in H <sub>2</sub> S. No anodic current.

# Table 2. POTENTIOSTATIC EVALUATION OF ANODE MATERIALS USING LOW-BTU FUEL GAS IN BINARY CARBONATE MELT AT 650°C

High-Btu fuel.

\*

\*\* ~1000 ppm H<sub>2</sub>S.

Table 3. CORROSION RESULTS FOR CANDIDATE ANODE CURRENT COLLECTOR MATERIALS

	Total	Period		
	Exposure	in H <sub>2</sub> S	Total	
t	to Low-Btu	(274 ppm),	Weight	
Composition, %	Fuel, hr	hr	Change, %	Comments
P-0 25: Mn-2 0: 04-1 5: P-26 0:				
N1-ZU; Fe-51.Z5 (SS-310)	1588	1301	+ 0.2	
Cr-50.0; N1-49.0; T1-1.0 (UNILOY)	1588	1301	+ 0.5	
Co-50.0; Cr-28.0; Fe-16.5; W-5.5	355	187	-20.3	
Fe-81.8; Al-15; Mo-3.2 (VE-441)	648	648	+82.9	
Cr-21.0; Mn-9.0; Ni-6.0; Fe-64	1588	1301	+ 0.5	
Fe-70; Al-10; Mn-20 (EX-20)	648	648	+26.7	
C-0.2; Cr-25.0; Ni-0.5; Fe-74.3 (SS-446)	1588	1301	+ 0.6	
Cr-22.0; Co-0.5; Al-5.0; Fe-73.5 (KANTHAL)	) 258	258	ł	Completely corroded.
C-0.15; Mn-2.0; S1-1.0; P-0.2; S-0.15;				
Cr-18.0; Ni-9.0; Mo-0.6; Fe-Bal.				
(SS-303)	1554	1554	- 5.3	
2-0.08; Cr-17.0; Ni-12; Mo-3.0;				
Fe-Bal. (SS-316)	1554	1554	+ 2.2	

MATERIALS	
COLLECTOR	AT 650°C
CURRENT	NATE MELT
F ANODE	Y CARBO
EVALUATION 01	GAS IN BINAR
OTENTIOSTATIC	LOW-BTU FUEL
e 4. P	USING
[ab]∢	

	Clear	ı Fuel	Fuel with	50 ppm H <sub>2</sub> S	
		Current 1 (at		Current i (at	
	<b>Open Circuit</b>	50 mV from rest	Open Circuit	50 mV from rest	
Composition, % 1	Potential, mV	potential) mA/cm <sup>2</sup>	Potential, mV	potential) mA/cm <sup>2</sup>	2 Comments
C-0.2; Cr-25.0; N1-0.5; Fe-74.3 (SS 446)	-1182	0.128	-1137	0.147	
C-0.25; Mn-2.0; S1-1.5; Cr-25.0; N1-20;					
Fe-51.25 (SS 310)	-1186	0.063	-1145	0.089	Black coating after test
C-0.08; Cr-17.0; NI-120; Mo-3.0;					
FeBal (SS 316)	-1173	0.156	-1164	0.197	Black coating after test
C-0.15: Mn-1.0; S1-1.0; Cr-12.5;					
FeBal (SS 410)	-1173	0.184	-1148	0.157	
C-0.15; Mn-1.0; Si-1.0; Ni-45.45;					
Fe-18.5; Cr-21.8; Co-2.5; Mo-9.0;					
W-0.6 (Hastalloy X)	-1167	0.236	-1147	0.207	
N1-80.0; Cr-20.0 (nichrome)	-1257	3.508			Corroded
Cr-22.0; Co-0.5; Al-5.0; Fe-73.5 (Kanthal	1)	0'0			Corroded
Fe-70; A1-10; Mn-20 (Ex 20)	-1347	0.218	-1222	0.911	
Fe-81.8; A1-15.0; Mo-3.2 (VE 441)	-1382	0.413			Crusted with thick
					black oxide.

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P78082503

# Figure 3. ANODES FROM ELECTROCHEMICAL HALF-CELL AFTER POTENTIOSTATTING IN Li/K CARBONATE MELT IN LOW-Btu FUEL CONTAINING 1000 ppm H<sub>2</sub>S AT 650°C



P78082505









Figure 7. STEADY-STATE POLARIZATION CURVE FOR Mg<sub>0.05</sub>La<sub>0.95</sub>CrO<sub>3</sub> USING LOW-Btu FUEL WITH AND WITHOUT 50 ppm H<sub>2</sub>S ADDED (Li/K Electrolyte, 650°C)







A78072282







### INFLUENCE OF ELECTROLYTE COMPOSITION ON ELECTRODE KINETICS IN THE MOLTEN CARBONATE FUEL CELL

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### ABSTRACT

Electrode kinetics for fuel oxidation on nickel and cobalt electrodes is discussed for three selected molten carbonate mixtures. Activation kinetics under the probable mixed-control conditions present in the electrochemical half-cell were determined using a potential step technique. With all melts, the highest exchange current values were found on nickel anodes, and the highest of these values were found for the melt comprised of 43.5 mole percent  $\text{Li}_2\text{CO}_3$ -31.5 mole percent  $\text{Na}_2\text{CO}_3$ -25 mole percent  $\text{K}_2\text{CO}_3$ . For this ternary melt the exchange current density on nickel varied from 78 mA/cm<sup>2</sup> for intermediate-Btu fuel to 22 mA/cm<sup>2</sup> for low-Btu fuel at 650°C. The exchange current density was found to have a reaction order of around 0.25 for hydrogen, carbon dioxide, and water. Electrochemical performance on the two anode materials in the three melts is discussed, and a tentative reaction mechanism for the oxidation reaction is suggested.

### INTRODUCTION

Little work has been previously reported on the dependency of electrode kinetics in the molten carbonate fuel cell on the electrolyte composition present in the tile.

Several factors must be considered in the selection of a molten carbonate mixture supported on the lithium-aluminate  $(\text{LiAlO}_2)$  matrix of the tile. These factors are a) ionic conductivity, b) solubility of reactants and reaction products, c) the diffusion coefficients of reactants and products, d) the rate of the electrochemical anodic and cathodic reactions, e) electrolyte vapor pressure, and f) stability of the lithium-aluminate matrix with each selected molten carbonate mixture. Electrolyte vaporization losses appear to be related to the hydroxide content in the molten carbonate mixture, with the highest concentrations occurring in lithium carbonate.<sup>1</sup> Projected electrolyte tile lifetimes have already been reported.<sup>2</sup> Reactant-gas solubility has generally been found to decrease with the increasing fraction of lithium carbonate. Maximum solubilities have been found with ternary mixtures rich in K<sub>2</sub>CO<sub>3</sub> and lean in Li<sub>2</sub>CO<sub>3</sub>.<sup>3</sup>

To date, little work has been reported on the effect of molten carbonate composition on the electrochemical performance of the molten carbonate fuel cell, using representative electrode materials. The electrode kinetics, particularly for the hydrogen-oxidation reaction,

have not been quantified to this time. It has also been difficult to correlate experimental data performed in electrochemical half-cells with conditions present at the porous electrode of a fuel cell because the relative contribution to cell polarization from diffusional effects of either reaction or reaction products will be expected to differ in each case. The small amount of data available on electrode kinetics for the hydrogen-oxidation reaction has been of a somewhat preliminary nature.<sup>2</sup> Polarization data to date for hydrogen oxidation has indicated little effect because of the nature of the metal, 4 indicating rapid activation kinetics for the anodic reaction with a probable strong dependency of rate on diffusional effects as a consequence. Experimental evidence has indicated that polarization at such electrodes for the hydrogen-oxidation reaction in molten carbonates may be dictated more by the local build-up of reaction products  $(H_20, C0_2)$ than by diffusion of hydrogen in the melt.<sup>5</sup> Some recent work has been reported on open-circuit potential measurements for hydrogen dissolved in lithium-carbonate/potassium-carbonate melts on gold electrodes<sup>6</sup> in which reasonable agreement was found between calculated and experimental thermodynamic values. Some half-cell work has already been reported for hydrogen oxidation on fully immersed<sup>7,8</sup> and partially submerged anodes in molten carbonate melts. 9,10 This latter work has shown that diffusion of reactants through the thin-film electrolyte meniscus plays a significant role in the overall rate of the anodic reaction. From chronopotentiometric measurements performed in a lithium-sodium carbonate melt, using a completely immersed smooth platinum electrode, diffusion control of the anodic process was indicated.<sup>11</sup>

Until this time, very little has been reported on the activation kinetics for the hydrogen-oxidation reaction on a nickel or cobalt electrode in molten carbonate melts. As will be discussed later, this requires the application of techniques that will enable effective separation of activation kinetics from the diffusion-control conditions that have been shown to exist in the electrochemical half-cell. The majority of electrode kinetic work in the area of molten carbonate melts has focused on oxygen reduction at gold electrodes, fully immersed in lithium-carbonate, sodium-carbonate, and potassium-carbonate electrolytes.  $^{12 \cdot 13}$  This work concluded that the exchange current density for the oxygen-reduction reaction was closely dependent on the partial pressures of CO<sub>2</sub> and O<sub>2</sub> to the respective powers of (CO<sub>2</sub> pressure) $^{-5/4}$  and (oxygen pressure) $^{3/8}$ . These kinetic data were obtained by analysis of current voltage characteristics obtained at different sweep rates under the diffusion-controlled conditions present.

Here we will discuss activation kinetic data for fuel oxidation in three molten carbonate mixtures with a view to identifying the preferred electrolyte composition for the electrolyte tile based upon such kinetic data. Electrolyte compositions chosen for evaluation during the course of this work have included binary and ternary mixtures of alkali-metal carbonates. Work has been focused particularly on the following electrolyte compositions: 62 mole percent  $Li_2CO_3$ - 38 mole percent  $K_2CO_3(Li/K)$ , which has a high ionic conductivity and a reasonably high reactant-gas solubility; 52 mole percent  $Li_2CO_3-48$ mole percent  $Na_2CO_3$ , (Li/Na), which combines good electrolyte conductivity and a high sodium content for low vapor pressure to minimize electrolyte vaporization losses; and the ternary 43.5 mole percent  $Li_2CO_3-31.5$  mole percent  $Na_2CO_3-25$  mole percent  $K_2CO_3$  (Li/Na/K) to evaluate electrochemical performance at temperatures below 650°C.

Electrochemical techniques used in the course of this work have included linear voltage sweep, steady-state potentiostatic, and potential step<sup>14</sup> methods. The latter technique was found particularly useful for identification of kinetic current values under the diffusion-controlled conditions present in the electrochemical half-cell.

### EXPERIMENTAL

Materials for the anode nickel wire and cobalt rod were purchased from commercial sources (Materials Research Corp., Orangeburg, New York). All measurements were performed in the electrochemical halfcell. Humidification of the inlet gas was performed by passing it through a column of water in a large test tube. A gold wire bubbled with 33.3%  $O_2-66.7\%$  CO<sub>2</sub> inside an alumina tube served as a reference electrode. The wire communicated with the melt through a small hole (0.015-inch diameter) at the bottom of the tube. The potential of the working electrode was controlled by a Wenking ST72 potentiostat. The potentiostat had a risetime of about 7 µs when a step voltage was applied. A piece of round gold foil was used as the counterelectrode. The electrolyte was prepared from a mixture of Li<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>CO<sub>3</sub> (Mallinckrodt, Analytical Reagent).

A Tacussel type GSTP2B pulse-sweep generator was used to control the potentiostat. The output voltage of the Tacussel generator was monitored with a digital voltmeter (Fluke, type 8020A). Steady-state, linear voltage sweep and transient pulse techniques were used to study the current/voltage relationships of the electrode. The signals were recorded on a Hewlett-Packard 7046 X-Y recorder. Signals from the transient techniques were displayed and photographed on a Tektronix Type 547 oscilloscope. To eliminate errors caused by mass-transfer effects, the transient potentiostatic technique was used so that more precise kinetic information could be obtained. The measurements were performed with appropriate IR compensation using a feedback circuit. A Lindberg Hevi-Duty SB furnace with 3-zone temperature control was used to heat the cell. The temperature of the melt was read by an alumina-sheathed thermocouple and was displayed on a digital readout (Newport Laboratories, Inc., Model 267A-KC1-07).

### RESULTS AND DISCUSSION

Before comparative activation kinetic data could be obtained for the hydrogen-oxidation reaction, it was essential to determine whether the rate of the anodic reaction in the electrochemical half-cell was dictated by diffusion or mixed control. The first objective was to gain some qualitative insight into the relative contributions to the overall rate by activation and diffusion control under such experimental conditions.

