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APPLIED BATTERY AND ELECTROCHEMICAL RESEARCH PROGRAM

REPORT FOR FISCAL YEAR 1980

Energy & Environment Division
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Report for Fiscal Year 1980

I. OVERVIEW

The Applied Battery and Electrochemical Research Program is managed by the Lawrence Berkeley Laboratory (LBL) for the Office of Advanced Conservation Technologies of the Department of Energy (DOE). This program provides the applied research base which supports four major DOE missions: Electric Vehicles, Dispersed Electric Load Leveling, Solar Electricity, and Energy and Resource Conservation. The general objective of the program is to help provide electrochemical systems that can satisfy economic, performance and schedule requirements of one or more of the four missions. The specific goal of the project is to identify the most promising electrochemical technologies and transfer then to industry and/or another DOE program for further development and scale-up.

General problem areas addressed by the program include the identification of new electrochemical couples for advanced batteries, the determination of technical feasibility of the new couples, improvements in components of batteries under development by other Electrochemical Systems projects funded by DOE, and the establishment of engineering principles applicable to batteries and electrochemical processes. Major emphasis is given to applied research which will lead to superior technical performance and lower life-cycle costs.

The Applied Battery and Electrochemical Research Program addresses four major tasks, including three research areas and a management task aimed at directing and monitoring the activities of the program participants:

Task 1: Exploratory Battery Research and Development
Task 2: Engineering-Science Research
Task 3: Materials Science
Task 4: Program Management

Research conducted in Fiscal Year 1980 Tasks under 1, 2, and 3 are outlined in Sections II, III and IV, respectively, of this report.

Highlights of the management activities in Fiscal Year 1980 are:

- Both the Implementation Plan and Program Charter for the Applied Battery and Electrochemical Research Program were approved by DOE.
- A mid-fiscal year review of the Applied Battery and Electrochemical Research Program was held in Rockville, Maryland, March 7, 1980.

- An annual LBL Electrochemical Contractors' Meeting was held in Berkeley, California, August 14-15, 1980. Presentations were given by 15 of LBL's 25 subcontractors, and 5 separate LBL in-house projects were reviewed.
- LBL staff members paid site visits to 16 of the 21 separate institutions performing subcontracted research for LBL, and site visits were paid to potential subcontractors at 5 other research institutions. LBL personnel also attended numerous scientific meetings, reviews and workshops.
- LBL provided partial support for the "Third International Meeting on Solid Electrolytes - Solid State Ionics and Galvanic Cells", September 15-19, 1980, Tokyo, Japan.

The LBL scientists participating in this program are: E. J. Cairns[†], L. C. DeJonghe,[*], J. W. Evans,[*] F. R. McLarnon[†], R. H. Muller,[*] J. S. Newman[*], P. N. Ross,[*] and C. W. Tobias.[*]

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E. J. Cairns, Division Head.

II. EXPLORATORY BATTERY RESEARCH

The Exploratory Battery R&D area provides for the study of new electrochemical couples, or of new approaches to known battery systems. High temperature systems under investigation include Ca/molten salt/FeS_2, Li/LiI·Al_2O_3/TiS_2, and Na/β"-Al_2O_3/SCl_4-NaCl-$AlCl_3$. Ambient temperature systems being studied are Li/SO_2/C and Zn/NaOH/$Fe(CN)_6^{\equiv}$. New electrode/electrolyte formulations for Zn/KOH/NiOOH and Li/organic electrolyte/TiS_2 cells are being investigated, and a status study of ambient temperature secondary lithium batteries was conducted.

Brief summaries of eight separate research projects follow.

A. STUDIES OF HIGH ENERGY CATHODES AND ANODES FOR MOLTEN SALT BATTERIES

LBL Subcontractor: The University of Tennessee
Principal Investigator: G. Mamantov
DOE Program Manager: A. Landgrebe
LBL Project Manager: E. Cairns
LBL Contract No.: 4502810
B & R Number: AL-05-10-05
FY 1980 BA/BO Released: 10K/60K

This program is concerned with the research and development of the rechargeable low temperature molten salt cell:

Na/Na^+ ion conductor/SCl_3^+ in molten chloraluminates.

The above cell operates at 180 - 250°C (the lower temperature limit is primarily determined by the resistance of β''-alumina, the usual Na^+ ion conductor) and has an open circuit voltage of 4.2V.

Studies during the past year have involved laboratory cell development, spectroelectrochemical studies of the oxidaton of sulfur in chloraluminate melts, a determination of a partial phase diagram for the system SCl_3AlCl_4 ($AlCl_3$ - NaCl, 63-37 mole %), and a preliminary characterization of two β''-alumina tubes that were used in laboratory cells.

B. STUDY OF THE STATUS OF AMBIENT TEMPERATURE SECONDARY LITHIUM BATTERIES

LBL Subcontractor:	EIC Corporation
Principal Investigator:	S. B. Brummer
DOE Program Manager:	A. R. Landgrebe
LBL Project Manager:	C. W. Tobias
LBL Contract No.:	4503510
B & R Number:	AL-05-10-05
FY 1980 BA/BO Released:	29K/29K

EIC has reviewed the status of the ambient temperature rechargeable lithium batteries.

Although there have been striking advances in recharging the Li electrode since 1975, reactivity of the as-plated Li has prevented more rapid development of these cells. It reacts with the solution, and protective insulating films form on its surface. These films lead to poor cycling efficiency and poor shelf-life. Ethereal solvents have shown the least reactivity towards Li and present the best current opportunities for the development of practical systems. Half-cell anode cycling efficiencies in excess of 98% have been found.

Among positive electrodes, the intercalation compounds, which take Li^+ into their lattices on discharge, show promise for high specific energy and long life. Prominent among the currently known candidates are TiS_2, amorphous MoS_3 and Cr_3O_8.

Complete Li/TiS_2 or Li/V_6O_{13} cells have shown 100-200 deep discharge cycles. Present data project to a developed performance of:

- ~130 Wh/kg
- ~50 W/kg
- 100-200 cycles
- ~$100/ kWh

C. CALCIUM/METAL SULFIDE BATTERY DEVELOPMENT

LBL Subcontractor:	Argonne National Laboratory
Principal Investigator:	M. Roche
DOE Program Manager:	A. R. Landgrebe
LBL Project Manager:	P. N. Ross
LBL Contract No.:	4505310
B & R Number:	AL-05-10-05
FY 1980 BA/BO Released:	315K/315K

A Ca-Al-Si/FeS_2 cell has been developed and has exhibited reasonably stable capacity through 3200 hr of operation. This system is expected to be capable of meeting the ultimate performance goals (e.g., 160 W-hr/kg) of this development program; FY 1980 work has led to identification of the various components needed to fabricate a high-performance calcium cell of reasonably long life. These components are: the Ca-Al-Si negative electrode; the $Fe_{0.93}Co_{0.07}S_2$ positive electrode; BN felt separator; iron negative and molybdenum positive current collectors, and LiCl-NaCl-$CaCl_2$ - $BaCl_2$ electrolyte. In the coming year, these components will be employed in a number of cells to evaluate their ultimate performance capabilities and demonstrate an extended cycle life.

D. RECHARGEABLE ALKALINE ZINC/FERRICYANIDE HYBRID REDOX BATTERY

LBL Subcontractor:	Lockheed Co.
Principal Investigator:	R. Hollandsworth
DOE Program Manager:	A. R. Landgrebe
LBL Project Manager:	F. R. McLarnon
LBL Contract No.:	4503710
B & R Number:	AL-05-10-05
FY 1980 BA/BO Released:	100K/73K

Lockheed's initial research efforts on this system were aimed at assessing technical and economic feasibility of the alkaline zinc/ferrcyanide rechargeable battery for utility load leveling applications. This battery meets the requirements for this application with cell voltages of 1.94 V on charge and 1.78 V on discharge (35 mA/cm^2, 40^oC), with peak power density of 4.5 kW/m^2. A mean energy efficiency of 84% was obtained after 950 4-hour cycles. Cell construction uses a sintered nickel porous flow-thru electrode for the redox electrode, a Nafion N-114 separator, and a cadium-plated iron substrate for zinc deposition.

Recent work has focused on evaluation of alternative substrates for the redox sintered nickel electrode, alternative substrates for the cadmium-plated iron, replacement of the Nafion membrane with one costing about $\$1/ft^2$, demonstration of zinc storage capacity of 300 mAh/cm^2 over many cycles, and the development of a mathematical model providing a mass and energy balance of the overall system as well as detailed analysis of mass transport across the cell separator.

An economically viable replacement electrode for the sintered nickel is believed to be graphite felt, as preliminary results indicate little, if any, loss in efficiency for this electrode. Alternative substrates for zinc deposition are copper and brass, which have undergone over 100 cycles with coulombic efficiencies of 97% and 99% respectively. Cadmium, by comparision, usually operates at a coulombic efficiency of 95% to 97%; hence, brass appears to very promising. Several polyethylene and polypropylene separators from RAI Research Corp. have undergone testing with very good results of electrolyte transference and low membrane resistivity. However, the mechanical durability of these 1.5 mil thick samples is very poor. Zinc storage capacity has been demonstrated at up to 284 mAh/cm^2 for 15 cycles.

E. PERFORMANCE CHARACTERIZATION OF A SOLID-STATE STORAGE BATTERY

LBL Subcontractor: Duracell, Inc.
Principal Investigator: R. Rey
DOE Program Manager: A. R. Landgrebe
LBL Project Manager: P. N. Ross
LBL Contract No.: 4504310
B & R Number: AL-05-10-05
FY 1980 BA/BO Released: 199K/94K

Duracell is pursuing a fundamental investigation of the electrode materials, electrolyte and electrode/electrolyte interfaces in a solid state storage battery based on the systems Li alloy/$LiI \cdot Al_2O_3$/metal sulfides. Accomplishments in FY 1980 are listed below:

1. Developed an hermetic glass-to-metal seal feedthrough for can cells.
2. Developed techniques to fabricate 5-cm diameter cells.
3. Achieved new performance levels for the Li-Si/TiS_2 system (packaging not included):
    - (a) Energy Efficiency 84-87% (c/10, 5 mA/cm^2)
      78-81% (c/5, 10 mA/cm^2)
    - (b) Specific energy 110-140 Wh/kg (c/10)
      60-88 Wh/kg (c/5)
    - (c) Peak Specific Power (15 sec. pulse)
      360 W/kg, (full charge)
      100-180 W/kg, (half-charge)

(d) Cell Life - 4½ months, 300 cycles

4. Demonstrated immunity of cells to deep thermal cycles
5. Demonstrated immunity of cells to efforts of long term open circuit storage at operating temperature.
6. Determined performance effects of different electrode loadings in Li-Si/TiS_2 with unoptimized electrodes.
7. Improved performance of Li-Si/TiS_2 system to the 100 Wh/kg, 37.5% capacity utilization level at 5 mA/cm^2 rate, 350°C.
8. Developed a three-electrode cell structure and began electrode polarization studies.

F. ALL-INORGANIC AMBIENT TEMPERATURE LITHIUM BATTERY

LBL Subcontractor:	Duracell, Inc.
Principal Investigator:	A. N. Dey
DOE Program Manager:	A. R. Landgrebe
LBL Project Manager:	P. N. Ross
LBL Contract No.:	4507410
B & R Number:	AL-05-10-05
FY 1980 BA/BO Released:	59K/40K

The aim of Duracell's project is to determine the chemistry of charging and discharging reactions of a $Li/SO_2/C$ battery. During the six months of this contract, Duracell has:

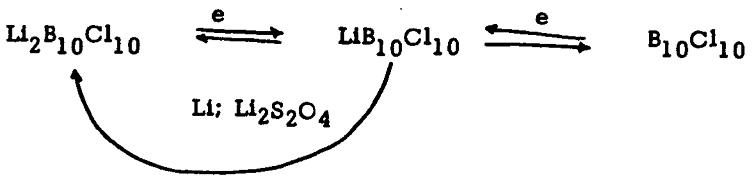
(1) Developed a hermetically sealed Li/SO_2 rechargeable cell incorporating a reference electrode.

(2) Demonstrated that $Li_2S_2O_4$ is the discharge product for inorganic electrolyte SO_2 cells and verified cell stoichiometry.

(3) Demonstrated the validity of their "scavenging" concept using overcharge products to destroy electrically isolated Li and $Li_2S_2O_4$ in the cell.

In the course of item 3 above, Duracell determined that the "all inorganic" electrolyte salt $Li_2B_{10}Cl_{10}$ is oxidized at ∿3.6V vs Li in a reversible one electron reaction to give a persistent product which was characterized by its visible absorption near 569 nm. It was demonstrated that this persistent product, $LiB_{10}Cl_{10}$ will oxidize both Li and $Li_2S_2O_4$ to prevent loss of active material in the cell.

The behavior of the salt $Li_2B_{10}Cl_{10}$ was examined further, and it was found possible to generate $LiB_{10}Cl_{10}$ by chemical means such as Ce^{IV} oxidation in solution. It was also found that $Li_2B_{10}Cl_{10}$ undergoes a second one electron oxidation at highly oxidizing potentials 4.2V vs Li. The oxidation product is unstable in CH_3CN and very near background but was studied by differential pulse polarography. The reactions of the electrolyte salt can be summarized as:



G. STUDIES OF LITHIUM ANODES IN NON-AQUEOUS ELECTROLYTES FOR AMBIENT TEMPERATURE BATTERIES

LBL Subcontractor:	Electrochimica Corporation
Principal Investigator:	M. Eisenberg
DOE Program Manager:	A. R. Landgrebe
LBL Project Manager:	P. N. Ross
LBL Contract No.:	4507210
B & R Number:	AL-05-10-05
FY 1980 BA/BO Released:	58K/49K

The following key points summarize Electrochimica's findings:

(1) There are signigicant electrocrystallization and general morphology effects caused by substrates, the solvent system the nature of the anions, additives, choice of substrate, and the applied current density.

(2) It was found that a nickel substrate is unfavorable for deposition of lithium; that such deposits are totally non-adherent and often accompanied by codeposition of salts and solvent reduction or polymerization products. Therefore, a nickel substrate cannot be employed for studies of deposition and stripping efficiencies of lithium.

(3) Dioxolane appears to be a very desirable solvent but shows an early tendancy towards polymerization, unless properly inhibited by use of triethylamine, triethyl phosphate or related inhibitors.

(4) Additions of DME to Dioxolane appear to be beneficial for morphology.

(5) Pre-electrolysis of an electrolyte to remove last traces of water may be a beneficial procedure for all secondary lithium batteries.

(6) A more dense deposit (not necessarily more adherent) results from $LiASF_6$ compared to $LiClO_4$.

(7) After initial SEM studies, it became clear that there is a need for classification of deposits in accordance to the relationship to the substrate and in accordance to its morphological coherence, quite aside from the electrocrystallization.

H. DEVELOPMENT OF A HIGH RATE INSOLUBLE ZINC ELECTRODE FOR ALKALINE BATTERIES

LBL Subcontractor:	Energy Research Corporation
Principal Investigator:	H. Vaidyanathan
DOE Program Manager:	A. R. Landgrebe
LBL Project Manager:	F. R. McLarnon
LBL Contract No.:	4506710
B & R Number:	AL-05-10-05
FY 1980 BA/BO Released:	59K/28K

This program concentrates on the development of Zn electrode/ electrolyte formations which result in insoluble discharge products and the development of special activated ZnO samples which are insoluble and/or have the ability to form a more conductive anodic film upon cycling. The latter property of the activated ZnO may permit the use of dilute KOH (15-20%) as the battery electrolyte in which ZnO solubility is limited.

Activated ZnO samples containing Fe, Cd, Ca, Ni, Co, Sn and In as dopants have been prepared. The solubilities of ZnO + 0.6 atom percent Co and ZnO + 0.6 atom percent Sn in KOH are less than that of unactivated ZnO.

The solubility of ZnO in KOH may also be reduced by adding complexing agents to the electrolyte. Thus electrolyte formulations consisting of: a) 30.5% KOH + 13.2% KF, b) 39% KOH + 1.65% H_3BO_3 and e) 28% KOH + 5% H_3BO_3 + 15% KF are capable of lowering the solubility of ZnO.

The current-potential profile obtained for a Teflon-bonded ZnO electrode by cyclic voltammetry shows regions of ZnO reduction, active dissolution and anodic film formation very similar to that obtained for a Zn wire electrode. The discharge products obtained at -1.32V (vs. Hg/HgO) exhibit maximum reactivity under cathodic polarization.

III. ENGINEERING-SCIENCE RESEARCH

A major thrust of the Engineering-Science Research supported by LBL's Applied Battery and Electrochemical Research Program is a deeper understanding of the complex transport processes that govern electrochemical processes. Phenomenological studies, advanced optical techniques and sophisticated modeling are valuable tools employed in these studies. A large fraction of LBL's in-house research program is directed toward this goal, and "Development of Electrochemical Synthesis and Energy Storage" is therefore listed as a project in Engineering-Science Research.

Projects grouped in this area include morphological and optical studies of battery electrodes in $Pb/H_2SO_4/PbO_2$, Zn/KOH/NiOOH, and metal/air cells; and a thermal management study of the high-temperature Li/molten salt/FeS Battery. Improvements in alkaline (Zn/NiOOH and Fe/NiOOH) battery performance are being sought through investigations of the effect of temperature on electrode kinetics, measurements of thermodynamic efficiencies, and detailed studies of electrode restructuring phenomena.

Brief summaries of the nine separate projects follow.

A. DEVELOPMENT OF ELECTROCHEMICAL SYNTHESIS AND ENERGY STORAGE

(LBL Research Projects)

Principal Investigators:	E. Cairns, L. DeJonghe, J. Evans, R. Muller, J. Newman, P. Ross and C. Tobias
DOE Program Manager:	A. R. Landgrebe
B & R Number:	AL-05-10-10
FY 1980 BA/BO Released:	620K/620K

INTRODUCTION

The overall aim of this program is to improve the energy efficiency, lower the capital cost, and increase the materials yield of electrochemical processes employed in the direct conversion of chemical to electrical energy in galvanic cells and in the production of materials by electrolysis. These goals are pursued in eight partially interdependent projects:

A. 1. Surface Morphology of Metals in Electrodeposition
(C. W. Tobias)

A. 2. Anodic Surface Layers on Battery Materials
(R. H. Muller)

A. 3. Analysis and Simulation of Electrochemical Systems
(J. S. Newman)

A. 4. Metal Couples in Non Aqueous Solvents
(C. W. Tobias)

A. 5. Improvements in Efficiency of Aluminum Reduction Cells
(J. W. Evans)

A. 6. Electrochemical Properties of Nasicon
(L. C. DeJonghe)

A. 7. Bifunctional Air Electrodes for Metal-Air Batteries
(P. N. Ross)

A. 8. Battery Electrode Studies
(E. J. Cairns and F. R. McLarnon)

A. 1. SURFACE MORPHOLOGY OF METALS IN ELECTRODEPOSITION

The objective of this project is to develop a pragmatic understanding of the processes governing the macrocrystallization of metals. This understanding is necessary for the design optimization of metal deposition processes, including those in rechargeable galvanic cells. Current projects include (a) The effect of hydrodynamic flow on the surface morphology of copper and of zinc, and (b) Dynamic modeling of surface profiles in electrodeposition and dissolution.

A.1.1. MICROSTRUCTURAL DEVELOPMENT DURING MASS TRANSFER CONTROLLED DEPOSITION

Andrew Kindler and Charles W. Tobias

The formation of powdery deposits during electrodeposition at the limiting current is a phenomenon familiar to all electroplaters. In the case of copper electrodeposition from solutions of $CuSO_4$-H_2SO_4 in channel flow, the powder particles are nodular in appearance when the electrode is viewed from the top under a scanning electron microscope. (Fig. 1, top two photos) None of the many attempts made to explain this phenomenon[1] is satisfactory. Our copper deposition experiment, conducted under carefully controlled hydrodynamic conditions, supports the hypothesis that mass transfer overpotential is a requirement for dentritic growth.

The nodules are dendritic structures that undergo morphological transformation during growth. As shown in Fig. 2 this results in the coverage of the dendrite tip by a mushroom cap. The transformation occurs because the growing dendrite disturbs the thin (approx. 20 microns thick in the experiment of Fig.1) mass transfer boundary layer. Therefore, the dendrite is no longer growing at the limiting current. Below the limiting current, solid coherent deposits similar to the mushroom cap are known to be formed.

Three lines of evidence support this explanation. First, the overpotential in galvanostatic copper deposition at the limiting current declines. It can be shown that a surface area increase cannot account for a decrease of this magnitude. (See Fig. 4) The drop in overpotential must be caused by the decrease of concentration overpotential resulting from mass transfer boundary layer disruption.

A second line of evidence was developed by performing copper electrodeposition under approximately potentiostatic conditions, and at limiting current. Under such conditions, the dendrite tip is always near limiting current because potentiostatic operation causes the current density to increase as the boundary layer is disrupted. This keeps the overpotential fairly constant. The resulting deposit was clearly dendritic and lacking any appearance of the beginning of morphological transformation. (See Fig. 3 top left photo) The same figure (Fig. 3 top right) shows a galvanostatic deposit formed by passing the same number of coulombs. The galvanostatic deposit does not show signs of mushroom capping, rather grape-like clusters are visible, which will eventually fuse as deposition continues. To prove that lack of mushroom capping is due to the shortness of the deposition time, compare bottom photo in Fig. 1 to the two top photos. Both deposits were produced under identical deposition conditions with the exception that the bottom photo shows a short-time deposit. The same sort of comparision can be made between the photographs in Fig. 2, which are simply cross sections of the deposits shown in Fig. 1. The top two and the bottom left photos are different views of the same sample. The lower right is a view from a short-time experiment, again without the mushroom cap.

The third line of evidence, is the observation[2] that dendrites grow on copper deposited from solutions of H_2SO_4-$CuSO_4$ when hydrogen is evolved. In this special case, copper is deposited at constant mass-transfer overpotential, η_c, near the limiting current. These are, of course, the previously stated conditions for dendrite formation. The η_c stays constant in this special case because any disturbance of the mass-transfer boundary layer will make copper deposition easier, thus diverting current from the hydrogen evolution reaction which by comparision becomes energetically less favored.

