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BERKELEY ELECTROCHEMICAL RESEARCH CENTER

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Introduction

About fifty years ago a group of researchers from the University of California at Berkeley (UCB) led by Dr. Ernest Lawrence established the foundation for the Lawrence Berkeley Laboratory (LBL). From this modest beginning has developed an intimate relationship between LBL and UCB. Today, LBL is a major multi-disciplinary national laboratory operated by the University of California for the United States Department of Energy (DOE). This close connection between LBL and UCB has spawned many collaborative programs that support the goals of DOE. One of these programs is the Electrochemical Energy Storage Program of the Berkeley Electrochemical Research Center (BERC).

BERC is the Lead Center for the U.S. Department of Energy's Technology Base Research Project for Electrochemical Energy Storage. BERC conducts and manages a wide range of electrochemical research, including exploratory research and development on new electrochemical systems, supporting research for advanced rechargeable-batteries and electrochemical technologies, materials science research for improved battery components, fundamental research to improve electrochemical energy conversion efficiency, and R&D on fuel-cell technology.

The very nature of electrochemistry requires an interdisciplinary approach to advance the technology effectively. This requirement is met at BERC through the close association of the Applied Science and the Materials and Molecular Research Divisions at LBL, and the Departments of Chemical Engineering and of Materials Science and Engineering at UCB. The facilities at both LBL and UCB are outstanding, and the technical expertise is world renowned. The stimulating academic/scientific environment of UCB and LBL provides a unique arena for research aimed at providing advanced batteries and other electrochemical technologies that exhibit high performance, long life, and low cost.

The LBL/UCB electrochemical engineering program, the first of its kind in this country, has been supported by DOE and its predecessor agencies since 1955. However, it is only recently that LBL was assigned the lead laboratory responsibility. Since 1979, BERC has managed a substantial portion of DOE's applied battery and electrochemical research, and BERC now provides technical guidance to about 40 research projects at various universities, national laboratories, industrial organizations, and non-profit research institutes. In addition, BERC is responsible for disseminating technical information, providing liaison between the governmental, industrial, and academic sectors, and evaluating and selecting both solicited and unsolicited research proposals. A vital component of this service is to facilitate the transfer of the most promising technology from the research laboratory to industrial organizations capable of its development and commercialization.

Major accomplishments of the electrochemical research program at BERC include:

- **Development of electrochemical engineering program to advance electrochemical technology**
- **Development of advanced modeling concepts for electrochemical systems**
- **Development of advanced optical techniques for the study of electrochemical phenomena**
- **Advancements in the characterization of organic and solid electrolytes for new battery technologies**
- **Advancements in the fundamental understanding of electrochemical process technology and electrocatalysis**

The various research projects conducted by BERC involve all major disciplines of electrochemical science and technology. These research areas include:

- **Electrochemical Energy Storage and Conversion**
- **Application of Novel Surface/Optical Techniques in Electrochemistry**
- **Electrocatalysis**
- **Solid Electrolytes**
- **Electrochemical Engineering**
- **Electrochemical Processes**

Brief descriptions of some of the research are presented in the following sections.

Electrochemical Energy Conversion and Storage

E.J. Cairns, F.R. McLarnon, J.S. Newman, and C.W. Tobias

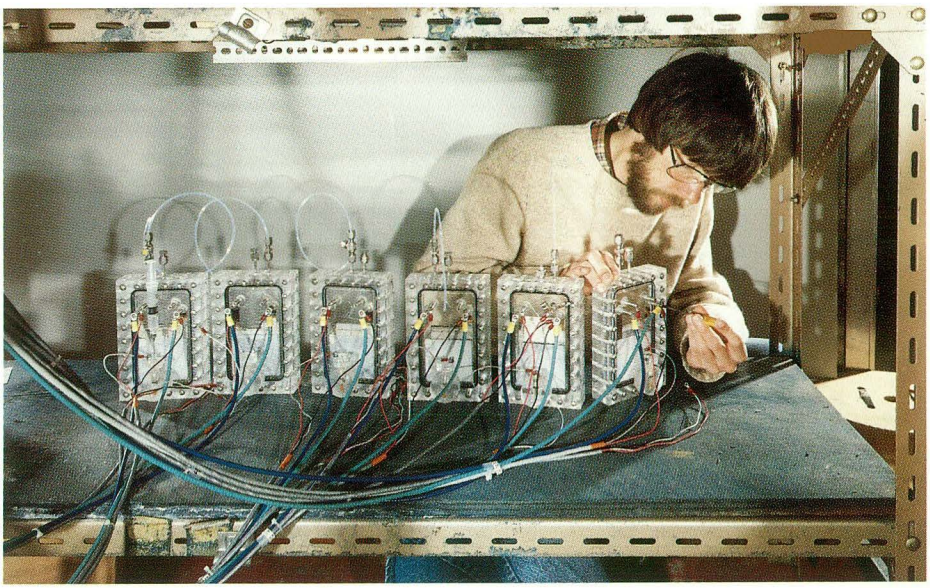
Electrochemical Couples in Nonaqueous Electrolytes