Linear voltage sweep measurements at various sweep rates are shown in Figure 1 for a completely immersed nickel wire anode in the ternary Li/Na/K melt at 650°C under conditions of bubbling (50 ml/min). Figure 2 shows the voltage sweep measurements taken with the fuel bubbling turned off immediately prior to the linear voltage sweep. The fuel composition during the course of these measurements corresponded to intermediate-Btu fuel, that is, 40% H<sub>2</sub>, 17% CO<sub>2</sub>, 10% CO and 33% H<sub>2</sub>O. (See Table 1.) In both cases, we can see a dependency of the current density measured on the voltage sweep rate; the higher the sweep rate, the higher the observed current density. If we compare the measured current at a fixed voltage sweep rate, higher values are obtained for the melt subjected to continuous bubbling during this measurement. For example, with a sweep rate of 0.15 mV/s in the anodic direction, the current densities measured at an anodic overpotential of 20 mV are found to be 0.35 and 0.11  $mA/cm^2$  for the melt with and without continuous fuel bubbling, respectively. For the completely immersed nickel wire, the dependency of current density on both the linear voltage sweep rate and on the fuel bubbling suggests diffusion or mixed control at the anode, either of the electroactive species or the reaction products away from the reaction site.

> Table 1. FUEL GAS COMPOSITION CALCULATED FROM THE WATER-GAS SHIFT EQUILIBRIUM REACTION AT 650°C

	<u>H2</u>	C02	<u>H<sub>2</sub>0</u>	<u></u>	CH4	_N <sub>2</sub> _
High-Btu (53°C)*	60.0	7.42	22.47	10.11		
Intermediate-Btu (71°C)*	40.5	16.4	32.8	10.3	`	
Low-Btu (36°C)*	21.16	9,16	5.54	17.76	1.13	45.25
Very-low-Btu (36°C)*	11.71	5,71	4,40	7.75	0.57	69.86
High-Btu (71°C)*	53.68	8.08	31.11	7.12		

\* Number in parentheses corresponds to the humidifier temperature.

Upon potentiostatting either nickel or cobalt working electrodes at high anodic overpotentials of about 200 mV, some changes were observed in later current voltage characteristics. This is reflected in the curves in Figure 3 for nickel and in Figure 4 for cobalt, both in low-Btu fuel. These measurements were performed over the temperature range of 550° to 700°C. Generally, the higher the melt temperature the higher the recorded current was at a given overpotential. These steady-state polarization curves differ from those obtained initially on new electrodes by exhibiting rapidly increasing currents at high anodic overpotentials (~ 150 mV for nickel and ~ 100 mV for cobalt). Upon removal of the high anodic potentials, approximately 30 minutes was required to reach the initial open-circuit potential. However, if upon removal of the anodic overpotential the working electrode is potentiostatted back to its initial open-circuit potential, then large (several mA/cm<sup>2</sup>) cathodic currents were observed. It can be speculated that the sudden increase in currents at high anodic overpotentials is because of electrode surface oxidation. The oxidation potentials of nickel and cobalt are expected to be within the potential range of these experiments.

A nickel or cobalt wire that is completely immersed in a molten carbonate electrolyte may be somewhat unrepresentative of those electrochemical conditions present at a porous anode within the molten carbonate fuel cell. It is usually assumed that the porous anode is covered with a thin film of the molten carbonate mixture, and that this is the more favorable site for the anodic reaction. Linear sweep measurements were performed on a nickel wire partially submerged in the melt (approximately 50%) so that the upper half of the nickel wire surface would approximate those electrochemical conditions expected at the porous electrode, With continuous fuel bubbling, linear voltage sweep measurements were performed with sweep rates between 0.15 mV/s and 150 mV/s, and a dependency of the current density on the voltage sweep rate was again observed (Figure 5), indicating the continued presence of diffusion- or mixed-control effects at a partially submerged nickel wire. The limiting current density obtained with a sweep rate of 0.15 mV/s at an overpotential of approximately 150 mV can be seen to be at around  $3 \text{ mA/cm}^2$ . In a porous electrode where the ratio of real to apparent area can be expected to be about 400, this current density would correspond to an apparent value of  $1.2 \text{ A/cm}^2$ .

The measurement of activation kinetic parameters under the diffusion- or mixed-control conditions have been performed using transient potentiostatic techniques<sup>14</sup> on both nickel and cobalt electrodes under conditions of total and partial immersion in the candidate molten carbonate electrolytes. This technique involves applying a voltage step to the nickel or cobalt working electrode, and recording the current as a function of time. Under such conditions of mixed or diffusion control, the assumption is made that at time zero only activation control will be present; that is, sufficient supply of

electroactive species will be present, together with minimal reaction products, so that any mass-transfer effects will be minimized. A typical oscillograph obtained using this transient potentiostatic technique is shown in Figure 6. A 20 mV anodic voltage step (from the resting potential) is shown for a nickel electrode (top traces). The bottom traces show the current variations on three different time scales between 0.05 ms and 2.0 ms/div. The kinetic current, i(o), was obtained by extrapolating currents between 0.3 and 0.5 ms to time zero. Here the kinetic current is found to be 39 mA/cm<sup>2</sup> for the Li/Na/K melt at 650°C in intermediate-Btu fuel. Care was taken so that the extrapolated current values were free of interference by capacitive currents. With appropriate IR compensation the capacitive current can be clearly distinguished. Following the transient capacitive spike (Figure 6) the current can be seen to decrease because of diffusional processes.

This potential step technique has been applied to both nickel and cobalt electrodes in the three candidate molten carbonate mixtures discussed earlier. This was performed using various fuel compositions and different temperatures so that comparative kinetic data could be obtained from the three candidate melts. Extrapolated current densities at time zero i(o) were plotted versus the applied potential steps  $\eta$ . Figure 7 shows a representative activation polarization plot for nickel in the Li/Na/K ternary melt using intermediate-Btu fuel. For an activation process the current-voltage is given by the relationship —

$$\mathbf{i}(\mathbf{0}) = \mathbf{i} \left[ \mathbf{e}^{\alpha} \mathbf{A}^{\mathsf{T}} \mathbf{F} / \mathbf{R} \mathbf{T} - \mathbf{e}^{-\alpha} \mathbf{C}^{\mathsf{T}} \mathbf{F} / \mathbf{R} \mathbf{T} \right]$$
(1)

In the low overpotential region, this equation can be approximated by,

$$i(0) \simeq i_{\alpha} (\alpha_{\lambda} + \alpha_{C}) \eta F/RT$$

or,

$$i_o \simeq \frac{RT}{(\alpha_A + \alpha_C)F} \frac{di(0)}{d\eta}$$
 (2)

Thus, the exchange current density,  $i_0$ , can be calculated from the slope of the current density, i(0), versus overpotential, n, curve. We assume a value of 2 for the sum of the apparent transfer coefficients  $\alpha_A$  and  $\alpha_C$  based on a total of two electron transfer processes and a stoichiometric number 1. For the specific case above  $i_0$  was calculated using Equation 2 to be 78 mA/cm<sup>2</sup> for a nickel electrode. This potential step technique was applied to electrodes that were both fully and partially immersed in molten carbonate mixtures. Under each experimental condition, the extrapolated current densities were in good agreement with values obtained from fully immersed electrodes, lending good support to the validity of this technique for separating

activation kinetic data under the diffusion- or mixed-control conditions present.

Exchange current density values were also obtained from Allen-Hickling plots of the potential step data. For the Allen-Hickling plot, Equation 1 can be rewritten as -

$$\log \frac{i}{e^{(\alpha_A + \alpha_C) \eta F/RT_{-1}}} = \log i_0 - \frac{\alpha_C \eta F}{2.303 RT}$$
(3)

If we assume  $\alpha_A + \alpha_C = 2$ , then a plot of

$$\log \frac{i}{e^{(\alpha_{A} + \alpha_{C}) \eta F/RT} - 1} \text{ versus } \eta$$
(4)

can give the value of  $\alpha_{C}$  from the slope and a value of  $i_{O}$  from the intercept.

Typical Allen-Hickling plots at  $650^{\circ}$ C for nickel and cobalt are compared in Figure 8 using intermediate-Btu fuel. From the intercept at zero overpotential, exchange current densities were generally found to be higher for nickel ( $85 \text{ mA/cm}^2$ ) compared with those for cobalt ( $28 \text{ mA/cm}^2$ ). Good agreement was found between exchange current density values obtained from low overpotential data and Allen-Hickling plots. The curves for the anodic and cathodic side of the Allen-Hickling plots shown in Figure 8 differ for both cobalt and nickel, probably indicating a change in the reaction mechanism between the anodic and cathodic direction.

From the anodic slope shown in Figure 8 for nickel, we obtain  $\alpha_A = 0.7$  and  $\alpha_C = 1.3$ , and for cobalt  $\alpha_A = 0.74$  and  $\alpha_C = 1.26$ . From the cathodic slope, for nickel we obtain  $\alpha_C = 0.48$  and  $\alpha_A = 1.52$ , and for cobalt  $\alpha_C = 0.59$  and  $\alpha_A = 1.41$ .

The above charge-transfer coefficients discussed for the ternary melt are representative of values obtained for all three melts with the temperatures and fuel compositions used in this work.

In the high anodic overpotential region, oxidation of the electrode surface may become significant, giving currents higher than that caused by fuel oxidation only. (See Figures 3 and 4.) This would result in higher  $\alpha_A$  values in the anodic region. To gain more insight into the validity of  $\alpha_A$  and  $\alpha_C$  values corresponding to fuel oxidation at nickel and cobalt electrodes, activation data were generated on a gold electrode in the Li/K melt at 650°C using intermediate-Btu fuel, as shown in Figure 9. The corresponding Allen-Hickling plot from this activation data is shown in Figure 10. Here we obtain  $i_0 = 16 \text{ MA/cm}^2$ ,  $\alpha_C = 1.56$  and  $\alpha_A = 0.44$ . Based on these results, we can tentatively conclude that the oxidation of fuel proceeds with  $\alpha_C = 1.5$  and  $\alpha_A = 0.5$  in the absence of electrode oxidation effects.

The dependency of the  $i_0$  on hydrogen content is shown for both nickel and cobalt for the Li/K, Li/Na/K, and Li/Na melts at 650°C in Figures 11, 12, and 13, respectively. In these figures, a straight line was drawn through the data points; however, those points falling off these lines should not be interpreted as experimental error, but rather as reflecting the interdependency between  $H_2$ ,  $CO_2$ ,  $H_2O$ , and COby way of the water-gas shift reaction,

$$H_2O + CO \stackrel{?}{\leftarrow} H_2 + CO_2. \tag{5}$$

Although the slope of these lines would indicate an empirical reaction order for hydrogen of approximately 0.5, this cannot be considered the true reaction order because it was not possible to independently vary the hydrogen content without changing the overall gas composition. (See Table 1.) The true reaction orders for hydrogen, carbon dioxide, and water in the fuel were calculated from the following equation:

$$i_{o} = \dot{k} (H_{2})^{a} (CO_{2})^{b} (H_{2}O)^{c}$$
 (6)

where  $\hat{k}$  is a proportionality constant; a, b, and c are the reaction order of H<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O, respectively.

Knowing the respective concentrations of  $H_2$ ,  $CO_2$ , and  $H_2O$ , then, by the water-gas shift reaction (Equation 5) the CO content is automatically fixed. If  $i_O$  is measured in four different fuels, then the four unknowns  $\vec{R}$ , a, b, and c can be determined. The above equation can be written in the logarithmic form -

$$\log i_0 = k + a \log (H_2) + b \log (CO_2) + c \log (H_2O)$$
(7)

where k = log k\*. Using  $i_0$  values obtained with fuel gas compositions corresponding to high-, medium-, low-, and very-low-Btu fuel (Table 1), Equation 7 can be written in a matrix form, e.g., for nickel in Li/K –

$$\begin{pmatrix} 1.54\\ 1.62\\ 1.34\\ 1.20 \end{pmatrix} = \begin{pmatrix} 1 & -0.22 & -1.13 & -0.65\\ 1 & -0.39 & -0.79 & -0.48\\ 1 & -0.67 & -1.04 & -1.26\\ 1 & -0.93 & -1.24 & -1.36 \end{pmatrix} \begin{pmatrix} k\\ a\\ b\\ c \end{pmatrix}$$
(8)

These linear simultaneous equations were solved on a programmable calculator to the solution,

$$\begin{pmatrix} k \\ a \\ b \\ c \end{pmatrix} = \begin{pmatrix} 2.02 \\ 0.258 \\ 0.275 \\ 0.178 \end{pmatrix}.$$

Thus, Equation 6 can be written as -

$$i_o = 104.7 (H_2)^{0.258} (CO_2)^{0.275} (H_2O)^{0.178}$$
 (9)

We can see that the reaction orders with respect to  $\rm H_2$  ,  $\rm CO_2$  , and  $\rm H_2O$  are close to 0.25.