The evidence presented reduces the phenomena of dendrites and nodules at limiting current to just one: dendrites. These dendrites form at the limiting current probably as a result of an instability phenomenon.[3] At limiting current the supply of copper ions at the metal/electrolyte interface approaches 0. Any projection from the electrode penetrating into the mass-transfer boundary layer will find itself in an environment relatively more rich in copper ions. It will therefore tend to grow faster than flat regions of the electrode. Some evidence supporting a mass-transfer explanation rather than a kinetic one is provided by Fig. 3, bottom photo. Here, a copper deposit formed on a rotating cylinder is shown. The fraction of the limiting current was only 54% so that η_c is negligible. The charge transfer overpotential, η_s, however, was 0.26 volt or about the same as in a powder-producing experiment run at 95% of limiting current. If η_s were responsible for producing dendrites, these should have formed on the rotating eylinder. Instead a smooth surface was obtained. Clearly, high mass-transfer overpotential (close to limiting current) is required for the growth of dendrites.

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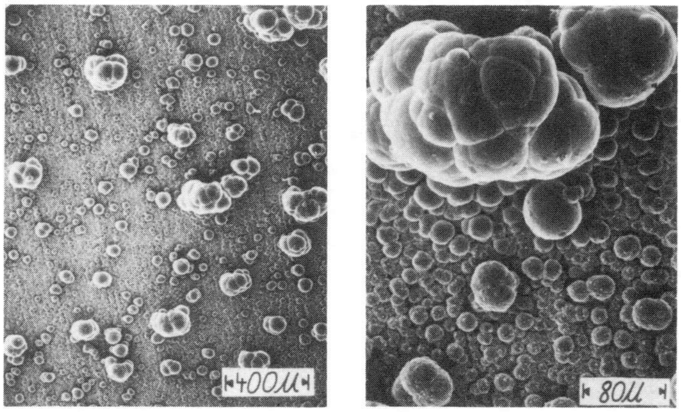
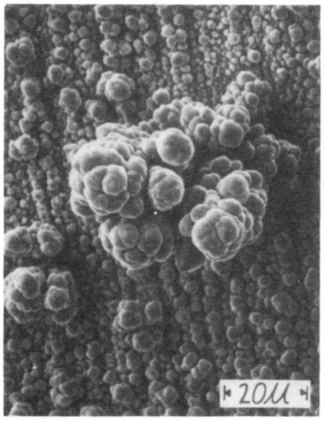
3. A. R. Despic and K. I. Popov "Transport Controlled Deposition and Dissolution of Metals," Modern Aspects of Electrochemistry, 7(1972) p. 223.



TOP VIEW GALVANOSTATIC
LIMITING CURRENT DEPOSIT



← SHORT TIME
DEPOSIT

FIG. 1. 0.228 M $CuSO_4$, 0.93M H_2SO_4, limiting current: 83.6 mA/cm^2
Re = 23,000, Galvanostatic.
Top two photos: Same experiment. 58.9 Coulombs/cm^2 passed.
Bottom: Same experimental conditions but 10.78 Coulombs/cm^2 passed.
(XBB 805-5761)

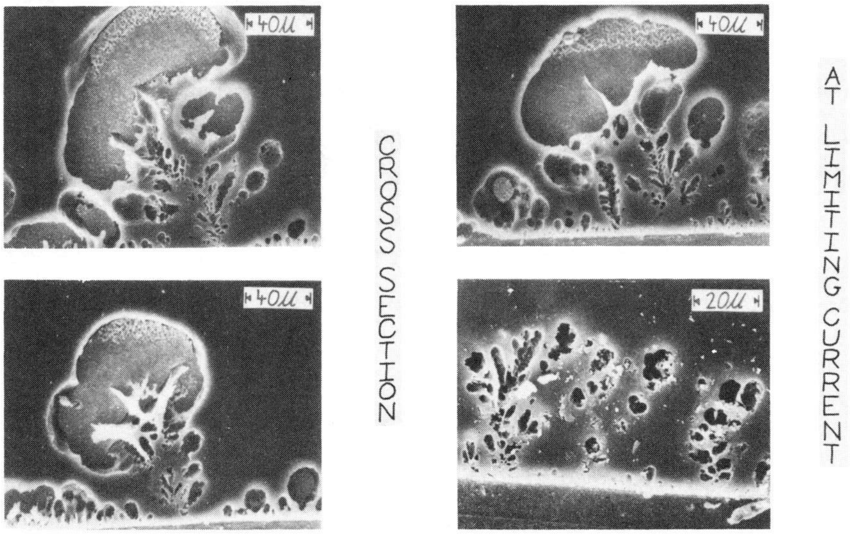
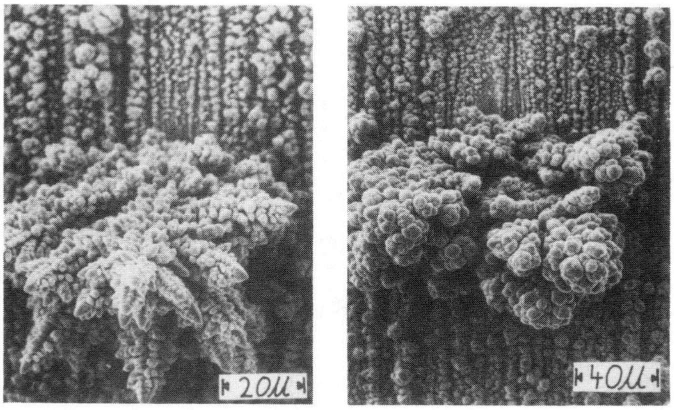
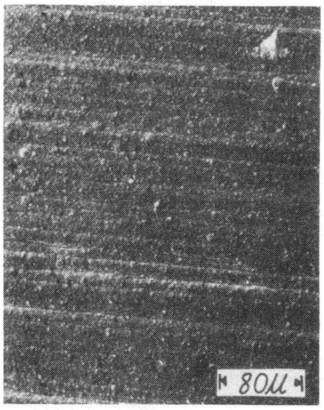


FIG. 2. Cross sections of photos in Fig. 1.
Top two and lower left: Same experiment, 58.9 Coulombs/cm^2 passed.
Lower right: 10.78 Coulombs/cm^2 passed.
(XBB 805-5762)



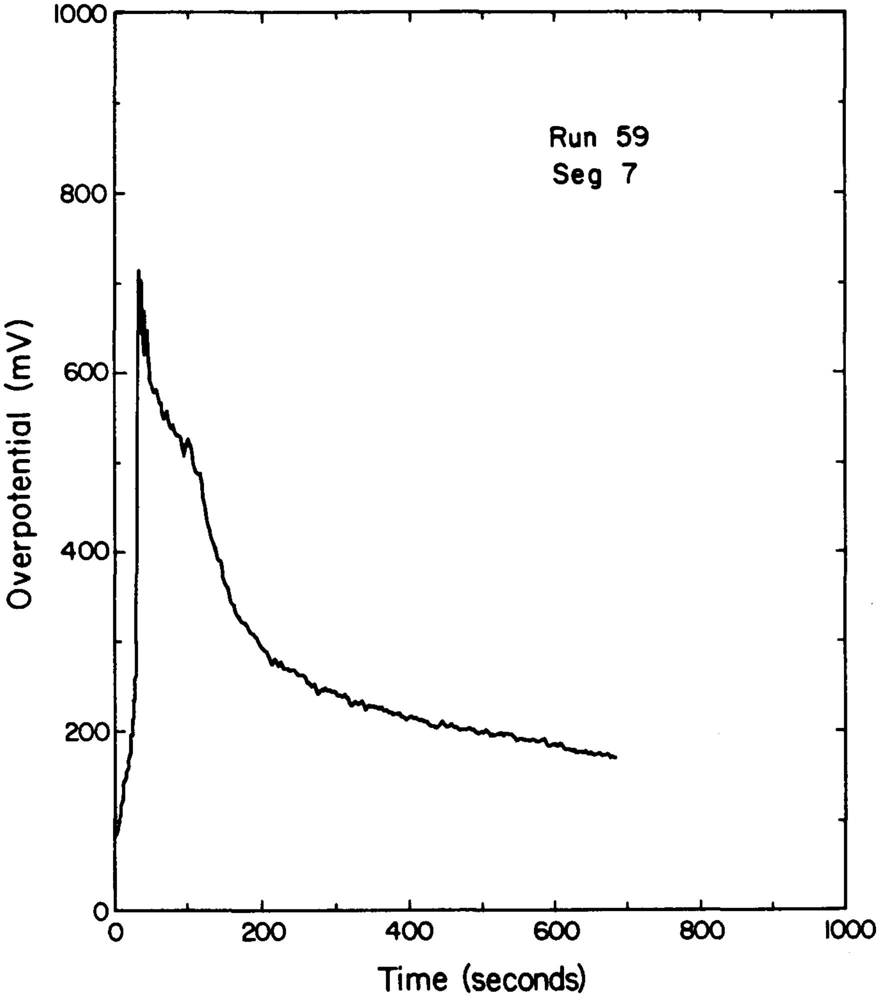
POTENTIOSTATIC GALVANOSTATIC



TOP: LIMITING CURRENT
BOT: HIGH SURFACE OVERPOTENTIAL

54% I_L

FIG. 3. Top: 0.228 M $CuSO_4$, 0.932 M H_2SO_4 Re = 23,000 9.9 Coulombs/cm^2.
Top Left: Potentiostatic - 0.600 volt.
Top Right: Galvanostatic at limiting current, 83.6 mA/cm^2.
Bottom: 0.4 M $CuSO_4$, 0.925 M H_2SO_4, Re = 185,000, 50.75 coulombs/cm^2, 273 mA/cm^2: 95% of limiting current density.
(XBB 805-5764)



XBL-813-455

FIG. 4. Decline of total overpotential with time during a galvanostatic run set at limiting current. Conditions: same as FIG. 1.

A. 1. 2. EFFECTS OF HYDRODYNAMIC FLOW ON THE ELECTROCRYSTALLIZATION OF ZINC FROM ACID ELECTROLYTES

James L. Faltemier, Vladimir Kommenic, Tetsuaki Tsuda, and
Charles W. Tobias

The influence of current density, hydrodynamic conditions, time of metal deposition, nature of zinc salt, and substrate conditions, on the quality of zinc deposits has been studied galvanostatically in a rotating-disk system containing a platinum cathode and a zinc anode.

A current density interval well below limiting current has been identified in which spiral-like striations form, reflecting the fluid motion over the surface of the electrode. Within this interval, increasing current density increase the number of spirals and decreases the time for their formation. Above some critical value a more uniform nucleation density occurs, and a smooth deposit is produced. Spirals were observed in 1 M $ZnCl_2$ solutions below 80 to 100 mA/cm^2, while in 1 M $ZnSO_4$ solutions spirals were observed below 10 mA/cm^2. The occurrence of spirals in both the highly-complexing $ZnCl_2$ and the non-complexing, less conductive, $ZnSO_4$ solutions confirms that the spiral phenomenon is not dependent upon complex-ion formation or mass transfer. Short-time experiments showed an nonhomogeneity on the electrode substrate at the lower current densities with zinc preferentially deposited along the scratch lines and more uniform nucleation density at the higher current densities.

Variable-current step and AC pulse techniques were used to detect the influence of the original substrate surface and of preferential sites on the formation of spirals. By prolonging, or eliminating spiral formation altogether, these methods showed the close relationship between surface defects, nucleation density, and spiral formation.

Rotating-ring electrodes were employed to examine the leading-edge effect in a rotating system. Experiments were conducted at a current density of 5 mA/cm^2 and at rotating speeds of 200, 400, 800, and 1,600 rpm in 1 M zinc sulfate solution (pH 2). The results may be summarized as follows:

(1) Spiral ridges originally appear from the outer edge of a ring electrode propagating inwards along the spiral pattern. Then, after about a 3 minute deposition, spirals appear at the inner edge propagating outwards. Spiral formation is much more pronounced at the outer edge. Finally, many protrusions in the intermediate region are connected to each other to form complete spiral ridges.

(2) At 200 rpm, spiral formation at the inner edge did not occur. This might suggest that spirals are not formed below a certain rotational velocity.

(3) The number of spirals increases with an increase of rotation speed.

(4) Melding of spirals after prolonged deposition is more pronounced at rotation speeds.

(5) The formation time of spiral grooves does not diminish with increasing rotation speed.

(6) Shapes of spirals closely resemble (but don't exactly correspond to) logarithmic spirals (i.e., $r = a^\theta$ or $\theta - \theta_o = \frac{1}{\ell n\ a}\ \ell n \frac{r}{r_o}$). The characteristic constant ($\frac{1}{\ell n\ a}$) seems to be nearly independent of the rotation speed.

A. 1.3. DYNAMIC MODELING OF SURFACE PROFILES IN ELECTRODEPOSITION AND DISSOLUTION

Geoffrey A. Prentice and Charles W. Tobias

A model for simulating the transient behavior of electrodes undergoing deposition or dissolution has been developed. The model accounts for ohmic drop, charge-transfer overpotential, and mass-transport effects. Finite-difference techniques were used in the computer simulations. A procedure to overcome the instabilities inherent in the calculation of secondary and tertiary current distributions has been developed.[1] With this procedure convergence has been attained for all reasonable values of the physical parameters. General guidelines for determining the computational parameters (convergence criteria, mesh size, time step interval) have been established, and error limits have been estimated.

Carefully controlled electrodeposition experiments were performed in a contoured, rotating-cylinder electrode system. Two sinusoidal profiles were machined on different stainless steel cylinders. The amplitude-to-wavelength (A_o/λ) ratio was 0.1 in both cases, but the actual dimensions were greater by a factor of 7 for the larger profile. Experiments were performed with these two cylinders where the Wagner number was varied between 2 and 20.

In the previous work[2] rough deposits were obtained at relatively high current densities (80 mA/cm^2) in an acid-copper bath. Because smoother matte deposits were obtained at lower current densities, all subsequent experiments were conducted near 25 mA/cm^2. The original stainless steel cylinder with an amplitude of 2 mm and a wavelength of 2 cm is depicted in Fig. 1. The resulting deposit after 46 h at 800 rpm is shown in Fig. 2. The deposit, obtained under similar conditions, on the smaller wavelength profile appears in Fig. 3.

When the Wagner number is low (high wavelength case), the current density variation on the profile is greatest. In these cases, a shoulder tends to form near the peak, where the current density and curvature variations are relatively high. As the shoulder grows, the increased curvature in that area causes current to be diverted from the peak, where a depression forms. When the Wagner number is high (low wavelength case), the current density is more uniform, and no depression at the peak occurs.

The kinetic parameters were determined from overpotential behavior determined on smooth copper rotating cylinders. These parameters, along with other physical property and geometric data, were incorporated in simulations of the growing sinusoidal profiles. Based on the deposit thickness, the simulated and experimental profiles generally agreed to within 10 percent (Fig. 4). The depression at the peak for the low Wagner number runs was predicted by the simulations.

The effects of mass transport on growing sinusoidal profiles were considered. The depletion of reactant concentration that accompanies the passage of cathodic current reduces the exchange current density. When this dependence is taken into account, a more uniform current distribution results. As the limiting current density is approached, the concentration overpotential becomes significant. The functional dependence of the concentration overpotential and surface overpotential on the current density is markedly different. Because the concentration overpotential increases rapidly at high fractions of limiting current, a broad flattening of the peak results when the current density at the peak approaches the limiting current density. The surface overpotential increases logrithmically in the high-current-density range. This slower increase in surface overpotential causes the resulting profiles to be more uniform. This contrasting behavior is shown in Fig. 5.

Simulations of sinusoidal profiles undergoing anodic dissolution were also performed. These simulations were compared with Wagner's analytical results.[3] Because of the assumptions that Wagner invoked in order to obtain a solution, his prediction of the time-dependent decrease in amplitude is accurate to within a few percent for an initial amplitude-to-wavelength (A_o/λ) ratio of less than 0.05. Numerical results were obtained for A_o/λ up to 0.3. The simulations performed at high A_o/λ up to 0.3. The simulations performed at high A_o/λ showed that the initial rate of change of amplitude, computed by Wagner, was in error by at least 20 percent.

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1. G. A. Prentice and C. W. Tobias, "Finite Difference Calculation of Current Distributions at Polarized Electrodes," Paper no. 96d, AIChE Annual Meeting, 1980.

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3. C. Wagner, J. Electrochem. Soc., 101, 225 (1954).

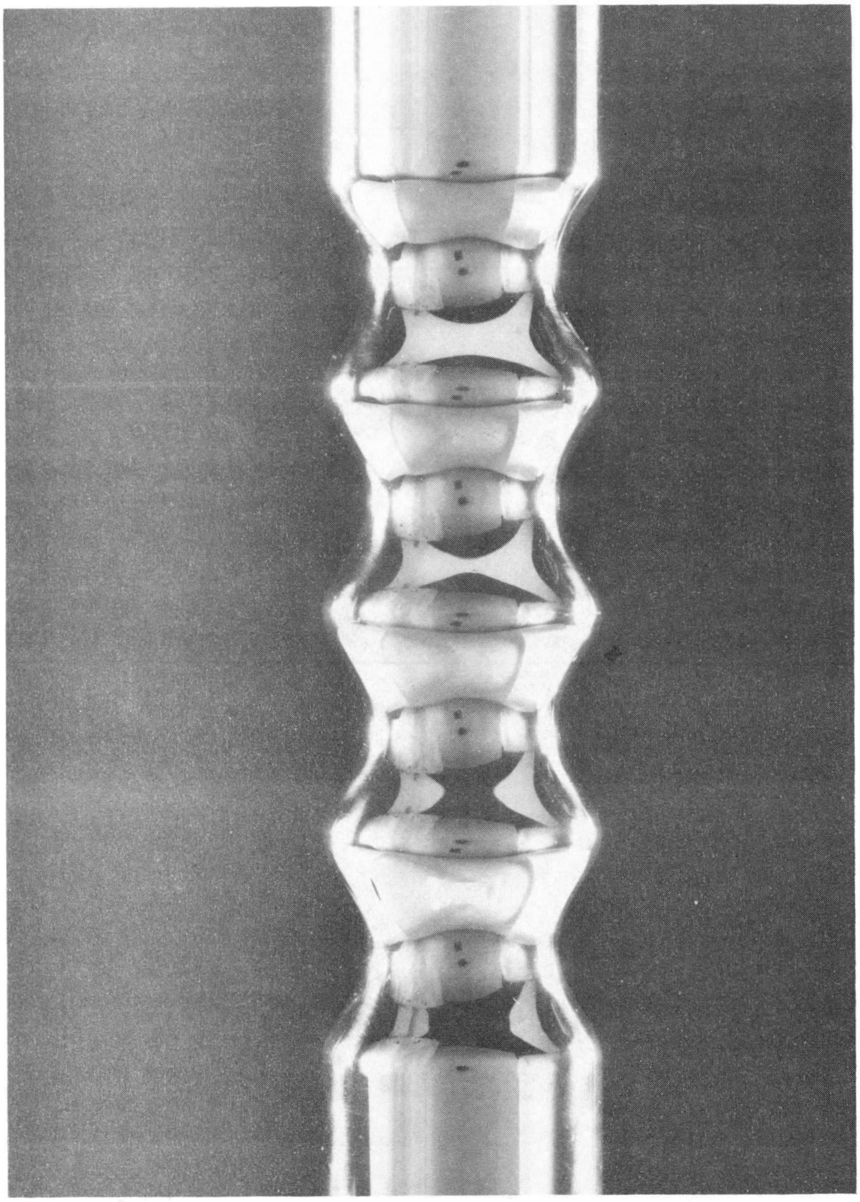


FIG. 1. Original rotating stainless steel electrode. Amplitude is 2 mm and wavelength is 2 cm. (CBB 798-11056)

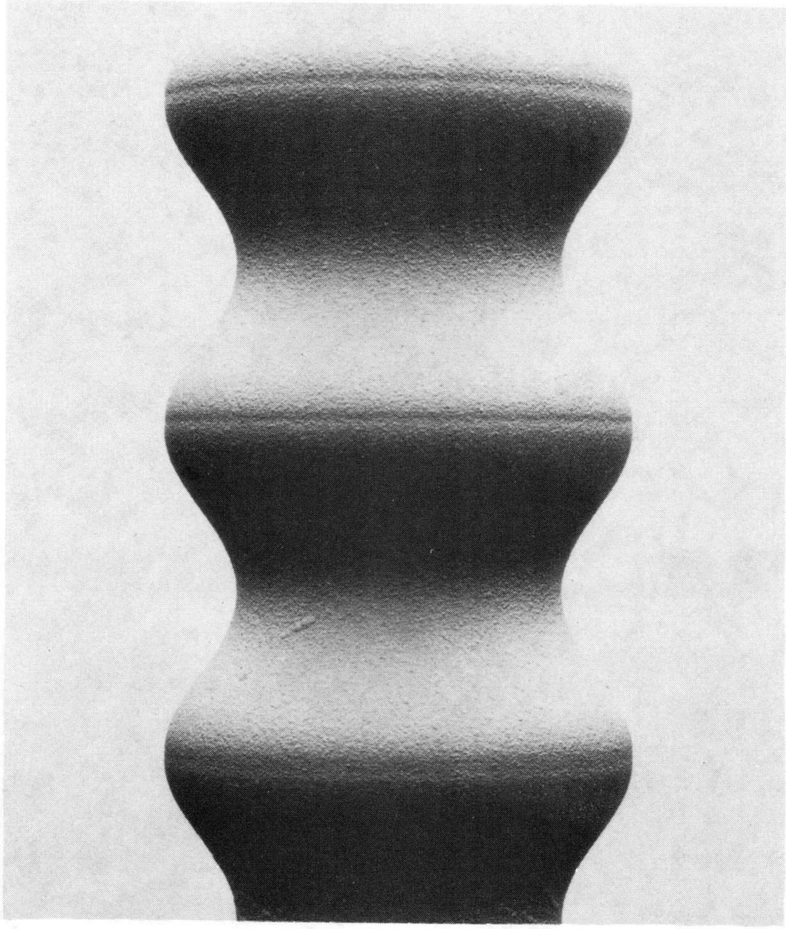


FIG. 2. Copper deposit after 46 h, 800 rpm, and an average current density of 25 mA/cm^2.
W = 2.7
(CBB 805-6272)

