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Energy Conversion and Storage Program

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APPLIED SCIENCE DIVISION ANNUAL REPORT

ENERGY CONVERSION AND STORAGE PROGRAM

FY 1988

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ENERGY CONVERSION AND STORAGE

INTRODUCTION

The Energy Conversion and Storage Program applies chemistry and chemical engineering principles to solve problems in *a*) the production of new synthetic fuels, *b*) the development of high-performance rechargeable batteries and fuel cells, *c*) the development of advanced thermochemical processes for energy storage, *d*) the characterization of complex chemical processes, and *e*) the application of novel materials for energy conversion and transmission. Projects focus on transport-process principles, chemical kinetics, thermodynamics, separation processes, organic and physical chemistry, and advanced analysis methods.

The electrochemical energy storage and conversion project develops advanced power systems for electric vehicle and stationary energy storage applications. Topics include identification of new electrochemical couples for advanced rechargeable batteries, improvements in battery and fuel cell materials, and the establishment of engineering principles applicable to electrochemical energy storage and conversion. Major emphasis is on applied research that will lead to superior performance and lower life-cycle costs.

Research in thermochemical energy storage and conversion focuses on new and innovative approaches to the more efficient utilization of thermal and solar energy. Gas-particle suspensions are being developed for use in direct solar-thermal conversion processes, and for the catalysis of important thermochemical reactions.

Coal-related research strives to develop improved, energy-efficient methods for processing waste streams from synfuel plants and coal gasifiers. Of particular interest are new techniques to remove compounds such as H_2S, NH_3 and phenols from effluents, and the establishment of a data base for physical, chemical and biological properties of the numerous compounds that are found in such streams.

Energy-related chemistry projects seek to identify and characterize the constituents of liquid fuel system streams, and devise energy-efficient means for their separation. Also of current interest is the development of advanced methods for production of alcohols from hydrocarbon fuels; the application of novel microstructured materials to develop super-insulating windows, new ceramics, and high-temperature superconducting films; and the use of ultrasensitive optical techniques to characterize high-temperature superconductor fabrication processes and biochemical reactions.

Technology Base Research Project for Electrochemical Energy Storage*

E.J. Cairns, K. Kinoshita, and F.R. McLarnon

The Lawrence Berkeley Laboratory (LBL) is lead center for management of the Technology Base Research (TBR) Project, which is supported by the Electrochemical Branch of DOE's Office of Energy Storage and Distribution. This project's research supports DOE development of electrochemical energy conversion systems for electric vehicles and stationary energy storage. Specifically, most promising electrochemical technologies will be identified and transferred to industry and/or to another DOE program for further development and scale-up.

The TBR Project identifies new electrochemical couples for advanced batteries, determines the technical feasibility of the new couples, improves battery components and materials, establishes engineering principles applicable to electrochemical energy storage and conversion, and investigates fuel cell and metal/air systems for transportation applications. Major emphasis is given to applied research that will lead to superior performance and lower life-cycle costs.

The LBL scientists participating in the project are E.J. Cairns, K. Kinoshita, and F.R. McLarnon of the Applied Science Division; and L.C. DeJonghe, J.W. Evans, R.H. Muller, J.S. Newman, P.N. Ross, and C.W. Tobias of the Materials and Chemical Sciences Division.

Research projects conducted by subcontractors are described in the report, *Technology Base Research Project for Electrochemical Energy Storage* (LBL-25507); in-house work is summarized in the next article and in the *Materials and Chemical Sciences Division 1988 Annual Report* (LBL-26455). Highlights of the subcontracted work follow.

EXPLORATORY RESEARCH

Efforts at Argonne National Laboratory (ANL) are focused on two advanced high-temperature rechargeable battery systems: *a)* $LiAl/FeS_2$ cells containing a dense upper-plateau (U.P.) FeS_2 electrode, a Li-Al electrode, and LiCl-LiBr-KBr electrolyte (m.p. 310°C); and *b)* Na/β''-$Al_2O_3/NaAlCl_4/NiCl_2$ cells ($Na/NiCl_2$ cells). Overcharge tolerance of U.P. FeS_2 for >250 cycles in $LiAl/FeS_2$ cells at 400°C was demonstrated, and the test is continuing. The performance of $Na/NiCl_2$ cells was shown to be sensitive to electrode thickness and to Ni particle size.

University of Pennsylvania and University of Minnesota investigations into the electrochemical properties of conducting polymers showed that the hydration/dehydration of poly(ethylene oxide) [PEO] profoundly influences the ionic transport of dissolved cations such as Ni^{2+} and Co^{2+}. Hot pressing and solvent casting were successfully used to prepare thin-layer electrochemical cells containing PEO.

APPLIED SCIENCE RESEARCH

Stanford University investigated sodium alloy (Na-Sn, Na-Pb) electrodes and $NaAlEt_4$ (Et = ethyl group) liquid electrolyte as replacements for the negative electrode/β''-Al_2O_3 assembly in $Na/FeCl_2$ cells. Constant-potential plateaus were identified for various compositions of alloys at 120°C. Thin films of $FeS_{1.5}$ (1-3 μm) were produced by high-rate atmospheric-pressure chemical vapor deposition (CVD), and tests of these materials in small Li/FeS_x cells are being conducted.

Studies at the Massachusetts Institute of Technology showed that chemical stability to Li at high temperatures was improved by a "passivating" layer of Ca on the surface of glasses, which are fast-ion conductors but are susceptible to attack by Li. These glasses are being developed for use in high-performance, rechargeable Li/S cells.

The Illinois Institute of Technology (IIT) has successfully electrodeposited Mo and Mo_2C layers from a FLINAK (LiF-NaF-KF) melt. Samples of these coatings are now being evaluated by an industrial developer of Na/S cells.

Brookhaven National Laboratory (BNL) and IIT are studying the electrodeposition of Zn in electrolytes for flow batteries. BNL's EXAFS (Extended X-ray Absorption Fine Structure) studies of supersaturated zincate solutions showed no evidence of chain or polymer formation as previously reported. IIT observed that pulse-reverse-voltage charging reduces formation of dendrites and produces more coherent Zn deposits than those obtained by alternating-voltage charging.

Spectroscopic techniques are being applied at Case Western Reserve University (CWRU) and Jackson State University to characterize the surface of reactive alkali and alkaline earth metals in organic electrolytes. Electron energy-loss spectroscopy of CO_2 adsorbed on K revealed two strong bands for CO_2 vibration. Raman spectra showed bands indicative of decomposition products from reactions of Li in 2-methyl tetrahydrofuran and propylene carbonate (PC).

Johns Hopkins University observed that Fe and Ni, in highly purified PC, exhibit similar electrochemical behavior near their corrosion potentials but that differences appear at high overpotentials. Fe retains its passive behavior up to the potential (E_p) at which PC is oxidized, whereas Ni begins to pit at about 500 mV below E_p.

*This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Storage and Distribution, Energy Storage Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

AIR SYSTEMS RESEARCH

Research at CWRU confirmed that a transition metal oxide must be present in heat-treated organic macrocycles to obtain active catalysts for oxygen reduction. These findings were observed with the organic macrocycles: dibenzotetraazaanulene, tetramethoxyphenyl porphyrin, and octaethyl porphyrin.

Experiments at Pinnacle Research Institute demonstrated that Mg is a better substrate than glassy carbon (GC) for Zn deposition during recharge of a Zn/air cell; about 0.52 Wh/g Zn was required for Zn deposition onto a Mg substrate, whereas the corresponding value needed for a GC substrate was 0.98 Wh/g.