We considered several reaction mechanisms for fuel oxidation that might give the  $i_0$  dependency shown in Equation 9. We have found the following reaction mechanism to satisfy this criterion.

$$\begin{array}{c} k_{1A} \\ H_{2} + 2M \stackrel{2}{\leftarrow} 2MH \\ k_{1C} \end{array}$$

$$\begin{array}{c} (10) \\ MH + CO_{3}^{-} \stackrel{k_{2A}}{\leftarrow} OH^{-} + CO_{2} + M + e^{-} \\ k_{2C} \end{array}$$

$$\begin{array}{c} (11) \\ MH + OH^{-} \stackrel{k_{3A}}{\leftarrow} \\ k_{3C} \end{array}$$

a. Equation 11 is the rate-determining step.

b. Langmuir adsorption isotherm.

c. There is low coverage,  $\theta$ , of MH.

The net current from Equation 10 is given by,

$$i_1 = F[k_{1A} C_{H_2} (1 - \theta)^2 - k_{1C} \theta^2],$$
 (13)

At equilibrium, when  $i_1 = 0$ ,

$$\frac{\theta}{1-\theta} = \left(\frac{\kappa_{1A}}{k_{1C}} \quad C_{H_2}\right)^{1/2} = \kappa_1^{1/2} \quad C_{H_2}^{1/2}$$
(14)

The net current from Equation 12 is -

$$i_3 = F(k_{3A} \ \theta \ C_{0H^-} \ e^{\beta_3 FV/RT} - k_{3C} \ C_{H_2 0} \ (1 - \theta) e^{-(1 - \beta_3) FV/RT})$$
 (15)

V is the potential difference between the electrode and the electrolyte. At equilibrium, when  $i_{\rm 3}$  = 0,

$$C_{OH}^{-} = \frac{k_{3C}}{k_{3A}} C_{H_2O} \frac{1}{(K_1 C_{H_2})^{1/2}} e^{-FV/RT}$$
(16)

For Equation 11 the net current is

$$i_{2} = F[k_{2A} \ \theta \ C_{CO_{3}} \ e^{\beta_{2}FV/RT} - k_{2C}C_{OH} - C_{CO_{2}} \ (1 - \theta)e^{-(1 - \beta_{2})FV/RT}]$$
(17)

Upon substitution for  $C_{OH}$  from Equation 16 into Equation 17 for the equilibrium potential,  $V_0$ , we can write, 1/2

$$e^{FV_0/RT} = \left[\frac{k_2 C}{k_2 A} \quad \frac{k_3 C}{k_3 A} \quad \frac{1}{K_1 C_{H_2}} \quad \frac{C_{H_2 O} \quad C_{CO_2}}{C_{CO_3}}\right]^{7-1}.$$
 (18)

Replacing V for Vo +  $\eta$  in Equation 17, where  $\eta$  is the overpotential, we obtain,

$$i_{2} = F \begin{cases} k_{2A} \ \theta \ C_{CO_{3}^{=}} e^{\beta_{2}F\eta/RT} \left[ \frac{k_{2C}}{k_{2A}} \ \frac{k_{3C}}{k_{3A}} \ \frac{1}{\kappa_{1}C_{H_{2}}} \ \frac{C_{H_{2}O} \ C_{CO_{2}}}{C_{CO_{3}^{=}}} \right]^{-\frac{\beta_{2}}{2}} \\ - k_{2C} \ \frac{k_{3C}}{k_{3A}} \ \frac{C_{H_{2}O}}{(K_{1}C_{H_{2}})} r/_{2}C_{CO_{2}} (1 - \theta)_{e} (-2 + \beta_{2})F_{\eta}/RT \ \left[ \frac{k_{2C}}{k_{2A}} \ \frac{k_{3C}}{k_{3A}} \ \frac{1}{\kappa_{1}C_{H_{2}}} \right]^{-\frac{\beta_{2}}{2}} \end{cases}$$

$$\frac{C_{H_2O} - C_{CO_2}}{C_{CO_3}} = \frac{-2 + \beta_2}{2}$$
(19)

From Equation 14 for low coverage we have  $\theta = K_1 C_{H2} C_{H2}$  and  $1 - \theta \simeq 1$ . Thus, Equation 19 becomes -

$$i_{2} = F \begin{cases} k_{2A} K_{1}^{1/2} C_{H_{2}}^{1/2} C_{CO_{3}^{-}} \begin{bmatrix} k_{2C} & k_{3C} \\ \overline{k_{2A}} & \overline{k_{3C}} \\ - k_{2C} & \frac{k_{3C}}{k_{3A}} & \frac{C_{H_{2}O}}{(K_{1}C_{H_{2}})^{1/2}} C_{CO_{2}} \begin{bmatrix} k_{2C} & k_{3C} \\ \overline{k_{2A}} & \overline{k_{3A}} \\ - \frac{1}{K_{1}C_{H_{2}}} & \frac{C_{H_{2}O} & C_{CO_{3}^{-}}}{C_{CO_{3}^{-}}} \end{bmatrix}^{-2+\beta_{2}} e^{(-2+\beta_{2})Fn/RT} \end{cases}$$

$$(20)$$

Comparing this with the general relationship for activation polarization,

$$\mathbf{i} = \mathbf{i}_{o} \left( e^{\alpha_{A} F \eta/RT} - e^{-\alpha_{C} F \eta/RT} \right)$$
(21)

we obtain -

$$\alpha_{\mathbf{A}} = \beta_2 \simeq 0.5$$
  
$$\alpha_{\mathbf{C}} = 2 - \beta_2 \simeq 1.5 \text{ for } \beta_2 \simeq 0.5.$$

The dependency of  $i_0$  on the gases (for  $\beta_2 = 0.5$ ) is

$$i_{o} \sim [c_{H_{2}}]^{0.25} [c_{CO_{2}}]^{0.25} [c_{H_{2}O}]^{0.25}$$
 (22)

The theoretical value of  $\alpha_A = 0.5$  compares reasonably well with our experimentally determined  $\alpha_A$  of 0.7 for nickel and cobalt and 0.5 for gold. Table 2 compares experimentally determined  $i_0$  values at 650°C with those calculated, assuming reaction orders of 0.25 for H<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O on a nickel anode in three different melts and with four gases. Similar data for cobalt is shown in Table 3.

The highest exchange current densities were measured on nickel and cobalt in the Li/Na/K ternary melt with all fuel compositions used. In these tables, we can see that good agreement exists between experimental and calculated i values.

We have seen in Figures 1 and 2 that currents were dependent upon the rate of fuel bubbling through the melt. The current increased further when the nickel wire was partially submerged. This suggests that in this system the current is limited by the rate of fuel gas delivery through the melt into the electrode. In the porous electrode of an actual fuel cell, the situation is rather different, however. Fuel gas is delivered directly at the electrode from the rear side while the front side is facing the electrolyte tile. Thus, the gas can reach electroactive sites directly, or through a layer of melt, or by diffusion through the metal. Diffusion of hydrogen through nickel may be quite significant.<sup>16</sup> Thus, there may be a very high local concentration of hydrogen in the porous electrode. The solubility of hydrogen in nickel at 650°C has been shown to be around 2.5 X 10<sup>-5</sup> g mol/cc atm,<sup>17</sup> and its diffusivity to be 3 X 10<sup>-5</sup> cm<sup>2</sup>/s<sup>-1</sup>.<sup>18</sup>

We have seen from Equation 9 that the exchange current density does not depend only on hydrogen concentration but also on the other fuel components. In particular, the significance of water present in the melt appears to play an important role on the overall reaction rate.

Some preliminary work was performed on the temperature dependency of the exchange current density on nickel and cobalt electrodes in the Li/Na/K melt over the temperature range of  $550^{\circ}$  to  $700^{\circ}$ C. No correction for changes in hydrogen concentrations caused by the temperature dependence of Equation 5 was made. However, the calculated changes over this temperature range was below 10%. Figure 14 shows plots of log i<sub>o</sub> versus 1/T for nickel and cobalt using low-Btu fuel.

The activation energy (AE) was calculated from the relationship,

$$\Delta E = \frac{R}{0.434} \frac{d (\log i_0)}{d (1/T)}$$
(23)
		Measured	_	Calculated
	· · · · · · · · · · · · · · · · · · ·		$mA/cm^2$ –	·
Li/K				<u>k* = 110</u>
High-Btu		35.0		34.70
Medium-Btu		42.0		42.17
Low-Btu		21.0		19.84
Very-Low-Btu		16.0		14.37
Li/Na/K				k*= 229.09
High-Btu		57.0		55.34
Medium-Btu		78.0		66.80
Low-Btu		30.0		31.44
Very-Low-Btu		22.0		22.78
Li/Na				k*= 135
High-Btu		44.0		41.70
Medium-Btu		54.0		50.70
Low-Btu		23.0		23.85
Very-Low-Btu				17.30

# Table 2. EXCHANGE CURRENT DENSITIES, i<sub>o</sub>, FOR NICKEL IN DIFFERENT MELTS AND USING VARIOUS GASES AT 650°C

Table 3. EXCHANGE CURRENT DENSITIES,  $i_{\rm O},$  FOR COBALT IN DIFFERENT MELTS AND USING VARIOUS GASES AT 650°C

	Measured	_	Calculated
		$-mA/cm^2$	
			•
Li/K			k*= 45
High-Btu	12.5		14.20
Medium-Btu	17.0		17.18
Low-Btu	10.7		8.08
Very-Low-Btu	6.5		5.90
Li/Na/K			<u>k*= 71.59</u>
High-Btu	30.0		22.60
Medium-Btu	26.0		27.50
Low-Btu	17.4		13.00
Very-Low-Btu	10.5		9.40
Li/Na		-	k*= 55.2
High-Btu	15.0		17.46
Medium-Btu	11.0		21.00
Low-Btu	8.0		9.90
Very-Low-Btu	6.7		7.20

Here we get activation energies of 6.65 kcal/mol and 7.31 kcal/mol for nickel and cobalt, respectively.

# CONCLUSION

Of the three molten carbonate compositions evaluated, the highest kinetic rates for fuel oxidation were found in the ternary melt of 43.5 mole percent Li<sub>2</sub>CO<sub>3</sub>-31.5 mole percent Na<sub>2</sub>CO<sub>3</sub> and 25 mole percent K<sub>2</sub>CO<sub>3</sub> with both nickel and cobalt anodes. The higher  $\alpha_A$  and i<sub>0</sub> values found for nickel and cobalt compared with those found for gold may indicate that surface oxide species could be responsible for the enhanced kinetics in the former two anode materials.

Comparison of the ionic conductivities at 600°C for all three melts gives values of 1.20  $cm^{-1}cm^{-1}$ , 1.15  $ohm^{-1}cm^{-1}$ , and 1.79  $ohm^{-1}cm^{-1}$  for, respectively, the Li/Na/K, Li/K, and Li/Na melts. If ionic conductivity were the only consideration, then clearly the Li/Na melt would be favored. This melt, however, does not have such favorable kinetics as the ternary melt.

From a consideration of gas solubility of the three candidate melts, the highest values for both fuel and oxidant appear to occur in the ternary melt,  $^{19,20}$  thereby possibly giving higher limiting current density values than the other two candidates. Some work has been reported<sup>21</sup> on the expected lifetimes of each of these melts, based upon projected carbonate vaporization losses and the corresponding extrapolated cell lifetimes. For the Li/Na/K, Li/K, and Li/Na carbonate melts at 600°C, projected cell lifetimes were, respectively,  $6.4 \times 10^5$  hours,  $6.3 \times 10^5$  hours, and  $10.3 \times 10^5$  hours. Clearly, the Li/Na melt has a 40% greater projected lifetime compared with the other two melts.

The Li/Na/K melt is worthy of further consideration because of a higher fuel and oxidant solubility, higher activation kinetics for fuel oxidation, and, particularly, because its lower melting point, compared with the other two candidates, offers the possibility of operating the molten carbonate fuel cell at temperatures somewhat below the normal operating temperature of  $650^{\circ}$ C. This lower operating temperature may not only extend the electrolyte tile life, but also that of the other fuel cell components. The relatively low activation energy values ( $\approx$  7 kcal/mol) from the ternary melt, using both nickel and cobalt electrodes, also acts as further encouragement for low operating temperatures without sacrificing too much kinetic performance for the fuel oxidation reaction. However, at lower operating temperatures, diffusional factors may become predominant under the probable mixed-control conditions present.

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Figure 2. DEPENDENCY OF POLARIZATION CURVE ON LINEAR VOLTAGE SWEEP RATE FOR A FULLY IMMERSED NICKEL WIRE (No Fuel Bubbling Into Melt at Time of Measurement)















Figure 9. CURRENT-VOLTAGE CHARACTERISTICS FROM TRANSIENT POTENTIOSTATIC EXPERIMENTS ON GOLD IN 650°C Li/K MELT WITH INTERMEDIATE-Btu FUEL



Figure 10. ALLEN-HICKLING POLARIZATION CURVE FROM POTENTIAL STEP DATA (Gold Electrode, Li/K Melt, Intermediate-Btu Fuel, 650°C)







## PREDICTION OF CURRENT DISTRIBUTION IN A MOLTEN CARBONATE FUEL CELL

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# ABSTRACT

A mathematical model has been developed to predict the performance of a molten carbonate fuel cell as a function of anode and cathode gas compositions, gas flow rates, and polarization characteristics. The effect of gas flow modes such as crossflow and coflow and the effect of higher pressures on the current distribution are studied. The predicted polarization curves agree well with the experimentally generated polarization curves. Conditions for incorporating a microscopic porous electrode model into the overall model development are briefly outlined.