Recent developments in advanced electrochemical cells and projected high-energy rechargeable batteries involve the use of alkali-metal negative electrodes. Application of reactive metal at near ambient temperatures requires new ionic media with high decomposition potentials and the ability to dissolve ionic compounds (or to form ionic states by reacting with the solute). The propylene carbonate family of solvents, which has been shown to allow the reduction of alkali metals at room temperature with reasonably high efficiency, is being investigated at BERC. Equilibrium potential measurements and fast-transient methods are employed to investigate the electrochemical properties of alkali metal and halogen couples in nonaqueous electrolyte systems. Various wet-chemical methods and x-ray diffraction, Auger, and emission spectra are employed for qualitative and quantitative analyses of metal purity and for measurements of current efficiency.

Battery Electrode Research

There are several rechargeable batteries that offer excellent energy and power characteristics but exhibit inadequate lifetime. These short lifetimes are often associated with slow, irreversible processes that can be observed only by cycling battery electrodes for extended periods. Battery lifetimes are also known to depend markedly upon such variables as electrode size, charging regime, and temperature. Projects are underway at BERC to study the behavior of realistic battery electrodes cycled under conditions similar to those expected in the intended application (e.g., electric vehicles). A multiple electrochemical-cell test apparatus that is computer-controlled allows the simultaneous and continuous operation of up to 16 cells. Battery electrodes can be tested under a wide variety of charging and discharging regimes, and the data are conveniently stored and displayed. This apparatus has been employed to cycle model batteries under realistic charge/discharge modes, and the results are used to evaluate various theories proposed to explain electrode capacity loss and to investigate means to improve cell lifetime.

Experiments are also being conducted to improve the performance and cycle life of zinc/nickel oxide batteries. Electrolyte modifications, electrode modifications, and pulsed-current charging are being used to increase cycle life and capacity. An electrochemical method is being investigated to improve the process for producing porous nickel-oxide electrodes, and impedance techniques are being used to understand the anodic behavior of zinc electrodes.



Electrochemical test cells are used to model the behavior of electrodes used in zinc/nickel oxide batteries and to investigate practical means for improving their performance.

High-Temperature Systems

Research on high-temperature systems is underway to identify materials suitable for use in high-temperature rechargeable alkali metal/sulfur cells and to optimize the design of sulfur electrodes for lithium/sulfur and sodium/sulfur cells. Research projects involve the study of phase equilibria in molten lithium polysulfide, examination of novel lithium-ion conducting electrolytes, study of corrosion-resistant current collectors in sulfur electrodes, and measurement of the diffusion coefficient of sodium ions in melts of sodium polysulfides.

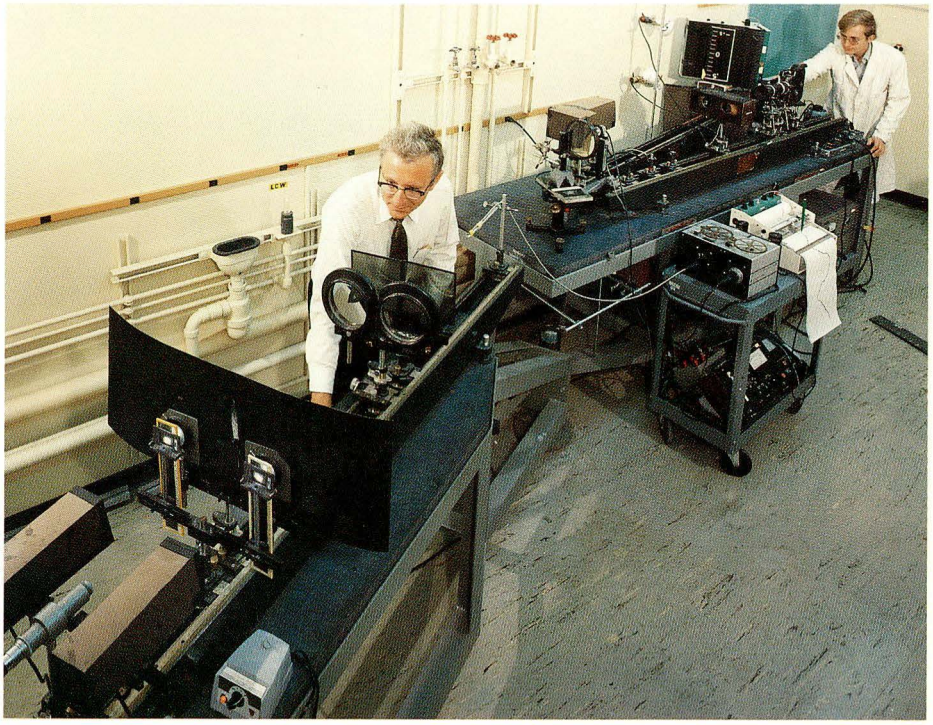
Application of Novel Surface/Optical Techniques in Electrochemistry

