

ELECTROCHEMICAL ENERGY STORAGE

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The objectives are to improve the performance and durability and to lower the costs of batteries and electrochemical processes employed in energy storage technologies.

Surface morphology of metals in electrodeposition

Transport processes involved in the electromacrocristallization of metals are being investigated under carefully controlled hydrodynamic conditions. Models are being developed for the description of current distribution involving combined mass and charge-transfer control. Current projects include the following:

- Observation of the development of surface morphology of zinc deposition from acid solutions — recent studies employing time-lapse photography confirmed LBL's earlier hypothesis regarding the evolution of imprints of hydrodynamic flow in the deposits. Initial nucleation is followed by growth and coalescence into protrusions that then grow outward causing secondary flows, enhanced deposition in regions receiving an improved supply of ions, and, finally, melding of protrusions into ridges.
- Deposition of copper from uninhibited acid sulfate solutions — it has been shown that the number density of large crystals decreases with Cu-ion concentration and with decreasing current density. Crystal size decreases with increasing concentration, and the average size is inversely related to number density.
- A model describing the current distribution at active/passive transition boundaries has been successfully tested. Results agreed well with experimental etch profiles obtained on a dissolving rotating cylindrical nickel anode, on which axially symmetric nonuniform distribution of current is caused to occur due to appropriate placement of the counter-electrode.

Anodic surface layers on battery materials

Structure, composition, and mode of formation of surface layers on battery electrode materials are determined from experimental observations to identify means for increasing energy efficiency and cycle life of battery electrodes. Present work is concerned with lithium in some representative

battery environments. Film formation in pure propylene carbonate solvent and its 1 M LiClO₄ and 1 M LiAsF₆ solutions has been observed in situ by ellipsometry and impedance measurements and ex situ by Auger electron spectroscopy, ion etching, secondary-ion mass spectrometry, and electron microscopy. The surface layers are found to be inhomogeneous: an inner, compact region is primarily responsible for the electrode behavior, although it is much thinner than the outer region with porosity increasing continuously toward the solution. Anodic and cathodic processes are found to involve different reaction mechanisms. Means to increase the ionic conductivity of the compact film are under investigation.

Metal couples in nonaqueous solvents

The objective of this project is to develop practical alternatives to aqueous (or high temperature molten-salt) systems for the efficient electrochemical reduction or oxidation of reactive metals. Current work is directed toward the elucidation of the role, in a quantitative sense, of solvent additives for improving solubility and conductance of single-solvent systems. Propylene- and ethylene-carbonate are used as main solvents with various ethers and esters as additives. A parallel effort at LBL (Anodic surface layers on battery materials) is aimed at clarification of the nature of films formed in these solvents and the resulting effect on electrode behavior.

Analysis and simulation of electrochemical systems

Mathematical models are developed to predict the behavior of electrochemical systems and to identify important process parameters. The accuracy and completeness of the models are tested experimentally. A one-dimensional model has been developed for the LiAl/FeS_x battery in conjunction with a major experimental program at Argonne National Laboratory. This model can be used to identify system limitations and to describe the actual phenomena associated with the LiAl/FeS_x battery during relaxation and charging.

Engineering analysis of gas generation

The objective of this project is to establish the influence of electrode geometry, surface morphology, and electrolyte composition on bubble size and residence time and to elucidate the role of free and forced convection as it affects overpotential behavior in gas-evolution processes. Current work is centered on a newly developed micromosaic electrode, which is prepared on a silicon wafer by integrated circuit manufacturing techniques. Bubbles nucleated at predetermined locations are allowed to detach and disturb the

concentration field around them. Current versus time behavior is observed simultaneously at various segments surrounding the segment on which the bubble was attached, using reduction of ferri- to ferro-cyanide ions as the vehicle for measurement of transport rates. In parallel with these experiments is the development of a theoretical model that describes the time-dependent concentration field around the bubble.

Electrode kinetics and electrocatalysis

The relationship between the kinetics of electrochemical reactions and the atomic structure of the electrode surface is being investigated. Catalytic surfaces under study include the Group VIII transition metals and metal oxides and the Group IB noble metals. Surface structures are varied by using single crystal methods and by dispersion of the catalytic phase onto inert substrates, as in commercial practice. Atomic structure is determined by low energy electron diffraction (LEED) in the case of single crystal surface and by high resolution transmission electron microscopy (ARTEM) in the case of the dispersed phases. Specific topics under study are the kinetics of oxygen reduction on active carbons impregnated with cobalt oxide, the chemical nature of heat-treated cobalt porphyrins immobilized on carbon surfaces, and hydrogen evolution from ordered zinc surfaces.

Electrochemical properties of solid electrolytes

The objectives of this work are to study the chemical and electrochemical stability toward molten sodium and to determine electrode polarization effects for various solid electrolytes. Nasicons ($\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$) with a variety of compositions were prepared, and their stability toward liquid sodium and liquid sodium polysulfide was determined.