The objective of this work was to develop a model capable of predicting the current distribution within the molten carbonate fuel cell as a function of gas compositions, gas flow rates, flow geometries, gas utilizations, and operating pressure. The half-cell reactions occurring in this cell are -

Anode:	$H_2 + CO_3^{=} \rightarrow CO_2 + H_2O + 2e^{-}$	(1)
	$CO + CO_3^{-} \rightarrow 2 CO_2 + 2e^{-}$	(2)
Cathode:	$2e^{-} + CO_{2} + 1/2 O_{2} \rightarrow CO_{2}^{-}$	(3)

The CO in the fuel may react electrochemically as shown above, but at the cell operating temperature of  $650^{\circ}$ C, the water-gas shift reaction -

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{4}$$

is more rapid, and the CO conversion to  $H_2$  contributes more to the current than the electrochemical reaction of CO. Hence, in the various stages of the model development, we have assumed that CO is electrochemically inert, and, therefore, Equation 2, as a direct faradaic reaction, is not considered

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The model development task was carried out in five stages:

- Predict current distributions for 100-cm<sup>2</sup> cells with crossflow configuration (where the fuel and oxidant gases flow perpindicular to each other). The water-gas shift reaction was not considered in this stage.
- Extend the model to include the shift reaction to study its contribution to the current density.
- 3. Modify the model for the coflow mode of operation and compare the current distributions with that predicted by the crossflow model, to obtain an insight into the effect of various flow configurations.
- Incorporate the effects of pressures greater than atmospheric on the current distribution predicted by the crossflow model.
- 5. Incorporate the microscopic porous electrode model in the crossflow model.

#### CROSSFLOW MODEL

#### Linear Polarization Model

In the 100-cm<sup>2</sup> cells operating at IGT, fuel and oxidant gases flow perpendicular to one another (crossflow). Figure 1 is a schematic diagram of the gas flows to the cell. The anode is porous nickel, which is 30 mils thick and has a mean pore size of around 5 $\mu$ . The cathode is also porous nickel which oxidizes to NiO. It is 15 mils thick and has a mean pore size of 12 to 14 $\mu$ . The electrolyte tile is typically a eutectic mixture of 62% Li<sub>2</sub>CO<sub>3</sub> - 38% K<sub>2</sub>CO<sub>3</sub> supported on a LiAlO<sub>2</sub> matrix.

In the initial modeling study, Equations 1 and 3 only were considered; the shift reaction (Equation 4) was neglected. The model was generated by formulating mass balances on the anode and cathode sides, which resulted in one equation each for local conversion at the anode and cathode. These two mass balance equations were solved simultaneously with the cell potential balance equation. The potential balance equation was obtained by combining the calculated Nernst potential (localequilibrium potential) and the assumed linear dependency of electrode overpotential on current density in such a way that the cell terminal potential was a constant.

# Mass Balance Equations

Figure 1 shows how the cell is divided into sections for computational purposes. Equations 5 through 11 show the dependency of the fuel and oxidant gas components on the gas flow rate, the length of the anode and cathode gas channels, together with current density.

## Mass Balance Equations

Figure 1 shows how the cell is divided into sections for computational purposes. Equations 5 through 11 show the dependency of the fuel and oxidant gas components on the gas flow rate, the length of the anode and cathode gas channels, together with current density.

Anode

H<sub>2</sub>: 
$$\frac{P}{RT L_C/n} \frac{d}{dx} \left(\frac{\Phi_A}{n} X_H\right) = -\frac{i_A}{2F} = -\frac{i}{2F}$$
 (5)

$$CO_2: \quad \frac{P}{RT L_C/n} \quad \frac{d}{dx} \quad (\frac{\Phi_A}{n} X_{CA}) = \frac{i_A}{2F} = \frac{i}{2F}$$
(6)

$$H_2 0: \quad \frac{P}{RT L_C/n} \quad \frac{d}{dx} \quad (\frac{\Phi_A}{n} X_W) = \frac{i_A}{2F} = \frac{i}{2F}$$
(7)

$$CO: \quad \frac{P}{RT L_C/n} \quad \frac{d}{dx} \quad (\frac{\Phi_A}{n} X_{CO}) = 0$$
(8)

Cathode

$$\operatorname{CO}_{2}: \quad \frac{P}{\operatorname{RT} L_{A}/m} \quad \frac{d}{dy} \quad \left(\frac{\Phi_{C}}{m} X_{CC}\right) = \frac{i_{C}}{2F} = -\frac{i}{2F}$$
(9)

$$O_2: \quad \frac{P}{RT L_A/m} \quad \frac{d}{dy} \quad (\frac{\Phi_C}{m} X_0) = \frac{i_C}{4F} = -\frac{i}{4F}$$
(10)

$$N_2: \quad \frac{P}{RT L_A/m} \frac{d}{dy} \quad (\frac{\Phi_C}{m} X_N) = 0 \quad (11)$$

Conversion of  ${\rm H}_2,\; \lambda,$  on the fuel side is defined as -

$$\lambda = \frac{\text{moles of } H_2 \text{ consumed}}{\text{moles of } H_2 \text{ in}} = \frac{\Phi_A^* X_H^* - \Phi_A X_H}{\Phi_A^* X_H^*}$$
(12)

where the ° superscript refers to the initial conditions; that is,  $\lambda = 1 - f_A \frac{X_H}{X_H^o} \tag{13}$ 

where

$$f_{A} = \frac{\Phi_{A}}{\Phi_{A}^{\circ}} \cdot$$

Conversion of CO  $_2,\ \mu,$  on the oxidant side is defined as -

$$\mu = \frac{\text{moles of CO}_2 \text{ consumed}}{\text{moles of CO}_2 \text{ in}} = \frac{\Phi_{C}^2 X_{CC} - \Phi_{C} X_{CC}}{\Phi_{C}^2 X_{CC}^2}$$
(14)

that is,

$$\mu = 1 - f_C \frac{X_{CC}}{X_{CC}^*}$$
(15)

where

 $f_{C} = \frac{\Phi_{C}}{\Phi_{C}^{\circ}} \cdot$ 

Combining Equations 12 and 13 for the hydrogen component of the fuel, we obtain Equation 16. Similarly, Equations 17 and 18 can be derived for the  $CO_2$  and  $H_2O$  fuel components.

 $f_A X_H = X_H^\circ - \lambda X_H^\circ$ (16)

$$f_A X_{CA} = X_{CA}^{\circ} + \lambda X_H^{\circ}$$
(17)

$$f_A X_W = X_W^\circ + \lambda X_H^\circ.$$
(18)

If Equations 16, 17, and 18 are added, then

$$f_A = 1 + \lambda x_H^{\circ}.$$
(19)

In a similar manner for the oxidant components at the cathode,

$$f_{C} X_{CC} = X_{CC}^{\circ} - \mu X_{CC}^{\circ}$$
(20)

$$f_{\rm C} x_{\rm O} = x_{\rm O}^{\circ} - \frac{\mu}{2} x_{\rm CC}^{\circ}.$$
 (21)

Adding Equations 20 and 21, then

$$f_{C} = 1 - \frac{3}{2} \mu X_{CC}^{\circ}.$$
 (22)

If dimensionless distance  $\xi$  is defined as

$$\xi = \frac{x}{L_A/m}$$
(23)

where  $L_A/m$  is the length of one section in the x-direction, then substituting Equations 13 and 23 into Equations 5, 6, and 7 results in Equation 24:

$$\frac{Pm}{R T L_C L_A} \quad \Phi^{\circ}_A \quad X^{\circ}_H \quad \frac{d\lambda}{d\xi} = \frac{i}{2F}$$
(24)

The current density can be defined as -

$$J = \frac{i}{A} = \frac{im}{I_{max}}$$
(25)

where  $I_{max}$  is the current density that would result if 100% conversion of the anode gas took place and the resulting current was uniformly distributed over the entire cell. Then,

$$A = \frac{2F P \Phi_{A}^{\circ} X_{H}^{\circ} m}{R T L_{C} L_{A}} \qquad (A/cm^{2})$$
(26)

and therefore

$$\frac{\mathrm{d}\lambda}{\mathrm{d}\xi} = \mathrm{J}.$$
(27)

If dimensionless distance  $\boldsymbol{\eta}_d$  is defined as

$$\eta_{\rm d} = \frac{y}{L_{\rm C}/n} \tag{28}$$

where  $L_C/n$  is the length of one section in the y-direction, then substituting Equations 15 and 28 into Equations 9 and 10 results in Equation 29:

$$\frac{Pn}{R T L_A L_C} \Phi_C^* X_{CC} \frac{d\mu}{d\eta_d} = \frac{1}{2F}$$
(29)

Let S denote the ratio of  $CO_2$  flow rate per cathode section to the H<sub>2</sub> flow rate per anode section; that is,

$$S = \frac{X_{CC}^{*} \Phi_{C}^{*} n}{X_{H}^{*} \Phi_{A}^{*} m}$$
(30)

Substituting Equations 26 and 29 into Equation 30, we obtain

$$\frac{d\mu}{dn_d} = \frac{1}{SA} = \frac{J}{S}.$$
(31)

Equations 27 and 31 are two mass balance equations, containing three unknowns,  $\lambda$ ,  $\mu$ , and J. To solve for these unknowns, a third equation is obtained from a potential balance.

# Potential Balance Equation

Figure 2 is a schematic representation of the potential gradient in a cell for both the open-circuit condition and when under load. The cell potential is given by -

$$V = (V_{CN} - V_{AN}) - iZ_{ohm} + \eta_C - \eta_A$$
(32)

The equilibrium potentials at the electrodes are -

$$V_{AN} = V_A^\circ + \frac{RT}{2F} \ln \left(\frac{X_W X_{CA}}{X_H}\right)$$
 and (33)

$$V_{CN} = V_{C}^{\circ} + \frac{RT}{2F} \ln (x_{O}^{1/2} x_{CC})$$
 (34)

where  $V^{a}_{A}$  and  $V^{c}_{C}$  are the standard anode and cathode potentials. Assuming a linear current-overpotential relationship, then

$$\eta_{A} = i_{A} Z_{A} = i Z_{A}$$
(35)  
$$\eta_{C} = i_{C} Z_{C} = -i Z_{C}$$
(36)

where  $Z_A$  and  $Z_C$  are effective electrode impedances (ohm-cm<sup>2</sup>). Substituting Equations 33 through 36 into Equation 32, we obtain

$$v + v_{A}^{\circ} - v_{C}^{\circ} = \frac{RT}{2F} \ln (x_{O}^{1/2} \quad x_{CC}) - \frac{RT}{2F} \ln (\frac{x_{W} \quad x_{CA}}{x_{H}}) - i_{A} (z_{ohm} + z_{A} + z_{C})$$
 (37)

Using the definition of conversions  $\lambda$  and  $\mu$  from Equations 13 and 15, Equation 37 can be written as

$$\frac{\mathbf{v} + \mathbf{v}_{A}^{2} - \mathbf{v}_{C}^{2}}{RT/2F} - \ln \left[ \frac{\mathbf{x}_{CC}^{2} (\mathbf{x}_{O}^{*} \mathbf{1}/2 \ \mathbf{x}_{H}^{*})}{\mathbf{x}_{W}^{*} \mathbf{x}_{CA}^{*}} \right]$$

$$= \ln \left[ \frac{(1 - \mu) (1 - 1/2\mu \ \frac{\mathbf{x}_{CC}^{*}}{\mathbf{x}_{W}})^{1/2} (1 - \lambda) (1 + \lambda \mathbf{x}_{H}^{*})}{(1 - 3/2\mu \mathbf{x}_{CC}^{*})^{3/2} (1 + \lambda \ \frac{\mathbf{x}_{H}^{*}}{\mathbf{x}_{W}^{*}}) (1 + \lambda \ \frac{\mathbf{x}_{CA}^{*}}{\mathbf{x}_{CA}^{*}})} \right] - \frac{\mathbf{J}\mathbf{z}\mathbf{A}}{RT/2F}$$
(38)

The first term on the right-hand side of Equation 38 is the Nernst loss, and the second term is the overpotential term. Substituting Equation 26 for A in the overpotential term, we obtain

$$\frac{JZ_A}{RT/2F} = JZ \frac{P \Phi_A^{\circ} X_H^{\circ} m}{L_C L_A} \left(\frac{2F}{RT}\right)^2$$
(39)

Rearranging Equation 38, we then have

$$\ln\left[\frac{(1-\mu)(1-\mu A_{1})^{1/2}(1-\lambda)(1+\lambda A_{2})}{(1-\lambda A_{3})^{3/2}(1+\lambda A_{4})(1+\lambda A_{5})}\right] - U - JE = 0$$
(40)

where

$$A_{1} = 0.5 X_{CC}^{\circ} / X_{0}^{\circ}$$

$$A_{2} = X_{H}^{\circ}$$

$$A_{3} = 1.5 X_{CC}^{\circ}$$

$$A_{4} = X_{H}^{\circ} / X_{W}^{\circ}$$

$$A_{5} = X_{H}^{\circ} / X_{CA}^{\circ}$$

$$U = \frac{V + V_{A}^{\circ} - V_{C}^{\circ}}{RT/2F} - \ln \left[ \frac{(X_{CC}^{\circ}) (X_{0}^{\circ})^{1/2} (X_{H}^{\circ})}{(X_{CA}^{\circ}) (X_{CA}^{\circ})} \right]$$
and  $E = \frac{Z m P \Phi_{A}^{\circ} X_{H}^{\circ}}{L_{C} L_{A}} \left( \frac{2F}{RT} \right)^{2}$ .