R.H. Muller and P.N. Ross

Optical Studies of Boundary Layers and Electrolyte Films

A detailed understanding of transport processes in many electrochemical systems is necessary to control current and potential distribution over large electrodes and to find means by which high current densities can be combined with uniform potential to achieve high space-time yields, product purity, and energy efficiency. Optical techniques are being applied at BERC to study mass-transport boundary layers. A traveling dual-emission laser interferometer has been built for such studies. By use of an optical theory that accounts for the deflection of light in refractive index fields, data on the boundary-layer thickness, the interfacial concentration, and the interfacial-concentration gradients are obtained.

Thin electrolyte films provide the reaction environment for gas electrodes. The factors responsible for the formation of electrolyte films on metal surfaces are being investigated by use of optical thin-film interference techniques. For this purpose, the optical theory of the formation of interference colors has been extended to apply to transparent films on metal surfaces. The present work is concerned with identifying the balance of surface forces that are responsible for the apparent stability of electrolyte films.



Double-beam optical bench for the measurement of electrolyte film thickness on gas electrodes by the analysis of white-light interference colors.

Electrochemical Surface Layers

Surface layers are responsible for the chemical properties of most metals in liquid and gaseous environments. The transformation of surface layers occurs in the charge and discharge of many batteries. Ellipsometry is used at BERC to investigate the mechanisms by which electrochemical surface layers are formed. The interpretation of ellipsometer measurements has been advanced by use of multi-dimensional theoretical models and spectral scanning. Simultaneous light scattering measurements are used for the characterization of particulate deposits and surface roughness. Multi-layer structures derived from optical interpretations are checked by transfer of specimens to ultra-high vacuum, where ellipsometry is combined with Auger spectroscopy and ion etching techniques. Topics presently under study include the formation of anodic films, the effect of adsorbed surface-active materials on phase nucleation and growth of metal deposits, and the composition and structure of protective films formed on alkali metals in nonaqueous solutions.

Analysis of Electrode Surfaces

Catalytic electrode materials are essential to technologies such as fuel cells, metal/air batteries, electrolyzers, and electro-organic synthesis. Physically meaningful mechanistic models are essential for the interpretation of electrode behavior and are useful in directing the research for new classes of electrocatalysts. The objective of this project is to develop an understanding of the detailed processes taking place in complex electrochemical reactions at catalytic electrode surfaces.

An experimental approach being used at BERC, and only a few other laboratories in the world, combines the study of liquid-solid interfaces by conventional electrochemical methods with the analytical methods of modern surface physics: Low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and photoemission spectroscopy (XPS and UPS). The atomic structure, composition, and chemical state of electrode surfaces can be determined with this formidable array of analytical techniques. Such detailed descriptions of the catalytic surface are being used to develop a quantitative theory of electrocatalytic reactions.