Work at SRI International showed that solution-phase inhibitors (*e.g.*, Bi, Ga, In, Mn, Sn) may provide an alternative to alloying for reducing the corrosion of Al in Al/air batteries. These inhibitors precipitate on the Al surface to suppress corrosion.

Los Alamos National Laboratory observed that steam-reformed methanol that was partially oxided to reduce the CO content to 10 ppm still showed significant performance losses in proton-exchange membrane (PEM) fuel cells. However, the direct injection of O_2 (2-3%) in the anode compartment of PEM fuel cells produced cell performance comparable to that obtained using CO-free fuel.

BNL's EXAFS studies of Pt electrocatalysts showed that phosphate anions are strongly adsorbed on Pt, whereas no anions are adsorbed from CF_3SO_4H electrolyte.

Advanced Electrode Research*

E.J. Cairns, F.R. McLarnon, T.C. Adler, M.J. Isaacson, K.G. Miller, S.A. Naftel, P. Ridgway, J. Rudnicki, R. Russo, and J. Weaver

The purpose of this research is to study the behavior of electrodes used in secondary batteries and fuel cells, and to investigate practical means for improving their performance and lifetimes. Systems of current interest include ambient-temperature rechargeable cells with Zn electrodes (Zn/air, Zn/NiOOH, Zn/AgO, Zn/Cl_2, Zn/Br_2, and $Zn/Na_3Fe(CN)_6$); rechargeable high-temperature cells (Li/S, $LiAl/FeS_2$, Na/S and $Na/NiCl_2$); and fuel cells. The approach used in this investigation is to study life- and performance-limiting phenomena under realistic cell operating conditions.

*This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Storage and Distribution, Energy Storage Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

ALKALINE ZINC ELECTRODES

Rechargeable alkaline Zn/air and Zn/NiOOH cells can be designed to deliver high specific energy and specific power, but they typically exhibit short lifetimes. The high solubility of Zn species in alkaline electrolytes tends to enhance physicochemical processes (active material redistribution, filamentary Zn growths, etc.) that degrade the cell's capacity and limit its life. Modeling and experimental investigations attempt to understand the complex transport processes within operating Zn electrodes and to characterize methods for reducing Zn species solubility in order to extend the lifetime of the Zn electrode.

A TWO-DIMENSIONAL MATHEMATICAL MODEL OF THE POROUS ZINC ELECTRODE

M.J. Isaacson, E.J. Cairns, and F.R. McLarnon

The first two-dimensional mathematical model of the porous Zn/ZnO electrode was developed, and the model predictions were compared to prior μ-electrode and cell cycling studies.[1] This model accurately predicted the influence of cell geometry and concentration gradients on the current density distribution, whereas one-dimensional models could not do so. The effect of the hysteresis in the ZnO precipitation/dissolution kinetics (*i.e.*, formation of a meta-stable supersaturated $Zn(OH)_4^{2-}$ solution during discharge) was also incorporated into the model. The ZnO precipitation rate constant could then be estimated by comparing simulation results to experimental data. The model predictions were in good agreement with experimental charge/discharge curves and μ-electrode data. The μ-electrode experiments and the model both showed that: *a*) KOH concentration changes are small during both charge and discharge, and *b*) $K_2Zn(OH)_4$ concentration gradients are larger during discharge than those during charge. The model predicted movement of Zn-active material from the middle of the electrode to the edge of the electrode, agreeing with experiments conducted in 30% KOH electrolyte in this laboratory.

The 0.42-mm-thick electrodes used in the simulation displayed a relatively uniform current density distribution, and the Zn active material was well utilized. However, concentration gradients magnify the non-uniformity of the current density distribution, and differences in the concentration field during charge and discharge cause a net movement of both ZnO and Zn metal. These differences in the concentration field result from hysteresis in the dissolution/precipitation reaction and from the presence of electrolyte reservoirs.

The results suggest that material redistribution may be minimized by the use of additives that decrease the stability of the supersaturated $Zn(OH)_4^{2-}$ solution and by redesigning the cell to minimize the effect of electrolyte reservoirs.

A MATHEMATICAL MODEL OF THE RECHARGEABLE Zn/NiOOH CELL

K.G. Miller, E.J. Cairns, and F.R. McLarnon

The one-dimensional, time-dependent model reported earlier has been implemented.[2] Designed to elucidate the cause of active material redistribution in the Zn electrode, this model takes into account transport of electrolyte species, heterogeneous reactions, kinetics, and variations in current density.

The model includes important phenomena that have been suggested as causes of Zn active material redistribution, with the exception of non-uniform current density distribution near the edges of the electrodes. To study the effects of different processes on the rate and extent of Zn redistribution, the model now simulates the Zn/NiOOH cell during the course of 20-50 deep-discharge cycles.

These simulations have yielded important conclusions. First, the dominant processes which determine the zincate $[Zn(OH)_4^{2-}]$ and hydroxide (OH^-) ion concentrations are the electrochemical reactions at both electrodes and the ZnO dissolution/precipitation reactions. Transport of electrolyte species across the membrane is generally much more important than transport in the direction parallel to the plane of each electrode. Also, transport of species in the pores of the electrodes is primarily due to convection, with diffusion and migration contributing little. Second, the electrolyte becomes supersaturated with $Zn(OH)_4^{2-}$ at the end of the first cycle, and the $Zn(OH)_4^{2-}$ concentration remains at elevated levels during subsequent cycles (compared to levels during the first cycle). Third, at the end of the first cycle, precipitation of ZnO in the NiOOH electrode has already occurred. After ZnO precipitation is initiated in the NiOOH electrode, this ZnO never redissolves completely, and the amount of precipitated ZnO increases as the cell is cycled. Finally, from preliminary studies, the most sensitive parameters in determining the Zn redistribution pattern are the values of the rate constants in the ZnO precipitation/dissolution reactions.

IN SITU SPECTROSCOPIC CHARACTERIZATION OF ZINC ELECTRODE PROCESSES

J. Weaver, E.J. Cairns, and F.R. McLarnon

The rates of solid-phase precipitation and dissolution in porous Zn electrodes are known to play important roles in the life-limiting material redistribution processes in this system. Neither the rates of precipitation/dissolution nor the identity of the precipitating/dissolving species are known. We are applying photothermal deflection spectroscopy (PDS) as a powerful, *in situ* technique to characterize this electrode. A model pore electrode system, amenable to microscopic and spectroscopic study, is being employed to simulate a real pore that exists in a rechargeable Zn battery electrode.

Two features of the model pore electrode are under investigation: *a*) the species formed on the electrode surface, and *b*) the concentration gradients generated in the electrolyte adjacent to the electrode. During FY 1988, PDS was used to study concentration gradients in a model pore electrode, and conventional light microscopy was used to observe surface species that form on the electrodes.

The electrodes in the model pore system are mounted in clear polished acrylic, which is in turn supported in a quartz optical cuvette. Alkaline electrolyte, saturated with ZnO, is kept in an electrolyte compartment. The size of the electrolyte compartment can be adjusted to a range of model pore dimensions by inserting spacers of various thicknesses between the acrylic support and the quartz cuvette. The entire cuvette arrangement is mounted on a support which allows alignment to submicron precision.