Equations 27, 31, and 40 were solved simultaneously to give  $\lambda$ ,  $\mu$ , and the current density at any point on the electrode surface.

A computer program was written to solve these three equations. The inputs to the computer program were 1) anode and cathode gas compositions and flow rates, 2) standard anode and cathode potentials from the Nernst Equation, 3) terminal voltages chosen from representative fuel cell data, 4) length of anode and cathode gas channels, 5) number of sections in the x and y directions across the cell, 6) temperature, 7) pressure and, 8) effective electrode impedance. The effective electrode impedence (input Z to the computer program) represents the sum of the cell resistance and the individual electrode overpotential terms. The cell resistance was obtained from current interruption measurements on 100-cm<sup>2</sup> cells. Representative electrode overpotentials ( $\eta_A$  and  $\eta_C$ ) were obtained from 3-cm<sup>2</sup> cells using various fuel and oxidant compositions at 7.5% H<sub>2</sub> utilization and 15% CO<sub>2</sub> utilization.<sup>1</sup>

Figure 3 compares experimental data obtained from  $100-cm^2$  cells and the predicted curve for a fuel composition obtained from reformed natural gas. The theoretical anode conversion was not found to agree exactly with that obtained experimentally (75%). Hence, Z was adjusted to get the experimentally obtained anode conversion. (Refer to section below, Variation in Effective Electrode Impedence, Z.)

# Inclusion of CO Shift Reaction in the Linear Polarization Model

In the next stage of the linear model development, hydrogen originating from the water-gas shift reaction (Equation 4) was included and the mass and potential balance equations were correspondingly modified. Figures 4 through 6 show experimental polarization curves for three different fuel gases, together with the predicted curves, both with and without consideration of the shift reaction. For fuels having a low initial CO content and a high  $H_2$  content (for example, a feed gas obtained by reforming methane, as in Figure 4), the contribution to the current density by the shift reaction is not significant. However, in the case of fuels with high CO contents (for example, fuels obtained by the partial oxidation of heavy oils or by the gasification of coal), the shift reaction contributes significantly to the current density,  $^3$  as can be seen in Figures 5 and 6. Also, the current distribution along the cell is generally more uniform than when no CO con-

#### Variation in Effective Electrode Impedance, Z

For fuels with low  $H_2$  contents, the current densities predicted with and without inclusion of the shift reaction were not in very good agreement with those values obtained experimentally from  $100-cm^2$  cells (Figures 5 and 6). In order to obtain better agreement with experimental data, we adjusted the effective cell impedance, Z, given by -

$$\mathbf{z} = \mathbf{R} \cdot \mathbf{A} + \frac{\mathbf{n}_{\mathbf{A}}}{\mathbf{i}} + \frac{\mathbf{n}_{\mathbf{C}}}{\mathbf{i}}$$
(41)

where R is the cell resistance, A is the area of the cell, i is the current density and  $n_A$ ,  $n_C$  are the anode and cathode overpotentials. For each inlet gas composition, representative cell resistance values, R, used were obtained as discussed previously using current interruption techniques on 100-cm<sup>2</sup> cells.

Consequently, the variable component of Z is the respective anode  $(n_A)$  and cathode  $(n_C)$  overpotential terms. Given this value of Z, along with the other inputs to the computer program, the model predicts the current density and average anode and cathode conversions. The average anode conversion initially obtained was generally different from the experimental 75% conversion achieved in bench-scale cells. Hence, the value of Z was adjusted to obtain the more representative anode conversion of 75%. The predicted average current densities, based on the new values of Z, agree to within 4% of the experimental current densities. Figures 7 and 8 compare the predicted polarization curves (obtained with the adjusted value of 2) with the experimental curve for two feed gases.

In general, it was observed that as the value assigned to Z was increased, the current distribution became more uniform. This is illustrated in Table 1.

From the adjusted value of Z, the overpotentials  $n_A$  and  $n_C$  are calculated at different loads, from Equation 41. In Figure 9 these are compared with the experimental overpotentials, which were extrapolated from 100-cm<sup>2</sup> cell data. The assumption of linear current/ overpotential relationship appears valid. However, one cannot draw conclusions about the relative contributions of mass transfer and activation overpotentials from Figure 9 because of the presence of an ohmic drop in the pores. (Refer to the section Incorporation of a Microscopic Porous Electrode Model.)

Table 1. UNIFORMITY OF CURRENT DISTRIBUTION AS A FUNCTION OF Z

Fuel: Product gas obtained by reforming natural gas (60% H<sub>2</sub>, 7.4% CO<sub>2</sub>, 22.6% H<sub>2</sub>O, 10% CO)

	Ratio of Highest to
Ξ, ohm/cm <sup>2</sup>	Lowest Current Density
0.6	4.8
0.8	4.2
1.0	3.8
1.2	3.4
1.4	3.1
1.6	2,95
5.0	1.7
10.0	1.4

# COFLOW MODEL

This corresponds to the situation where both fuel and oxidant gases flow in a direction parallel to each other. Here the current distribution is expected to be less uniform compared with the cross-flow configuration. The computer model was modified to predict the current distribution across the  $100-\mathrm{cm}^2$  fuel cell using this flow configuration.

Figures 10 and 11 compare the average current distribution along the 10-cm cell length for the crossflow and coflow configuration for two representative feed gases. Particularly high current densities are seen at the cell entrance for the coflow configuration, where both fuel and oxidant are at their highest concentrations. Figures 12 and 13 compare the predicted polarization curves for the coflow and crossflow configurations. Overall average current densities were predicted. However, the values were found to be only slightly lower for the coflow mode. The crossflow configuration would appear to be preferred to the coflow mode because the predicted current distribution is more uniform.

# EFFECTS OF PRESSURE ON CURRENT DISTRIBUTION IN LINEAR MODEL

Increasing the operating pressure of the molten carbonate fuel cell can be expected to result in performance improvements (Nernst gains) due to the increase in the partial pressures of the reactants. Higher pressures should also produce increases in gas solubilities and mass transport rates in the selected molten carbonate mixture, which should result in improved electrochemical performance.

Enhanced cell performance at pressures above atmospheric have been confirmed in practice with  $100-cm^2$  cells.<sup>1</sup> High pressure favors the carbon deposition and methane reactions:

$$2 \operatorname{CO} \stackrel{?}{\downarrow} \operatorname{C} + \operatorname{CO}_2 \tag{42}$$

$$CO + 3H_2 \stackrel{2}{\leftarrow} CH_4 + H_2O \tag{43}$$

Equilibrium inlet compositions were calculated at different pressures, at 650°C, taking into account Equations 42 and 43 and the water-gas shift reaction (Equation 4).

The mass and potential balance equations were therefore rewritten to take into account the conversions of  $CH_{i_4}$  and CO, both of which are assumed not electrochemically active compared with  $H_2$ . A new computer program was developed to predict the current distribution at higher operating pressures.

Figure 14 compares experimental and predicted polarization curves for steam-reformed naphtha at a pressure of 10 atmospheres. The fuel inlet equilibrium composition at 10 atmospheres and 650°C for steamreformed naphtha corresponds to 31% H<sub>2</sub>, 11.1% CO<sub>2</sub>, 43.4% H<sub>2</sub>O, 4.1% CO and 10.4% CH<sub>4</sub>, compared with the composition at 1 atmosphere and 650°C of 52.7% H<sub>2</sub>, 10.4% CO<sub>2</sub>, 25.2% H<sub>2</sub>O and 10.7% CO. The predicted current densities are found to be in very good agreement with the experimental values. The experimental data used in this comparison were obtained at constant flows rather than at constant conversion.

#### INCORPORATION OF A MICROSCOPIC POROUS ELECTRODE MODEL

The development of a porous electrode model is necessary for the integration of electrode kinetic data and the mass transfer and ohmic resistances in the crossflow performance model. In the work discussed above, a constant effective cell resistance (impedence), Z, has been used. This is equivalent to assuming that under probable conditions present at the fuel cell electrodes, to a first approximation the individual electrode overpotentials varied linearly with current density, Such an assumption is reasonable if the local current density inside a pore is small compared to the exchange current density <u>and</u> compared to the limiting current density. It has been estimated earlier<sup>4</sup> that the limiting current densities at the anode and at the cathode are at least  $1 \text{ A/cm}^2$  or larger.

The majority of work to date on the oxygen-reduction reaction in molten carbonate mixtures has been performed on gold electrodes,<sup>4</sup> where estimated  $i_0$  values can be calculated to be 0.01 mA/cm<sup>2</sup> for typical oxidant conditions.

As discussed previously, the local current density within the porous electrode is probably low enough to allow that the linear polarization model be used as a good first approximation for predicting the current distribution. However, the porous electrode model should also take into consideration ionic resistivity along the assumed thin film of electrolyte within the pore, and diffusional resistance because of the transport of dissolved reactants across the film. These resistances may cause an apparent increase in the overpotential (between the electrode terminal and the reference electrode), over and above that expected from kinetic relationships.

If the transport of reactants in the gas phase in not rate-limiting, as has been previously shown,<sup>4</sup> then ohmic resistances, kinetics, and mass transfer remain as possible rate-limiting factors. Their relative significance is indicated by the dimensionless parameters -

$A_1 = \frac{\kappa \delta RT}{\frac{i FL^2}{O}}$	( <u>kinetic resistance</u> ) ohmic resistance)	(44)
$A_2 = \frac{\delta^2 \kappa RT}{D_{\ell} C_{\ell} n F^2 L^2}$	( <u>mass transfer resistance</u> ) ohmic resistance	(45)
$A_3 = A_2/A_1$	( <u>mass transfer resistance</u> ) kinetic resistance)	(46)

Table 2 presents typical values of these parameters for a 100-cm  $^2$  fuel cell.\* Table 3 presents the structural data of the electrodes.

\* Basis – Fuel composition: 35.16% H<sub>2</sub>, 23.5% CO<sub>2</sub>, 34% H<sub>2</sub>O, 7.25\% CO (average of inlet and outlet compositions); Oxidant composition: 60.8% N<sub>2</sub>, 11.96% O<sub>2</sub>, 23.9% CO<sub>2</sub>, 3.4% H<sub>2</sub>O (average of inlet and outlet compositions). Values of D<sub>0</sub>, C<sub>0</sub>, and  $\kappa$ are from Reference 4. i<sub>o</sub> values of 40 mA/cm<sup>2</sup> for the hydrogen reaction and 1 mA/cm<sup>2</sup> for the oxygen reaction were used in estimating these parameters. This porous electrode model has been integrated with our crossflow configuration. Preliminary predicted polarization curves from this model, however, require that the exchange current density for the oxygen-reduction reaction on nickel oxide be significantly higher than 0.01 mA/cm<sup>2</sup> (as previously reported on a gold electrode).<sup>5</sup>

# Table 2. CHARACTERISTIC DIMENSIONLESS RESISTANCE RATIOS IN A $100\text{-}\mathrm{cm}^2$ FUEL CELL

	Anode	Cathode
$A_1 = \frac{\text{kinetic}}{\text{ohmic}}$	0.021	3.39
$A_2 = \frac{\text{mass transfer}}{\text{ohmic}}$	0.005	1.86
$A_3 = \frac{\text{mass transfer}}{\text{kinetic}}$	0.24	0.55

# Table 3. STRUCTURAL DATA OF ELECTRODES

	Anode	Cathode
Pore Radius	2.5 µm	6.5 µm
Pore Length	30 mils	15 mils
Porosity	70%	80%
Pore Density	$3.57 \times 10^{6}$	$6.03 \times 10^{5}$
Internal/External Area	427	94
Film Thickness	0.5 µm	0.5 µm

Assuming a constant exchange current density for both the hydrogen oxidation (40 mA/cm<sup>2</sup>) and oxygen-reduction reactions along the cell length, preliminary calculations have indicated that  $i_o$  values of around 2 mA/cm<sup>2</sup> for the latter reaction were necessary to achieve a satisfactory fit with experimental polarization curves.