Electrocatalysis

K. Kinoshita and P.N. Ross

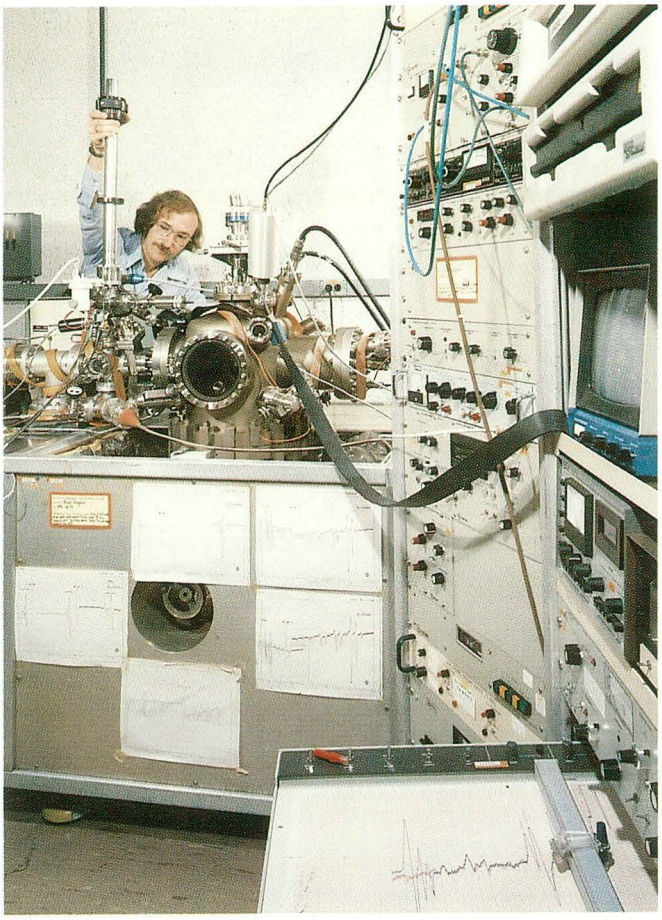
Fuel Cell Electrocatalysts

New types of electrocatalytic materials have resulted from research at BERC. These are Pt_3M intermetallic materials, where M is a Group-IVb or -Vb metal, e.g., Ti or Ta. These intermetallic catalysts have a higher catalytic activity than Pt for oxygen reduction in phosphoric acid. The mechanism of the activity enhancement is under current study using the techniques described in the previous section. LEED, AES, and XPS studies have shown that in acid solution the Pt_3M surface is converted to a $PtMO_x$ structure, which is different from the oxide phase of either pure element. The working electrocatalyst surface has been found to be uniquely formed in solution, illustrating the importance of determining the structure and composition of electrodes used as electrocatalysts.

Electrocatalyst/Support Studies

These studies provide supporting research in air-electrode technology for DOE metal/air battery projects. Metal/air systems have, in principle, the highest specific energy (>100 Wh/kg) of all ambient-temperature systems because one of the electroactive species (oxygen) need not be contained within the battery. However, practical development of this technology has been slow, owing to problems in developing suitable air-electrode materials. In electrically rechargeable metal/air batteries, the positive electrode must be bifunctional, both evolving and consuming oxygen.

Investigations are under way to determine the stability of carbon blacks in bifunctional air electrodes. To determine the stability of the carbon phase, BERC has developed a ^{14}C tracer method that produces in situ determination of carbon loss. Corrosion of acetylene black in the potential region for oxygen evolution was studied using the ^{14}C tracer method. This investigation is continuing with the focus on determining the role of carbon surface structure on corrosion rates.



Custom-designed apparatus for direct coupling of a thin-layer electrochemical cell with a UHV incorporating the analytical methods of electron spectroscopy.