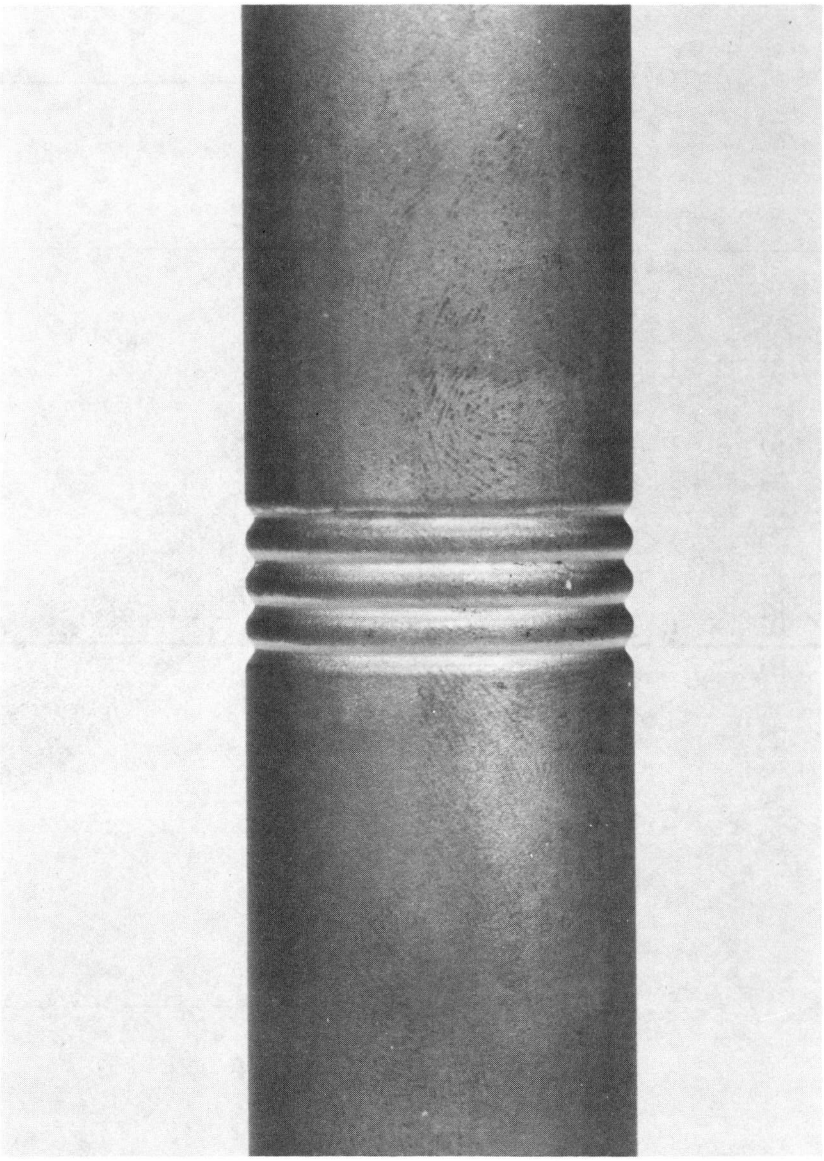
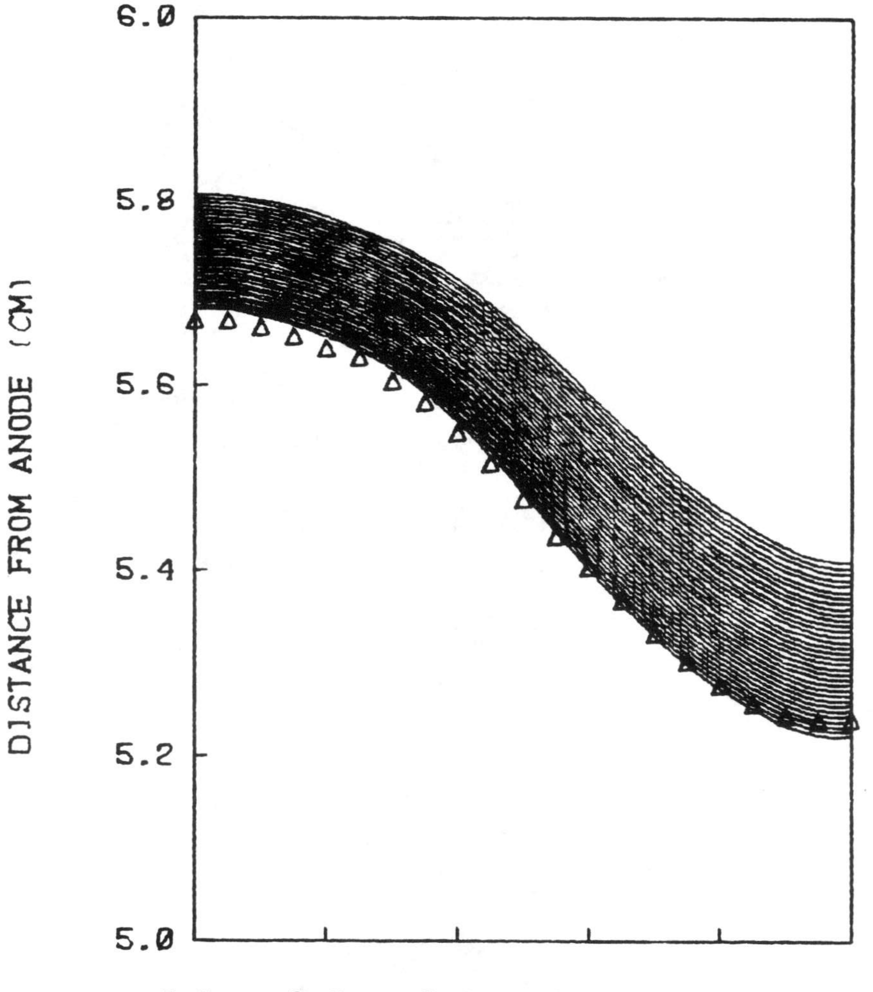


FIG. 3. Copper Deposit on small scale sinusoidal electrode. 20 h, 800 rpm, average current density of 25 mA/cm^2. W = 18
(XBB 807-8913)



XBL 808-10851

FIG. 4. Half wavelength of simulated and experimental profiles from Figure 2. The upper curve depicts the original profile, and the lowest curve is the simulated final profile. The experimentally obtained profile is denoted by triangles.

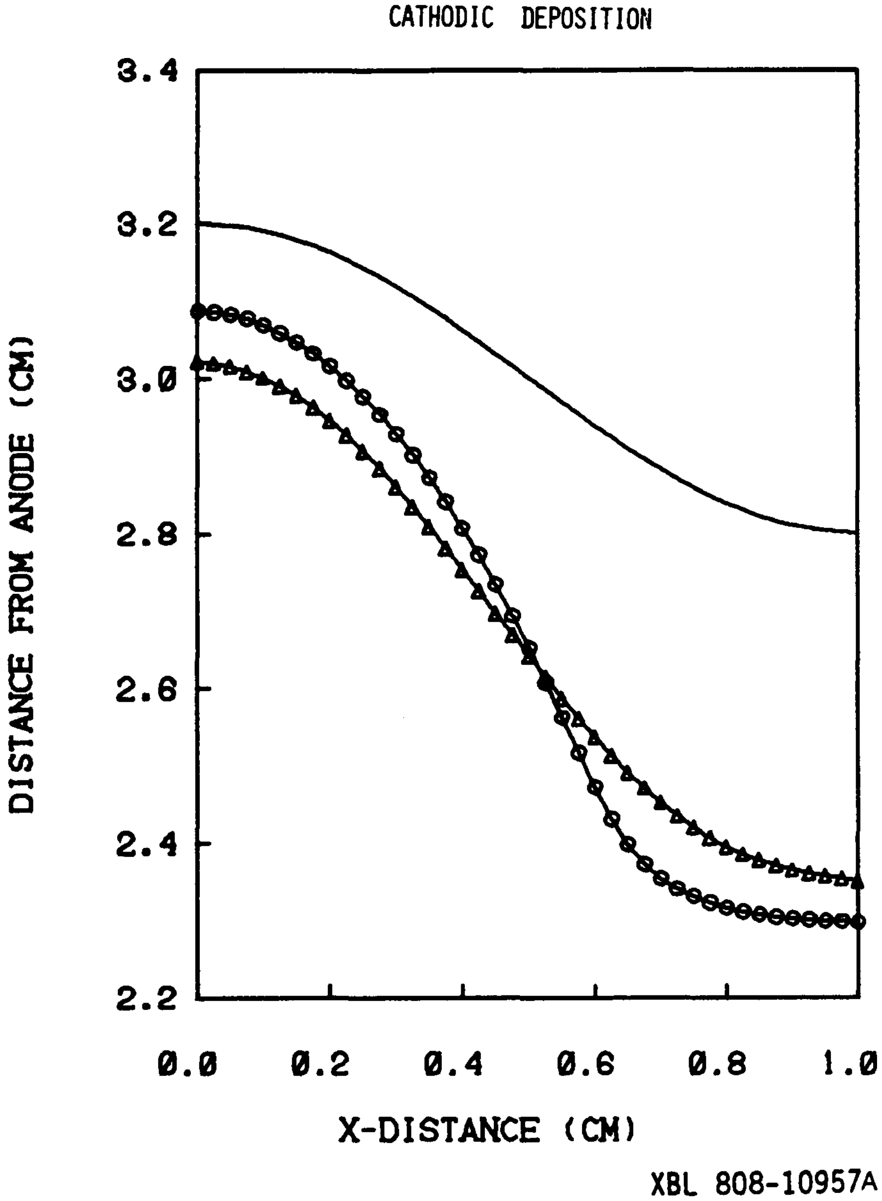


FIG. 5. Simulated deposition on a sinusoidal profile. (o) W = 0.5, 99% of limiting current, (Δ) W = 1.3.

A. 2. ANODIC SURFACE LAYERS ON BATTERY MATERIALS

The purpose of this work is to provide direct experimental information about formation and properties of surface layers on battery electrode materials.

A. 2. 1. ELLIPSOMETRIC STUDIES OF LITHIUM IN PROPYLENE CARBONATE SOLUTIONS*

Felix Schwager and Rolf H. Muller

The use of lithium in ambient-temperature batteries which employ non-aqueous solvents is largely made possible by the formation of surface layers which inhibit thermodynamically favored spontaneous reactions. These surface layers may, however, hinder the delivery of electric power upon discharge, when the metal is dissolved, and they are generally considered responsible for the poor performance of lithium electrodes upon recharging, when metal is re-deposited from the solution. This work is undertaken to determine structure, composition, and mode of formation of surface layers in some representative battery environments in order to identify approaches to improve electrode behavior.

Film formation on lithium, immersed in pure propylene carbonate solvent and its 1 M $LiClO_4$ and 1 M $LiAsF_6$ solutions, has been observed in situ by ellipsometry and ex situ by Auger electron spectroscopy, ion etching, and secondary-ion mass spectroscopy.

The following conclusions are drawn from ellipsometer measurements under open-circuit conditions:

(1) Ellipsometer measurements are possible although refractive indices of some potential film materials are close to that of the solution (Table 1).

(2) Film growth continues throughout the 15 day period of observation.

(3) Film growth rates strongly depend on electrolyte composition. They decrease in the order: pure solvent, 1 M $LiAsF_6$, 1 M $LiClO_4$.

(4) Film growth is not greatly affected by the addition of small amounts (1000 ppm) of water to $LiClO_4$ solutions.

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*Brief version of LBL-11846

(5) Interpretation of ellipsometer measurements requires the use of inhomogeneous film models with refractive index decreasing from the metal substrate to the solution side, indicative of increased porosity in that direction (Fig. 1).

(6) A high real part of the refractive index of the film material near the metal substrate is essential for a satisfactory interpretation of measurements and indicates the presence of Li_2O or possibly LiCl (Table 1).

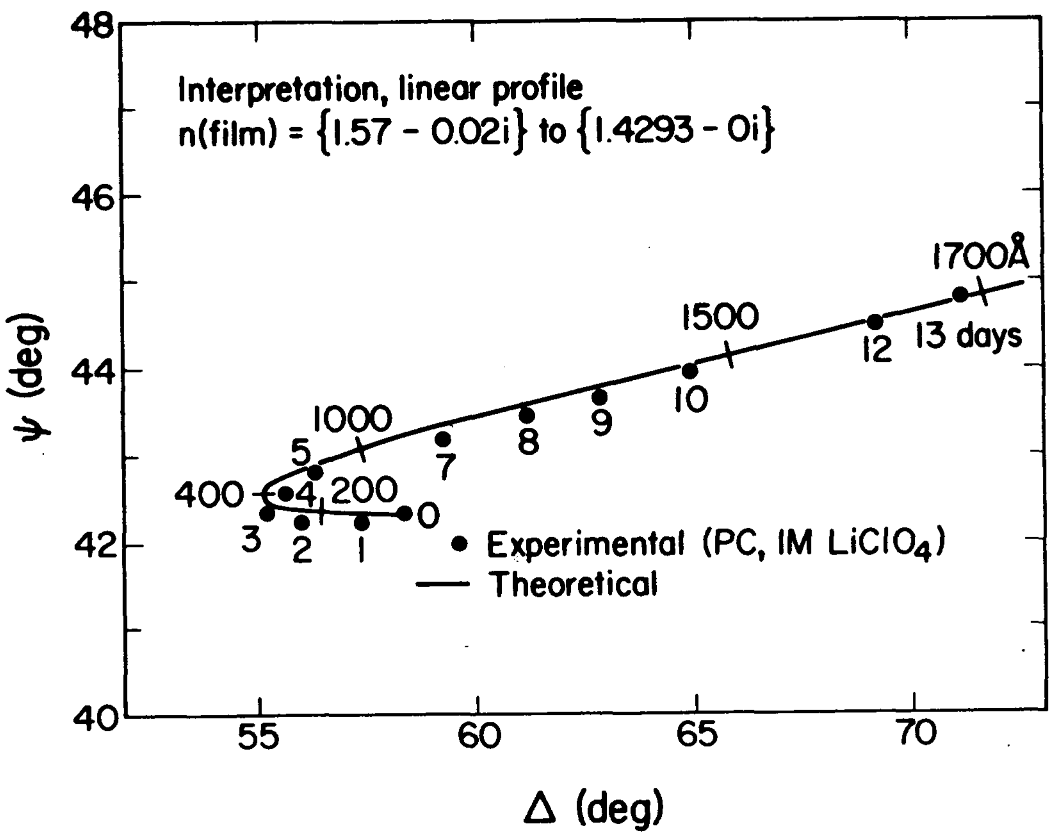
The inhomogeneous porous film model has been confirmed by changing the immersion medium of the film from solution to vacuum. The evaporation of solvent from the pores results in a considerable change in effective film refractive index. The same film thickness was derived.

Depth profiling by argon-ion etching and Auger spectroscopy confirmed the film thickness derived by ellipsometry and was consistent with the presence of Li_2O rather than LiCl near the substrate. The presence of carbon throughout the film may indicate a partial content of Li_2CO_3. Chlorine content was also uniform but small. Secondary-ion mass spectroscopy only partially agreed with Li_2CO_3 calibration results.

TABLE 1

Refractive Indices of Potential Film Materials, Solution, and Substrate

LiOH	1.466
Li_2CO_3	1.50
Li_2O	1.644
LiCl	1.662
PC, 1 M $LiClO_4$	1.429
Li	0.25 - 2.3i



XBL 809-2047

FIG. 1. Ellipsometer parameters Δ and ψ for film formation on Li in 1M $LiClO_4$ under open circuit. Measurements and interpretation for an inhomogeneous film with refractive index 1.57-0.02 i at the substrate side, decreasing linearly with distance to 1.429 (refractive index of solution) on the solution-side.

A. 2. 2. TRANSIENT ELECTROCHEMICAL MEASUREMENTS ON LITHIUM IN PROPYLENE CARBONATE SOLUTIONS

Yordan Geronov and Rolf H. Muller

Galvanostatic pulse measurements have been conducted to determine thickness, conductivity and kinetics of formation of surface layers formed on lithium with solutions of 1 M $LiClO_4$ and 0.5 M $LiAsF_6$ in propylene carbonate solvent. The electrode capacitance was derived from the rate of initial potential increase with short (5 to 10μs) current pulses. IR-free overpotential values were obtained from the response to long (20 ms) pulses.

The film thickness was computed from the capacitance measurements for a plane-parallel film geometry with an assumed film dielectric constant. The series-connected double-layer capacitance was neglected. Exchange current densities were determined from micropolarization measurements. Film resistivity was derived from current flow at steady-state overpotential.

Film thickness derived from capacitance measurements is typically about 5 times lower than that obtained by ellipsometry. The difference supports the concept of an inner, compact film section that controls capacitance, adjacent to electrolyte-filled porous sections facing the solution. The thickness of the compact section reaches a steady-state (Fig. 2) in contrast to the ellipsometer measurements which show a continuing overall film growth. The continued increase in overall film thickness therefore appears to be due to growth of the porous sections. Higher water content results in faster film growth but unchanged steady-state thickness with perchlorate and hexafluoroarsenate solutions.

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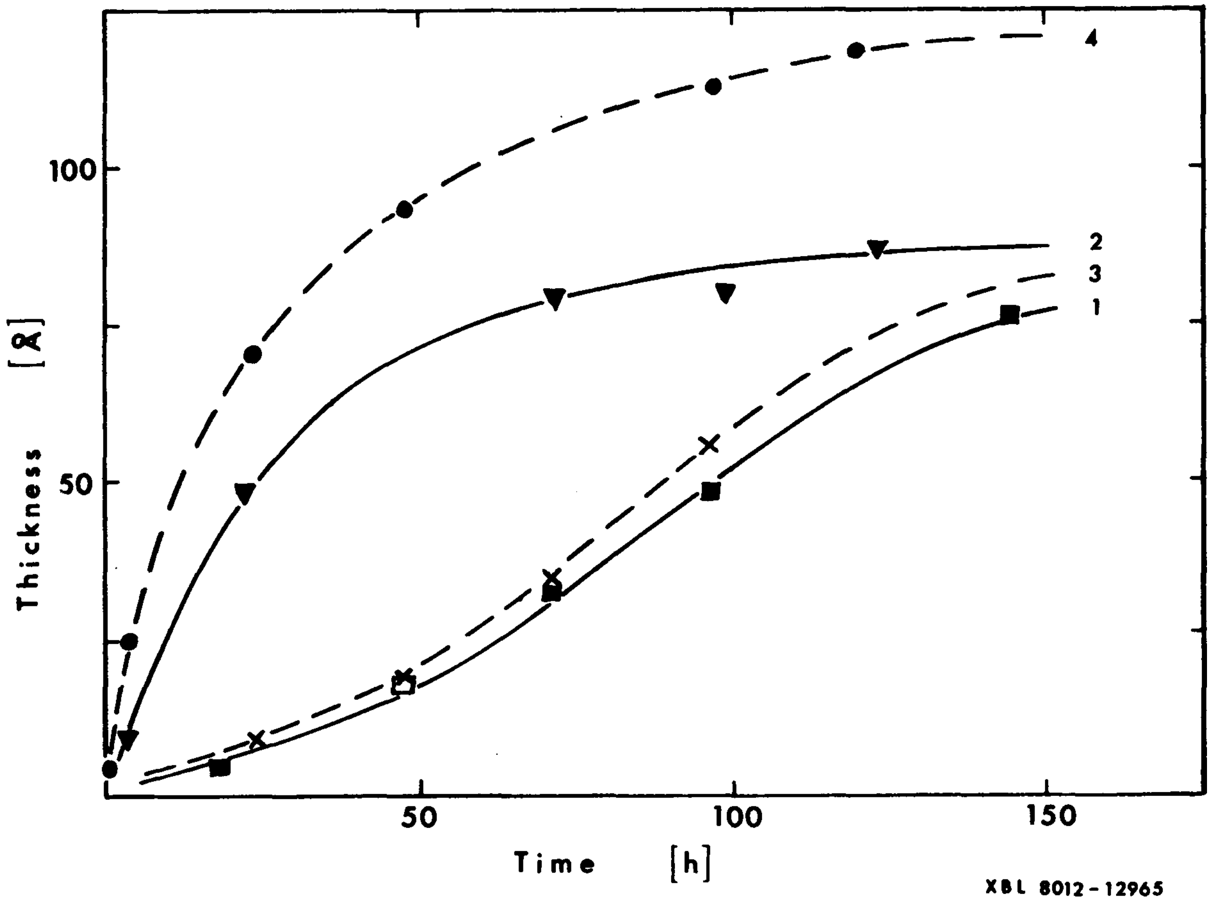
*Brief version of LBL-11126.

Film conductivities of 2.7×10^{-9} Ω^{-1} cm^{-1} and 5.1×10^{-9} Ω^{-1} cm^{-1} have been determined for immersion in solutions of $LiClO_4$ and $LiAsF_6$ respectively. An increase in the water content of $LiClO_4$ solutions to 1000 ppm resulting in lower film conductivity but did not affect film conductivity with pure propylene carbonate or $LiAsF_6$ solutions.



XBL 8012-12965

FIG. 2. Growth of compact surface layer on lithium in different propylene carbonate solutions. Film thickness derived from capacitance measurements under the assumption of dielectric constant = 4.9.
1-1M LiClO$_4$
2-same with 1000 ppm H_2O added
3-0.5M LiAsF$_6$
4-same with 1000 ppm H_2O added

A.3. ANALYSIS AND SIMULATION OF ELECTROCHEMICAL SYSTEMS

This work supports the development of energy-storage systems by means of mathematical models and by experiments designed to test the accuracy and completeness of the models. A one-dimensional model has been developed for the Li(Al)-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 Li(Al)-FeS$_x$ battery during relaxation and charging.

A.3.1. MATHEMATICAL MODELING OF THE LITHIUM-ALUMINUM, IRON SULFIDE BATTERY*

Richard Pollard and John Newman

The lithium-aluminum, iron sulfide battery is under development for use in electric-vehicle propulsion. A mathematical model of the LiAl/LiCl, KCl/FeS cell has been used to study the behavior of the system during relaxation and charging. The changes which take place in the cell during relaxation and charging conditions could influence the dependence of cell performance on the number of completed cycles. Therefore, it is important to identify the factors that can limit the system during these modes of operation. The governing differential equations used to study the cell discharge behavior (see ref. 1) can be used directly in this analysis, and it is only necessary to replace the initial composition and porosity with the appropriate distributions and to modify the model for negative electrode kinetics.