Several constant-current experiments were carried out, during which PDS data were collected at various locations along the length of the electrode. As expected for anodic Zn oxidation, PDS experiments indicated that the concentration of soluble Zn species is higher near the electrode surface, and for cathodic Zn electrodeposition the reverse is true. For both anodic and cathodic experiments, the gradients became smaller near the closed end of the model pore electrodes (*i.e.*, away from the counter electrode). These results are now being compared with those predicted by a one-dimensional numerical model of the transient diffusion processes in this system.

The progress of reactions on the electrode surface has also been observed with a light microscope. A grey oxide film typically grows toward the closed end of the model pore anode during the course of the experiment, in agreement with earlier observations by others.

METHODS TO IMPROVE THE LIFETIME OF THE ZINC/NICKEL OXIDE CELL

T.C. Adler, F.R. McLarnon, and E.J. Cairns

Zinc redistribution is a major failure mode of the Zn/KOH/NiOOH cell and is associated with the high solubility of the zincate species in the alkaline electrolyte. A typical procedure for preparing a Zn/NiOOH cell to undergo repeated charge/discharge cycling is to subject it to extended low-current-density charges and discharges ("formation cycles") that establish a Zn metal reserve and "condition" the NiOOH electrode. A series of formation-cycle experiments has shown that as much as 15% of the original Zn is deposited in the NiOOH electrode during the first few formation cycles; this surprising result indicates that Zn redistribution is well established before normal cell cycling even begins!

Three approaches have successfully reduced Zn redistribution: *a*) reducing the concentration of zincate species in the electrolyte by reducing its alkalinity, *b*) binding the Zn-active material in a nearly insoluble calcium zincate complex, and *c*) employing optimized cell charging waveforms. Efforts during FY 1988 have been directed toward combining these three approaches.

Electrode/electrolyte combinations that exhibit low Zn species solubilities often exhibit high Zn electrode overpotentials when the cell is charged, and concomitant zincate-ion gradients in the electrolyte increase the likelihood of dendritic shorting. By maintaining the cell voltage at 1.93 V and reducing the cell current accordingly, the problems associated with high-overpotential charging can be avoided. The LBL computer-controlled electrochemical cell test-cycling system was adapted to provide this constant-voltage, limited-current mode of charging (CVLC); subsequently all cells have been charged in this mode.

Prior attempts to combine alkaline-fluoride electrolytes (which exhibit reduced zincate-ion solubility and are compatible with pure Zn/ZnO electrodes) with Zn-Ca electrodes showed inconsistent results, apparently due to difficulty in forming the calcium-zincate complex in this electrolyte. During FY 1988, several Zn-Ca/KOH-KX/NiOOH cells (X=halide) were constructed and tested. These cells exhibited problems during formation cycles, probably because of reduced availability of soluble zincate ion for reduction during charge. This problem was alleviated by first forming the Zn-Ca electrode in a cell containing an electrolyte with a high Li-ion content (KOH-KX electrolytes exhibit reduced Li ion solubility). Low-zincate-solubility electrolyte was then added to the cell, and the cell was cycled successfully in CVLC mode. Starved-electrolyte cells prepared in this manner are now being tested.

HIGH-TEMPERATURE CELLS

The high-temperature Na/S cell offers very good performance, and recent improvements to the process for manufacturing the ceramic β''-Al_2O_3 electrolytes indicate that acceptable cell lifetimes may be realized. However, the performance of the sulfur electrode has not been optimized, and the phenomena which govern its operation are poorly understood. In addition, Na/S cells cannot tolerate overcharge and overdischarge, a problem that complicates the design of cell-string configurations for battery applications. Ongoing work is aimed at developing and confirming an advanced mathematical model of the sulfur electrode and exploring variants of Na/S (and Li/S) cells that can tolerate limited overcharge and overdischarge.

MATHEMATICAL MODELING OF THE SODIUM/SULFUR CELL

S.A. Naftel, F.R. McLarnon, and E.J. Cairns

A comprehensive model of the sulfur electrode in Na/S cells has been developed.[3] The cell being modeled is of the tubular central-sodium type, and it incorporates a thin layer of α-alumina felt around the β''-alumina solid electrolyte in order to prevent deposition of sulfur on the solid electrolyte during cell charge. The model, consisting of a set of non-linear PDE's, describes the diffusion, migration, and convection processes that take place during operation of such a cell. The linearized equations are solved on a digital computer *via* implementation of the Newman-IAD method, a finite-difference technique for solving second-order linear PDE's.

The model was written in FORTRAN 77 and is being debugged; significant results are expected during FY 1989. An attempt will be made to predict the effect of various charge-discharge regimens upon cell operation.

FUEL CELLS

Fuel cells can be designed to exhibit acceptable lifetimes for a number of applications, and a handbook describing the status of fuel cells is available.[4] However, the performance of the O_2 electrode in fuel cells requires improvement, and development of an efficient direct-methanol fuel cell would represent a major advance over reformed-hydrocarbon fuel cells.

APPLICATION OF PHOTOTHERMAL DEFLECTION SPECTROSCOPY TO CHARACTERIZE DIRECT METHANOL ELECTROOXIDATION

J.D. Rudnicki, R.E. Russo, O. Haas, F.R. McLarnon, and E.J. Cairns*

Photothermal Deflection Spectroscopy is being used to study electrochemical interfaces.[5] PDS is a versatile, *in situ* technique which measures both absorption of light at the electrode surface and electrolyte concentration gradients formed near the electrode surface. By measuring the absorption of light at the surface as a function of wavelength, the absorption spectrum of the surface is determined. Such a spectrum can be used to identify the species on the electrode surface. The sensitivity of the technique is high enough to detect the absorption of light and concentration gradients due to the formation of less than one molecular layer of species on an electrode surface. The information provided by PDS helps determine reaction mechanisms, and with this knowledge methods to improve the efficiencies of electrode reactions can be formulated.

Platinum electrodes have been studied because of their high electrocatalytic activity for methanol oxidation, and supported-Pt electrodes would be good candidates for use in direct-methanol fuel cells. The Pt surface can be modified by the presence of a small amount of another species on the electrode surface (either adatoms or admolecules) resulting in a synergistic increase in the catalytic activity. One method of accomplishing this modification is underpotential deposition (UPD), and the UPD of Pb on Pt has been studied. The PDS results provided information which showed that the UPD process is different than that which would be expected from standard

* Paul Scherrer Institute, Switzerland

electrochemical experiments. The study of UPD of other species on Pt is in progress.

The versatility of PDS has been expanded. Many types of electrodes, including smooth Pt, Cu, polymer films on carbon or a fine screen, and porous UO_2 have been studied as electrode surfaces. Improvements in the signal-to-noise ratio have been made, and increased sensitivity has allowed the experimental data to be obtained in a shorter time. Work has also been started to expand the spectral range of PDS into the near- and mid-infrared.

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THERMOCHEMICAL ENERGY STORAGE AND CONVERSION

Direct Solar Thermal Conversion Processes*

A. Hunt, I. Hodara, F. Miller and J. Noring

This research explores advanced concepts in the direct conversion of concentrated solar energy to thermal and chemical forms. Of the four research areas, two involve purely solar thermal processes; the others address the solar heating of catalysts to drive useful chemical reactions. The unifying theme is the absorption of concentrated solar energy by small particles and its conversion to other forms. The concept of entrained particle absorbers was first demonstrated in 1982 with the solar test of the Small Particle Heat Exchange Receiver (SPHER). This approach may be used to heat gases to high temperatures for driving turbogenerators and for supplying heat for industrial processes; it may also be used to convert solar energy to chemical forms suitable for storage or transport.[1]

RADIANT HEATING OF GAS-PARTICLE SUSPENSIONS

This research was undertaken to understand the thermal and optical processes in the radiant heating of gas-particle mixtures. In FY 1988, we completed development of a cylindrical receiver model and related experimental work to study the operation of an idealized receiver system. Our goal was to understand the absorption of radiation by the particles, the heating and expansion of the gas, and the resulting temperature, density, and flux profiles within a solar receiver. The results of our research will provide a basis for designing future direct-absorption receivers.