Refinement of this porous electrode model will include the concentration dependencies of  $i_0$  for both the anodic and cathodic reactions, as determined from our electrochemical half-cell data, and will be discussed at a later time.

# CONCLUSIONS

The current distribution in  $100-cm^2$  cells with crossflow of fuel and oxidant gases has been modeled assuming linear polarization; the predicted polarization curves are in good agreement with the experimental curves.

The current distribution is more uniform in the crossflow configuration than the coflow mode, although the average current densities of the crossflow and coflow modes differ only slightly.

At higher operating pressures, the methane-reaction equilibrium needs to be considered. The current densities thus predicted agree very well with the experimental values obtained using a  $100-cm^2$  cell operated under pressure.

# NOMENCLATURE

cm on, cm
cm on, cm
cm on, cm
on, cm
m <sup>2</sup>
cm <sup>2</sup>
, cm
nel, cm
direction
ow direction
e cathode
e anode

- $\delta$  = film thickness
- i = exchange current density

L = pore length

D<sub>o</sub> = diffusivity of gas in electrolyte

 $C_o$  = solubility of gas in electrolyte

Subscripts

A = anode

C = cathode

- H = hydrogen
- $CA = CO_2$  in anode gas
- $CC = CO_2$  in cathode gas

W = water

- CO = carbon monoxide
- 0 = oxygen
- N = nitrogen.

#### ACKNOWLEDGEMENT

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 $\lambda$  = ANODE GAS CONVERSION

 $\mu$  = CATHODE GAS CONVERSION

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UNDER LOAD



$$\begin{split} \psi^{*}_{A} &= \text{STANDARD AYODE POTENTIAL} \\ \psi^{*}_{C} &= \text{STANDARD CATHODE POTENTIAL} \\ \psi^{*}_{AH} &= \text{AYODE NERNST POTENTIAL} \\ \psi^{*}_{CH} &= \text{CATHODE NERNST POTENTIAL} \\ \psi^{*}_{CH} &= \text{CATHODE METAL POTENTIAL} \\ \psi^{*}_{CH} &= \text{CATHODE METAL POTENTIAL} \\ \psi^{*}_{AE} , \psi^{*}_{CE} &= \text{ELECTROLYTE POTENTIALS} \\ \vdots \psi^{*}_{C} &= \psi^{*}_{CH} - \psi^{*}_{CE} \\ \eta^{*}_{A} &= \psi^{*}_{AH} - \psi^{*}_{AH} \\ \eta^{*}_{C} &= \psi^{*}_{CH} - \psi^{*}_{CH} \\ \eta^{*}_{C} &= \psi^{*}_{CH} - \psi^{*}_{CH} \\ \text{SUPERSCRIPT CQ INDICATES EQUILIBRIUM CONDITIONS} \end{split}$$

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Figure 2. SCHEMATIC REPRESENTATION OF THE POTENTIAL GRADIENT IN A CELL









Figure 5. PREDICTED POLARIZATION CURVES FOR PARTIAL OXIDATION OF HEAVY OILS (With and Without the CO Shift Reaction) COMPARED WITH EXPERIMENTAL DATA



Figure 6. PREDICTED POLARIZATION CURVES FOR LOW-Btu COAL GAS (With and Without the CO Shift Reaction) COMPARED WITH EXPERIMENTAL DATA



Figure 8. COMPARISON OF THE EXPERIMENTAL CURRENT DENSITY WITH PREDICTED CURRENT DENSITIES (Fuel: Low-Btu Coal Gas)





Figure 9. COMPARISON OF PREDICTED AND EXPERIMENTAL OVERPOTENTIALS



Figure 10. VARIATION IN CURRENT DENSITY WITH CELL LENGTH FOR REFORMED NATURAL GAS (With and Without the CO Shift Reaction) FOR THE COFLOW AND CROSSFLOW CONFIGURATIONS





Figure 11. VARIATION IN CURRENT DENSITY WITH CELL LENGTH FOR LOW-Btu COAL GAS (With the CO Shift Reaction) FOR THE COFLOW AND CROSSFLOW CONFIGURATIONS



Figure 12. PREDICTED POLARIZATION CURVES FOR REFORMED NATURAL GAS USING COFLOW AND CROSSFLOW CELL CONFIGURATIONS (CO Shift Reaction Not Considered)





Figure 14. COMPARISON OF EXPERIMENTAL AND PREDICTED POLARIZATION CURVES FOR REFORMED NAPHTHA AT 10 atm PRESSURE

# HEAT RELEASE AND EMF OF NONISOTHERMAL MOLTEN SALT FUEL CELLS

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# ABSTRACT

Expressions based on nonequilibrium thermodynamics are presented for the emf and local heat production of a nonisothermal fuel cell operating in steady state. Using these expressions, contributions to the local heat release rate can be attributed to: separate electrode Peltier heats, electrode overpotentials, Joule heating, electrolyte diffusion and thermal diffusion potentials, and bulk electrolyte Peltier and Thomson heats. The sizes of these terms and of the various terms contributing to the emf have been estimated for molten carbonate fuel cells.

# 1. INTRODUCTION

In an operating fuel cell, the amount of heat produced or absorbed at any point varies with location in the cell. This is so not only because fuel and oxidant gas utilization causes the cell operating conditions to be nonuniform across the electrode faces, but also because there are many different physical and chemical mechanisms responsible for the heat release. As a result, the cell is likely to operate in a nonisothermal mode. Knowledge of the strengths and locations of the various heat sinks and sources is required in order to fully assess the importance of nonisothermal effects on cell performance.

Using linear irreversible thermodynamics, we have recently completed an analysis of a nonisothermal fuel cell that enables us to identify all of the heat release mechanisms and their loci of operation within the cell. <sup>1</sup> We have also obtained an expression for the emf of such a cell. <sup>1</sup> In this presentation we use these results to estimate the sizes of the various effects contributing to the heat release and emf of a molten carbonate fuel cell at an average temperature of 923 K operating at a current density of 160 mA/cm<sup>2</sup>. Our analysis was limited to a cell satisfying the following set of conditions and limitations: 1) The cell is in a nonisothermal steady state under load. 2) The cell half reactions involve dissolved gas species and electrolyte anions. 3) The electrolyte may be a mixture, but only a single anionic species is permitted. 4) Gas-electrolyte interfaces are in close proximity to the electrodes. 5) Uniform conditions pertain at each electrode and gas-electrolyte interface. 6) The metal used for the reference leads differs from that used for both electrodes. 7) Gas phase transport is neglected. 8) Constant pressure conditions prevail.

A schematic diagram of the cell is depicted in Fig. 1. For future use we note that the subscripts A and C refer to anode and cathode, subscript i denotes electrolyte ions with N being reserved for the anionic species  $CO_3^{-}$ , subscript e is used for electrons, and the letters h, w, o, d, c, m will designate the following gaseous species: H<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub>. As usual, F will stand for the Faraday. For this presentation we specialize a bit further and consider only monovalent cations, e. g. Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>. The specific half-reactions at the cathode and anode are, as usual.

$$\frac{1}{2}O_2 + CO_2 + 2e^- = CO_3^-$$
(1)

$$H_2 + CO_3^{=} = H_2O + CO_2 + 2e^{-}$$
 (2)

The effects of CO and  $CH_4$  reactivity will be included only indirectly by assuming gas phase equilibrium for anode fuel mixtures.

A detailed derivation and additional discussion of the general results presented here will appear elsewhere.  $^1$ 

#### 2. NONISOTHERMAL CELL EMF

# 2.1 General Expression

Using the procedures presented by Haase<sup>2</sup>, we were able to obtain the following expression for the potential difference  $\Delta \varphi$  between points 1 and 2 of the reference leads. (Refer to Fig. 1.)

$$\Delta \varphi = \varphi_2 - \varphi_1 = E(T_A) - IR - \eta_A(T_A) - \eta_C(T_C)$$
  
- (2F)<sup>-1</sup> 
$$\sum_{i \neq N} \int_A^C t_i [(\nabla \mu_{iN})_{T, P} + (^* \Omega_{iN}/T) \nabla T] \cdot d\mu$$
  
+ (2F)<sup>-1</sup> 
$$\int_A^C *_{S_N} \nabla T \cdot d\mu - (2F)^{-1} \int_{T_A}^{T_C} (S^{(g)} + 2^* S_e) dT$$

The terms in this equation will be interpreted and evaluated in the following sections.

2.2 Nernst Potential

The Nernst open circuit potential  $E(T_A)$  of the cell is calculated at the anode temperature for the prevailing gas conditions. For the molten carbonate cell E is typically about 1 volt.

2.3 Ohmic Loss

The IR term is the familiar ohmic potential loss attributable to the finite conductivities of the electrolyte and electrodes. (In practical cells, electrode contact resistances might also be important.) Considering only the ohmic loss in the electrolyte we may rewrite the product of cell current I and resistance R in terms of cell current density j, specific conductivity  $\kappa$  and electrode separation l:

 $IR = i\kappa^{-1}\ell$ 

For molten carbonate/lithium aluminate tiles  $^{3}$  K $\approx$ 1 ohm  $^{-1}$  cm  $^{-1}$ , then for j = 160 mA/cm<sup>2</sup> and &=2 mm, we find

IR = 32 mV

2.4 Overpotentials

At 160 mA/cm<sup>2</sup> the sum of the anode and cathode overpotentials,  $\eta_A + \eta_C$ , is about 100 - 150 mV. We note that the total measureable electrode overpotential does not include the "concentration overpotential" arising from changes in the activity (chemical potential) of the anion from its open circuit value in the vicinity of each electrode. These thermodynamically indeterminable potential changes have been
combined with the diffusion and thermal diffusion potentials resulting in the measurable quantities discussed next.

# 2.5 Measurable Diffusion Potential

The next term,

$$-\Delta \varphi_{\mathbf{D}} = (2\mathbf{F})^{-1} \sum_{i \neq \mathbf{N}} \int_{\mathbf{A}}^{\mathbf{C}} t_{i} (\nabla \mu_{i\mathbf{N}})_{\mathbf{T}, \mathbf{P}} \cdot d\boldsymbol{\mu}$$

is formally the emf of a concentration cell with transference. It can also be interpreted as the measurable part of a diffusion potential resulting from composition gradients that may be established when current is passing through the cell. In the above expression  $t_i$  is the Hittorf (internal) transference number of cation i relative to  $CO_{3}^{\sim}$ ,  $\mu_{iN}$  is the chemical potential of the i'th electrolyte <u>component</u>,

$$\mu_{iN} = 2\mu_i + \mu_N$$

and the integral is to be evaluated along a path from the anode to the cathode. The possible occurrence, consequences and size of  $\Delta \varphi_D$  in molten carbonate cells have been the subject of several recent reports. <sup>4-7</sup> A likely upper limit for  $\Delta \varphi_D$  is given<sup>4</sup> by  $\Delta \varphi_D = RT/2F \approx 40 \text{ mV}$ , at 923 K, but more refined calculations<sup>5</sup> and experiments<sup>6</sup>, <sup>7</sup> give values that are usually less than 10 mV.

2.6 Measurable Thermal Diffusion Potential

We choose to call the next term,

$$-\Delta \varphi_{\mathrm{TD}} = (2F)^{-1} \int_{A}^{C} \sum_{i \neq N} t_{i} ({}^{*} Q_{iN} / T) \nabla T \cdot d\ell$$

the measurable part of the thermal diffusion potential. This nomenclature is somewhat arbitrary, but it does reflect the origin<sup>2</sup> of the term. The  $^{*}Q_{iN}$  are the heats of transport of the electrolyte components,

$${}^{*}Q_{iN} = 2{}^{*}Q_{i} + {}^{*}Q_{N}$$

They can be determined from measurements made in Soret (currentless) steady states for which we find

$$(\nabla \mu_{iN})_{T,P} + (^* \Omega_{iN} / T) \nabla T = 0$$
 (3)

The  $^{\sim}Q_{iN}$  can also be related to thermocell measurements:

$$(2F)^{-1} \sum_{i \neq N} t_i^* Q_{iN} / T = \epsilon_{\infty} - \epsilon_0 . \qquad (4)$$

Here,  $\varepsilon_0$  and  $\varepsilon_{\infty}$  are the initial and steady state thermoelectric powers of a thermocell consisting of a mixed electrolyte and of electrodes reversible to the anion<sup>2</sup>. Data for  ${}^*Q_{1N}$  in molten carbonate mixtures are apparently lacking, making it difficult to estimate the size of  $\Delta\phi_{\rm TD}$ . If we use results for  $\varepsilon_0$  and  $\varepsilon_{\infty}$  for molten nitrate systems<sup>8</sup>, we may get a crude idea of the magnitudes involved. (Although their net charges are different, NO<sub>3</sub> and CO<sub>3</sub> are isoelectronic and have similar geometries.) At the highest temperature studied, 340°C, the largest difference reported for the LiNO<sub>3</sub>/AgNO<sub>3</sub> system was

$$\epsilon_{\rm m} - \epsilon_{\rm o} = 58 \,\mu V/K$$

A considerable overestimate of  $\Delta \varphi_{TD}$  should be afforded by putting \*Q = TS where S is the molar entropy of a molten alkali carbonate, S  $\approx 200 \text{ JK}^{-1}\text{mol}^{-1}$ . Then

$$\frac{\Delta \varphi_{\rm TD}}{\Delta T} \approx \frac{{}^{*}{\rm Q}}{2{\rm FT}} \approx 1 \, {\rm mVK}^{-1}$$

2.7 Transported Anionic Entropy

The next term

$$\frac{1}{2F} \int_{A}^{C} * S_{N \overset{\nabla}{\sim}} T \cdot \overset{d}{\sim}$$

arises when the change in chemical potential of the anions caused by a temperature gradient in the electrolyte is combined with the contribution of  ${}^{*}Q_{N}$  to the thermal diffusion potential not already included in the preceding term. Using an extension of the Third Law, conventional values of the transported entropy  ${}^{*}S_{N}$  can be obtained from the thermocell measurements as discussed by Haase<sup>2</sup>. We defer the size estimate to Section 2.9.