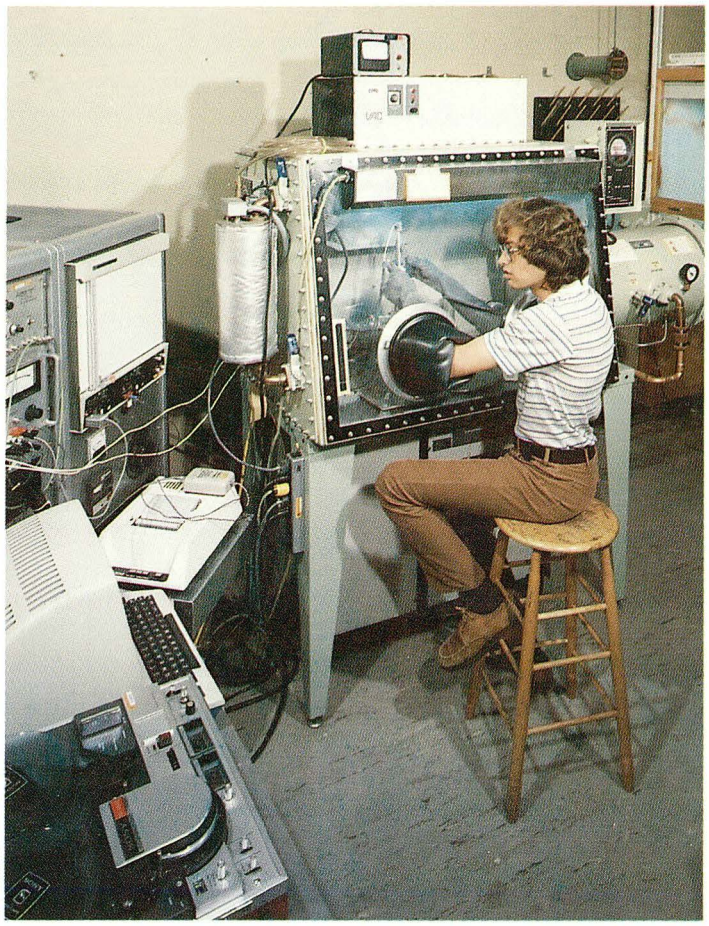
Solid Electrolytes

L.C. De Jonghe

Sodium Beta Alumina Studies

Several electrochemical storage systems are currently under consideration, and those employing molten sodium and sodium polysulfides separated by a ceramic membrane are among the most promising. The key factor in the eventual commercialization of these sodium/sulfur systems is the lifetime and failure statistics of the electrolytes. Solutions to this problem are being investigated at BERC.

The rapid degradation of solid electrolytes, involving penetration of a sodium-filled crack from the negative to the positive electrolyte surfaces, is being studied by a variety of techniques. A sensitive acoustic-emission detection system is used which permits the collection of failure statistics as a function of current density and provides information concerning the effect of temperature, electrolyte microstructure and composition, and impurity levels on the maximum permissible current densities. In addition, a broad range of analytical techniques are employed. These include galvanometric measurements, AC complex admittance measurements, microanalytic transmission electron microscopy, and high-resolution scanning and transmission electron microscopy.



Acoustic emission detection system records the failure initiation of sodium beta-alumina solid electrolytes in an experimental sodium/sulfur cell at 300°C.

Electrochemical Engineering

R.H. Muller, J.S. Newman and C.W. Tobias

Mass and Charge Transport in Cell Processes

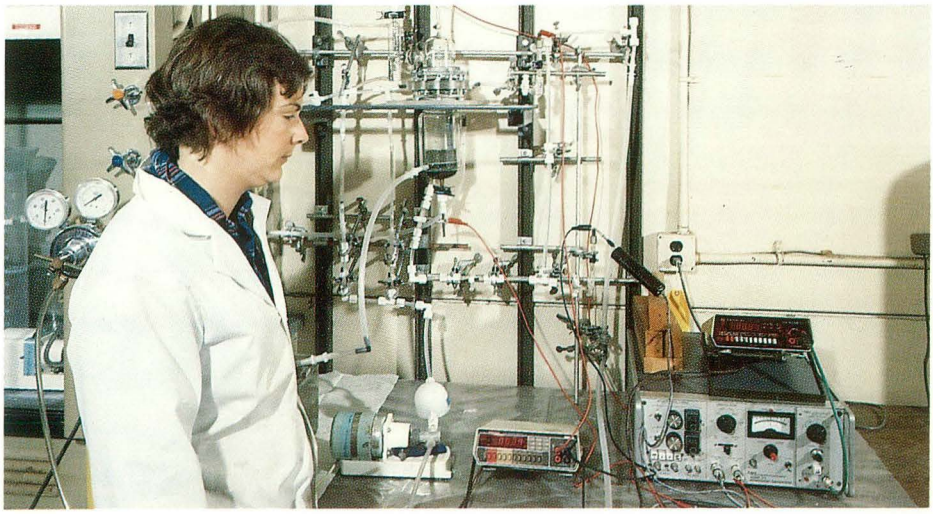
Only in the last 20-30 years have rigorous scientific methods been applied to the analysis of electrolytic processes and their interactions in complete cells. BERC has been a leader in the United States in the characterization of electrolytic transport phenomena and in the optimization of operating efficiency and capital costs of cells.

Mass- and charge-transport studies at BERC include investigations of the combined influence of electrode geometry, surface potential, and ionic transport under well-defined hydrodynamic conditions and determinations of limiting rates and current distributions under conditions characteristic of electrochemical machining and electroforming. These studies involve such techniques as the measurement of limiting currents along segmented electrodes, the use of double-beam laser interferometry to observe directly the mass-transfer boundary layer, and the evaluation of mass-transfer rates by means of rotating electrodes, capillary cells, and suspended inert particles—complemented by computer-implemented numerical models.

Other research involves mass-transport studies in electrochemical cells with flow-through cathodes consisting of a porous fixed bed of carbon flakes and chips mounted on a metal current collector. Experiments indicate that this cell may be attractive for the processing of mercury-contaminated brine solutions; similar studies are being conducted on lead. Future experiments are designed to elucidate further the mass-transfer characteristics of this system and to yield mass-transfer-coefficient data that can be used for scale-up.

