TECH HIGHLIGHTS

In celebration of the Society's Centennial, Tech Highlights presents an "All-Star" collection of 25 significant articles that have appeared in ECS journals during a portion of the Society's history. A citation search dating back to 1945 revealed a number of articles, including those highlighted here, that have been cited hundreds of times in the scientific literature. Unfortunately, the search could not be extended back to 1902, when Transactions of The Electrochemical Society *was first published, but the highlighted articles are representative of the leading role ECS has played for 100 years in advancing the theory and practice of electrochemical and solid-state science. The papers appear in order of decreasing citation frequency—the first 13 appear with summaries, and the last 12 papers are listed in the sidebar on page 19.*

Reaction Rates in Ionic Solutions

In a paper presented in 1942 at the 82nd ECS general meeting, Professor **PETER J. W. DEBYE** of Cornell University in New York presented an important extension of Smoluchowski's 1916 theory on reaction rates in ionic solutions. The earlier theory employed a purely diffusional treatment that Debye extended to include electrostatic effects arising from the presence of net charges. Debye, the 1936 Nobel Prize winner in Chemistry, derived the influence of intermolecular forces on reaction rates for dilute solutions (where Coulomb forces between the two reactants predominate) and for concentrated solutions (where other fundamental forces typical of strong electrolytes, including the screening effect, are important). Debye's research at this time was focused on macromolecular and colloid chemistry, and this new reaction rate theory was useful in understanding reactions such as the coagulation of colloid suspensions. It also clearly built on the mathematical and physical foundation of his numerous other publications on X-ray scattering, molecular dipole moments, molecular polarizability, electrolyte theory, and macromolecular light scattering.

From: Trans. Electrochem. Soc., ***82****, 265 (1942)*

Low Temperature Surface Cleaning of Silicon for MBE

Molecular beam epitaxy (MBE) can produce device quality Si films if the substrate is properly cleaned prior to epitaxial growth. High temperature (1200°C) thermal etching in ultra high vacuum (UHV) provides the required cleanliness but is often undesirable because it increases the densities of dislocations, stacking faults, and other defects. Further, it can result in unwanted thermal diffusion of impurities. In 1986, **AKITOSHI ISHIZAKA** and **YASUHIRO SHIRAKI** of Hitachi in Japan described a low temperature cleaning method consisting of (1) wet chemical treatments to degrease the surface and eliminate carbon contamination, (2) repeated wet chemical oxidation (boiling HNO_2 and/or NH_4OH:H_2O_2) and oxide removal (dilute HF) steps to further clean the surface, (3) formation of a thin, volatile oxide layer (via a brief dip in a boiling solution of aqueous HCl:H_2O_2), and (4) low temperature (< 800°C) desorption of the volatile oxide under UHV. Crystalline Si films grown on these substrates were shown to be of high quality by a combination of Auger electron spectroscopy, high-energy electron diffraction, and X-ray photoelectron spectroscopy.

From: J. Electrochem. Soc., ***133****, 666 (1986)*

The Shape of Electrochemical Polarization Curves

Polarization measurements are used to characterize the relationship between overpotential and current for electrode reactions. Early studies of electrode reaction mechanisms demonstrated that, in many cases, the current is exponentially related to the overpotential. In 1905, Tafel formulated the well-known equation that relates these quantities. However, in 1957, **M. STERN** and **A. L. GEARY** of the Electro Metallurgical Company in New York observed that considerable uncertainty in the interpretation of polarization curves still existed. They published a theoretical study of polarization curve behavior for both noncorroding and corroding electrode systems. The authors concluded that deviations from Tafel behavior for a noncorroding electrode at low overpotentials are due primarily to the reverse reaction of the oxidation-reduction system, and at high overpotentials to concentration polarization and/or ohmic potential drop effects. For corroding electrodes, the forward and reverse reactions for both of the oxidation-reduction systems forming the corrosion couple were required to calculate polarization curves that reasonably explained experimental results published in the literature.