Figure 1 shows composition profiles across the cell sandwich for several times after interruption of the current at the end of a discharge. In the negative electrode, the back becomes cathodic with respect to the front portions, and local concentration cells with the reaction

$$\mathrm{LiAl} \rightleftarrows \mathrm{Li}^+ + \mathrm{Al} + e^- \qquad (1)$$

are established. Although these concentration cells promote a uniform electrolyte composition, they accentuate the nonuniform utilization of reactants since there is no mechanism for equalization of local state of charge within the alloy. In the positive electrode, the possibility of simultaneous reactions exists. Adjacent to the current collector, FeS reacts with lithium ions according to the reaction

$$2\mathrm{FeS} + 2\mathrm{Li}^+ + 2e^- \rightleftarrows \mathrm{Li_2FeS_2} + \mathrm{Fe} \qquad (2)$$

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*Brief version of LBL 10421, January 1980.

whereas, near the front of the electrode, Li_2S reacts anodically with iron according to the reaction

$$2Li_2S + Fe \rightleftarrows Li_2FeS_2 + 2Li^+ + 2e^-. \qquad (3)$$

Heat is not generated in the cell during relaxation, and the temperature falls in accordance with the specified rate of heat transfer to the surroundings. As a result precipitation of the electrolyte may also occur.

After the current is switched off, there is an initial rise in cell voltage. The magnitude of this step change can, in principle, be used as a basis for the estimation of cell resistance. However, the influence of double-layer capacity is not included in this model, and the final total cell voltage, prior to interruption, predicted by the discharge model may be much lower than expected in practice. Therefore, separate calculations are necessary to estimate the interruptor resistance. Double-layer effects are not included since they are not generally regarded as being significant during normal cell operation.

Following the initial rise, the voltage gradually approaches the equilibrium open-circuit cell potential. The shape of the voltage-relaxation time curve is determined by the specific reactions which occur in the individual electrodes.

Figure 2 shows simulated composition profiles at different stages of a constant-current charge. The parameter λ represents the overall state of charge. The composition profiles represent the combined effects of diffusion, migration, and electrochemical reaction. A relaxation time of two hours was included between the initial discharge and the start of the charging process. Without relaxation, the profiles are very similar and there is little trace of the starting composition profile after the charge is completed.

The average cell temperature in Figure 2 falls from 753.5 to 740.0 K during the charge, as a result of reversible heat effects and heat transfer to the surroundings. This drop in temperature causes the saturation limit for KCl to rise and precipitation begins at the reaction front in the negative electrode when $\lambda = 85.9$. If the cell is not relaxed before charging, the temperature falls over a higher range (769.4 to 751.6 K) and precipitation is delayed until $\lambda = 91.1$. The difference in charging behavior caused by the temperature drop during relaxation emphasizes the need for careful thermal management of battery modules.

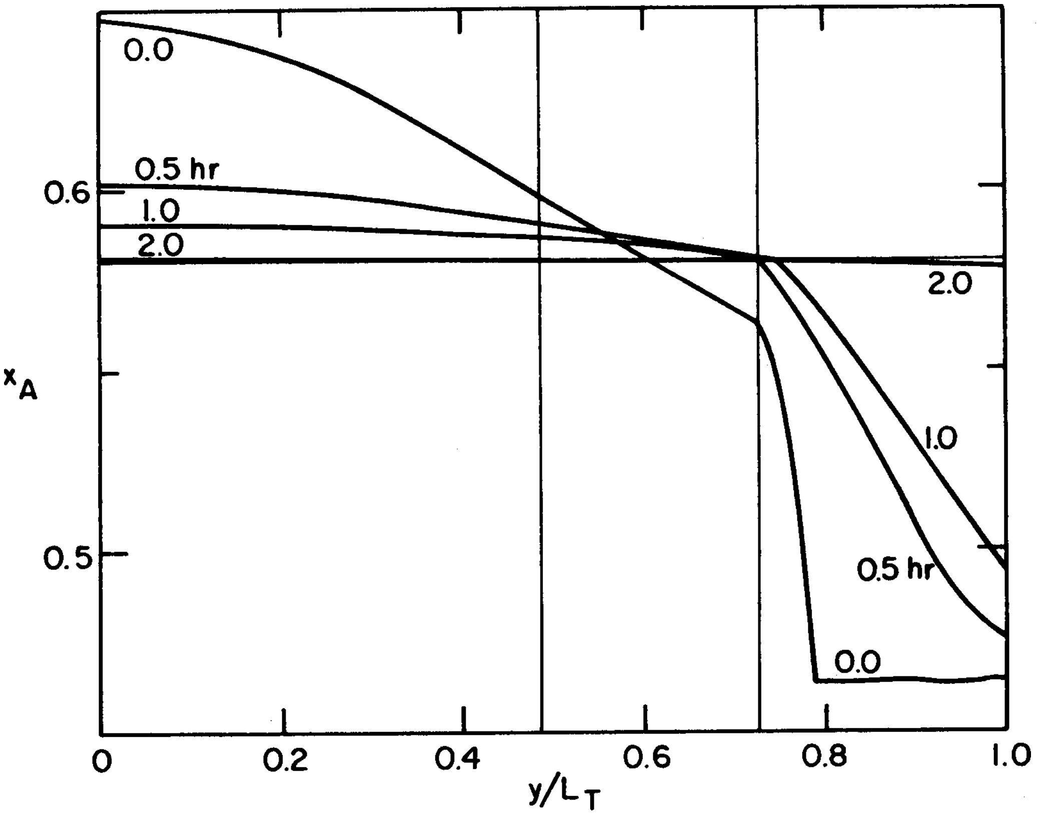
Figure 3 shows the fraction of active material utilized within the negative electrode, for the example in Figure 2. The region closest to the electrode/separator interface is recharged first, and the reaction front moves back through the electrode as the alloy is completely reconverted to β-LiAl. Relaxation of the electrolyte composition results in an increase in nonuniform utilization of reactants compared to the unrelaxed examples.

The complementary reaction distribution for the positive electrode is shown in Figure 4. A sharp reaction front moves through the electrode as Li_2FeS_2 is consumed. This mechanism also predominates in the unrelaxed case, but the final distribution of unreacted material is shifted from the back of the electrode.

In summary, the analysis indicates that composition variations become less pronounced during relaxation, but the local state of charge within the electrodes can become more nonuniform. The results obtained are sensitive to the details of the heat balance used in the calculation, and this reflects a need for precise thermal management of LiAl/FeS battery modules.

References

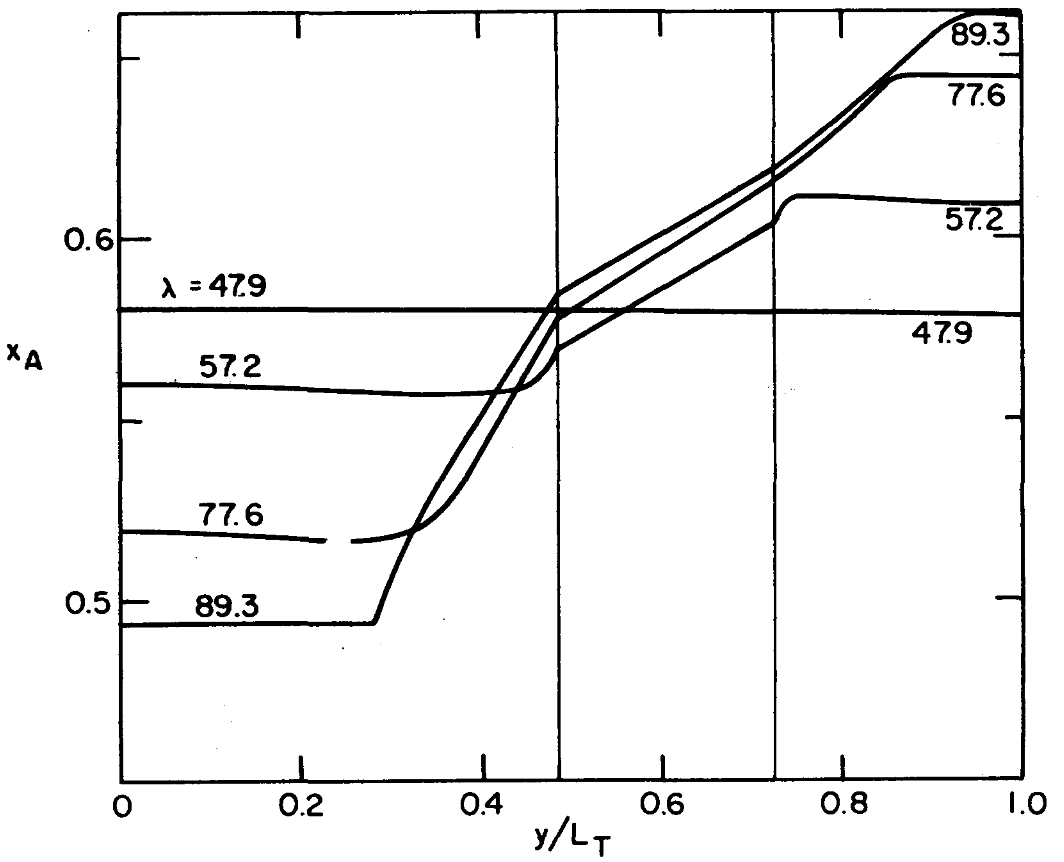
(1) R. Pollard and J. Newman, LBL 10420, January 1980.



XBL 7912-14569

FIG. 1. Position dependence of mole fraction of LiCl at different times after current interruption. Simulation parameters: $Q_- = 2800$ C/cm^3, $Q_+ = 4630$ C/cm^3, $L_- = 0.32$ cm, $L_S = 0.16$ cm, $L_+ = 0.18$ cm, $N = 5.5\times10^7$ cm^{-3}, $h_o = 8.25\times10^{-2}$ W/m^2·K, $R_g = 1.55$ Ω cm^2, $h = 0.004$ cm, $w = 0$, $-c^{\beta}_{Li}/(c^{\beta}_{Li})_{sat} = 1.0$ $D_\beta = 4\times10^{-8}$ cm^2/s. Parameters at start of previous discharge: $\varepsilon^o_- = 0.39$,

$\varepsilon_s = 0.75$, $\varepsilon^o_+ = 0.555.$, $T_o = 470°C$, $I = 41.6$ mA/cm^2, $x^o_A = 0.58$. Initial stage of charge, $\lambda(t = 0) = 47.9\%$. Additional parameters specified in Tables 1 and 3 of Reference 1.



XBL7912-14567

FIG. 2. Position dependence of mole fraction of LiCl at different states of charge for a constant current charge of -41.6 mA/cm^2. A relaxation time of 2 hours is included between the end of the previous discharge and the beginning of the charging process. Simulation parameters: T(t = 0) = 480.4°C, see also Fig. 1.

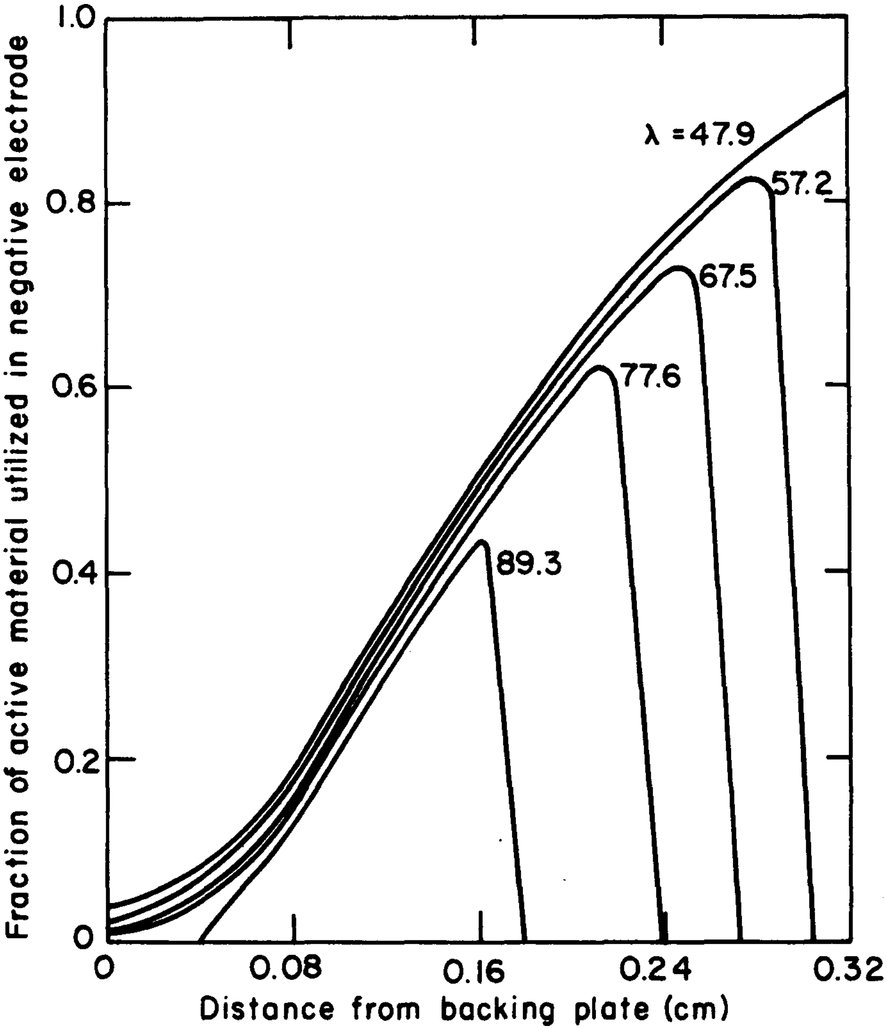


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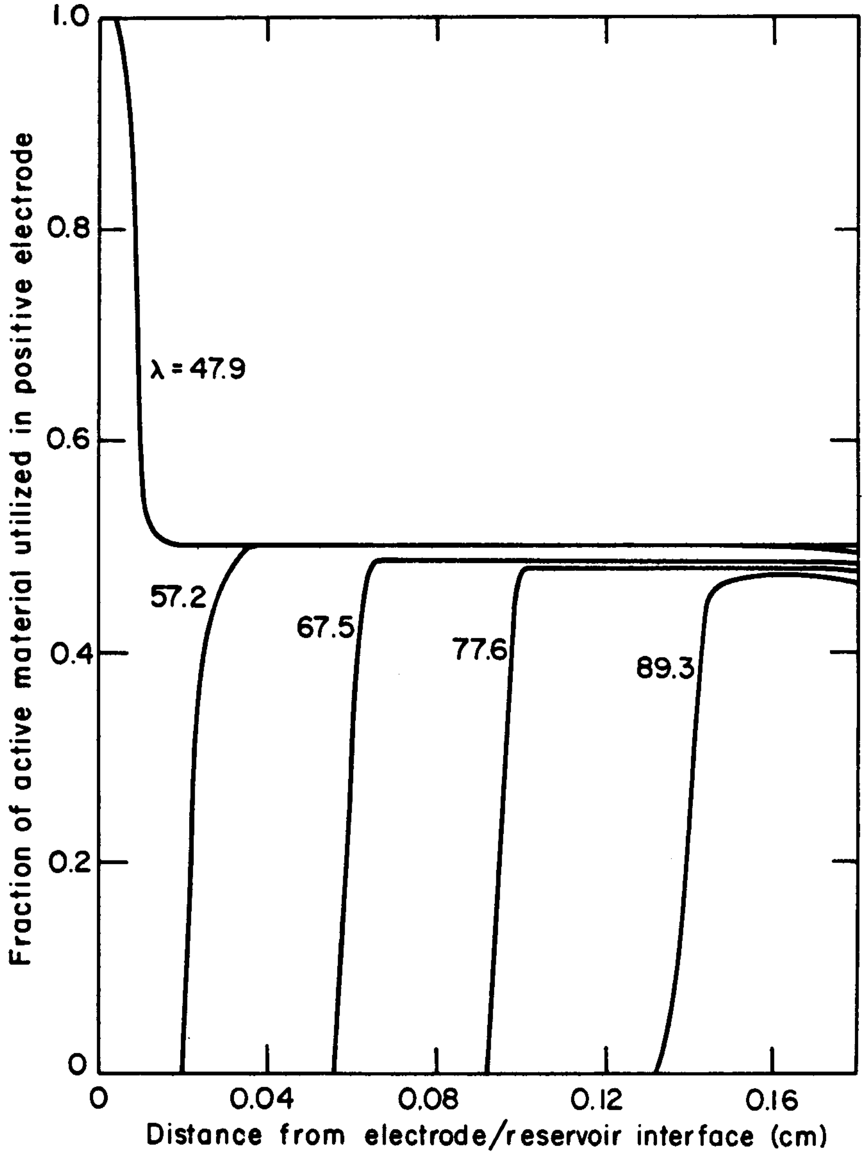
FIG. 3. Fraction of active material utilized in negative electrode at different overall states of charge during a constant current charge of -41.6 mA/cm^2. A relaxation time of 2 hours is included between the end of the previous discharge and the beginning of the charging process. Simulation parameters are as in Fig. 1.



XBL7912-14561

FIG. 4. Fraction of active material utilized in positive electrode at different overall states of charge during a constant current charge of -41.6 mA/cm^2. A relaxation time of 2 hours is included between the end of the previous discharge and the beginning of the charging process. Simulation parameters as in Fig. 1.

A. 4. METAL COUPLES FOR NON-AQUEOUS SOLVENTS

Charles W. Tobias

The objective of this project is to develop practical alternatives to aqueous, or high-temperature molten salt systems for the efficient electrochemical reduction and oxidation of reactive metals. Past accomplishments include the efficient reduction of potassium metal from $KAlCl_4$ dissolved in propylene carbonate. Current work concerns the determination of the thickness and chemical nature of surface films on lithium in propylene carbonate electrolytes.

A. 5. IMPROVEMENTS IN EFFICIENCY OF ALUMINUM REDUCTION CELLS

James W. Evans

Approximately 100 billion kWh of electrical energy are consumed each year in the U.S. in the electrolytic production of aluminum in Hall-Héroult cells. There is therefore considerable incentive to improve the performance of such cells and reduce the energy consumed per unit of metal produced.

Part of a cell is shown in the cross section in Fig. 1. The molten "cryolite" electrolyte (at about 950°C) serves as a solvent for aluminum oxide. Passage of current from the carbon anode through this electrolyte to a pool of molten aluminum at the bottom of the cell causes the reduction of the aluminum oxide, aluminum metal being generated at the surface of the aluminum pool and carbon dioxide gas bubbles at the surface of the anode. Unfortunately a portion of the aluminum generated is lost by a mechanism which consists of the dissolution of aluminum into the cryolite and its turbulent convection to the anode where it is re-oxidized by carbon dioxide bubbles. This loss of product (loss of current efficiency) should be reduced if means can be found to reduce the turbulent convection in the electrolyte. Motion of the electrolyte and the resulting turbulence are mainly due to electromagnetic stirring forces within the cell. A typical Hall-Héroult cell has a current of 100-200 kA; such currents generate strong magnetic fields. The interaction of the currents and the fields yields electromagnetic forces which stir both the molten cryolite and molten aluminum giving velocities of the order of 10 cm/s.

The electromagnetic forces have a second effect. These forces result in a distortion (bowing) of the interface between the metal and cryolite. Parasitic energy consumption (resistive heating of the electrolyte) can be reduced by bringing the anodes as close as possible to the metal surface, without contacting it. This is difficult to achieve if the surface is significantly bowed. The magnetic field within the cell, and consequently the electromagnetic forces, are a function of the arrangement of electrical conductors ("bus-bars") in the vicinity of the cell. It is therefore evident that some bus-bar arrangements will yield more or less bowing of the interface and current efficiency loss than others. The objective of the present investigation is by means of mathematical models, to determine what changes in cell design (e.g. bus-bar arrangements) result in cells with high current efficiency and little distortion of metal-cryolite interface.

A.5.1. CURRENT INEFFICIENCIES IN ALUMINUM REDUCTION CELLS

Stephen Lympany and James W. Evans

The mathematical computations entail the solution of Laplace's equation to determine the current density distribution in the cell. Knowing the currents within the cell and external bus-bars, the magnetic field within the cell can be computed and subsequently the electromagnetic forces acting on metal and cryolite. The turbulent fluid flow equations for the cryolite and metal are then solved, with the forces as input, to yield velocities and turbulence levels in both liquids, together with the shape of the metal-cryolite interface. Knowing the turbulence level within the cryolite, the rate of mass transfer of dissolved aluminum can be calculated, yielding the cell current efficiency.

Two common Bus-bar arrangements for the Hall-Héroult cells in the U. S. are "end-riser" arrangements and "quarter-riser" arrangements which differ in the way current is brought from one cell to an adjacent one. The computed cryolite velocities for end riser cells and quarter riser cells are depicted in Fig. 2. The cell is shown looking from above (the motion of the cryolite being predominantly in a horizontal plane). Also shown in the figure are velocity vectors for a novel riser which represents a first attempt at a bus-bar arrangement giving a better cell performance. The velocities are seen to be significantly different for the three riser arrangements; there are four circulation loops for the end riser arrangement, as opposed to two for the other riser arrangements, and the more complex circulation pattern results in higher turbulence levels in the molten cryolite and, consequently, lower computed current efficiency as indicated in Table 1.