Surface Morphology of Metals in Electrodeposition

Although the electrolytic deposition and dissolution of metals have many industrial applications, e.g., galvanic cells, a clear understanding of the deposition processes (electrocrystallization) is lacking, especially where substantial thicknesses of metal are involved (macrocrystallization). Research at BERC is directed to understanding these macrocrystallization processes and their interactions, which is essential to the design of efficient, low-cost galvanic cells.



An electrochemical cell with a porous flow-through cathode is used to remove mercuric ions from contaminated brine solutions.

Studies of the surface morphology of metals include observations of thick deposits for groove patterns in flow cells and at rotating disk electrodes. Deposit roughness is measured by a profilometer and more detailed images of surface structure are obtained by SEM. Electrolyte properties, including transport coefficients, are investigated by classical methods. Nucleation frequency function of electrode overpotential is observed on rotating disk electrodes using steady-state and transient techniques. A special flow cell is used for time-lapse photography to record macroscopic crystal growth in the electrodeposition of zinc.

Modeling of Electrochemical Systems

Mathematical models, which are useful in the design of electrochemical systems, are being developed to calculate the concentration, potential, and current distribution in a thin-gap flow cell, and to predict the performance characteristics of liquid-junction cells. Although previous models have assumed that the interelectrode gap is much larger than the diffusion boundary layer thickness, the present model allows the gap to be thin enough for the boundary layers to interact. The model also can take into account multiple reactions at the electrodes. An experimental program is currently being designed to verify the completeness of the mathematical model.

Engineering Analysis of Gas Evolution

Despite the wide industrial application of electrochemical gas evolution, the complex phenomena involved in this process are not well understood. BERC is conducting studies to establish the influence of electrode geometry and surface structure, electrolyte composition, and free and forced convection on gas-evolution processes. Gas coverage and detachment, and gas behavior in suspension, are observed by normal and high-speed cinematography using a channel-flow cell incorporating an easily changeable, coplanar 1-X 1-cm illuminated electrode surface. A novel cell with an electrode consisting of a 10 × 10 quadratic planar matrix of 100-micrometer-square platinum surface elements, electrically isolated from each other, is being used to study the nucleation, growth, and coalescence of bubbles at predetermined locations by simultaneous monitoring electrode potentials and currents at 100 surface elements within a square millimeter.

Electrochemical Processes

J.W. Evans, R.H. Muller and C.W. Tobias

Electrochemical Machining

The shaping of metals and conductive refractory materials by high-speed anodic dissolution (electrochemical machining) has achieved considerable industrial importance. Two problems in the technical operation of this process are the prediction of the cut geometry and surface finish. Research is aimed at replacing the costly trial-and-error procedures now in use with predictive processes. For simple chemical systems, predicted shapes computed from current distributions agree well with experiments. The formation of resistive surface layers has been found to be essential for the attainment of bright, polished surfaces. Conditions under which such surface layers are formed, however, and their chemical and electrical properties need to be better known to include them in the predictions.

Electrorefining of Metals

Electrodeposition of metal from an aqueous solution, or a molten salt, is an important operation in the production of aluminum, magnesium, copper, nickel, cobalt, zinc, and many other metals. Modern electrochemical engineering has yet to have an impact on such electrodeposition steps; some have changed little in several decades and are characterized by high capital, labor, and energy costs. Research aimed at improving these operations is underway at BERC. Representative of this research is work on the use of fluidized-bed electrodes in the electroreduction of copper, cobalt, silver, and other metals from aqueous solutions. By using cathodes consisting of fluidized beds of metal particles, the current per unit volume of cell can be increased by more than an order of magnitude. Research on fluidized-bed cathodes is being carried out in cells ranging up to 1,500 amperes and amongst recent discoveries is a cell design that has a higher current than the conventional cell but consumes less electrical energy. Recently research was begun on the application of this new cell design to batteries.

In electrochemical cells used in "electrorefining" to purify copper, nickel and several other metals, the flow of electrolyte (concentration-gradient-driven natural convection) and mass transport determine the production rate and purity of the product. An investigation into flow and mass transport in such electrorefining cells is being carried out at BERC. A computer model for the turbulent recirculating flow has been developed and is being tested against cell velocity measurements made using Laser- Doppler velocimetry. Research is also underway to reduce the energy consumed in the electrochemical production of aluminum. A mathematical model for the Hall-Heroult cell has been developed and is currently being evaluated.