From: J. Electrochem. Soc., ***104****, 56 (1957).*

EMF Measurements on Galvanic Cells with Solid Electrolytes

As early as 1904, many researchers (including Fritz Haber) showed that electromotive force (emf) measurements on galvanic cells containing solid electrolytes would yield important thermodynamic information. In 1957, **CARL WAGNER** (recipient of the Society's Olin Palladium Medal in 1951) and **KALEVI KIUKKOLA** of the Massachusetts Institute of Technology reported results of detailed emf measurements that allowed them to accurately determine the standard molar free energy of formation of CoO, NiO, Cu_2O, Ag_2S, Ag_2Se, PbS, and several phases of the Ag-Te system. In a typical experiment, a sandwich arrangement of three separate tablets (*e.g.*, a mixture of a metal and its oxide, a ZrO_2/CaO solid electrolyte, and a mixture of another metal and its oxide) was placed between two Pt disks. This cell was then placed in a furnace so that potentiometric measurements could be made at temperatures as high as 1150°C. The authors compared their emf and standard free energy values with literature results (both experimental and theoretical) and discussed possible causes for some of the observed discrepancies.

From: J. Electrochem. Soc., ***104****, 379 (1957)*

Surface-State Charge of Thermally Oxidized Silicon

In the early 1960s, the thermally oxidized silicon surface was the subject of intense investigation due to its extreme technological importance. In 1967, **B. E. DEAL** (who was later honored as an ECS Fellow in 1991), **M. SKLAR, A. S. GROVE**, and **E. H. SNOW** of Fairchild Semiconductor in California reported the results of an extensive experimental investigation of the effects of oxidation conditions, silicon orientation, annealing treatments, oxide thickness, and electric fields on the surface-state charge (Q_{ss}) of thermal oxide and on the spatial distribution of Q_{ss} within the oxide. Their experiments, primarily capacitance-voltage measurements on metal-oxide-semiconductor (MOS) structures, indicated that Q_{ss} is an intrinsic property of the silicon dioxide-silicon system and that it can be reproducibly controlled over the range 10^{10}-10^{12} cm^{-2}. The intrinsic nature of the surface-state charge was surmised from its relative immobility and by its high degree of reproducibility. The authors further concluded that Q_{ss} appeared to be due to an excess silicon species introduced into the oxide layer, near the silicon, during oxidation.

From: J. Electrochem. Soc., ***114****, 266 (1967)*

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AC Impedance Study of Li Diffusion in WO_3 Films

The electrochemical insertion of metal atoms into tungsten oxide is accompanied by a dramatic clear-to-blue color change caused by injection of electrons into the conduction band. This electrochromic phenomenon has been extensively studied and is the basis for several technological applications of these materials today. In 1980, **C. Ho, I. D. Raistrick**, and **R. A. Huggins** of Stanford University in California reported the results of an electrochemical investigation into the thermodynamics and kinetics of Li-WO_3 electrochromism. They performed coulometric titration and ac impedance measurements on thin film WO_3 working electrodes immersed in a supporting electrolyte of $LiAsF_6$ in propylene carbonate. The counter and reference electrodes were pure Li metal. They observed that, at low ac frequencies, diffusion of neutral lithium limits the coloration rate of the oxide. At high frequencies, however, the kinetics of the electrochemical reduction of lithium ions was determined to be the rate-limiting step.