# 2.8 Other Entropic Corrections

In the last term, S<sup>(g)</sup> represents the combination of partial molar entropies

$$S^{(g)} = S_{d} + \frac{1}{2} S_{o}$$

which arise when the cathode half-cell potential is referenced to the anode temperature. The nearly negligible transported entropy of electrons in the reference leads,  ${}^{*}S_{e,r}$  appears because of the contact potentials between reference leads and electrodes and the thermal diffusion potentials in the reference leads.

#### 2.9 Thermocell Measurements

The measurements on thermocells mentioned in Section II. 6 have been made by Jacobsen and Broers  $(JB)^9$  for molten carbonate mixtures. Apparently, JB measured the initial thermoelectric power  $\epsilon_0$ , given by

$$2Fe_0 = {}^*S_N - 2{}^*S_{e,r} - S^{(g)} - \sum_{i \neq N} t_i - \frac{{}^*Q_{iN}}{T}$$
 (5)

and their results can be used to estimate the size of the sum of terms discussed in Sections 2.6, 7 and 8.  $JB^9$  also estimated that  $\Sigma t_j {}^*Q_{jN}/T$  was a small term, hence we also have

$$\epsilon_0 \approx \epsilon_{\infty}$$
 (6)

where

$$2Fe_{\infty} = {}^{*}S_{N} - 2{}^{*}S_{e,r} - S^{(g)}$$
 (7)

The value

$$z_0 \approx 1 \,\mathrm{mV/K}$$

found by JB indicates that comparatively small potential drops will occur in cells with electrode temperatures differing by only a few degrees.

#### 3. HEAT RELEASE

# 3.1 General Expression

The local heat release rate  $\dot{Q}(watts/cm^3)$  for the cell described in the introduction is given by the following expression<sup>1</sup>:

$$-\dot{Q} = j^{2} \kappa^{-1} + (2F)^{-1} j \cdot \sum_{i \neq N} [(\nabla \mu_{iN})_{T,P} + (^{*}Q_{iN}/T) \nabla T]$$
  
+  $(2F)^{-1} j \cdot [T (\nabla^{*}S_{N})_{T,P} + T (\delta^{*}S_{N}/\delta T)_{X,P} \nabla T]$   
-  $\dot{Q}_{A} - \dot{Q}_{C}$ 

As in the case of the cell potential, we identify each term and provide an estimate of its size in the following sections.

3.2 Joule Heating

The Joule heating term  $j^2 \kappa^{-1}$  is easy to identify. For our earlier choices of  $\kappa = 1$  ohm<sup>-1</sup> cm<sup>-1</sup>, j = 160 mA/cm<sup>2</sup> we find

$$j^2 \kappa^{-1} \approx 26 \, \mathrm{mW/cm}^3$$
.

The heat evolved per unit area of electrode surface can be estimated for a cell with electrode separation l=2 mm as

$$j^2 \kappa^{-1} \ell \approx 5 \text{ mW/cm}^2$$
.

# 3.3 Measurable Diffusion and Thermal Diffusion Potentials

The next two terms

$$(2\mathbf{F})^{-1} \mathbf{j} \cdot \sum_{i \neq N} t_i [(\nabla \mu_{iN})_{T,P} + (^* \mathbf{Q}_{iN}/T) \nabla T]$$

represent the energy dissipated (or absorbed, depending on sign) by the passage of current through what we termed earlier the measureable part of the diffusion and thermal diffusion potentials. Probably, these two terms will be of opposite sign. (As can be seen from Eq. (3), they cancel in the Soret steady state.) We also anticipate only small temperature differences between electrodes. An overestimate of the size of these two terms should therefore be obtained by using the earlier estimated value of 40 mV for just the diffusion potential,  $\Delta \phi_{T}$ . For the 2 mm cell, we thus find

$$j \left| \frac{\Delta \varphi_D}{\ell} \right| \leq 30 \text{ mW/cm}^3$$

and per unit electrode area we have

$$j\Delta\phi_D \leq 6 \text{ mW/cm}^2$$

#### 3.4 Bulk Peltier and Thomson Effects

The next two terms are very interesting from a conceptual point of view. By analogy with the formal expressions occurring in the theory of metallic thermoelectric effects<sup>2</sup>, it is reasonable to identify Tj  $\cdot$   $(\nabla^* S_N)_T$  as the heat evolved or absorbed with passage of current because of a bulk electrolyte Peltier effect. In the steady state under discussion, the effect arises because of the possible composition dependence of the transported entropy of the anions. Likewise, the other term Tj  $\cdot$   $(\partial^* S_N / \partial T)_X \nabla T$  is a formal representation of a bulk electrolyte Thomson heat that arises from the possible temperature dependence of  $*S_N$ .

Information regarding the temperature and composition dependence of  ${}^{*}S_{N}$  is lacking. For the sake of making an estimate, let us attribute half of the standard deviation reported by JB<sup>9</sup> in their measurements of  $\varepsilon_0$  (Eq. (5)), to a variation in  ${}^{*}S_{N}$ . Then after noting the the simplification

we find (for *l*=2 mm)

$$jT \left| \frac{\Delta^* S_N}{l} \approx 7 \text{ mW/cm}^3 \right|$$

and per unit electrode area

$$jT \Delta^* S_N \approx 1 \text{ mW/cm}^2$$

#### 3.5 Electrode Heat Release

Because of our assumption of close proximity of gas/electrolyte interfaces and electrodes, the following contributions may be included as part of the heat release/absorption rates at the anode,  $\dot{Q}_A$ , and the cathode,  $\dot{Q}_C$ : 1) the enthalpy change of gas dissolving or evaporating, 2) the transported enthalpy flux of dissolved gas species, and 3) the changes in electrochemical enthalpy and heats of transport for <u>all</u> species involved in the half reactions. The ponderous expression that results will be presented and discussed elsewhere<sup>1</sup>. It is far more instructive here to integrate  $\dot{Q}_A$  and  $\dot{Q}_C$  over the volumes  $V_A$ ,  $V_C$ enclosing the electrode and gas/electrolyte interfaces and divide by the electrode areas  $\mathcal{A}_A$ ,  $\mathcal{A}_C$ :

$$\dot{q}_{A,C} = \mathcal{A}_{A,C}^{-1} \int \dot{Q}_{A,C} dV_{A,C}$$

We then find for the individual cathode and anode heat release/absorption rates (in  $mW/cm^2$ ) the expressions

$$2F \dot{q}_{C} = j \left( \Delta \tilde{H}_{C} + {}^{*}Q_{N} - 2{}^{*}Q_{e} \right)$$
(8)

$${}^{2F}\dot{\mathbf{q}}_{\mathbf{A}} = \mathbf{j} \left( \Delta \widetilde{\mathbf{H}}_{\mathbf{A}} + 2^{*} \mathbf{Q}_{\mathbf{e}} - {}^{*} \mathbf{Q}_{\mathbf{N}} \right) \quad . \tag{9}$$

where the half cell enthalpy change,  $\Delta \hat{H}$ , is the appropriate linear combination of gas phase partial molar enthalpies for neutral species and of electrochemical enthalpies for charged species partaking in the half reactions, Eqs. (1) and (2). Equations (8) and (9) can be readily manipulated into the form

$$\dot{\mathbf{q}} = \mathbf{j} \left( \frac{\mathbf{T} \Delta \mathbf{S}^{\mathbf{P}}}{2\mathbf{F}} - \eta \right)$$
(10)

where  $\eta$  is the absolute value of the electrode overpotential and  $\Delta S^{P}$  is the steady state Peltier entropy of the electrode half reaction. For the estimates of Section 2.4, we find

 $j(\eta_A + \eta_C) = 16 \text{ to } 24 \text{ mW/cm}^2$ 

The size and behavior of  $\Delta S^{\mathbf{P}}$  will be considered in detail in the next section.

#### 4. ELECTRODE PELTIER HEAT RELEASE

# 4.1 General Considerations

Aspects of this problem have been treated previously. See in particular the work of Agar<sup>10</sup>, and Jacobsen and Broers<sup>11</sup> in which the Peltier entropy for a half reaction taking place on an electrode immersed in an electrolyte of uniform composition has been formulated. Our results, as indicated, apply to the steady state in which any possible composition gradients have been fully established. The difference between the Peltier entropies in these two extremes is slight, and is given by the term  $\Sigma t_1^* \Omega_{\rm iN}/T$  which we have seen to be small. Needless to say, in the case of a pure molten salt  $^*\Omega_{\rm iN} = 0$  and the two Peltier entropies become identical. In the remainder of this section, we intend to consider the gas pressure and composition dependence of the molten carbonate steady state Peltier entropies. Initially, we treat only the hydrogen half reaction at the anode. We will shortly consider the complications introduced by the shift and methanation equilibria. Using the classical thermodynamic expressions for ideal gas entropies, we can write

$$\Delta S_{C}^{P} \stackrel{\cdot}{=} \Delta S_{C}^{\theta} + R \ln \left( X_{o}^{1/2} X_{d} \right) + \frac{3}{2} R \ln P$$
(11)

and for the H<sub>2</sub>(h) half reaction at the anode

$$\Delta S_{A,h}^{P} = \Delta S_{A,h}^{\theta} - R \ln \left( X_{w} X_{d} / X_{h} \right) - R \ln P$$
(12)

For  $\Delta S^{\theta}$  we have the following combinations of gaseous standard state entropies  $S^{\circ}$  and transported entropies \*S of charged species:

$$\Delta S_{C}^{\theta} = {}^{*}S_{N} - 2{}^{*}S_{e} - S_{d}^{o} - \frac{1}{2}S_{o}^{o}$$
$$\Delta S_{A,h}^{\theta} = S_{w}^{o} + S_{d}^{o} - S_{h}^{o} + 2{}^{*}S_{e} - {}^{*}S_{N}$$

These two quantities depend primarily on T, and, through  ${}^{*}S_{N}$  and  ${}^{*}S_{e}$ , on electrolyte composition and electrode material. This last dependence is unimportant because  ${}^{*}S_{e}$  is negligibly small, usually on the order of 1 J/K-mol. Furthermore, Jacobsen and Broers<sup>9</sup> found no indication of any appreciable composition dependence or temperature dependence for  $\Delta S^{\theta}$ . This last point must mean that the individual temperature variations of the  $S^{\circ}$ 's and  ${}^{*}S_{N}$  very nearly cancel. From the JB<sup>9</sup> work and Eqs. (6) and (7), we find for various molten carbonate mixtures in the temperature range 800 - 1150 K, the average values

$$\Delta S_{C}^{\theta} = -217 \text{ JK}^{-1} \text{ mol}^{-1}$$

and

$$\Delta S_{A, h}^{\theta} = 162 \ JK^{-1} mol^{-1}$$

Using Third Law entropies for the gaseous species we also obtain at 923 K,  ${}^{*}S_{N} \approx 170 \text{ JK}^{-1} \text{mol}^{-1}$ , an appreciable quantity.