An analytic model of a long cylindrical receiver was developed to predict temperature and flux distribution in a gas-particle suspension flowing along the axis of the receiver. The model provides information regarding gas densities and the effects of flow direction and gives detailed performance predictions for our experimental receiver, which was constructed to test the model.

The receiver system consists of a vacuum-insulated cylindrical receiver, carbon-particle generator, light source, and associated instrumentation. The light source produces a collimated beam of light along the axis of the tube with a peak intensity of over 80 suns. Carbon particles are mixed with air and directed in either a co- or counter-current flow direction with respect to the direction of the incident light. Thermocouples measure the temperature profile along the entire axis at 6 different radial positions and at fixed points within the receiver. The receiver was completed in FY 1988 and the measurements were compared with the model predictions.

There was general agreement between the modeled and experimental results for the counter-current case but the experiment showed more rapid heating than predicted for the co-current case. Much of the difference can be attributed to non-idealities in the experiment, but further research is required to resolve the remaining discrepancies.

CARBON-PARTICLE ABSORBERS IN LIQUID SALTS

The DOE Solar Thermal Program is developing an advanced direct-absorption receiver based on a liquid medium of Na/K nitrate salt for heat transfer and storage. The salt flows over a plate exposed to concentrated solar radiation from a field of heliostats. Because the pure salt is transparent to solar radiation, current designs call for the salt to be doped with cobalt oxide particles. We investigated the use of carbon particles as an alternative absorber. They are less abrasive and are slowly oxidized in the hot salt. Oxidation of the particles effectively eliminates problems of agglomeration and settling encountered with the cobalt oxide particles. A hot stage transmissometer was designed and built to study the oxidation, agglomeration, and settling properties of the carbon particles.

Calculations compared the mass loading of carbon and cobalt oxide as a function of particle size. On the basis of weight, our calculations showed carbon to be a better absorber than cobalt oxide.

RADIANTLY HEATED CATALYSTS FOR THERMOCHEMICAL ENERGY STORAGE

This research explores the use of concentrated sunlight to initiate endothermic catalytic reactions in gases for high-temperature thermochemical energy storage cycles. Direct radiant heating of catalyst particles to drive gas reactions has several important advantages. Enhanced heat transfer occurs because heat is supplied directly to the reaction site (in contrast to conventional reactors, where heat is supplied through pipe walls and thereby leaves the catalyst the coolest part of the system). A radiantly heated catalyst particle becomes the hottest part of the reactor, dramatically increasing the reaction rate. Additionally, a semiconducting catalyst particle can photocatalyze the reaction because the absorbed photons produce energetic photocharges. In small particles, these charges can reach the gases adsorbed on the surface to initiate the reaction.

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We studied the endothermic dissociation of SO_3 to SO_2 and O_2 as a means of thermochemically storing solar energy. Experiments used hematite (iron oxide) particles fixed on a substrate and illuminated with a solar simulator. We constructed a new system for SO_3 storage and transfer and fabricated a new reaction cell. Experiments confirmed that the rate of reaction was enhanced by radiant heating as compared to isothermal heating in a furnace.

RADIANTLY HEATED CATALYSTS FOR ENERGY TRANSPORT

We investigated the feasibility of direct radiant reactors for the chemical transport of energy. In this concept, individual solar concentrators convert solar energy to chemical energy. The energy-rich gases from the collectors are piped at ambient temperatures and are combined at a central conversion site where they pass over a catalyst to produce high temperatures to drive a steam-Rankine cycle.

The reaction studied was the CO_2 reforming of methane over a catalyst at high temperature to produce H_2 and CO. Analytic models of the optical, thermal, and chemical interactions were formulated. Reticulated alumina, alumina aerogel, and fiber arrays were considered as substrates for the absorbing rhodium catalyst particles. We analyzed the mass transport, optical, and thermal properties of the reactor designs.

The uncatalyzed CO_2 reforming of methane was studied experimentally. The results of these experiments showed that the reaction may be carried out without a catalyst if sufficiently high temperatures are achieved.

In FY 1989, our solar thermal research will continue by carrying out collaborative projects with the German aerospace organization (DFVLR). The first project will quantify the losses from a radiantly heated gas-particle receiver. The second project will measure the effects of concentrated solar radiation on carbon particle oxidation rates.

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Microstructured Materials*

A. Hunt, F. Hibbler, and K. Lofftus

This research develops new microstructured materials *via* advanced chemical processing. Liquid organo-metallic compounds are reacted to form a solid network that contains solvent. The solvent is then removed without changing the microstructure by a supercritical drying technique developed at LBL. A low-density, porous solid called "aerogel" results. Several single- and mixed-metal oxide compositions were made this way using different starting compounds. Three projects employ this technique: one develops silica aerogel for insulating windows; another explores the preparation of new ceramic materials for high temperature applications; and a third, new project, is exploring the preparation of high critical point superconductoring films using sol-gel processing.

SILICA AEROGEL, A TRANSPARENT SUPERINSULATOR

Silica aerogel is a transparent, porous insulating solid with many applications. We have developed aerogel as a transparent insulator for high-thermal-performance windows (R-20 per inch). Three major technological barriers to its commercialization have been overcome in the past six years of research and development at LBL. A safer, more economical supercritical drying process was developed and patented, the clarity of aerogel was improved, and methods to produce good-quality aerogel with alternate non-toxic starting compounds were developed.[1] In addition, economic studies indicated that mass-produced aerogel will be a cost effective insulator. This year's activities involved primarily scale-up and technology-transfer.

A new large autoclave for CO_2 substitution and supercritical drying of samples up to 12 inches square was constructed and tested. Instrumentation was developed to monitor the fluid level and composition in the autoclave. New molding techniques were developed and large alcogel samples were prepared for drying. The dried aerogel samples were encapsulated between glass, and several were evacuated.

The last stage of this project included technology transfer to private industry. Encouraged by the DOE tech-

*This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Solar Heat Technologies, Solar Buildings Division, and the Office of Energy Systems Research, Energy Conversion and Utilization Technologies (ECUT) Division, and the Office of Energy Storage and Distribution of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

nology transfer program, Quantum Optics, Inc. was founded to commercialize the manufacture of aerogel products in the United States and Canada using the CO_2 substitution process. A key first application of aerogel may be for refrigerator insulation.

POROUS MICROMATERIALS DEVELOPMENT

Micromaterials research at LBL develops new methods to produce microporous materials and precursors based on sol-gel chemistry and supercritical solvent extraction techniques. These techniques have enabled us to create new and unusual materials. Low-density materials with controlled microporosity promise applications including high-temperature insulators, porous materials for filters, catalyst substrates and superconducting aerogels. New composite ceramics may be possible because very fine-grained aerogels have significantly lower sintering temperatures[2] than conventional ceramic powders, thereby reducing the tendency for the components to react with each other.

During FY 1988, we improved methods to prepare mixed-oxide ceramic materials, studied the effects of varying solvents and pH on microstructure, and developed analytic techniques to study the structural development of gel materials.[2] Research into the production of bulk superconducting YBCO aerogels was also carried out. New methods to prepare zirconia alcogels were developed and zirconia aerogels were prepared using the supercritical drying process.