*From: J. Electrochem. Soc., **127**, 343 (1980)*

Structural Evaluation of Silicon Oxide Films

Silicon oxide films are extensively used in the fabrication of semiconductor devices. **W. A. Pliskin** (who was later honored as an ECS Fellow in 1991) and **H. S. Lehman** of IBM in New York produced an extensive study in 1965 that described a variety of physical and chemical analysis methods for characterization of oxide films. They demonstrated the utility of these methods by analyzing films formed by thermal oxidation, thermal evaporation, reactive sputtering, anodic oxidation, lead catalyzed oxidation, CO_2 oxidation, and thermal decomposition of tetraethoxysilane. Analysis was performed by a combination of infrared spectroscopy (in several frequency regions), selective etchants formulated from HF and HNO_3, optical interference microscopy, and electrical testing of oxide-passivated diodes. In addition to illustrating the power of this suite of characterization methods, the authors concluded that porous and strained oxides can be densified to be indistinguishable from thermal oxides, that steam is more effective than dry oxygen in densification procedures, and that surface hydroxyl groups can be removed by densification.

*From: J. Electrochem. Soc., **112**, 1013 (1965)*

Thermodynamics of Electron/Hole Formation in Ge, Si, GaAs, and GaP

The forbidden energy gap of a semiconductor is the standard Gibbs energy for formation of electrons and holes. In 1975, **C. D. Thurmond** of Bell Laboratories in Murray Hill, New Jersey used data on energy gaps of Ge, Si, GaAs, and GaP to obtain the standard Gibbs energy, enthalpy, and entropy for electron/hole formation in these important semiconductor materials. Thurmond used previously published experimental data, of energy gaps within limited temperature ranges, to estimate the values of the standard thermodynamic functions for temperatures ranging from 0 K to the respective melting points of the semiconductors. Decreases in energy gaps with temperature are predominantly due to the relatively large entropies resulting from the interactions of electrons and holes with the lattice. The author also noted that the observed increases in enthalpies with temperature are indicative of positive heat capacity changes accompanying electron/hole formation.

*From: J. Electrochem. Soc., **122**, 1133 (1975)*

Resistance for Flow of Current to a Disk

To avoid distortion of the potential field and the velocity distribution near a rotating disk electrode, the reference electrode is typically located some distance from the rotating disk. However, the ohmic drop between the reference and the working electrodes must be quantified. In a Technical Note published in 1966, **John Newman** of the Lawrence Radiation Laboratory and the University of California-Berkeley quantified the resistance between a disk imbedded in the surface of an insulator and a counter electrode located at infinity. Assuming no deviations from primary current distribution, he showed that even if the reference electrode is placed along an axis orthogonal to the plane of the disk and 0.5 mm away, the resistance remains greater than 10% of that between the disk and the counter electrode. Further, at small distances from the disk, the resistance is a strong function of distance. Thus, to more accurately estimate the resistance between the reference and working electrodes (and therefore accurately quantify the ohmic potential drop), he concluded that it is better to locate the reference electrode some distance from the disk. Newman received the Society's Olin Palladium Medal in 1991 and was honored as an ECS Fellow in 1995.

*From: J. Electrochem. Soc., **113**, 501 (1966)*

Electropolishing Silicon in Aqueous Hydrofluoric Acid

Among the first investigations of the electrochemistry of silicon in hydrofluoric acid solutions was that by **Dennis Turner** of Bell Telephone Laboratories, Murray Hill, New Jersey in 1958. Earlier work by A. Uhlir, also at Bell Labs, had identified a divalent silicon dissolution reaction. Turner observed that this reaction occurred at current densities below that for the tetravalent silicon electropolishing reaction and produced a thick, solid layer in p-type silicon. The solid layer has since been identified as porous silicon, which remains today a material of great scientific and technological interest for applications in silicon-on-insulator circuit fabrication, chemical vapor sensors, microelectromechanical systems, and electroluminescent devices. Turner showed that the anode film contained fluoride ion and that hydrogen evolution occurred at the anode during the divalent reaction. He proposed that the divalent reaction produced an unstable silicon subfluoride that is oxidized to tetravalent silicon with concomitant production of hydrogen gas. Turner's proposed reaction is still generally accepted as the divalent electrochemical reaction that produces porous silicon. Turner was honored as an ECS Fellow in 1991 and received the Society's de Nora Award in 2000.