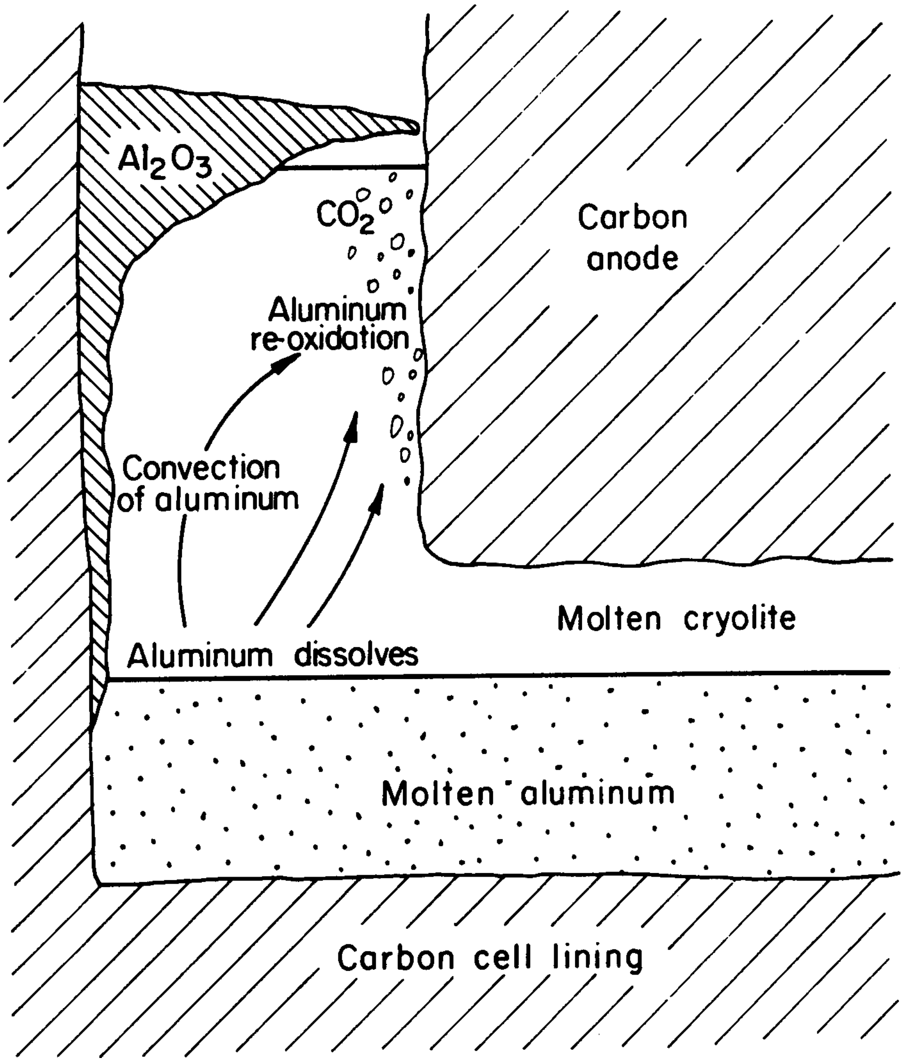
Aluminum cells are typically equipped with aluminum covers to prevent escape of cell gases. It can be conjectured that replacement of these covers by steel ones could be managed at little expense and would have the effect of shielding the inside of the cell from magnetic fields generated by the bus bars, reducing electromagnetic forces and improving cell performance. Table I reveals that such replacement improves the current efficiency of end riser cells, but not of quarter riser cells. The reasons are beyond the scope of this short report, but are covered in a full length report (LBL # 11675) on this project.

Fig. 3 depicts the contours for the metal-cryolite interface. The end riser design is seen to be somewhat inferior to the quarter riser design in that the interface is more bowed. The novel riser design, which appeared superior to the end riser design in terms of current efficiency is seen to be inferior in terms of interface topography. It is stressed that this novel riser arrangement is a first attempt at improving cell design and other arrangements will be studied in an attempt to find arrangements superior to both in terms of current efficiency and cell topography.

TABLE I

Computed current efficiencies for various designs of Hall-Héroult cell

	Cell with usual aluminum covers	Steel cell covers
End riser	93.8	92.9
Quarter riser	88.6	90.3
Novel riser	93.4	93.4



XBL 784-8016

FIG. 1. Sketch of part the cross section of a Hall-Héroult cell showing the transport of part of the aluminum product to the anode region where it is re-oxidized with consequent current efficiency loss.

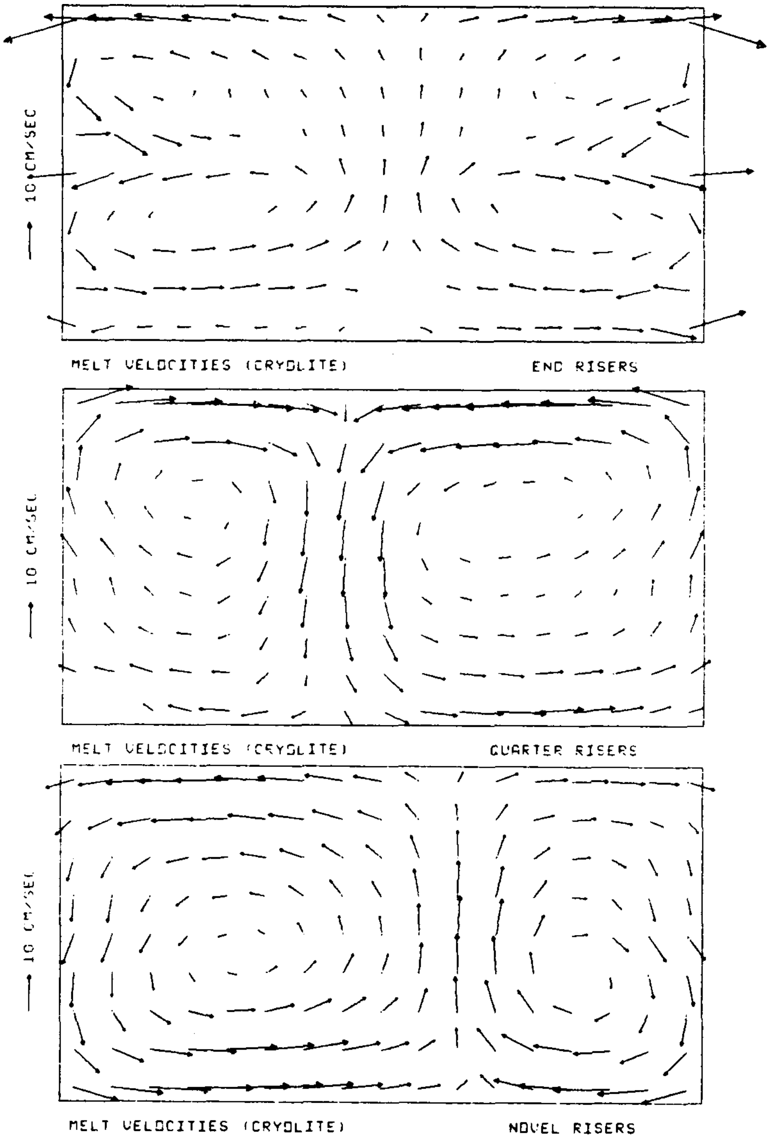


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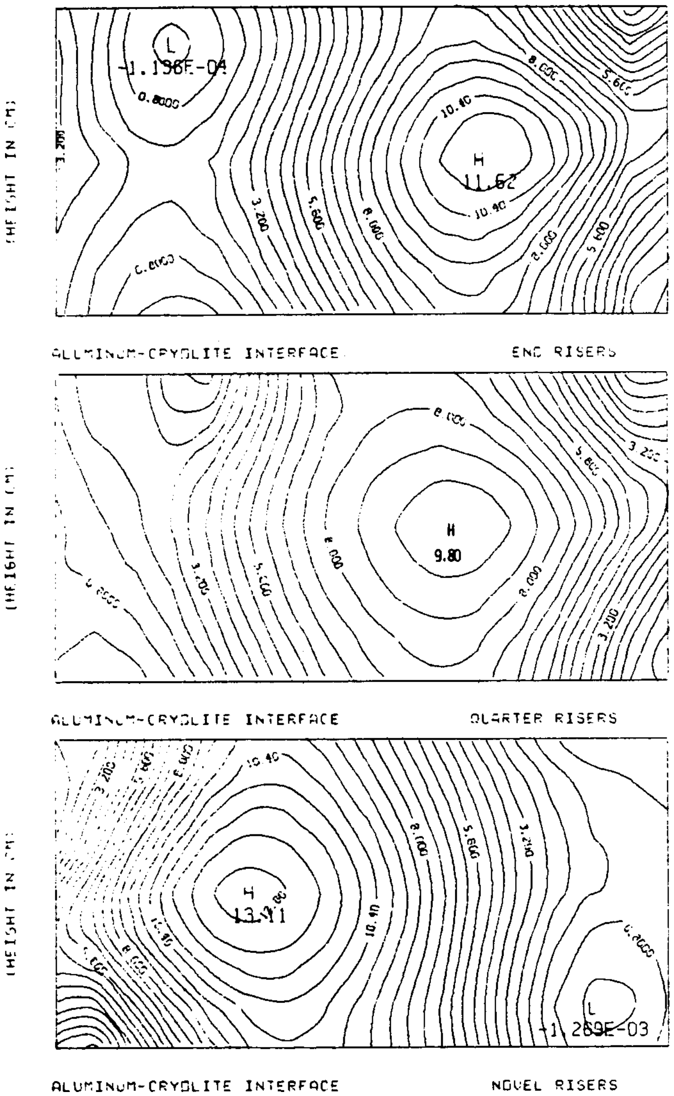
FIG. 2 **Computed velocities in the molten cyrolite electrolyte for three arrangements of the "riser" bus-bar bringing current to the cell.**



XBL 809-11703

FIG. 3 Computed contours for the metal-cryolite interface showing the least amount of bowing for the quarter riser arrangement.

A. 6. ELECTROCHEMICAL PROPERTIES OF NASICON

One of the more attractive systems for load leveling or for vehicle propulsion, is based on the sodium/sulfur electrochemical couple with a ceramic electrolyte. To date, sodium-beta alumina is the most developed ceramic electrolyte. The search for fast ion conductors is continuing to provide alternatives to the sodium-beta alumina ceramic electrolytes. One of these is the three dimensional sodium ion conductor Nasicon, ($Na_{1+x}Zr_2 Si_x P_{3-x} O_{12}$). Naiscon possesses some advantage, especially in the fabrication stage, over beta" alumina. Its resistivity is potentially lower at 300°C than that of sodium-beta" alumina polycrystalline electrolyte. The research intends to examine the properties of Nasicon so that they can be critically compared with sodium-beta" alumina solid electrolytes.

A.6.1. PROPERTIES OF NASICON

David C. Hitchock, Craig P. Cameron, Herbert K. Schmid, and Lutgard C. DeJonghe

Nasicon, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ has been prepared in different compositions by the sol gel process. Two compositions were prepared and tested, x=2 and x=2.3. The samples were either sintered or hot pressed. The best results were obtained by the hot pressing of Nasicon in which the graphite mold had been coated with hexagonal boron nitride powder. After preparation, the specimens were immersed in molten sodium held at 300°C, for times up to two weeks. In all cases, there was a chemical attack of the Nasicon by the molten sodium. The most pronounced degradation was found for Nasicon compositions with x=2, the least degradation was observed for Nasicon specimens with x=2.3. A crack pattern could usually be observed on the immersed samples as shown in Fig. 1. The mechanical strength of the samples was very severely decreased by the formation of the cracks. X-ray analysis before and after the immersion showed that an unidentified compound, possible a phosphate, with the most prominent reflection at 4.3 Å, was severely attacked by the molten sodium. Additionally, it was found that the lattice parameter of the Nasicon was increased by approximately 2% due to the immersion in the sodium. The stresses that are generated due to this lattice expansion as well as a dissolving of the second phase could account for the severe degradation of the Nasicons prepared in contact with molten sodium.

Some Nasicons were also examined in the transmission electron microscope. Electron beam irradiation was found to destroy the crystal structure very rapidly, although this destruction was slower at 500 kV than 100 kV. The microstructure of the polycrystalline Nasicon before and after destruction by the electronbeam in the high voltage electron microscope is shown in Figure 2. Interestingly, the amorphous Nasicon formed a relic of the original crystalline structure in which the grain boundaries apparently formed an amorphous structure of different density or different composition. The ionic resistivity of the samples was determined by AC admittance measurements over the range of frequencies up to 5 Mhz and for a range of temperatures between 50°C and 424°C. The immersion of Nasicon with $x=2$ in sodium for about 90 hours increased the resistivity by two orders of magnitude. This could be attributed to the formation of cracks and to the reaction of the Nasicon with the sodium.

The lowest ionic resistivity at 300°C that was found so far for Nasicon prepared in this laboratory was 2.5 Ω - cm with an activation energy of approximately 4 k cal.

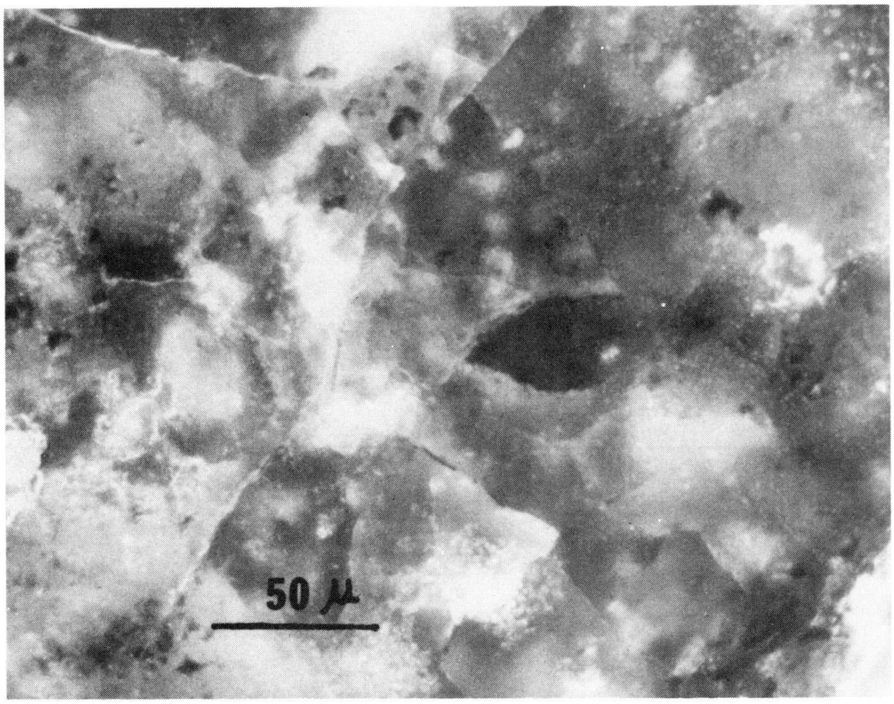


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FIG. 1. Cracks due to chemical attack of Nasicon by Na at 350°C for one week.

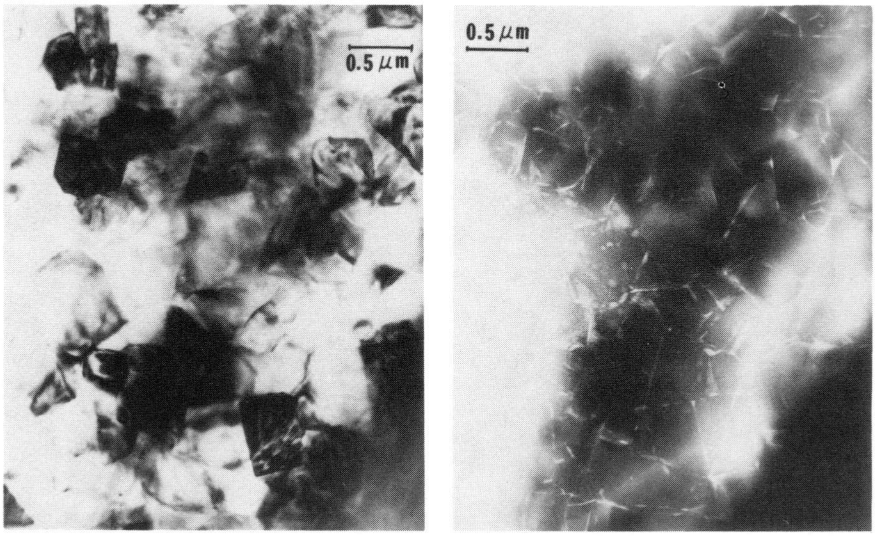

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FIG. 2. Relic formation after irradication of 500kV in the transmission electron microscope.

A. 7. BIFUNCTIONAL AIR ELECTRODES FOR METAL-AIR BATTERIES

The objective of this program is to conduct supporting research in air-electrode technology for DOE metal-air battery projects. Two metal-air system are currently in active development, the mechanically recharged Al-air system and the electrically recharged Fe-air system. It is expected that two new projects will be starting in FY 81, the mechanically recharged Zn-air and a hydrogen-air fuel cell optimized for transportation application. Both of these new projects will require low cost, efficient, unifunctional, air-electrode technology, as does the Al-air system. Metal-air systems are, in principle, high-energy and high-power-density systems (>100 Wh/kg, >100W/kg) owing to the fact that one of the electroactive species need not be contained within the battery or vehicle. However, practical development of this technology has historically been slow due to problems in finding a suitable air-electrode technology. The problem has been particularly grievous in the electrically recharged systems, where the positive electrode must both evolve and consume oxygen (bifunctional). Materials stability is a problem at the potentials required for oxygen evolution. Combined with the catalytic properties the electrode materials must have, the number of materials known to have suitable properties has been limited, and these materials have been too costly in electrodes using then existing technology, e.g., Pt black electrodes. The intrinsic difficulties in the electrically rechargeable electrode have caused emphasis to shift to mechanically recharged metal-air concepts where only a unifunction air electrode is required. Recent advances in gas-fed electrode technology in numerous fuel-cell projects indicate that efficient, low-cost, unifunctional electrodes can be developed. The bifunctional air electrode, however, appears to require a major breakthrough in both catalytic and materials technology.

A. 7. 1. OXYGEN REDUCTION WITH CARBON SUPPORTED METALLIC CLUSTER CATALYSTS IN ALKALINE ELECTROLYTE[+]

Philip N. Ross and Lee R. Johnson

Renewed interest in metal-air batteries and hydrogen-air fuel cells for vehicle application stems, at least in part, from the tremendous improvements in air-electrode technology that have occurred during the phosphoric-acid-fuel-cell development. Since a mechanically recharged battery requires only a unifunctional electrode, it seems reasonable to investigate the phosphoric-acid-fuel-cell-type electrode for use in alkaline electrolyte. In this electrode concept, a high-surface-area carbon is used both as the support for maintaining dispersion of the active catalyst and as the current collector. The active catalyst can, in principle, be any highly dispersed (<100 Å crystallites) material of interest. In the first phase of the program, we have examined selected Group VIII transition metals dispersed as metallic clusters on a turbostratic carbon-black (Vulcan SC-72, Cabot) material, e.g. Ni. Ru, Rh, Pd, Ag, Ir, and Pt, and in going work are examining certain Pt and Ag intermetallic clusters, e.g., Pt_3Ti or Ag_3Ti, dispersed on the same carbon support.

The metallic clusters were prepared by a combination of impregnation and ion-exchange techniques (1) with hydrogen reduction at 473 K. The metallic phase was confirmed by x-ray diffraction, and the metal dispersion was determined using transmission electron microscopy (TEM). Figure 1 shows a TEM micrograph of the Pt cluster catalyst, from which the cluster size was observed to be 20-30 Å. For Ni, Ru, Rh, Ir, and Pt, the metal loading was adjusted to give a

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[+] Brief version of LBL-11891.

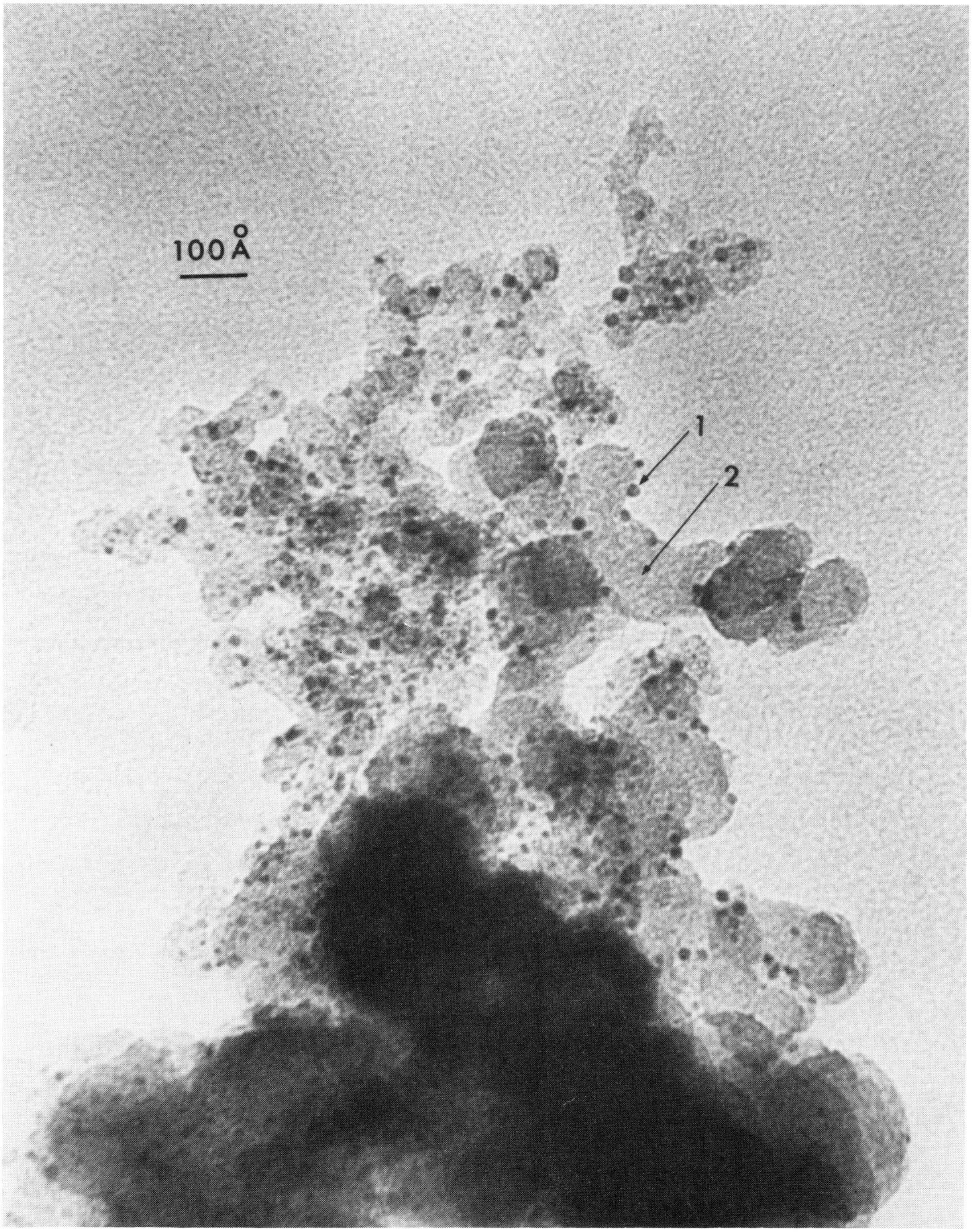

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FIG. 1. Transmission electron micrograph of Pt clusters dispersed on Vulcan XC-72 carbon black.

close grouping of crystallite sizes in the 20-30 Å range. Pd and Ag clusters could not be prepared in the same size range with reasonable metal loading (>5 w/o). Instead, Ag cluster sizes in the 100-200 Å range were utilized with 2.5 w/o metal loading, and Pd clusters in the 20-30 Å range were prepared at 1.3 w/o. Effective metal surface areas were calculated from the TEM measured "surface average diameter" using procedures developed in previous work (1).