SOL-GEL PROCESSING FOR SUPERCONDUCTING CERAMIC FILMS

A new project in the chemical fabrication of superconducting materials using sol-gel processing was initiated this year as part of the high-T_c thin film research effort at LBL. This approach offers the advantages of inexpensive fabrication methods for coating tapes and fibers, lower processing temperatures, very fine structure, and good homogeneity. The project, which started late in FY 1988, began exploring two approaches to preparing starting materials for YBCO films. In one approach separate alkoxides of yttrium, barium, and copper are prepared and mixed, before controlled hydrolysis is carried out. Alternatively, mixed alkoxides of two or three of the metals are prepared before hydrolysis. Transesterification methods were developed to prepare liquid copper alkoxide starting compounds.

The porous micromaterials area will concentrate on preparing composite aerogel materials and improved zirconia aerogels. The superconducting film project will explore the preparation of YBCO and other high-T_c compounds.

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Light Scattering Studies*

To study how light interacts with microstructures, we are conducting basic experimental and analytical studies of light scattering. In addition to the scattering measurements carried out in conjunction with our solar thermal conversion and microstructured materials research, we also have several projects to investigate light scattering in the biological sciences.

OPTICAL MEASUREMENTS OF THE INTRACELLULAR POLYMERIZATION OF HbS

A. Quintanilha, A. Hunt, K. Lofftus, H. Salamon, and R. Macy

Using a new, real-time light-scattering technique, we are measuring the kinetics of intracellular polymerization of Hemoglobin S (HbS) in red blood cells of individuals affected by sickle cell disease. This polymerization appears to be a major factor in capillary occlusion and crisis in the disease. In the kidney (frequently damaged in sickle cell disease) intracellular HbS polymerization is stimulated by dehydration, deoxygenation, and increased acidification; we have therefore simulated these conditions *in vitro* to study their effects on HbS polymerization in very dilute suspensions of red blood cells. The polarization-sensitive light-scattering technique developed earlier was used to measure the degree of polymerization.[1]

Our results indicate that the amount of induced circular polarized light, measured as a function of angle, increases when cells are placed in the dehydrating hypertonic medium representing the kidney environment. Furthermore, successive cycles of deoxygenation-reoxygenation appear to induce progressively larger steady-state values of this component of the scattered light. Comparison of our results with published data[2] on the amount of polymerized HbS measured using nuclear magnetic resonance (NMR) spectroscopy have been encouraging. A recently developed theoretical basis for our observations[3] shows that our results can be predicted using scattering theory.

Two additional observations are important in the pathophysiology of patients affected by sickle cell disease or sickle cell trait: *a)* our finding that the rates of polymerization and depolymerization as a function of changing

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oxygen tension are different; *i.e.*, the rate of polymerization is much slower than the rate of depolymerization; and *b)* red cells from subjects with sickle trait, despite their significantly lower levels of HbS, show evidence of polymerization at low oxygen tensions and in hypertonic media. The first observation is important in determining whether the transit time of red cells through the kidney (~24 sec) is enough for polymerization of HbS to occur; the second observation can probably be related to kidney function abnormalities that develop in sickle trait patients.

MODELING BIOLOGICAL PARTICLES TO PREDICT OPTICAL PROPERTIES OF THE OCEAN

A. Hunt, M. Quinby-Hunt, K. Lofftus, and D. Shapiro

This project combines a modeling and experimental approach to study light scattering in the ocean. Measurement of the intensity and polarization of scattered light as a function of angle can be used to investigate the nature of the particles and to predict the propagation of light in the ocean. The particle population in the ocean is often dominated by live organisms of defined size, shape, and optical properties. Using various theories, we can predict light scattering from such organisms.

Approximate and exact models were implemented as computer programs to predict light scattering variously shaped particles. Using Mie theory, rigorous calculations of scattering from spherically symmetric particles were performed for unrestricted particle size and optical properties. Models based on Rayleigh-Debye theory were used for a restricted range of sizes and optical properties to predict scattering for spherical and nonspherical shapes. The range of validity of the non-rigorous theories was determined by comparing the results with rigorous theories for spherical geometries.[4]

The scattering properties of single, immobilized marine organisms were measured.[5] Cells of the dinoflagellate *Prorocentrum micans* were immobilized and measured in a transparent silica gel. The technique provides a convenient method to perform scattering or other optical measurements on immobilized cells without interference of a substrate in a liquid medium.

In FY 1989, the kinetics of HbS polymerization will be studied in red cells containing differing amounts of HbS, HbF, HbA. We plan to investigate whether a history of oxidative stress to these red cells (with and without polymerized HbS) affects their rheological properties. We will also use other components of the scattered light to distinguish between intracellular polymerization of HbS and the resulting shape changes of the cells.

Models will be used to predict the complete scattering behavior of well characterized marine organisms. Populations of several marine organisms will be cultured, measured, and compared to the model predictions to determine the sensitivity of the technique to characterize marine populations in the ocean.

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High-Temperature Superconducting Films: Electrical Characterization*

P. Berdahl and L. Williams

This new research on high-critical-temperature superconducting films, initiated in May, 1988, focuses on a.c. electrical characterization of the films. The required measurements include resistance *vs* temperature and critical current *vs* temperature. The critical current is generally defined as the maximum current that the superconductor can carry before a measurable resistance appears. The magnetic field dependence of the critical current density will also be obtained. Measurements of a.c. and d.c. magnetic susceptibility will be performed.

After some analysis and literature review, an automated a.c. electrical characterization technique was chosen which uses low-frequency excitation and phase-locked synchronous amplification to measure the small voltages required. A suitable closed-cycle helium refrigerator and cryostat were ordered to support the measurements. The synchronous detection scheme permits smaller voltages to be measured than is the case with d.c. techniques. Furthermore, the range of frequencies and magnetic fields employed (*e.g.*, 5-1000 Hz, 10^{-2} to 10 tesla) are those expected for applications of superconductors in future electric power systems.

The basic electrical characterization measurements described here primarily support the investigators syn-

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thesizing high-T_c films. However, in FY 1989, we will begin to investigate details of the onset of resistance in the presence of magnetic fields, a phenomenon poorly understood due to the motion of magnetic flux lines. To obtain evidence for weak current links in the films, we will also examine the relation between critical currents measured by transport techniques and those measured by magnetization techniques.

High-Temperature Superconductors: Fundamentals and Their Applications*

P. Berdahl

This work was a part of an extensive multilaboratory technology assessment entitled "Assessment of Energy Productivity Applications of High-Temperature Superconductivity." The purpose of the work was to provide an overview of selected applications of superconductivity, with emphasis on fundamental processes and novel concepts. The balance of the larger Assessment included analyses of various technological areas: motors, transportation, materials production, separations technology, electromagnetic pumping, magnetic heat pumping, materials fabrication, and power electronics. Thus, the work reported here provided an overview of the technologies, with emphasis on basic physical principles and how these principles constrain technology development. Further, the analysis was extended to include study of the emerging material properties of new superconductors.

Magnetic pressure provides an important illustrative example of how physical principles constrain technology development. Most electrical applications of superconductivity utilize electromagnets. The design of any electromagnet requires that provision be made for structural support to contain the magnetic field. For an ordinary iron-core electromagnet with copper windings, with a field of 1 tesla, this pressure is only 400 kPa (60 psi). However, this pressure is proportional to the square of the field, so that for a high-field superconducting solenoid, containment of the magnetic pressure is a major problem. At 20 tesla, the record for a (very low temperature) superconducting solenoid, the pressure is larger than that at the bottom of the ocean.