*From: J. Electrochem. Soc., **105**, 402 (1958)*

Structural Features of Oxide Coatings on Aluminum

Anodization of aluminum in aqueous acid electrolytes produces oxide coatings that can be specifically tailored to suit the requirements of many different applications. Anodic oxides are used to improve corrosion, wear, and abrasion properties of structural aluminum alloys, and can also be used for decorative surface finishes. These oxides are also used as sensing elements in commercially-available capacitive moisture hygrometers and as ordered porous templates for fabrication of electronic, optoelectronic, photonic, microanalytical, and microelectromechanical devices. In 1953, **F. Keller, M. S. Hunter,** and **D. L. Robinson** of the Aluminum Company of America in Pennsylvania examined the structural features of oxides formed by anodization of aluminum in sulfuric, oxalic, chromic, and phosphoric acid electrolytes. Electron microscopy revealed that the coatings are composed of close-packed cells of hexagonal oxide, with each cell containing a single pore. Pore morphology, pore size, and the thickness of both the cell wall and the barrier oxide at the bottom of the pore were all shown to be dependent on the anodization electrolyte and the forming voltage. Their pioneering work has had a significant impact on the aluminum anodization industry because it provided important information on processing-structure-property relationships for anodic oxide coatings.

*From: J. Electrochem. Soc., **100**, 411 (1953)*

Lithium Intercalation into Carbon Electrodes

Carbonaceous electrodes have been widely used in rechargeable lithium batteries because of the well-established ability of carbon to intercalate large quantities of lithium to form Li_xC_6 ($0 < x < 1$). It is now generally agreed that the formation of a solid electrolyte interphase (SEI) at the surface of the carbon electrodes, as a result of the reaction of Li_xC_6 with nonaqueous solvents, plays an essential role in assuring the stability and the cyclability of such electrodes. The reaction between Li_xC_6 and nonaqueous solvents was observed more than a decade ago. In 1990, **R. Fong, U. von Sacken,** and **J. R. Dahn** at Moli Energy Limited in Canada reported the results of their study on this phenomenon using Li/graphite and Li/petroleum coke electrodes in a mixture of propylene carbonate and ethylene carbonate electrolyte. They found that the reactions were irreversible and only occurred on the first discharge of the cells. These irreversible reactions were associated with electrolyte decomposition and caused the formation of a passivating film or SEI on the surface of the carbon electrodes. The reactions proceeded until all the available surface of the carbon was coated with SEI. In subsequent cycles, these cells were found to exhibit excellent reversibility.

*From: J. Electrochem. Soc., **137**, 2009 (1990)*

Ternary Phase Formation in Cathode Reactions of Lithium Batteries

Sulfides and oxides of transition metals have been exploited as cathode materials for ambient temperature batteries using lithium metal anodes. Very little was known concerning the cathode reaction mechanisms of these materials, or even of the reaction products, until 1976 when **M. S. Whittingham** of the Exxon Research and Engineering Company in New Jersey reported the results of his study on cell reactions between lithium and several transition metal oxides and sulfides. Whittingham found that ternary phases, rather than simpler lower lithium oxides or sulfides, as had been previously proposed, were formed during the cell reactions. The structure of the ternary product depended upon the crystal lattice of the initial reactant, and minimum structural change occurred during intercalation reactions. The reversibility of the discharge reaction was maximized when no chemical bonds were broken during discharge, as in the Li/TiS_2 system. When some chemical bonds were broken, as for V_2O_5 and TiS_3, partial or difficult reversibility was found. The Li/CuS cell exhibited only primary characteristics because all chemical bonds were broken during the discharge.

*From: J. Electrochem. Soc., **123**, 315 (1976)*

The All-Star List Continues...