Specific catalytic activity was defined as the current per unit weight of metal at an electrode potential of 0.85 V (vs. a reversible hydrogen electrode) using pure oxygen as the oxidant gas. The specific activities for oxygen reduction in 20% NaOH at 343 K are summarized in Table 1. The specific activity of the Ni catalyst was improved by using KOH-LiOH electrolyte rather than NaOH while the other catalysts were relatively indifferent to the alkali metal cation. The nickel catalyst was oxidized *in situ*, and the LiOH presumably resulted in lithium doping and improved activity.

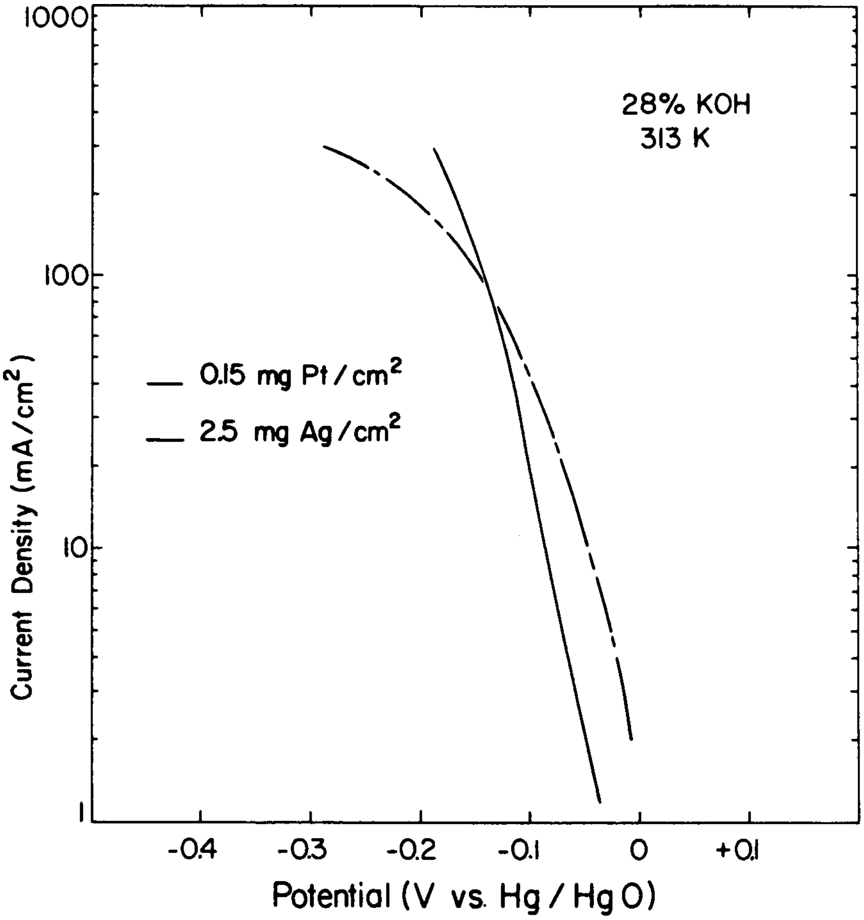
The activity measure of interest for development purposes is the catalyst cost to achieve the required performance characteristics, *i.e.*, the product of specific activity, required catalyst loading, and catalyst cost. In terms of cost effectiveness, Pt and Ag are the metals of choice. However, the polarization characteristics of the two electrocatalysts are very different, as shown by the curves in Figure 2, due to differences in reaction mechanism. For operation at high current density (>100 mA/cm^2), the Pt catalyst is the most cost effective catalyst of all the materials examined in this study. Actual testing of subscale (1 cm^2) H_2-air fuel cells (35% KOH, 70°C) have indicated the total (anode plus cathode) Pt cost would be only $60 per m^2 cell area for a vehicle fuel cell with sustained power density of 240 mW/cm^2 at 40% thermal efficiency. For operation at low current density (<50 mA/cm^2) and/or high (>55%) faradaic efficiency, the Ag cluster catalyst appears to be the more

TABLE 1

Activity of Metal Clusters for Oxygen Reduction in Alkaline

20% NaOH 345 K

Metal	Crystallite Size (Å)	mA/mg @ 0.85 V (RHE)	Tafel Slope (mV)
Pt	20-30	600	50
Ru	20-30	60	60
Ir	20-30	18	50
Rh	20-30	30	50
Pd	15-25	12	60
Ni	30-50	7	60
Ag	100-200	36	100



XBL 811-59

FIG. 2 Polarization curves for oxygen reduction with Teflon-bonded gas diffusion electrodes using Pt and Ag cluster catalysts. 20% O_2/80% N_2 ambient pressure.

cost effective, although there are problems with Ag dissolution under certain conditions of use.

The intermetallic cluster catalysts Pt_3Ti and Ag_3Ti have both shown improved polarization behavior relative to the pure metallic clusters. The improvement was particularly dramatic for Ag_3Ti, where the catalytic activity per unit weight of Ag increased nearly an order of magnitude. The reasons for the improved activity appear twofold: an improved dispersion of the metal on the carbon support and a basic alteration of the catalytic properties of the noble metal via a ligand effect. Ti is often used as a catalyst support in alkaline electrolyte, particularly for electrolysis. Based on our results with the Ti intermetallic compounds, we would expect to see a strong metal-support interaction (SMSI) for Pt or Ag dispersed on Ti. We are currently looking for these SMSI effects.

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A.7.1. ROTATING RING-DISC STUDIES OF OXYGEN REDUCTION ON Pt AND Ag IN ALKALINE ELECTROLYTE†

Philip N. Ross and Daniel A. Scherson

Previous studies in this laboratory have shown that Pt and Ag are the most important pure metals for use as catalysts of the metal cluster type in alkaline electrolyte. The characteristic polarization curves for these two catalysts are, however, dramatically different suggesting that different reaction mechanisms are operative. The mechanism of oxygen reduction on a wide variety of electrode materials may be analyzed in terms of a reaction pathway

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†Brief version of LBL-10700.

involving a direct 4-electron reduction of oxygen in parallel with a pathway involving the (2-electron) intermediate hydrogen peroxide. The most general description of the reaction pathways is shown in Figure 1. The 4-electron path is distinguished by the absence of O_2H^- as an intermediate. The rotating ring-disc electrode (RRDE) is useful in distinguishing between paths involving free O_2H^- (in equilibrium with H_2O_2) as an intermediate. Peroxide desorbing from the disc electrode is transported to the ring electrode by convection where it is oxidized; the ring current is equal to the rate of peroxide desorption times the collection efficiency of the ring. The general scheme in Figure 1 takes into account recycling of the oxygen produced by heterogeneous catalytic (non-electrochemical) decomposition of peroxide. The quantitative evaluation of rate constants k_1, k_2 and k_3 from RRDE data is simplified if the rate of the heterogeneous process, k_4, can be measured independently, and by making separate kinetic measurements on oxygen and peroxide-containing solutions. The catalytic decomposition of peroxide on both the Pt and Ag surfaces is extremely rapid, so measurement of k_4 is not a simple matter.

We have developed a new chronopotentiometric technique for the independent measurement of k_4 which makes no assumptions as to the order of reaction or the relative magnitude of the kinetics. An exact solution was found for the problem of convective diffusion to a rotating disc with a prescribed initial concentration profile and a current step at the disc surface. The steady-state (initial) surface concentration can be determined from the transition time τ by use of the parametric plots in Figs. 2 & 3. The surface concentration, C_o is related to the rate constant, k_4, reaction order, n, and the rotation rate, Ω, by the expression

$$\ln C_o = \frac{1}{1+n} \ln \Omega^{1/2} + \frac{1}{1+n} \ln \frac{K}{k_4}$$

where K is a known constant. A plot of ln C_o vs. ln $\Omega^{1/2}$ yields a straight line from which both the reaction order and rate constant can be determined from the slope, m, and intercept, b, as

$$n = \frac{1-m}{m} \quad \text{and} \quad k_4 = K \exp[1-(1-n)b]$$

A particularly attractive feature of this method is that the reaction order can be obtained in a single experiment.

Experiments on the Pt and Ag disc electrodes are in progress. In preliminary experiments, it is clear that the direct 4-electron path is predominant on Pt, whereas for Ag the reaction proceeds exclusively via the 2-electron pathway. Recycling via peroxide decomposition is thus very important for Ag, and in porous electrodes with Ag catalysts, the steady-state level of peroxide is probably quite high. Free peroxide would be expected to lower electrode life by accelerating corrosion of cell components and by loss of hydrophobicity of the electrode structure.

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† Brief version of LBL-10700; accepted for publication in J. Electroanal. Chem.

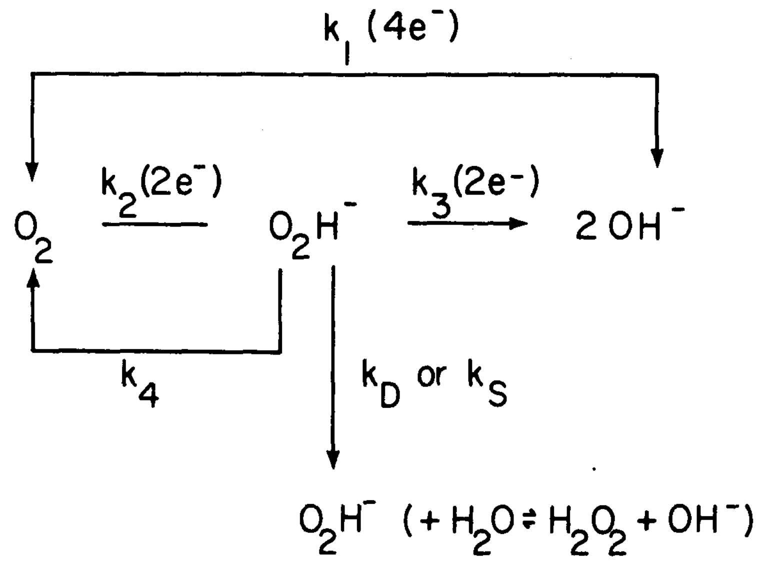

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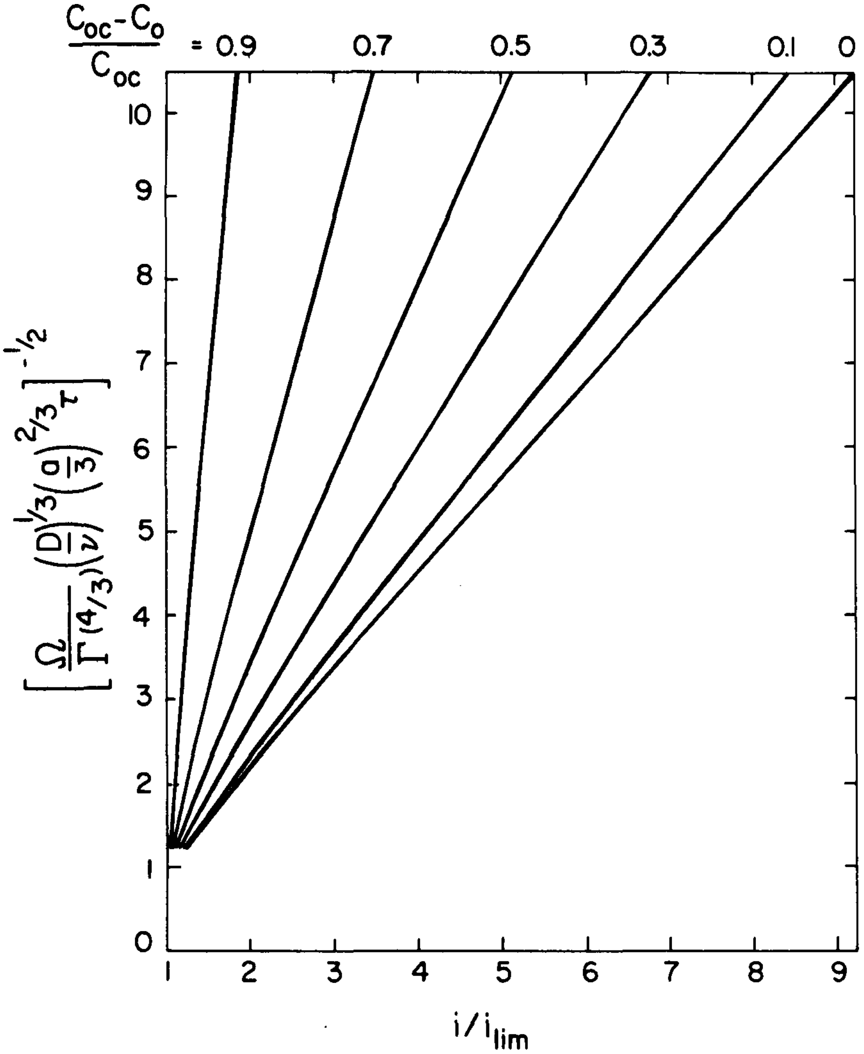
FIG. 1. General reaction sequence for oxygen pathways in alkaline electrolyte.



XBL 811-61

FIG. 2 Theoretical relationship of the transition time, τ, to the current step, i, for selected values of $(C_\alpha - C_o) / C_\alpha$.

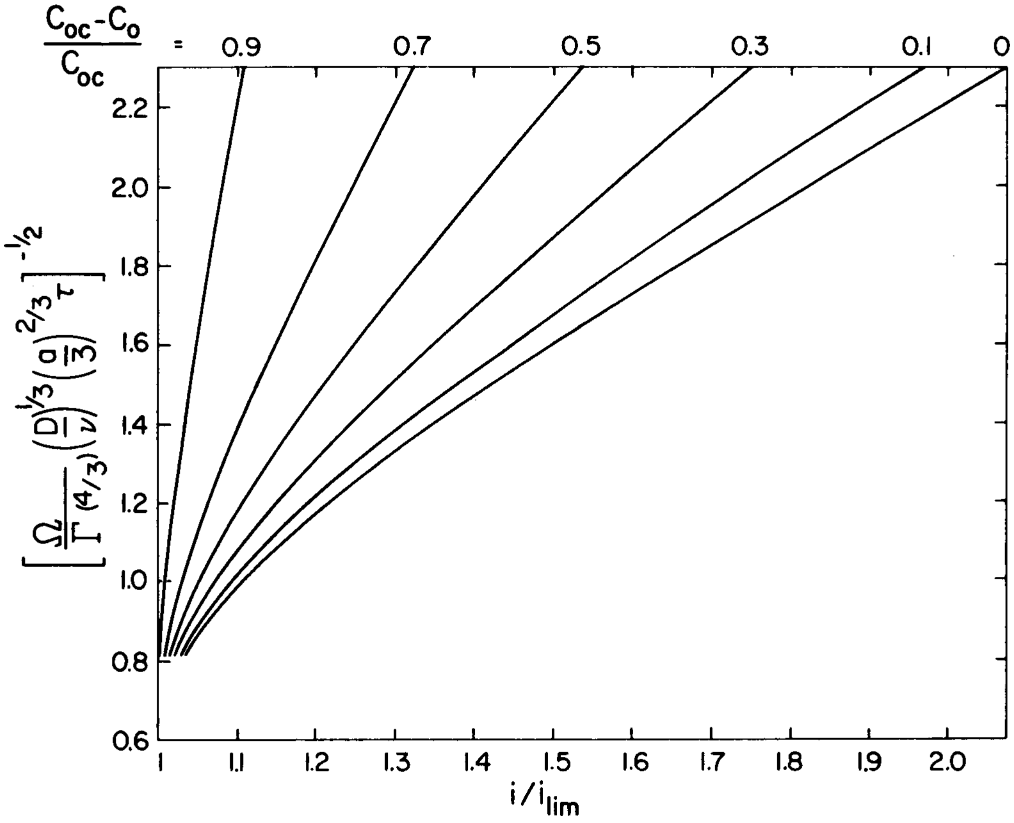


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FIG. 3 Expanded Region of FIG. 2.

A. 8. BATTERY ELECTRODE STUDIES

The purpose of the project is to study the behavior of electrodes used in secondary batteries and to investigate practical means for improving their performacne and lifetime. Systems of current interest include ambient-temperature rechargeable cells with zinc electrodes ($Zn/NiOOH$, Zn/AgO, Zn/Cl_2, Zn/Br_2, Zn/Air and $Zn/Fe(CN)_6^{\overset{\equiv}{-}}$) and rechargeable molten salt cells (Li-Al/FeS, Li-Al/FeS_2, Li-Si/FeS, Li-Si/FeS_2 and Na/β-$Al_2O_3/NaCl$-$AlCl_3$-SCl_4). The approach used in this investigation is to study the life- and performance-limiting phenomena under realistic cell operating conditions. Further background information can be found elsewhere[1-3].

Investigations have centered on the zinc electrode, which exhibits satisfactory performance in rechargeable alkaline cells ($Zn/NiOOH$, Zn/AgO) but has an inadequate cycle life. The short lifetime and continual capacity loss of the zinc electrode are closely related to a phenomenon known as shape change[4-6], the redistribution of active material over the face of the electrode as the cell is cycled.

A.8.1. Computer-Control of Electrode Performance Experiments

(M. Katz, E. Cairns, and F. McLarnon)

Cycle-life performance testing of battery electrodes requires contiuous control and/or monitoring of a variety of cell parameters (electrode overpotential, cell current, temperature). Design of a suitable control system must take into consideration a variety of possibly conflicting requirements: the system should be capable of continuously cycling up to 50 cells simultaneously and independently.

It must be reliable, accurate, cost-effective, and flexible enough to permit a wide variety of cell charge/discharge regimes. It also must lend itself to convenient data reduction, storage and display.

An appropriate computer-controlled test system has been designed, constructed and partially tested. The system configuration is shown in Figure 1. The heart of the system is a microcomputer (DEC LSI 11/23) with 128K of RAM and 2 hard memory disks (RL01), each with 5 megabytes of storage. The CPU is provided with a 16-bit I/O card and a 4-channel D/A card. Two prototype current controllers were constructed to permit operation of eight independent cells from a single power supply.

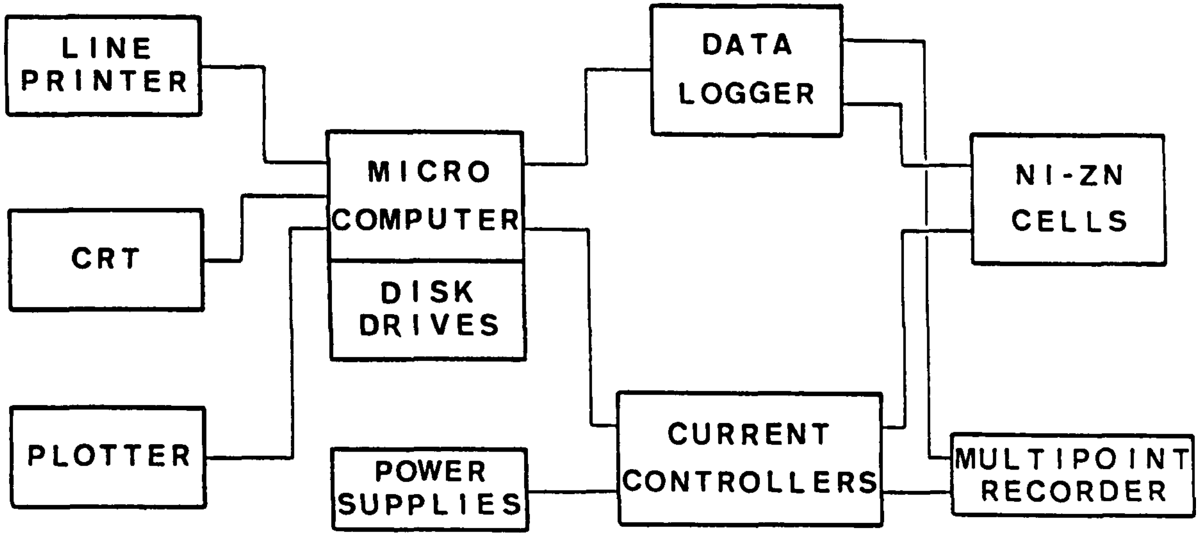

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FIG. 1 Test System
Microcomputer: DEC LSI 11/23, RL01 Disk Drives
Line Printer: LA-120
Data Logger: Fluke 2240B

A. 8.2. ZINC ELECTRODE RESEARCH

(J. Nichols, E. Cairns, and F. McLarnon)

It has been recognized [2,4-7] that reduced solubility of zinc species in alkaline electrolyte would reduce shape change and thereby improve the lifetime of Zn/NiOOH and Zn/AgO cells. The focus of this project is to identify candidate electrolytes and characterize the effect of lowered zinc solubility on the cycle-life performance of Zn/NiOOH cells.

A tri-electrode cell (see Fig. 2) was designed, constructed and tested. A 2.6 A-hr Zn electrode is sandwiched between two 1.3 A-hr NiOOH electrodes. Vacuum-table methods were employed to construct teflon-bonded zinc electrodes, and the nickel electrodes were generously supplied by battery manufacturers.[8] Analytical techniques[9] for the determination of zinc, hydroxide and carbonate concentrations are being adapted to selected battery electrolytes.