Because  $\Delta S^{\theta}$  is the largest term in either Eq. (11) or Eq. (12), we see that the cathode is highly exothermic and the anode is nearly as endothermic. The power densities that correspond to these Peltier entropies can be computed using Eq. (10). At 160 mA/cm<sup>2</sup>, we find

$$\dot{\mathbf{q}}_{\mathbf{C}}^{\mathbf{\theta}}$$
 = - 166 mW/cm<sup>2</sup>

and

$$\dot{q}_{A}^{\theta} = 124 \text{ mW/cm}^{2}$$

Thus to maintain a thermal steady state, besides removing net heat from the cell, approximately  $120 \text{ mW/cm}^2$  must be transferred from the cathode to the anode. This value is comparable to the electrical power density output,  $jV = (160 \text{ mA/cm}^2)(0.8V) = 128 \text{ mW/cm}^2$ , but the temperature gradient needed to effect this transfer directly through the electrolyte is small. We find

$$\frac{\Delta T}{l} = \frac{1}{k_{T}} (120 \text{ mW/cm}^2) \approx 1.3 \text{ K/mm}$$

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where we have conservatively taken the thermal conductivity  $k_{\rm T}$  of a molten carbonate/lithium aluminate tile to be one-half of the value estimated for a carbonate melt<sup>12</sup>. On this basis we can expect that only small temperature differences will exist between electrodes across the cell. Inclusion of the remaining terms of Eq. (11) and (12), which are discussed below, will not alter the general conclusions reached above, although the precise numbers may change somewhat.

#### 4.2 Pressure Dependence

The predominant pressure dependence of  $\Delta S^P$  arises from the gas phase species and is given by the  $\ln P$  terms in Eqs. (11) and (12). In Fig. 2 we present the pressure dependence of the heat release rates that can be obtained from Eqs. (10), (11) and (12):

 $\begin{bmatrix} \dot{\mathbf{q}}_{\mathbf{C}} \end{bmatrix}_{\mathbf{P}} = \mathbf{j}(\mathbf{3RT}/\mathbf{4F}) \, \boldsymbol{\ell}_{\mathbf{n}\mathbf{P}}$  $\begin{bmatrix} \dot{\mathbf{q}}_{\mathbf{A}} \end{bmatrix}_{\mathbf{P}} = - \mathbf{j}(\mathbf{RT}/\mathbf{2F}) \, \boldsymbol{\ell}_{\mathbf{n}\mathbf{P}}$ 

It is easy to see that a constant current density cathode exothermity, anode endothermity and overall cell exothermity decrease with increasing P. It is also clear that pressure variations would have to be quite extreme in order to effect substantial changes in overall cell exothermicity.

#### 4.3 Cathode Composition Dependence

The composition dependence of the cathode heat release rate is easily obtained from Eqs. (10) and (11) as

$$[\dot{q}_C]_X = j(RT/2F) \ln(X_o^{1/2}X_d)$$

In Fig. 3, a plot of  $[\dot{q}_C]_X$  versus  $X_d$  for air/CO<sub>2</sub> mixtures is presented. The noble mixture (2/3 CO<sub>2</sub>, 1/3 air) is the least exothermic, but changes in  $\dot{q}$  with composition are small.

# 4.4 Anode Heat Release for Fuel Mixtures

The anode heat release can be considered as arising from the electro-oxidation of H<sub>2</sub>, with possible additional contributions from the electrochemical reaction of CO and CH<sub>4</sub> as well as from the water gas shift reaction

$$H_2 + CO_2 = H_2O + CO$$
 (13)

and the methanation reaction

$$4 H_2 + CO_2 = CH_4 + 2 H_2O$$
 (14)

Provided the latter two reactions always remain in equilibrium, the question of the electrochemical reactivity of CO and  $CH_4$  need not be addressed, and a complete mathematical description of the heat release can be given as follows.

Aside from the heat of transport of the charged species which can be added in later, the amount of heat released, dH, by small (dn) changes in the numbers of moles of the involved species is

$$dH = \sum_{\alpha} H_{\alpha} dn_{\alpha} + \tilde{H}_{N} dn_{N} + \tilde{H}_{e} dn_{e}$$
(15)

where the sum on  $\alpha$  extends over h, w, d, c and m. Here,  $H_i$  is the usual partial molar enthalpy of gaseous substance i and  $H_j$  is the electrochemical enthalpy of charged substance j:

 $\widetilde{H}_{j} = H_{j} + z_{j}F\varphi_{j}$ 

where  $z_j$  is the charge, and  $\phi_j$  is the electrical potential of the phase in which species j is found.

The changes in the dn in Eq. (15) are not arbitrary, but are constrained by the requirement of maintaining equilibrium, at constant T and P, before and after the shift and methanation reactions have proceeded a small extent:

$$K_{s} = \frac{wc}{hd} = \frac{(w + dn_{w})(c + dn_{c})}{(h + dn_{h})(d + dn_{d})}$$
(16)

$$K_{m} = \frac{mw_{i}^{2}}{h^{4}dP^{2}} = \frac{(m + dn_{m})(w + dn_{w})^{2}n_{f}^{2}}{(h + dn_{h})^{4}(d + dn_{d})P^{2}}$$
(17)

For simplicity of notation we have also used the letters m, c, d, h and w to denote the number of moles of each gaseous substance. The initial  $n_i$  and final  $n_f$  numbers of moles present are

 $n_{i} = m + c + d + h + w$ 

 $n_{f} + n_{i} + \sum_{\alpha} dn_{\alpha}$ .

We also need the equation

$$-d\xi = dn_{N} = dn_{c} + dn_{h} + 4 dn_{m}$$
(18)

to define the variable  $\xi$  which measures the extent to which the electrochemical reaction of H<sub>2</sub> has proceeded. We next expand Eqs. (16) and (17) and retain only terms linear in dn. We then combine the resulting expressions with Eq. (18) and with the stoichiometric relations that arise from the conservation of C, H and O atoms and of charge in order to obtain from Eq. (15) the expression

$$\Delta \widetilde{H}_{A} \equiv \frac{dH}{d\xi} = \Delta \widetilde{H}_{A,h} - \frac{\beta \mu + \gamma \nu}{\alpha \beta - \gamma^{2}} \Delta H_{s} + \frac{\gamma \mu + \alpha \nu}{\alpha \beta - \gamma^{2}} \Delta H_{m}$$
(19)

where  $\triangle H_{A,h}$  is the electrochemical enthalpy change for the anodic  $H_2$  half reaction and  $\triangle H_s$  and  $\triangle H_m$  are the enthalpy changes for the water gas shift and methanation reactions:

$$\Delta \widetilde{H}_{A,h} = H_w + H_d + 2 \widetilde{H}_e - \widetilde{H}_N - H_h$$
$$\Delta H_s = H_c + H_w - H_d - H_h$$
$$\Delta H_m = H_m + 2 H_w - 4 H_h - H_d$$

The other quantities appearing in Eq. (19) are defined as

$$\alpha = 1/h + 1/c + 1/w + 1/d$$

$$\beta = 1/m + 4/w + 16/h + 1/d - 4/n_i$$

$$\gamma = 2/w + 4/h + 1/d$$

$$\mu = 1/h + 1/w - 1/d$$

$$\gamma = 1/d - 4/h - 2/w - 2/n_i$$

For the mixed reaction system under consideration, Eq. (17) is appropriate for use in Eq. (9). The terms in  $\Delta H_s$  and  $\Delta H_m$  obviously account for heat released or absorbed as the water gas shift and methanation reactions take place in order to maintain the equilibrium disturbed by the electro-oxidation of  $H_2$ .

Using a different starting point, Jacobsen and Broers<sup>11</sup> have also treated the problem of heat release from a mixed reaction system at the anode. Aside from the difference noted in Section IV. 1., Eqs. (9) and (19) can be shown to be identical with their results.

For cells running on low BTU gasifier output mixtures, the effects of the  $\Delta H_{s}$  and  $\Delta H_{m}$  terms are not too large. At 923 K,  $\Delta H_{s} = 35.6 \text{ KJ mol}^{-1}$  and  $\Delta H_{m} = -189.1 \text{ KJ mol}^{-1}$ , but for the fuel mixture consisting of 17.7 mole%H<sub>2</sub>, 16.6% CO, 4.7% H<sub>2</sub>O, 9.2% CO<sub>2</sub>, 0.74% CH<sub>4</sub> and 51.1% N<sub>2</sub>, we find  $(\beta\mu + \gamma\nu)/(\alpha\beta + \gamma^{2}) \Delta H_{s} = 3.3 \text{ kJ mol}^{-1}$  and  $(\gamma\mu + \alpha\nu)/(\alpha\beta - \gamma^{2}) \Delta H_{m} = 28.9 \text{ kJ mol}^{-1}$ . The contribution of the  $\Delta H_{s}$  term is quite small compared to  $T_{\Delta}S_{A,h}^{\Theta}$  which equals 150 kJ mol<sup>-1</sup> at 923 K. The  $\Delta H_{m}$  term is somewhat larger, but is still only 20% of  $T_{\Delta}S_{A,h}^{\Theta}$  at this low CH<sub>4</sub> concentration. Under full equilibrium conditions, the CH<sub>4</sub> content would decrease with fuel utilization in a working cell. Then, because  $\beta \rightarrow \infty$  as  $m \rightarrow 0$ , the  $\Delta H_{m}$  term will become even less important. If, on the other hand, CH<sub>4</sub> does not remain in equilibrium because of slow reaction kinetics, Eq. (19) is inappropriate. In the limit of complete unreactivity of CH<sub>4</sub>, we have

$$\Delta \widetilde{H}_{A} = \Delta \widetilde{H}_{A, h} - (\mu/\alpha) \Delta H_{s}$$

but intermediate cases require further consideration.

# 4.5 Anode Composition Dependence

For simplicity we consider  $CH_4$  to be unreactive, but we do include the effects of shift equilibrium, Eq. (13). Then in view of the smallness of the  $\Delta H_s$  term, the anode heat release composition dependence will be adequately described by the equation

$$[\dot{q}_A]_X = -j(RT/2F) \ln(X_w X_d/X_h)$$

which follows from Eqs. (10) and (11).

We first consider the variation of endo- or exothermicity of fuel gas mixtures lying on the carbon deposition boundary (CDB). This will be of interest because such mixtures typify inlet conditions at the anode. The present calculations were performed for fuel mixtures lying just on the CDB at T = 923 K, P=1 and 10 atm and with no methane present. The composition along the CDB is readily calculated using the analytical methods of Broers and Treijtel<sup>13</sup>. The results are presented in Fig. 4. The most notable feature of the results is the drastic increase in endothermicity with increasing H<sub>2</sub>/CO ratio.

Also of interest is the variation of the heat release with composition changes arising from utilization of fuel. In Fig. 5, results of a representative calculation are plotted. For an initial fuel mixture we took 17.9% CO, 19.1% H<sub>2</sub>, 8.6% CO<sub>2</sub>, 4.4% H<sub>2</sub>O and 50.0% N<sub>2</sub> at a temperature of 923 K and a pressure of 1 atm. This is a typical output of a low BTU, air blown gasifier, allowed to equilibrate with added H<sub>2</sub>O to prevent carbon deposition. To give an indication of the composition of the mixture we plotted power density (mW/cm<sup>2</sup>) at 160 mA/cm<sup>2</sup> versus the sum of the H<sub>2</sub> and CO mole fractions divided by the initial value of the quantity. Throughout the calculation  $X_c \approx X_h$ . The arrows ( $\uparrow$ ) on the figure mark points at which the indicated % of fuel (CO + H<sub>2</sub>) has been expended. The results show a steady decline in endothermicity with increasing utilization. The range of variation in the anode heat release is also large compared to that found in the cathode (Fig. 3).

# V. SUMMARY

The most important contributions to the cell heat release rate are the large, exothermic cathode Peltier heat and the somewhat smaller, but endothermic, anode Peltier heat. These individual electrode heat release rates have variations from changes in gas pressure and composition that are comparable in size to the additional exothermic heat release derived from the ohmic drop in the electrolyte and from the electrode overpotentials.

Other smaller, but conceptually interesting contributions to the heat release rate arise when current is passed through an electrolyte containing composition and temperature gradients. These contributions are caused by potential drops that we termed "measurable parts of the diffusion and thermal diffusion potentials" and by bulk electrolyte Peltier and Thomson heats.

It was also interesting to find that the cathode-to-anode heat flux required to maintain a nearly isothermal steady state is comparable in size to the electrical power density output of the cell. The small temperature gradient (1 - 2 K/mm) needed to sustain this heat flux through the electrolyte/tile, implies that the temperature difference between electrodes should be small at any point in the cell. As a result, only small voltage losses (1 mV/K) should occur because of temperature differences between electrodes. Effects of temperature variations in the plane of an operating cell are beyond the scope of this investigation.

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Fig. 1 Schematic cell diagram. Electrode Temperatures,  $T_A$ ,  $T_C$ . Reference points 1 and 2 at temperature T.





Fig. 2 Pressure dependence of electrode Peltier heat release rate.



Fig. 3 Gas composition dependence of cathode Peltier heat release rate for CO<sub>2</sub>/air mixtures.



Fig. 4 Gas composition dependence of anode Peltier heat release rate along methane free carbon deposition boundaries.



Fig. 5 Gas composition dependence of anode Peltier heat release rate as a function of % fuel utilization (**↑**).

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