A result of the analysis of materials properties is illustrated (Figure). Most applications require current densities of 10^5 A cm^{-2} or above, at fields above 1 tesla. Therefore, except possibly for thin films, additional materials research is required to raise current-carrying capacity of

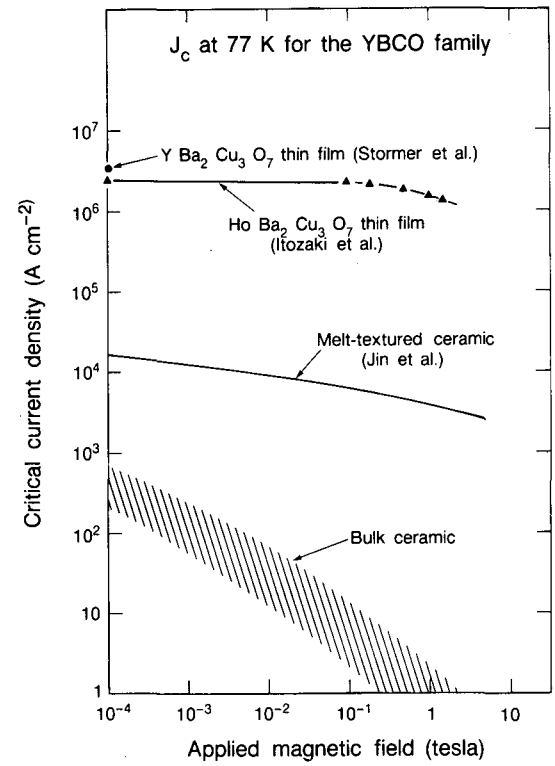

Figure. Critical current measurements *vs* applied magnetic field for a high-temperature superconducting material at 77 K (XBL 8811-9783).

YBCO (*i.e.*, $YBa_2Cu_3O_7$) before this material can be used in applications. The present situation with respect to other high-temperature superconductors is similar.

Solid State Radiative Heat Pump*

P. Berdahl

Work on this novel concept for cooling was largely concluded in FY 1987. However, publication and presentation of the results extended into FY 1988.

The Solid State Radiative Heat Pump concept utilizes non-equilibrium infrared radiation flows to produce radiative cooling and heating effects. The non-equilibrium radiation flows are caused by non-equilibrium populations of electrons and holes, produced electrically in narrow-bandgap semiconductors. The quantum efficiency for non-equilibrium electron-hole pairs to produce photons is

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a key material figure of merit for prospective heat pump materials. A comprehensive study of quantum efficiency for radiative recombination in InSb was published.[1] Efficiencies as high as 5% were achieved at room temperature by the use of p-type (Cd) doping.

From a slightly different perspective, production of a radiative cooling effect by reducing the ordinary thermal emission from a semiconductor can be regarded as "negative luminescence": when electrically excited, system emits less infrared radiation than it does when unexcited.[2,3]

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COAL-RELATED RESEARCH

Processing of Condensate Waters from Coal Gasification*

C.J. King, T. Grant, and L. Poole

Condensate waters from low-temperature coal-gasification processes contain large amounts of dissolved phenols, ammonia, and acid gases. The goal of this project has been to develop effective and economical physicochemical treatment technology for removing these substances.

IRREVERSIBLE ADSORPTION OF PHENOLS ONTO CARBON

Adsorption of phenols by carbon is hampered by incomplete regeneration and consequent needs for adding fresh carbon. We have shown that irreversible adsorption of phenols is the result of oxidative coupling reactions accelerated by the carbon surface. Methods used included mass-spectrographic identification of reaction products and determination of the effects of temperature, pH, type of phenol, type of carbon, and various chemical treatments of the carbon surface. Irreversible adsorption can be reduced by use of low temperature, low pH, frequent generation, mild oxidation of the carbon, and an oxygen-free environment.

EXTRACTION OF AMMONIA WITH LIQUID ION EXCHANGERS

Cyanex 272, a commercial phosphinic acid extractant (American Cyanamid Corp.), has been shown to have optimal acidity for extraction of ammonia from the highly buffered condensate waters. Stripping and thermal degradation studies have established the appropriate range of temperatures for regeneration by stripping of ammonia from the extract.

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Removal of H_2S from Coal-Derived Gases*

S. Lynn, T. Colson, R. Hix, and C. Stevens

When coal is gasified, most of its sulfur is converted to H_2S and must be removed before the gas can be used as a fuel or as synthesis gas. The UCB Sulfur Recovery Process (UCBSRP) is being developed as a general method for removing H_2S from gases. The H_2S is absorbed in a polyglycol ether, then reacted in the liquid phase with SO_2 to form marketable elemental sulfur and water. The process allows high specificity and flexibility; H_2S can be reduced to the part-per-million level or below in the presence of CO_2 and the other components of gasified coal. The CO_2 may be left in the original gas stream or it may be co-absorbed and recovered as a separate, sulfur-free product. The process thus has application both to syngas and hydrogen production from O_2-blown gasifiers and to power production using an air-blown gasifier.

PROCESS CONFIGURATION STUDIES

Two major goals of this project are to demonstrate the feasibility of replacing conventional industrial gas treatment technology with the UCBSRP technology and to compare the costs of the UCBSRP with those of conventional processes. One promising application of the UCBSRP is the removal of H_2S and CO_2 from a synthesis gas after a water gas shift (WGS) reactor in a process for producing high purity hydrogen.

In the production of high-purity hydrogen from gasified coal (Figure), the effluent from coal gasification is quenched with water to remove NH_3, HCl, and particulates and to cool the gas to about 430°F. To increase the H_2 content of the gas, the gas is fed to a WGS reactor, where CO is reacted with H_2O to form CO_2 and H_2. In addition, this reactor also converts some of the COS in the