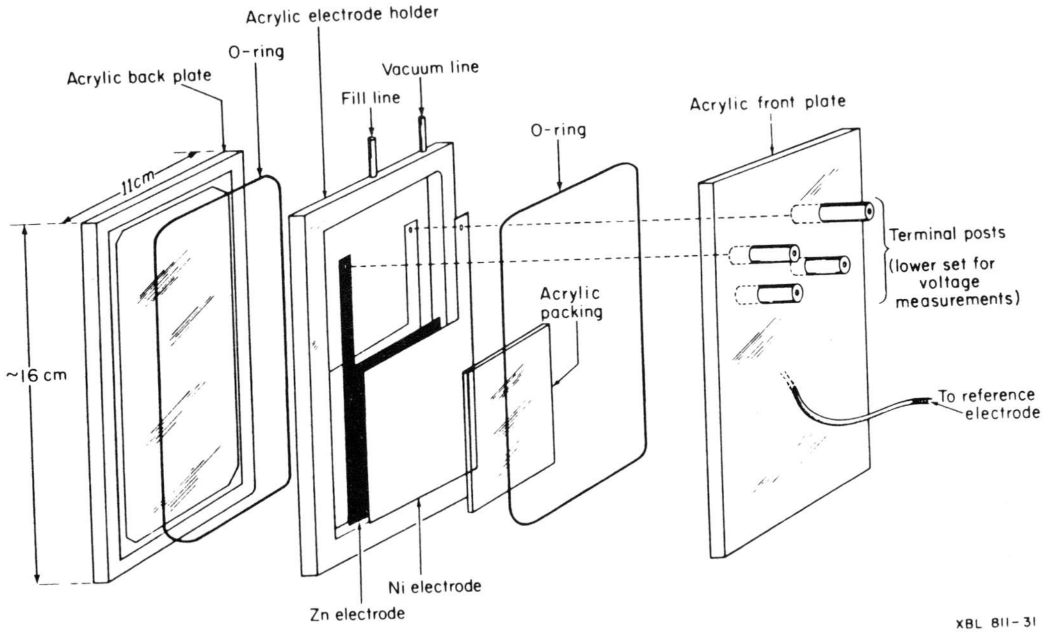

FIG. 2. Test Cell

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RESEARCH PLANS FOR CALENDAR YEAR 1981

A.1. SURFACE MORPHOLOGY OF METALS IN ELECTRO-DEPOSITION

C. W, Tobias, Investigator

Our differential nucleation theory, tentatively attributed to be the cause for the generation of regular macroscopic deposition patterns in the deposition of zinc from acid solutions will be subjected to critical experimental evaluation. According to this hypothesis, uneven growths of different crystal facets lead to protrusions, which generatie secondary flows (e.g. roll cells) in the presence of free or forced convection past the surface. This secondary flow causes small, periodic variations of concentration, and hence of potential, in a direction normal to the flow. Since nucleation density is potential dependent, the rate of growth of metal deposit tends to follow the spatial periodicity of potential produced by secondary flow. The effect of electrolyte composition including that of lighting absorbed surface active agents on the propagation and persistance of surface patterns will be systematically investigated and interpreted.--Simulation of advancing or receding electrode profiles, under mixed mass transfer/charge transfer control, will include a number of models of practical significance.

A.2. ANODIC SURFACE LAYERS ON BATTERY MATERIALS

R. Muller, Investigator

Further evidence for the inhomogeneous porosity of surface layers will be sought and means will be investigated to increase the ionic conductivity of the innermost nonporous part which seems to provide the protective function. A study of film behavior under anodic and cathodic polarization, where surface roughness is greatly increased, will benefit from use of a new laser light source and digital data acquisition system.

A.3. ANALYSIS AND SIMULATION OF ELECTROCHEMICAL SYSTEMS

J. Newman, Investigator

Experimental work will continue on the electrochemical removal of lead from wastewater. The model of the lithium/iron sulfide battery will be extended. A mathematical model will be developed to describe the concentration profiles and current distribution in a thin-gap flow cell containing a redox couple.

A.4. METAL COUPLES IN NON AQUEOUS SOLVENTS

C. W. Tobias, Investigator

This project will be directed toward the exploration of criteria for the efficient recovery, refining, and galvanic cycling of certain of the group II and III metals, notably magnesium, calcium and aluminum. In addition to the propylene carbonate family of solvents, other solvent options will be considered as well. Progress in this project will depend upon the availability of graduate research assistants.

A.5. IMPROVEMENT IN EFFICIENCY OF ALUMINUM REDUCTION CELLS

J. W. Evans, Investigator

Computations will be carried out for many alternative cell designs in an attempt to find ones that are superior in terms of current efficiency and freedom from distortion of the metal-electrolyte interface. Initiation of research aimed at testing the results of the predictions. Initiation of research on motion of the cryolite-metal interface (motion detrimental to cell performance).

A.6. ELECTROCHEMICAL PROPERTIES OF NASICON

L. C. DeJonghe, Investigator

Continued efforts are planned in the preparation of Nasicons of slightly varying compositions, in which certain elements may be added to improve sintering and to improve its resistance to chemical reaction with sodium. Once such composition has been clearly defined, the electrochemical stability of the Nasicon will be tested.

Electrochemical measurements will be made on the Nasicon/molten sodium interface, for pure and impure sodium. Potential static and galvanostatic techniques will be used to identify the important electrode reactions.

A.7. BIFUNCTIONAL AIR ELECTRODES FOR METAL-AIR BATTERIES

P. N. Ross, Investigator

Studies of Pt and Ag intermetallic catalysts for oxygen reduction will continue. Rotating ring-disc methods will be applied to the study of intermetallic catalysts found to be of interest in the study of bimetallic cluster catalysts. Carbon corrosion studies will begin to develop carbon support materials that are more resistant to oxidation than Vulcan XC-72. Studies of gas evolution in porous, hydrophobic, polymer-bonded type structures will be initiated. The objective of the latter studies is to determine how the electrolyte wetting in the catalyst layer changes during gas evolution, and what material properties are important in controlling electrolyte displacement.

A.8. BATTERY ELECTRODE STUDIES

E. J. Cairns, Investigator

The computer-controlled electrode testing system will be completely implemented, and cycle-life testing of Zn/NiOOH cells will be initiated. Work on rechargeable molten-salt cells will begin.

1980 PUBLICATIONS AND REPORTS

I. REFEREED JOURNALS

1. Richard Pollard and John Newman, "Transient Behaviour of Porous Electrodes with High Exchange Current Densities," Electrochim. Acta, 25, 315-321 (1980).
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II. OTHER PUBLICATIONS

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III. REPORTS

See also "Refereed Journals" and "Invited Talks"

1. Y. Geronov, F. Schwager and R. H. Muller, "Film Formation on Lithium in Polypropylene Carbonate Solutions under Open Circuit Conditions", LBL - 11126.
2. Richard Pollard and John Newman, "Mathematical Modeling of the Lithium-Aluminum, Iron Sulfide Battery, I. Galvanostatic Discharge Behavior," January, 1980.
   LBL-10420
3. Richard Pollard and John Newman, "Mathematical Modeling of the Lithium-Aluminum, Iron Sulfide Battery, II. The Influence of Relaxation Time on the Charging Characteristics," January, 1980.
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5. J. W. Evans, Y. Zundelevich and D. Sharma, "A Mathematical Model for Prediction of Currents, Magnetic Fields, Melt Velocities, Melt Topography and Current Efficiency in Hall-Héroult Cells," LBL-11675.

6. P. N. Ross, "Oxygen Reduction with Carbon Supported Metallic Cluster Catalysts in Alkaline Electrolyte", LBL-11891.

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2. Milan M. Jaksic and Charles W. Tobias, "Hydrodynamic Flow Visualization by the Electrochemical Method," paper presented at the International Symposium on Flow Visualization, Ruhr-University Bochum, Germany, September 9-12, 1980.
3. Henry H. Law and Charles W. Tobias, "The Kinetic Stability of Potassium in Propylene Carbon Electrolytes," paper presented at the 158th meeting of the Electrochemical Society, Hollywood, Florida, October 5-10, 1980. Extended abstracts, Vol. 80-2, No. 39, pp. 106-108, 1980. Based on LBL-11487.
4. Henry H. Law and Charles W. Tobias, "The Morphology of Potassium Deposited from Propylene Carbonate Electrolyte," paper presented at the 158th meeting of the The Electrochemical Society, Hollywood, Florida, October 5-10, 1980. Extended Abstracts, Vol. 2, No. 392, p. 991-92. Based on LBL-11253.
5. Charles W. Tobias, "Prospects and Problems in Electrochemical Engineering," invited address delivered in the frame of the International Symposium on Electrochemistry in Industry - New Directions, celebrating the centennial of Case Institute of Technology, Cleveland, Ohio, October 20-22, 1980.
6. Geoffrey A. Prentice and Charles W. Tobias, "Finite Difference Calculations of Current Distributions at Polarized Electrodes," paper presented at the 73rd Annual Meeting of the American Institute of Chemical Engineers, Chicago, Illinois, November 16-20, 1980. Based on LBL-11058.
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11. Rolf H. Muller, "Lithium Surface Layers," Applied Battery and Electrochemical Research Program Review, Berkeley, California, August 14-15, 1980.

12. John Newman, "Modeling of Li-Al/FeS Batteries," Department of Energy Battery and Electrochemical Contractors' Conference, Arlington, Virginia, December 11, 1979.

13. John Newman, "Engineering of Electrochemical Storage Batteries." Invited address before the Department of Chemical Engineering, Texas A&M University, College Station, Texas, March 21, 1980.

14. John Newman, "Elecrochemical Modeling." Address at the review of the Lithium-Iron Sulfide Battery Program, Argonne National Laboratory, Argonne, Illinois, June 26, 1980.

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16. Pier Filippo Marconi and John Newman, "Mathematical Modeling of Hybrid-Redox Flow-Through Porous Electrode Cells for Energy Storage, the Fe/Fe^{2+}/Fe^{3+} System." Presented at the 31st Meeting of the International Society of Electrochemistry, Venice, Italy, September 22-26, 1980.

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18. L. C. DeJonghe, "Solid Electrolyte Batteries," National Defense Academy, Yokosuka, September, 1980, Japan.

19. C. W. Tobias, "Morphology of Metals in Electrodeposition," Review of the Applied Battery and Electrochemical Research Program, Lawrence Berkeley Laboratory, Berkeley, California, August 14-15, 1980.

20. E. J. Cairns, "Electric Powered Vehicles," invited lecture at Energy Forum Series, sponsered by the Energy Resources Committee of the Engineering Council of Sacramento Valley, Sacramento, California, January 15, 1980.

21. E. J. Cairns, "Advanced Batteries," invited lecture at Advanced Energy Conversion Short Course, Arizona State University, Tempe, Arizona, March 17-21, 1980.

22. E. J. Cairns, "Electric Vehicles and Better Batteries," invited lecture at College of Engineering, University of California-Davis, Davis, California, April 24, 1980.

23. E. J. Cairns, "Rechargeable Molten-Salt Cells," invited lecture at ECS Meeting, Hollywood, Florida, October 5-10, 1980, Abstract No. 641.

24. E. J. Cairns, "Batteries of the Future - Vehicles," invited plenary lecture and panelist at Symposium on Electrochemistry in Industry--New Directions for Case Centennial Celebration, Case Institute of Technology, Case Western Reserve University, Cleveland, Ohio, October 20-21, 1980.

25. E. J. Cairns, "Electric Vehicles," invited lecture at Mellon Institute Fuel Economy/Synfuel Steering Group Meeting, Scottsdale, Arizona, November 6-7, 1980.

B. INVESTIGATION OF THE NATURE AND STRUCTURE OF DEPOSITS ON LITHIUM AND ALUMINUM ANODES

LBL Subcontractor:	University of Southampton
Principal Investigator:	M. Fleischmann
DOE Program Manager:	S. Ruby
LBL Project Manager:	R. Muller
LBL Contract No.:	4504410
B & R Number:	AL-05-10-10
FY 1980 BA/BO Released:	28K/17K

The objectives of this project are to investigate the nature of this interface between aluminum electrodes and aqueous alkaline electrolytes, and between lithium electrodes and organic solvent/electrolyte systems. The major part of the work is aimed at the application of in-situ structural techniques which are being developed. The major technique used is in-situ Raman spectroscopy. A Coderg T800 Raman spectrometer system with triple-dispersion monochromator and high optical throughput is employed.

Most of the work which has been carried out so far has been aimed at measuring the Raman spectra of aluminum oxide films and of aluminum/aluminum oxide/electrolyte interfaces using relatively pure samples of aluminum. It was confirmed that α alumina (corundum) has a readily detectable Raman spectrun (S.P.S. Porto and R. S. Krishnan, 47, 1099 (1967). On the other hand, λ alumina has a very weak spectrum. The extremely weak (and at this time still unconvincing) spectra which have been obtained therefore indicate that layers of aluminum oxide on electrodes consist of λ alumina; in fact; these oxide films are usually designatedby using repetitive scanning and signal averaging of the spectra. The oxide layers are photosensitive, and resonance enhancement of the lattice mode by using an appropriate blue laser line has been sought. No enhancement lattice mode has been observed, but this may in part be due to these lines being obscured by increases in the fluorescence. Current work has therefore been concentrated on measurements with alloys and these experiments are leading to the first major breakthrough with this system. For example, measurements with the alloy 98Al/1 Mg/1 Si (an alloy known to form oxide films containing color centers) are yielding spectra containing bands due to the oxide lattice, incorporated anions and some indication of incorporated water. The spectra are sensitive to alloy and solution composition.

The presence of OH groups could not be determined to the vibrational spectrum of the oxide. Initial measurements using infrared spectroscopy, looking for OH species, were more promising.

C. BASIC DEVELOPMENT OF NICKEL/ZINC BATTERIES

LBL Subcontractor:	Lockheed Missiles and Space Corporation
Principal Investigator:	T. Katan
DOE Program Manager:	S. Ruby
LBL Project Manager:	F. R. McLarnon
LBL Contract No.:	4503610
B & R Number:	AL-05-05-05
FY 1980 BA/BO Released:	93K/34K

The objective of this research program is to generate basic data to assure proper development of zinc/nickel oxide batteries for electric vehicles. At the present state of development, the zinc electrodes in these batteries have limited cycle life, and the utilized nickel is costly. Immediate goals are to determine the factors causing the limited zinc electrode lifetime, to recommend corrective action, and to determine the minimum amount of nickel that can be spread into a porous electrode.

Fundamental studies are conducted to characterize the processes causing limited zinc life, such as dendrite growth and shorting, electrode shape change, and premature passivation. Basic engineering studies are conducted to yield the optimal electrode structure and thickness. Ideal porosity, pore size, and specific surface area are determined to guide electrode manufacture.

The experimental program uncovered the sequence of processes occurring during zinc discharge to zinc oxide, and determined the presence of hydrogen as a precursor to dendrite growth during charge. A general law for dendrite growth rate was derived.

Other findings include the occurrence of electrochemical displacement of isolated zinc fragments, the exfoliation and loss of nickel capacity on overcharge, and the gradual loss of zinc electrode performance after 300 to 400 cycles without apparent morphological change. This latter "premature passivation" was found to be removed by addition of fresh electrolyte.

D. RESEARCH ON LEAD-ACID BATTERY ELECTRODES

LBL Subcontractor:	Naval Research Laboratory
Principal Investigator:	S. M. Caulder and A. C. Simon
DOE Program Manager:	S. Ruby
LBL Project Manager:	P. N. Ross
LBL Contract No.:	4505710
B & R Number:	AL-05-05-05
FY 1980 BA/BO Released:	125K/64K

The primary objective of NRL's research on lead-acid battery electrodes is to investigate the atomic structure of PbO_2. Correlations between microstructure, electrolyte stratification, current density and electrolyte concentration are being sought.

In continuation of the investigation of PbO_2 molecular structure and origin of electrochemical activity, alpha PbO_2 was synthesized by available chemical and electrochemical methods, with variations in the preparation parameters. It was found that electrochemical methods gave preferred orientations which varied with experimental conditions. Chemically prepared alpha PbO_2 showed broad Bragg diffraction peaks, indicating poor crystallinity. The best of the chemical preparations was subjected to high-resolution neutron diffraction, which confirmed the poor crystallinity, and in addition revealed traces of beta PbO_2 structure.

The recently-completed determination of beta PbO_2 structure had shown that previously published parameters for beta PbO_2 were in error. Using the corrected parameters for beta PbO_2, these were subtracted from the neutron patterns for the chemically prepared alpha PbO_2 to obtain the molecular parameters and crystal structure for alpha PbO_2.

It was also found that in the preparation of the PbO_2, variations in the pH and lead ion concentrations influence the x-ray diffraction pattern. Since pH and lead ion concentration changes occur in the working electrode, as a result of electrolyte stratification and diffusion gradients, corresponding changes in PbO_2 microstructure would be expected to occur.

The necessary data to compare changes in molecular structure on this basis is not yet available. Research is proceeding to make a study of the changes in electrode potential and microstructure that occur with changes in current density, and how this relates to electrolyte stratification and microstructural changes at various depths within the electrode.

In the batteries investigated so far it is indicated that loss of capacity and reduced cycle life at high rate discharges is a function, not only of stratification, but also of poor current distribution produced by inadequate conductivity as a result of poor current collector design. The electrode potentials at different vertical distances in the electrode also behave in an erratic manner that cannot be explained only by differences in pH or IR drop but must also take into account differences in microstructure and, possibly, differences in electrochemical activity of the PbO_2.

E. THERMAL MANAGEMENT OF BATTERY SYSTEMS

LBL Subcontractor:	Gould, Inc.
Principal Investigator:	H. F. Gibbard
DOE Program Manager:	S. Ruby
LBL Project Manager	F. R. McLarnon
LBL Contract No.:	4505810
B & R Number:	AL-05-10-10
FY 1980 BA/BO Released:	86K/58K

Objectives of this project are the determination of heat generation rates, measurement of temperature distributions, analysis of heat transfer rates, and evaluation of thermal management strategies for Li-Al/FeS batteries. Accomplishments in FY 1980 are listed below:

1. A constant temperature furnace designed for cell tests has been built, and the temperature distribution in the test chamber varies less than 1°C at temperatures up to 500°C.
2. A high-temperature calorimeter has been designed for measuring cell heat generation; the designed ranges of temperature and heat flow are room temperature to 500°C and 0-25 W.
3. With a nonactive cell in a vacuum-foil insulated vessel, the effective thermal conductivity in the direction normal to electrode plates has been measured to be 0.48 W/mK. It has also been observed that melting of electrolyte begins at the top of the cell at 354°C.

4. A preliminary study has been carried out to predict the heat generation rate in a 50 kWh battery and the cooling requirements of a temperature-control system for the battery.
5. A heat-transfer analysis has been performed to investigate the effect of heat loss along feedthroughs (which penetrate the insulated vessel) on the total heat loss and the battery temperature. The prediction is consistent with experimental observations and shows an unacceptably high conduction heat loss from the cell nearest the entry point of the power leads.
6. The hardware and software have been assembled for automated data acquisition and cycling of cells. The system has performed satisfactorily in tests on a zinc/nickel oxide cell cycled on S.A.E. schedule D for electric vehicles.
7. The temperature distributions in a three-cell and a ten-cell cycling battery have been measured. The results indicate that the electrical insulation between cells and the heat generation in reversed cells could cause thermal problems.
8. A cooling system has been designed for a ten-cell battery module. The data from a test with a relatively low cooling rate show that the system functions effectively. However, the data also indicate that a large temperature gradient may result if high cooling rates are applied.

F. TEMPERATURE LIMITATIONS OF PRIMARY AND SECONDARY ALKALINE BATTERY ELECTRODES

LBL Subcontractor:	SRI International
Principal Investigator:	M. McKubre
DOE Program Manager:	S. Ruby
LBL Project Manager:	F. McLarnon
LBL Contract No.:	4505610
B & R Number:	AL-05-10-10
FY 1980 BA/BO Released:	65K/87K

SRI has sought to use the "high information" electrochemical methods previously applied to understanding temperature limitations of Ni, Fe, and Zn electrodes in NaOH, and extend these measurements to KOH solutions. Some refinement of techniques has been undertaken--specifically in the construction of a closed loop digital feedback variable speed RRDE motor assembly. Considerable attention has also been paid to the development of stepped-frequency AC impedance measurements under minicomputer control as a quantititve tool yielding mechanistic information in battery electrode studies.

Particular emphasis has been directed towards the phenomena previously identified as critical to the operation of alkaline battery electrodes. These are, (1) to determine the mechanisms of irreversibility of Ni associated with deep or prolonged discharge at elevated temperatures; (2) to quantify the extent of Fe (II) and Fe (III) dissolution at elevated temperatures, and to determine the influence of KOH concentration on dissolution kinetics; and (3) To quantify the dissolution and to study passivation and oscillation phenomena of Zn, as a function of KOH and $Zn(OH)_4^{2-}$ concentration.

Five temperatures have been used at 25° intervals in the range 0° to 100°C. Two electrolyte concentrations (30 and 35 wt%) are being used. These were chosen as being typical of alkaline battery electrolyte concentrations, and are close to the composition of maximum electrolyte conductivity at all temperatures.

G. THERMODYNAMIC FRAMEWORK FOR ESTIMATING THE OVERALL, THERMAL, COULOMBIC, AND VOLTAGE EFFICIENCIES OF ALKALINE BATTERIES AS A FUNCTION OF CONCENTRATION AND TEMPERATURE

LBL Subcontractor:	Ohio State University
Principal Investigator:	D. Macdonald
DOE Program Manager:	S. Ruby
LBL Project Manager:	F. R. McLarnon
LBL Contract No.:	4505110
B & R Number:	AL-05-10-10
FY 1980 BA/BO Released:	65K/18K

Assessment of the efficiencies of various alkaline battery systems requires a detailed knowledge of the thermodynamic properties of metals in concentrated hydroxide solutions over a wide range of concentration and temperature. Of particular interest is the change in Gibbs energy and enthalpy for the cell reaction, because these quantities can be used to define the voltaic, coulombic, and thermal efficiencies of the system. Once these are known, a rational choice may be made between various systems for the most efficient use of energy.

In order to define the thermodynamic properties of a metal in concentrated hydroxide solution over the appropriate temperature range (-20°C to 120°C), it is necessary to take into account the non-ideal nature of the hydroxide medium. For example, the activity of water cannot be assumed to equal one (Raoult's Law standard state); experimental data demonstrate that a_{ω} may be as low as 0.3 depending upon the temperature and concentration. Also, the activity of water depends upon the identity of the cation (Li^+, Na^+, or K^+), contrary to the behavior in dilute hydroxide systems. The cation also affects the activity coefficient of the hydroxide ion in solution, and the actual concentration of this species because of ion pairing. Although quantitive data for ion-pairing are not extensive, those that are available indicate that the extent of ion-pairing increases along the series $K^+<Na^+<Li^+$. Finally, our previous work has demonstrated that the pH of a concentrated hydroxide solution is not linearly related to the logarithm of concentration; the variation of activity coefficient and the extent of ion pairing forces the pH through a maximum as the molality of hydroxide increases over the range of 1 mol kg^{-1} to 10 mol kg^{-1}. Because thermodynamic stability of a metal is conveniently defined in terms of potential-pH space, the deviation of concentrated hydroxide solutions from ideal behavior is very important.