Electrolyte flow measurements which are made here using a Laser-Doppler velocimeter, are used to validate results of a numerical model for electrochemical cells.

Facilities and Equipment

The Berkeley Electrochemical Research Center has a wide range of standard facilities and advanced, specialized systems that are available to the various research projects. Major items of specialized equipment include the following.

Electrochemical Cells and Flow Loops

- Cell (1 cm interelectrode gap) and flow loop (40 × 15 cm channel type), for the study of effects of hydrodynamic flow (to Re = 120,000) on the distribution of reaction rates (limiting currents) and on the development of surface textures in electrodeposition of metals. Segmental currents to electrically isolated electrode segments may be simultaneously measured and recorded with the aid of microprocessors and an HP 9825 computer. A power source with current ramp capable of very fast rise times and current up to 100 amperes is available.
- Cells with very small gaps (200-500 micron) and flow loop for the study of electrode phenomena at high electrolyte flow velocities (to 100 meter/sec) involving high pressure drops (to 5000 psia).
- Cell and flow loops for the in situ study of effects of gas evolution on cell resistance and for the in situ study of development of surface morphology of metals, notably of zinc in deposition from acid solutions.
- Electrochemical cells (50, 150, and 1,000 amperes) with fluidized cathodes. These cells employ a bed of metallic particles as a cathode, fluidized by upward flowing electrolyte, titanium anodes with a catalytic coating, and a ceramic or polymer diaphragm separator. The cells are used in a study of electrodeposition of copper or cobalt from aqueous solutions.
- Electromachining apparatus (500 amperes, modified Hanson-Van Winkle-Munning model), which is equipped with means for measuring electrolyte flow rate, electrode potential, etc, for the study of high rate dissolution processes of metals and refractory compounds.
- Electrochemical cell containing a concentric coaxial cylindrical electrode pair, with the center electrode rotating, suitable for studies on tertiary current distribution (using profiled rotating electrodes), and for the observation of mass transfer effects in active/passive transition.
- Cell with micromosaic electrodes for measurements of potential and/or current to 2-100 electrically isolated, co-planar platinum surface elements. This electrode is prepared on a three-inch diameter silicon wafer, by semiconductor device manufacturing techniques. The surface elements are separated by 2-micron wide dielectric (SiO_2) contours. A microprocessor controls current (or potential) to all channels. The micromosaic electrode is particularly useful for studies of interfacial transport events.

Instrumentation

- Computer-controlled self-compensating spectroscopic ellipsometer with Auger UHV chamber for study of electrode-surface layers. Spectral range 370-720 nm, maximum scan rate 114 nm/sec, Azimuth rotation speed 1000-4000 deg/s, dynamic range 35-140 deg., and resolution 0.001-0.0003 deg.
- Optical bench for spectroscopy and time-lapse photography of polarized white-light optical interference in thin liquid films.
- Auger Electron Spectrometer and LEED apparatus coupled to a electrode system to permit direct transfer of the electrode from the electrochemical cell to a high-vacuum chamber for surface analysis.
- Traveling dual-emission laser interferometer, developed by BERC for the study of developing boundary layers along electrode surface.
- Computer-controlled, multiple-channel system for electrochemical experiments, developed at BERC for the study of battery electrode processes.
- Laser-Doppler velocimeter for measurement of electrolyte velocities in a cell where convection is driven by concentration gradients or bubbles.
- High-speed motion picture camera (''Hycam'') for the recording of fast events in electrolytic gas evolution.

Berkeley Electrochemical Research Center

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  The Electric Power Research Institute
- **Minerals and Primary Materials Processing Program**
  The National Science Foundation

In addition to the research areas described in the preceding section, other electrochemical research is currently being pursued in the College of Chemistry at UCB. The faculty members and a brief description of their electrochemical areas of interest follows:

Leo Brewer
application of EMF measurements to investigate high-temperature thermodynamic properties of binary and ternary-transition metal systems