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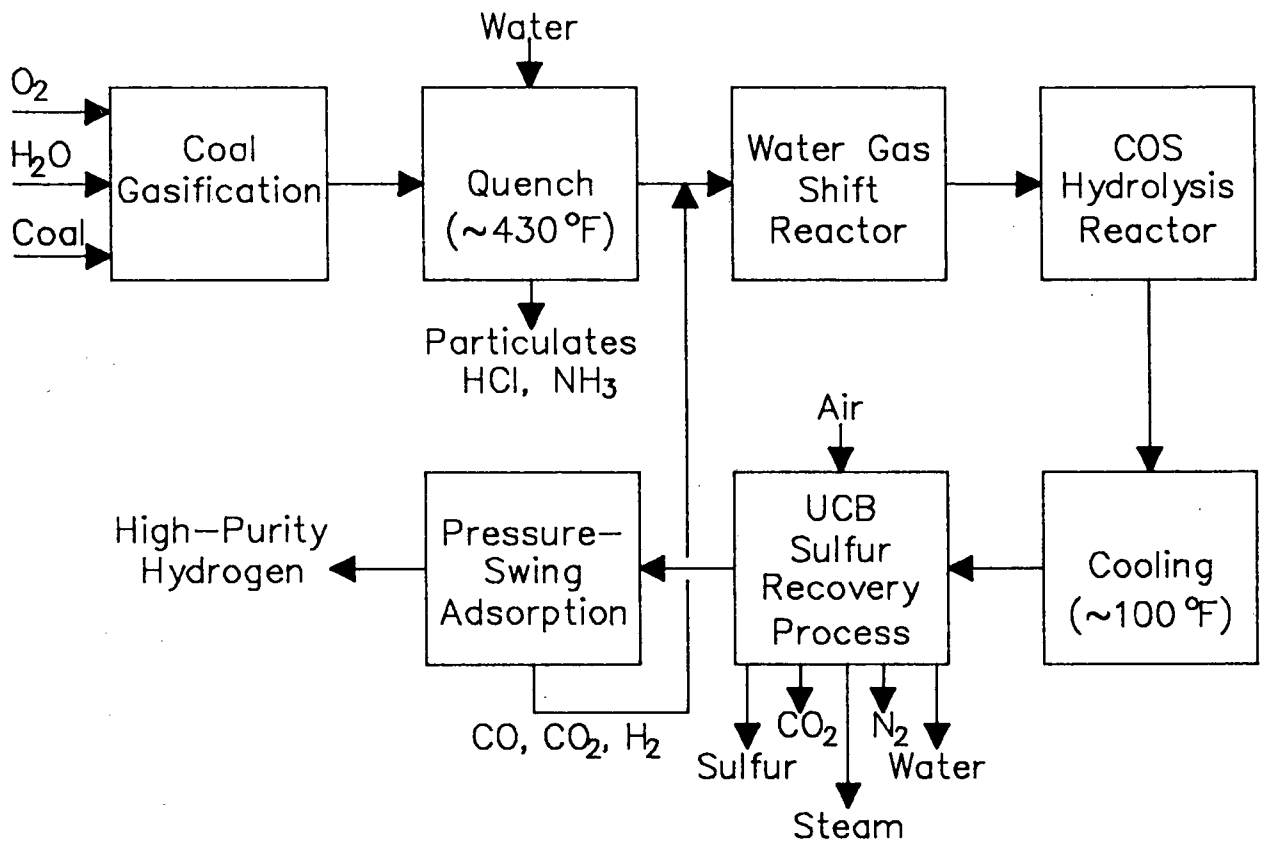

FIGURE. Block flow diagram proposed for producing high-purity hydrogen from gasified coal (XBS 8811-3939).

gas to H_2S via hydrolysis. The gas is then fed to a COS hydrolysis reactor to complete the conversion. This gas is cooled to about 100°F and sent to the UCBSRP where the H_2S and CO_2 are recovered as elemental sulfur and a purified (99+%) CO_2 stream. The treated gas from the UCBSRP is then fed to an adsorption unit for final purification. The products from the adsorber are a high-purity (99.999+%) H_2 stream and an impurity stream containing inert gases (N_2 and Ar) and any unreacted CO. Part of this stream may be recycled to the WGS reactor to recover CO, but the remainder must be purged to remove inert gases from the system.

SULFUR CRYSTALLIZATION

A major potential advantage of the UCBSRP is the purity of the crystalline sulfur that is produced. The sulfur crystallizes from solution both as a result of cooling and as a result of chemical reaction between H_2S and SO_2. In the former case, the degree of supersaturation is relatively low because the solubility of sulfur in the solvent varies only a few grams per liter over the temperature range of interest. A substantially higher concentration of sulfur can result from the chemical reaction.

The crystallizer consists of a well-stirred 2-liter vessel. Hot saturated feed enters at the top, and the vessel walls are cooled. Cold effluent exits at the bottom of the vessel as a sulfur/solvent slurry. A sample of the effluent slurry is collected when the system is at steady state and the size distribution of the sulfur crystals is determined. The first set of experiments, in which only the residence time was varied, indicated that the mixed-suspension, classified-product-removal (MSCPR) model can be used to correlate the data. Changes in residence time produce changes in nucleation and growth through their common driving force: super-saturation. The effect of supersaturation manifests itself in the general slope of the curves when the data are plotted. Although the slurry density changes slightly with residence time for a MSCPR crystallizer, large changes in slurry density were made by altering the feed temperature in the second set of experiments.

The addition of water to the solvent is equivalent to reducing the water-free solvent temperature with respect to sulfur solubility. Increasing the water concentration in the solvent should therefore produce a variable slurry density effect similar to that when the crystallizer feed temperature is reduced. Although the growth rate remains relatively invariant for different water concentrations with similar residence times, the nucleation rate increases less with increasing growth rate (decreasing residence time) when water is present.

ABSORPTION WITH CHEMICAL REACTION

Tray efficiency data are needed for two process situations. In one, H_2S at very low concentration is being absorbed by a chemically reactive solution of SO_2. In the other, gaseous SO_2 in the low parts-per-million concentration range is absorbed by lean process solvent. Both are of interest for using the UCBSRP to effect stringent sulfur removal. The equipment consists of a single sieve tray (or section of packed column) placed in a test section through which gas and liquid streams pass. Murphree tray efficiencies are determined from the mass balances and previously obtained solubility data. During FY 1988, this equipment was used to determine tray efficiencies for SO_2 absorption while varying liquid flow, gas flow and weir height. Similar data were obtained for H_2S absorption.

A computer program that incorporates the Murphree vapor tray efficiencies of H_2S and SO_2 and the reaction between these two components was written to solve the absorber operating problem. The column was assumed to be isothermal (a good assumption due to the small amount of H_2S being absorbed) and isobaric (a good assumption for columns at high pressure). Mass balance and equilibrium equations were written for each stage, and the resulting system of equations was solved by the multivariate Newton-Raphson technique. The column temperature and pressure, number of stages, feed flows and compositions, component tray efficiencies, reaction rate constant and tray volume must be specified. This model will be modified as experimental data for reactive absorption are obtained.

The crystallizer is being modified to accept separate feeds of dissolved H_2S and SO_2. Sulfur will be produced by chemical reaction. The absorption of H_2S enhanced by the presence of SO_2 in the solvent will be studied and the results used to develop a model that incorporates previous work on reaction kinetics.

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ENERGY-RELATED CHEMISTRY

Organometallic Synthesis and Catalysis Studies*

The Organometallic Chemistry Group focuses on two areas of research: *a)* reactions of polynuclear heteroaromatic nitrogen (PHN) compounds with organorhodium and organoruthenium complexes as well as catalysis studies on the regioselective hydrogenation of PHN compounds with the above-mentioned complexes as homogeneous catalysts; *b)* biomimetic catalysis directed toward the synthesis and catalytic activity of mimics of monooxygenase enzymes. The conversion of small hydrocarbons to their respective alcohols (*e.g.*, methane to methanol) is the major goal of this project.

BONDING OF POLYNUCLEAR HETEROAROMATIC NITROGEN LIGANDS TO (PENTAMETHYLCYCLOPENTADIENYL)RHODIUM DICATION: THE ROLE OF NITROGEN VERSUS π-COMPLEXATION ON THE REGIOSELECTIVE HYDROGENATION OF THE NITROGEN RING*

R.H. Fish, H-S. Kim, J.E. Babin, and R.D. Adams

The reactions of quinoline (**1**), isoquinoline (**2**), 1,2,3,4-tetrahydroquinoline (**3**), and 2-methylquinoline (**4**) with (pentamethylcyclo- pentadienyl)rhodium dication [$Cp^*Rh(acetone)_3^{2+}$, $Cp^*Rh(acetonitrile)_3^{2+}$, or $Cp^*Rh(p-xylene)^{2+}X_2$; X = PF_6 or BF_4] were studied to ascertain nitrogen (N) versus π-bonding. Ligands **1** and **2** were found to form N-bonded rhodium complexes, while ligand **3** preferred π-coordination (η^6). Ligand **4** was found to provide both π- and N-bonded complexes. A single-crystal x-ray structural analysis of a derivative of [$Cp^*Rh(quinoline)(acetonitrile)_2^{2+}$, $Cp^*Rh(quinoline)(\mu-hydroxo)]_2^{2+}$ verified the N-bonding of ligand **1** to the rhodium metal center. We also found that the abovementioned Cp^*Rh^{2+} synthetic precursors were excellent catalysts or catalyst precursors for the selective hydrogenation of **1**, **2**, and **4** to their corresponding tetrahydro derivatives. This latter result defines the important role of N-bonding for regioselective nitrogen ring reduction.[1]

*These studies was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy and the Electric Power Research Institute under Contract No. DE-AC03-76SF00098.