The goal of the present program is to define the thermodynamic properties of iron, nickel, zinc, aluminum, sodium, and lithium in concentrated lithium hydroxide, sodium hydroxide and potassium hydroxide solutions over the temperature range -20° to 120°C. Our initial activity has involved a detailed review and assessment of data in the literature for the properties of concentrated hydroxide solutions. Sufficient vapor pressure data have been located to provide a reasonably precise description of the thermodynamic properties of concentrated sodium hydroxide and potassium hydroxide solutions over the concentration and temperature ranges of interest. However, insufficient data are available for concentrated lithium hydroxide. Accordingly, the vapor pressure data for this system will be determined experimentally, and an apparatus for these measurements is now being set up.

A detailed statistical analysis of existing thermodynamic data for concentrated hydroxide solutions is currently being performed. The principal goal of this analysis is to determine the most appropriate function for describing the variation of water activity with concentration and temperature. Once this has been accomplished, the functions will be used to compute the hydroxide activity and hence the pH of the medium. These data will then be used to construct stability diagrams for metals of interest in concentrated LiOH, NaOH, and KOH as a function of temperature.

H. AN ELECTROCHEMICAL AND MORPHOLOGICAL STUDY OF THE EFFECT OF TEMPERATURE ON THE RESTRUCTURING AND LOSS OF CAPACITY OF ALKALINE BATTERY ELECTRODES

LBL Subcontractor:	Ohio State University
Principal Investigator:	D. Macdonald
DOE Program Manager:	S. Ruby
LBL Project Manager:	F. R. McLarnon
LBL Contract No.:	4506610
B & R Number:	AL-05-10-10
FY 1980 BA/BO Released:	53K/6K

Capacity loss on cyclic charging/discharging of porous iron, nickel, and zinc electrodes in alkaline electrolytes is a serious limitation of practical battery systems. The loss of charge capacity can be attributed, in part, to a degradation of particle-particle electronic contact caused by the cyclic formation and reduction of oxidation products. This cyclic process exerts stresses on the bridges between neighboring particles because of the high (>1) Pilling-Bedworth ratios of the oxidation products. The goal of this program is to investigate the mechanism(s) of charge capacity loss with emphasis on studying the effect of temperature on those processes which lead to restructuring of the porous electrode and degradation of interparticle contacts.

Significant progress has been made in a number of important areas. Design and construction of the electrochemical cell and solution reservoir have been completed. Both components were fabricated from PTFE, which is expected to be inert in the aggressive concentrated hydroxide environments of interest. Care has been taken to establish a uniform current distribution at the face of the porous electrode; this is necessary to ensure the applicability of uniform transmission line models for the analysis of experimental impedance data. The equipment required for the preparation of porous electrodes has also been assembled, including dies for pressing powders into compacts and the furnace which will be used for sintering.

AC impedance and ellipsometric studies of planar nickel surfaces in aqueous solutions have been initiated. These studies are being carried out to provide data which may be used later in this program for interpreting the impedance data obtained for porous electrodes after cyclic charging/discharging. These initial studies have demonstrated that, in the case of nickel, hydrogen evolution involves two clearly-defined relaxations which can be attributed to coupling between discharge reaction and subsequent recombination reaction and double layer charging. On passive nickel, two high-frequency relaxations are also observed, but at low frequencies the electrochemical properties are dominated by diffusion. These initial studies, which were carried out in buffered phosphate and borate solutions, are now being extended to concentrated hydroxide solutions.

A transmission line model of finite length has been set up to interpret the AC impedance data from the porous electrode studies. An important feature of this model is that account is taken of the resistance of the "metal" phase; that is, resistance resulting from the degradation of metal particle-particle contacts due to restructuring of the electrode. Analysis of a discretized transmission line model has yielded analytical functions for the current and potential distributions and the impedance of the system in terms of system parameters, such as solution resistance, resistance of the "metal" phase (including particle-particle contact resistance) and the impedances of the wall-solution and current collector (pore base)-solution interfaces. Non-linear regression analysis techniques are being developed to interpret experimental data in terms of the transmission model outlined above.

I. RESEARCH ON ALKALINE ZINC SECONDARY ELECTRODES

LBL Subcontractor:	Linfield Research Institute
Principal Investigator:	D. Hamby
DOE Program Manager:	S. Ruby
LBL Project Manager:	F. R. McLarnon
LBL Contract No.:	4506910
B & R Number:	AL-05-10-10
FY 1980 BA/BO Released:	21K/8K

The aim of this project is to characterize sources of overpotential and capacity deterioration in alkaline zinc electrodes operated under conditions of severely limited convective flow. Of special interest is the evaluation of predictions of hydroxyl ion depletion as a failure mode for porous zinc electrodes.

Previous experimental data did not show agreement with the predicted hydroxyl ion depletion, but experimental uncertainities were such that a firm conclusion could not be reached. Accordingly, a new cell was designed, constructed and operated. Experiments with this new cell have been impeded by two major problem areas: difficulty with standard analytical techniques and unexpected early passivation of the planar zinc electrode.

The initial results have been inconclusive; there appears to be some agreement between theory and data, but the scatter is too great and the number of data points too few to allow a firm conclusion.

IV. MATERIALS RESEARCH

Materials Research seeks to identify, characterize, and improve the materials and components to be used in batteries and electrochemical processes. Basic investigations of new materials for battery components have led to the discovery of a novel all-solid electrode structure for possible use as negative electrodes in molten-salt cells. New ternary lithium-transition metal oxides have been identified as possible electrode reactants for use in similar systems. Projects aimed at developing improved separators for high-temperature Na/S and Li/S cells are focusing on such materials as β''-alumina, NASICON, conducting glasses, and novel superionic conductors. New polymeric separators are being studied for use in ambient-temperature Li/TiS_2 cells, and composition profiles in molten-salt electrolytes are being analyzed.

Summaries of nine research projects are presented in the following pages.

A. NEW BATTERY MATERIALS

LBL Subcontractor:	Stanford University
Principal Investigator:	R. Huggins
DOE Program Manager:	S. Ruby
LBL Project Manager:	L. C. DeJonghe
LBL Contract No.:	4503110
B & R Number:	AL-05-10-10
FY 1980 BA/BO Released:	20K/250K

The objectives of this research are to understand and evaluate the important structural, thermodynamic and kinetic parameters related to the use of materials as electrolyte or electrode components in high-performance lithium-based secondary battery systems, and to investigate a number of materials that might be useful for such purposes. It therefore has a rather exploratory flavor, and is oriented toward longer-range improvements in presently-visible battery systems or to the development of new alternatives, rather than toward solving specific problems in systems undergoing development or in production.

Significant advances have been made in this program in several areas. Activities can be categorized in terms of areas potential long range application as relating to electrolytes, negative electrode materials (in which the lithium activity is typically very high), and positive electrode materials (with low lithium activities). In the latter two groups, mixed conduction, in which both ionic and electronic species are highly mobile, is often highly advantageous. In addition to work on materials, a considerable amount of effort has been expended in this program to develop experimental and theoretical methods which can be employed to evaluate new materials and relevant phenomena. This is especially important in this area of materials science and engineering at the present time, because of its unusual features.

An important characteristic of the approach being taken in this program is the emphasis upon the relationships between fundamental thermodynamic and kinetic parameters, e.g. phase equilibria, equilibrium potentials, chemical diffusion within solid phases, etc., and the microscopic and macroscopic electrochemical phenomena. The microscopic structural basis for the observed properties is also given much attention. This combination of viewpoints and approaches has proven to be very useful in sorting out and explaining observed phenomena, as well as providing a basis for understanding and, in some cases, predicting important quantities.

During the course of the past year's program several new approaches which might have important practical, as well as scientific, consequences have been demonstrated. Three of these represent substantial deviations from the directions followed heretofore in the area of battery-related materials. One of these involves the investigation of ternary lithium-transition metal oxides as possible positive electrode reactants in lithium-based systems. It has been shown that several of these materials deserve serious consideration as candidates to replace the metal sulfides that are used for this purpose in several present approaches. Although they have comparable electrochemical behavior, these oxides have great potential advantage over sulfides with regard to container, seal, and current collector corrosion problems.

A second new approach involves the discovery of a new molten salt electrolyte that can be used in the presence of elemental lithium at intermediate temperatures for both primary and secondary cells. It appears that this salt can be used at temperatures as low as 135°C, and with positive electrodes with very low lithium activities - and thus high voltages. This electrolyte, based upon lithium nitrate, is highly oxdizing, and causes the formation of a very thin layer of lithium oxide on the surface of the lithium. This layer has the fortunate property of being a good solid electrolyte for lithium ions, has a very low electronic conductivity, and is relatively insoluble in the molten salt. As a result, lithium can be passed in either direction through it, making it possible to produce reversible solid lithium electrodes. Although the practical importance of this discovery is still far from demonstrated, it does represent a major new direction in molten salt cells which could have substantial advantages over the high-temperature approaches presently receiving a great deal of developmental attention.

The third especially interesting development from this program is the introduction of a novel approach to an all-solid electrode structure that may have kinetic properties comparable to the traditional fine particle, liquid electrolyte - permeated structures. While work in this new direction is also very young, it does lead to the possibility of several major deviations from current practice. The important feature in this case is the use of a composite microstructure containing finely-dispersed reactant phases in a metallic matrix that has a very high chemical diffusion rate for the reactant species, e.g. Li. Work on this program has lead to the identification of several candidate matrix materials which have the requisite thermodynamic and kinetic properties, and initial experiments have indicated that such an approach behaves as predicted. The use of all-solid electrodes, rather than the more typical powder-containing structures, presents some attractive alternative possibilities for cell design and fabrication. The achievement of a microscopically reversible internal morphology might lead to a truly reversible electrode structure, a long sought-after goal.

B. FABRICATION OF THIN-WALLED SOLID ELECTROLYTE TUBES

LBL Subcontractor:	Johnson Controls
Principal Investigator:	D. J. Merlau
DOE Program Manager:	S. Ruby
LBL Project Manager:	L. C. DeJonghe
LBL Contract No.:	4505410
B & R Number:	AL-05-10-10
FY 1980 BA/BO Released:	54K/19K

The objective of this project is to develop a fabrication technique using commerical tube wrapping equipment to determine whether tubes formed from cast tape provide a viable alternative to tubes formed by more conventional methods. In the fabrication technique lithia stabilized β''-alumina powder prepared by the "zeta" process is continuously cast onto silicone coated release paper. The tape is slit while on the release paper to widths suitable for sprial tube winding. Two ply tubes are formed using a Rockport STW spiral tube winder with the inner ply tape-side-out and the outer ply tape-side-in. The resultant tube consists of two plies of ceramic tape with release paper on the inner and outer surfaces. The ceramic tape layers are solvent bonded by applying solvent to either or both plies. The release paper is removed after the tubes have dried. One end of the tube is sealed using heat and pressure to deform a tape disk insert until it bonds to the tube wall. The organics are removed and the tube is fired in a two step sintering process in α-alumina tubes. Tubes prepared by this fabrication method tend to retain their geometry better and have fewer wall delaminations than hand rolled lap joint tubes. Resistivity and mechanical strength tests will be made to determine the effect of the spiral tube cell performance.

C. FABRICATION AND CHARACTERIZATION OF POLYCRYSTALLINE NASICON CERAMIC ELECTROLYTES

LBL Subcontractor:	Ceramatec, Inc.
Principal Investigator:	R. Gordon and G. Miller
DOE Program Manager:	S. Ruby
LBL Project Manager:	L. C. DeJonghe
LBL Contract No.:	4507310
B & R Number	AL-05-10-10
FY 1980 BA/BO Released:	172K/47K

Scaled-up fabrication procedures have been developed for NASICON ($Na_{1+x}Zr_2Si_x P_{3-x}O_{12}$) electrolytes (x=2.0-4) involving (1) the mechanical mixing of raw materials ($Na_3PO_4 \cdot 12H_2O$, SiO_2 and ZrO_2 or mixtures of $ZrSiO_4$ and Na_3PO_4), (2) calcination at 1160°C, (3) dry milling (ball, vibratory and attrition), (4) isostatic pressing and (5) sintering at 1230-1260°C. Small electrolyte tubes (16mm OD x 200mm long) possess acceptable dimensional tolerances, mass densities over 3.20 g/cm^3, sodium ion resistivities under 5-7 ohm-cm at 300°C and maximum strengths of approximately 115 MPa.

Electrolytes prepared at the x=2.0 composition, which contain a small amount of ($\leq$5 w/o) of residual free zirconia (ZrO_2), have demonstrated marginal to poor static corrosion resistance in liquid sodium at 300-400°C and low endurance ($\leq$5 Ah/cm^2) in dynamic sodium-sodium test cells operated at 300-340°C. Static corrosion resistance in liquid sodium (300-350°C) can be improved by either changing the overall composition to x=2.4 or by using hot-pressing (or hot isostatic pressing) in lieu of or in addition to conventional pressureless sintering techniques.

Sol-gel and slurry-solution spray drying techniques are being investigated to prepare NASICON electrolytes with a homogeneous distribution of components. Single-phase NASICON electrolytes have been prepared from gel-processed powders formulated at the x=2.3 composition. Compositions with excess soda and phosphate or a deficiency in zirconia are also under investigation. Attention is being given to controlling the potential loss of soda and phosphate during the firing operations.

D. ELECTRICAL CONDUCTION AND CORROSION PROCESSES IN FAST LITHIUM ION CONDUCTING GLASSES

LBL Subcontractor:	Massachusetts Institute of Technology
Principal Investigator:	H. Tuller and D. Uhlmann
DOE Program Manager:	S. Ruby
LBL Project Manager:	L. C. DeJonghe
LBL Contract No.:	4503810
B & R Number:	AL-05-10-10
FY 1980 BA/BO Released:	67K/67K

The objectives of this project are to achieve an improved understanding of how glass composition and structure correlate with fast ion transport and chemical durability and to identify glasses with optimized alkali-ion transport rates, chemical durability and thermal stability.

Attention has been focussed onto glasses in the system Li_2O-$(LiCl)_2$-B_2O_3, which corresponds to that of crystalline boracite. Substitutions of Cl for O in these glasses were found to result in systematically increasing Li ion conductivity, and decreasing T_g and density. Other results indicate that σ might continue to increase if Cl content could be increased beyond the apparent glass solubility limit.

A systematic study of molten Li metal attack on glasses was initiated. Glasses in the Li_2O-B_2O_3 system remained coherent and did not dissolve upon exposure to molten Li. After removal from the molten Li, all specimens were observed to form a black reaction product layer. The rate of formation of this layer was found to decrease with increasing Li content. Similar films were found to form on glasses in the Li_2O-$(LiCl)_2$-B_2O_3 system.

Resistivities measured during low current density tests on glasses in a Li/glass/Li cell agreed well with values determined by AC complex impedance measurements. At current densities greater than 1 mA/cm^2, variations of cell voltages with time indicated the occurrence of electrical breakdown phenomena.

E. A STRATEGY FOR PROVIDING THERMODYNAMIC DATA ON ELECTROLYTE SOLUTIONS NEEDED FOR ADVANCED ENERGY TECHNOLOGIES

LBL Subcontractor:	National Bureau of Standards
Principal Investigator:	R. Goldberg and B. Staples
DOE Program Manager:	S. Ruby
LBL Project Manager:	J. S. Newman
LBL Contract No.:	4504510
B & R Number:	AL-05-10-10 AL-05-10-15
FY 1980 BA/BO Released:	50K/40K

The program by NBS to provide systematic coverage of activity and osmotic coefficient data for important classes of electrolytes has resulted in the following accomplishments:

1. The evaluation of the activity and osmotic coefficients for solutions of bi-univalent compounds of zinc and cadium at 25°C is in press (J. Phys. Chem. Ref. Data).
2. A manuscript on the evaluation of the activity and osmotic coefficients for some uni-bivalent aqueous electrolytes such as Li_2SO_4,Na_2CO_3 at 25°C has been completed and is in press. (J. Phys. Chem. Ref. Data).
3. A computational scheme has been developed for the evaluation of the thermal properties such as relative molal enthalpy and apparent molal heat capacity of aqueous systems. This program is analogous to that previously developed for activity and osmotic coefficients.
4. An annotated bibliography on the thermodynamic and transport

properties of sulfuric acid will be completed early in the coming contract year.

5. A manuscript containing the evaluated activity and osmotic coefficients of aqueous sulfuric acid at 25°C has been completed.

F. PHYSICAL CHEMISTRY OF MOLTEN SALT BATTERIES

LBL Subcontractor:	Oak Ridge National Laboratory
Principal Investigator:	J. Braunstein
DOE Program Manager:	S. Ruby
LBL Project Manager:	J. Evans
LBL Contract No.:	4506210
B & R Number:	AL-05-10-10
FY 1980 BA/BO Released:	70K/61K

Current induced composition gradients were demonstrated in the molten LiCl-KCl eutectic mixture, the electrolyte of a LiAl/LiCl-KCl/FeS_x battery. The gradients were produced by electrolysis of the salt between LiAl electrodes at currents of 50-100 mA cm^2, and quenching. Analysis of composition profiles in quenched samples was by atomic absorption spectroscopy in a scanning electron microscope (SEM/EDX), which gave good distance resolution. Work is in progress to improve the precision of the SEM/EDX measurements to that demonstrated in model systems.

G. POLYMERIC ELECTRODES FOR AMBIENT TEMPERATURE LITHIUM BATTERIES

LBL Subcontractor:	University of Pennsylvania
Principal Investigator:	W. Worrell and G. Farrington
DOE Program Manager:	S. Ruby
LBL Project Manager:	L. C. DeJonghe
LBL Contract No.:	4505210
B & R Number:	AL-05-10-10
FY 1980 BA/BO Released:	134K/74K

The objective of this program has been to explore the preparation, physical properties, and electrochemical characteristics of polymers suitable for use in solid state batteries. Efforts concentrated on synthesizing and characterizing polyethylene oxide (PEO) - alkali metal salt complexes. One of these materials, $(PEO)_4$-Li-Trifluoroacetate (LiTFA) has been reported to be a good solid electrolyte for lithium ions. As such it might be used as a separator in solid state lithium cells. We have prepared films of $(PEO)_4$ LiT FA, studied their physical properties, measured their ionic conductivities, and used them in a number of solid state $Li/(PEO)_4LiTFA/TiS_2$ electrochemical cells.

All our experimental results are consistent with the conclusion that $(PEO)_4$LiTFA polymer films are indeed solid electrolytes which conduct lithium ions. Preparing the films involves relatively simple solution casting, although careful control of solution concentration is necessary to produce single-phase products. When dried, the films lie flat and are easy to work with in electrochemical applications. The conductivity of $(PEO)_4$LiTFA is less than 10^{-11} $(ohm\ cm)^{-1}$ at $30^{o}C$ and rises to about 10^{-4}

$(\text{ohm cm})^{-1}$ at 140°C. Trace solvent remaining from the solution casting process has no apparent influence upon conductivity. However, small quantities of water vapor absorbed by the films increase their ionic conductivities by about 10^2 below 70°C. NMR results suggest that the principal charge carriers in the films are lithium ions. Protons and trifluoroacetate ions appear to only undergo local motions. $Li/(PEO)_4LiTFA/Li_xTiS_2$ cells have potentials consistent with those measured using non-aqueous liquid electrolytes.

H. PRINCIPLES OF SUPERIONIC CONDUCTION

LBL Subcontractor: Massachusetts Institute of Technology
Principal Investigator: B. Wuensch
DOE Program Manager: S. Ruby
LBL Project Manager: L. C. DeJonghe
LBL Contract No.: 4507910
B & R Number: AL-05-10-10
FY 1980 BA/BO Released: 66K/4K

The objectives of this program are to provide insight into the mechanisms of fast-ion conduction in alkali ion conductors of potential relevance to battery systems. This will be done through specification of the probability distribution and thermal motion of the mobile ions through precise neutron scattering techniques. The materials to be studied will be new potential conductors or crystal-chemically modified forms of phases which have already been demonstrated to be useful conductors.

Attempts have been made to synthesize phases in the system $K_{6-n}M^{n+}Si_6O_{15}$, a potential new fast-ion conductor. Solid-state reactions produced glassy products because of the high silica content. Hydrothermal reaction at 190° produced a crystalline phase which has yet been identified. A large number of crystal-chemical variations of the NASICON structure type ($Na_3Zr_2Si_2PO_{12}$) are possible, as Zr may be replaced by other octahedrally coordinated cations and/or Si and P replaced by tetrahedral cations. Only two solid solution systems have been examined and the influence of variation in Na content and framework size on the conduction properties is unknown.

Powders have been successfully synthesized through solid-state reaction in three NASICON-like systems.

$Na_{1+x}\ Zr_2\ Si_x\ V_{3-x}\ O_{12}$

$Na_{1+x}\ Zr_2\ Ge_x\ V_{3-x}\ O_{12}$

$K_{1+x}\ Zr_2\ Ge_x\ V_{3-x}\ O_{12}$

Products were obtained for ranges of compositions corresponding to $x=1.5$, 2.0, 2.5, 3.0. NASICON-like phases were obtained for $x \geq 2.0$, 2.0 and 1.5, respectively, in the three systems.

I. RESEARCH ON NOVEL MEMBRANES FOR LITHIUM BATTERIES

LBL Subcontractor:	Case Western Reserve University
Principal Investigator:	M. Litt
DOE Program Manager:	S. Ruby
LBL Project Manager:	L. C. DeJonghe
LBL Contract No.:	4508010
B & R Number:	AL-05-10-10
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Polyethylene glycol, M. Wt. $\sim$ 1000, has been purified and the ditosylate ester has been synthesized. This is the initiator and will be the central block of the triblock polymer.

The monomer tolyl oxazoline has been synthesized and purified. Initial yields were very low but now are 80 - 90%.

A high-pressure gel permeation chromatography, HPGPC, has been set up and standardized. The resolution of HPGPC has been increased by incorporation of two more chromatographic tubes. It is now working and shows that the polyethylene glycol being used has a narrow molecular weight distribution.