Nasicons were fabricated by a sol-gel method. The specimens were immersed in sodium for periods of up to several weeks at 300 °C. Analysis with X-rays showed that the lattices of all electrolytes had undergone changes as a result of chemical reaction with sodium. Changes of the lattice dimensions were sufficient to cause electrolyte fracture, and it was determined that these lattice changes were not due to processing. It was found that minor alumina contamination could lead to the formation of a sodium aluminosilicate intergranular phase that was rapidly attacked by sodium. Elimination of contamination by alumina dramatically increased the resistance to chemical degradation of the electrolyte. Nevertheless, after about 10 weeks of immersion at 300 °C, the electrolytes again showed the same type of degradation that was observed in the more rapidly degrading electrolytes containing some alumina. It is therefore necessary to reexamine the stability of Nasicons at various compositions before work proceeds on cell development involving the sodium/sodium polysulfide electrochemical couple. Preliminary

experiments are showing that a decrease in the phosphorous content of the solid electrolyte can increase the susceptibility to chemical attack by molten sodium.

Battery electrode studies

The behavior of rechargeable electrodes in both aqueous and molten salt electrolytes is being studied, and means to improve their performance and lifetime are being investigated. A computer-controlled test system has been designed and constructed to allow the simultaneous and continuous cycling of 16 or more electrochemical cells with a wide variety of charge and discharge profiles, including pulse charging and Environmental Protection Agency (EPA) power profile discharging. This test system has been employed to study the cycle-life behaviour of 1.4-A h zinc/nickel oxide cells. Several electrolytes that exhibit reduced solubility of ZnO demonstrated improved capacity retention and lower Zn materials distribution when compared to 'standard' 31 wt.% KOH electrolyte. A parallel study of the effect of various pulsed-charging waveforms on Zn/NiOOH cell cycle-life performance identified a charging characteristic (30 ms on/90 ms off, 16-mA/cm² peak current density) that resulted in improved capacity retention when compared to constant-current charging.

Improvement in efficiency of aluminum reduction cells

The objective of this project is the improvement of the performance of electrolytic cells used in the production of aluminum. Of particular interest are the current efficiency of the cells and the deformation of the molten aluminum/molten salt interface within the cells. Both are strongly affected by electromagnetic forces acting on the aluminum and molten salt. These forces are a function of the cell design and operating practice. The interface deformation is significant in that it prevents the reduction of the distance between the aluminum and the carbon anodes. Such a reduction would enable the energy consumption of a cell to be greatly diminished. A mathematical model has been developed at LBL to predict cell performance as a function of parameters under control of the cell designer or operator. Computed current efficiency for a 185-kA 'quarter riser' cell design typical of those used in the aluminum industry is 93 percent, a figure falling within the range 85 to 95 percent expected from industrial measurements. An interface deformation of 9 cm is computed, which is also in line with actual measurements. A large number of alternative cell designs have been examined using the mathematical model. Most proved inferior to the quarter riser design, but a few were superior. In particular, one cell design that used a novel connection whereby current is withdrawn from underneath the cell, rather than the side of the cell, showed an interface deformation of only 1.8 cm.

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BIBLIOGRAPHY OF CONVECTIVE TRANSPORT CORRELATIONS

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The objectives are to search scientific and technical literature for references on experimentally established convective mass transfer and heat transfer correlations and to abstract, index, review, and publish as a bibliography, essential information useful for detailed analysis of convective transport phenomena in energy storage systems.

A preliminary search of prominent electrochemical and chemical engineering journals since 1970 has been made. Seventy publications were identified in addition to those recorded in previous surveys of mass transfer correlations (e.g., J. R. Selman and C. W. Tobias, *Adv. Chem. Eng.*, 10 (1978) 211). A start has been made with a computer search covering a wide spectrum of journals, using the Lockheed DIALOG online bibliographic retrieval systems. The information in the publications collected thus far has been recorded on a disk file using the following nine-digit classification code: (1) flow containment (9 categories); (2) flow regime and phase (10 categories); (3) flow geometry (9 categories); (4) type of convection (10 categories); (5) electrode movement (6 categories); (6) electrode geometry, if single element (9 categories); (7) electrode geometry, if multiple element (6 categories); (8) reactant (10 categories); and (9) supporting electrolyte (8 categories).

The MIDASFILE system of Prime, Inc., has been adopted for index-sequential processing. Initial difficulties in using this very efficient retrieval system have been resolved, and filing preliminary data has been completed. Preliminary contacts have been made to establish a panel of experts to advise on search procedures and to review the first draft report. Those contacted expressed a willingness to participate, but on a correspondence basis rather than as traveling consultants.

A first draft report will be completed by December 1, 1982. This will contain all available mass-transfer correlations and an initial selection of heat-transfer correlations. A review of the search procedures and the first draft report will be requested from the review panel in December 1982. A second draft will be completed by August 1983.