14 Conduction Characteristics of the Lithium Iodide-Aluminum Oxide Solid Electrolytes, C. C. Liang (P. R. Mallory and Co., Inc., Burlington, MA).
*J. Electrochem. Soc., **120**, 1289 (1973)*

15 The Anodic Oxidation of Iron in a Neutral Solution. I. The Nature and Composition of the Passive Film, M. Nagayama and M. Cohen (National Research Council, Ottawa, Ontario, Canada).
*J. Electrochem. Soc., **109**, 781 (1962)*

16 Polymer Films on Electrodes. VII. Electrochemical Behavior at Polypyrrole-Coated Platinum and Tantalum Electrodes, R. A. Bull, F.-R. F. Fan, and A. J. Bard (University of Texas, Austin, TX).
*J. Electrochem. Soc., **129**, 1009 (1982)*

17 Lightweight Rechargeable Storage Batteries Using Polyacetylene, $(CH)_x$ as the Cathode-Active Material, P. J. Nigrey, D. MacInnes, Jr., D. P. Nairns, A. G. MacDiarmid, and A. J. Heeger (University of Pennsylvania, Philadelphia, PA).
*J. Electrochem. Soc., **128**, 1651 (1981)*

18 Thermodynamic Potential for the Anodic Dissolution of n-Type Semiconductors. A Crucial Factor Controlling Durability and Efficiency in Photoelectrochemical Cells and an Important Criterion in the Selection of New Electrode/Electrolyte Systems, A. J. Bard (University of Texas, Austin, TX) and M. S. Wrighton (Massachusetts Institute of Technology, Cambridge, MA).
*J. Electrochem. Soc., **124**, 1706 (1977)*

19 Environmental Factors Affecting the Critical Potential for Pitting in 18-8 Stainless Steel, H. P. Leckie and H. H. Uhlig (Massachusetts Institute of Technology, Cambridge, MA).
*J. Electrochem. Soc., **113**, 1262 (1966)*

20 The Preparation and Properties of Vapor-Deposited Epitaxial $GaAs_{1-x}P_x$ Using Arsine and Phosphine, J. J. Tietjen and J. A. Amick (RCA Laboratories, Princeton, NJ). *J. Electrochem. Soc., **113**, 724 (1966)*

21 A Mathematical Model of the Coupled Fluid Mechanics and Chemical Kinetics in a Chemical Vapor Deposition Reactor, M. E. Coltrin, R. J. Kee, and J. A. Miller (Sandia National Laboratories, Albuquerque, NM and Livermore, CA).
*J. Electrochem. Soc., **131**, 425 (1984)*

22 Electrostatic Binding of Metal Complexes to Electrode Surfaces Coated with Highly Charged Polymeric Films, N. Oyama and F. C. Anson (California Institute of Technology, Pasadena, CA).
*J. Electrochem. Soc., **127**, 247 (1980)*

23 Anodic Oxidation of GaAs in Mixed Solutions of Glycol and Water, H. Hasegawa and H. L. Hartnagel (University of Newcastle upon Tyne and The Merz Laboratories, Newcastle upon Tyne, United Kingdom).
*J. Electrochem. Soc., **123**, 713 (1976)*

24 The Use of Metal-Organics in the Preparation of Semiconductor Materials. I. Epitaxial Gallium-V Compounds, H. M. Manasevit and W. I. Simpson (North American Rockwell Corporation, Anaheim, CA).
*J. Electrochem. Soc., **116**, 1725 (1969)*

25 Electrochemistry of Manganese Dioxide in Lithium Nonaqueous Cell. III. X-Ray Diffractional Study on the Reduction of Spinel-Related Manganese Dioxide,
T. Ohzuku, M. Kitagawa, and T. Hirai (Osaka City University, Osaka, Japan).
*J. Electrochem. Soc., **137**, 769 (1990)*

Tech Highlights was prepared by Zenghe Liu of the California Institute of Technology, Yanrong Zhu of the University of Cincinnati, David Pendlebury of ISI-Thomson Scientific, Inc., and Diane Kozelka, Terry Guilinger, and Mike Kelly of Sandia National Laboratories.