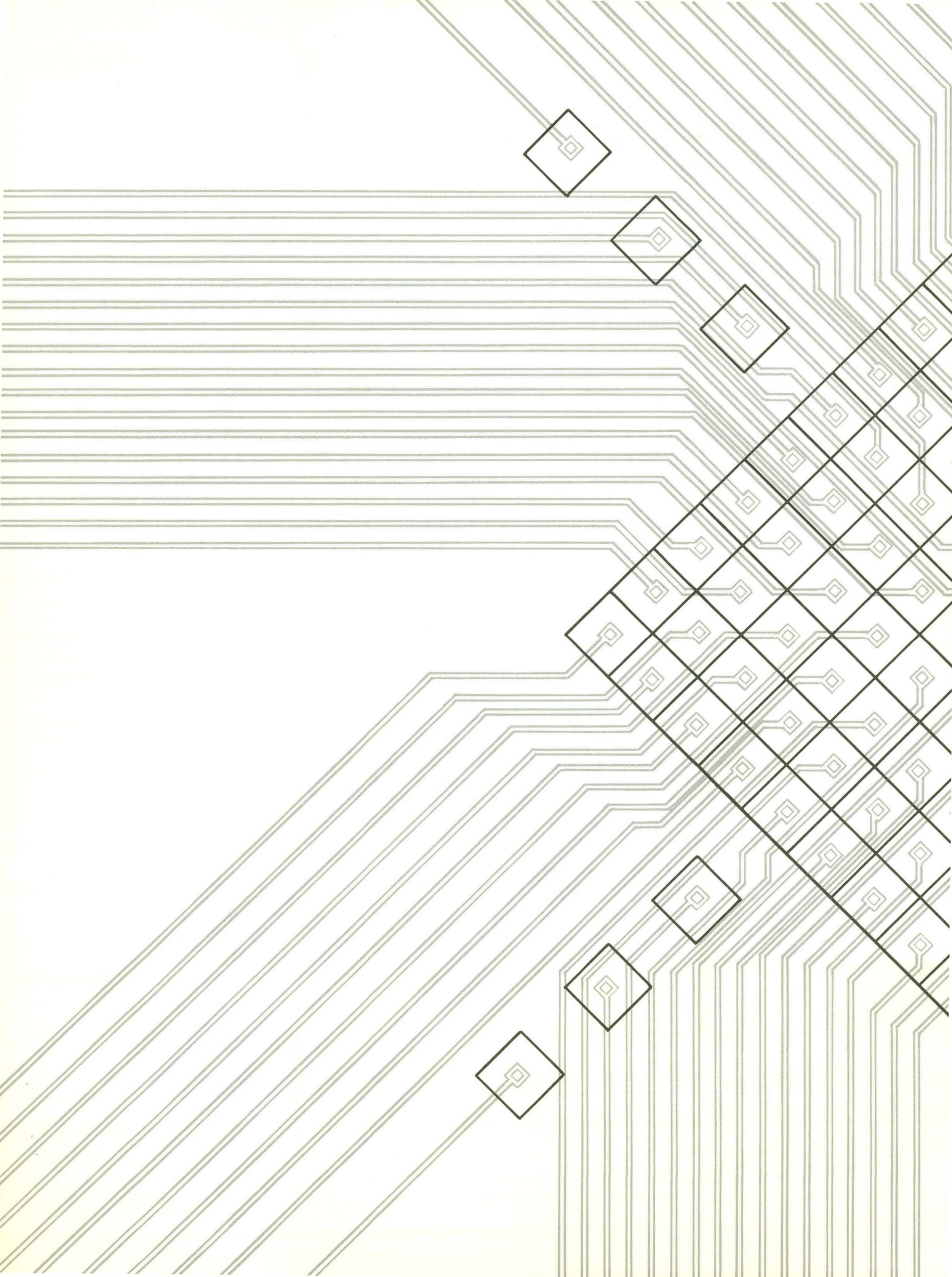
Scott Lynn
electrochemical studies on the development of small-scale chlorine generators

Marcin M. Majda
electrochemical studies to elucidate the mechanism and kinetics of electron transport and the dynamics of ion migration in thin films on electrode surfaces; electrocatalysis

James N. Michaels
application of high-temperature electrochemistry to analyze and influence vapor-phase catalytic reactions and electrocatalytically-enhanced reactions

Kenneth S. Pitzer
theoretical and experimental studies of aqueous electrolytes at high temperatures and high pressures

Angelica M. Stacy
electrochemical synthesis of inorganic compounds; intercalation studies of transition metal polychalcogenides

The Technology Base Research Project, which is managed by BERC for DOE, provides funds for applied research that is focused on (1) secondary batteries and fuel cells for electric vehicles, (2) secondary batteries for stationary energy storage, and (3) energy-efficient electrochemical conversion technology. Summary reports that provide an overview of BERC activities are published annually by the Lawrence Berkeley Laboratory. BERC welcomes both requests for information and proposals to conduct electrochemical energy storage research; such inquiries should be directed to the manager of the Electrochemical Energy Storage Program:

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