MODELING THE DINUCLEAR SITES OF IRON BIOMOLECULES: SYNTHESIS AND PROPERTIES OF $Fe_2O(OAc)_2Cl_2(bipy)_2$ AND ITS USE AS AN ALKANE ACTIVATION CATALYST

J.B. Vincent, J.C. Huffman, G. Christou, Q. Li, M.A. Nanny, D.N. Hendrikson, R.H. Fong, and R.H. Fish

The study of synthetic models containing the $[Fe_2(\mu-O)(\mu-O_2CR)_2]^{2+}$ core established in the oxygen carrier protein hemerythrin (Hr) has received additional impetus and importance with the realization that such units may also be present in other dinuclear iron biomolecules. These include the purple acid phosphatases (PAP), ribonucleotide reductases (RR), and methane monooxygenases (MMO). By using a variety of tridentate N-based ligands (L), synthetic materials of formulation $[Fe_2O(O_2CR)_2L_2]$ have been prepared, establishing the accessibility and stability of this unit outside a polypeptide environment. The tridentate ligands, however, block all terminal binding sites, precluding investigation of native substrate or substrate-analogue binding. Use of bidentate ligands to overcome this problem has led to dimerization of the $[Fe_2O(O_2CR)_2]^{2+}$ unit to yield products containing $[Fe_4O_2(O_2CR)_4]^{4+}$. However, we reported a procedure that uses 2,2'-bipyridine (bipy) to allow access to a $[Fe_2O(O_2CR)_2]^{2+}$ product; in addition, we described the structure, properties, and alkane activation reactivity of $Fe_2O(OAc)_2Cl_2(bipy)_2$, which possesses Cl^- ligands bound to the now-available sixth coordination sites.[2]

CARBON-HYDROGEN ACTIVATION CHEMISTRY: HYDROXYLATION OF C_2, C_3, AND $CycloC_6$ HYDROCARBONS BY MANGANESE CLUSTER CATALYSTS WITH A MONOOXYGEN TRANSFER REAGENT

R.H. Fish, R.H. Fong, J.B. Vincent, and G. Christou

The C-H bond activation of alkanes with homogeneous catalysts that mimic the active site of monooxygenase enzymes is currently an extremely important and intense area of research. Although considerable effort has been focused on mimics of cytochrome P450 (which has a metallo-porphyrin center as the active site) few examples have been reported on non-porphyrin complexes. The interest in non-porphyrin complexes as C-H activation catalysts coincides with recent reports on methane monooxygenase enzymes, which have tentatively been assigned, via EXAFS analysis, as having a μ-oxo diiron non-porphyrin active site.

The reported metallo-non-porphyrin C-H activation catalysts are predominantly mononuclear metal complexes, whereas two studies were directed towards metal clusters containing iron. We reported that a series of manganese clusters (Figure) originally synthesized as models for the photosynthetic water oxidation enzyme site in green plants are novel C-H activation catalysts for the hydroxylation of C_2, C_3, and cycloC_6 hydrocarbons in the presence of a monooxygen transfer reagent. To our knowledge, this is the first reported attempt to evaluate the C-H bond reactivity of small hydrocarbons using non-porphyrin metal clusters as catalysts.[3]

$Mn_3O(O_2CCH_3)_6(py)_3$	$[Mn_3O(O_2CCH_3)_6(py)_3](ClO_4)$
1	**2**
$Mn_4O_2(O_2CPh)_7(bipy)_2$	$[Mn_4O_2(O_2CPh)_7(bipy)_2](ClO_4)$
3	**4**

FIGURE. Manganese-cluster catalysts for hydroxylation of C_2, C_3, and cycloC_6 hydrocarbons.

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Energy-Related Organic Compounds (EROC): A Microcomputer Information Database of Potential Pollutants*

C.G. Daughton and J.F. Thomas

A commercial-scale "synthetic fuels" industry (*e.g.*, coal gasification, shale oil production) would generate vast quantities of liquid and solid wastes comprising highly complex assemblages of organic compounds from numerous chemical classes. These compounds are the subject EROC (Energy-Related Organic Compounds), a menu-driven relational database for MS-DOS microcomputer retrieval of physicochemical/biological properties, process-stream occurrence, chemical nomenclature, and full bibliographic citation information for all referenced data.

When completed, EROC will comprise three integrated modules: BCS (Bibliographic Citation System), CPSS (Chemical Properties, Structures, and Synonyms), and PSCC (Process-Stream Chemical Characterization). The third module, PSCC, is in the initial stages of development. The first two modules have been completed and are designed to function also as stand-alone software applications.

BCS is an information management system for all aspects of bibliographic citation. No experience in database use or programming is required of the user. BCS is fully menu-driven for all aspects of data entry, editing, data retrieval and report generation. The structure of BCS is completely "normalized"; the number of fields has been minimized, and code "look-up" tables have been used where appropriate. All references are linked with the other modules via unique accession numbers. Version β-1.0[1] is currently available from Dr. Christian Daughton.

CPSS is a fully menu-driven information system that describes the chemistry of organic compounds found in waste materials. CPSS allows retrieval of information concerning molecular structures, reactions, physicochemi-

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cal properties, chemical names/synonyms, miscellaneous chemical information, and comprehensive chemical nomenclature. Each compound (current total 1700) is assigned a unique identification number for relational linking among the numerous data tables. CPSS contains a wide selection of physicochemical properties that would be of use in designing or implementing environmental fate models.

With CPSS, querying for particular chemical classes requires no knowledge of chemical structure. Instead, use is made of a comprehensive hierarchical menu system based on numerous attributes of chemical structure. Queries for practically limitless combinations of functional groups can be executed simply by selecting appropriate functional group names. Complex queries are made possible by the use of an iterative filter system.

CPSS contains an index of all alternative names for each compound. These include CAS, IUPAC, common, trivial, and trade names, and acronyms. Compounds can be queried on the basis of any of their names, roots, or approximations. The synonyms facility serves as a cross-referenced thesaurus of chemical names. Currently, for 1700 compounds there are 5784 synonyms.

CPSS nomenclature encompasses a broad spectrum of terminology that could potentially be of relevance to any of the other EROC modules. Representative classes of information include *a)* nearly all of the potentially relevant prefixes and suffixes in organic chemistry that comprise "substitutive nomenclature"; line structures and definitions are given for chemical radical names; *b)* common abbreviations and acronyms, especially those used in the fields of chemistry and the environment; *c)* information on the elements of the periodic table; *d)* units of measure; *e)* common and uncommon prefixes and suffixes; *f)* thorough listing and definition of chemical classes, including representative line structures; *g)* listing and line structures for all common aromatic and heteroatomic ring systems; and *h)* other related nomenclature for organic and analytical chemistry, chemical engineering, and toxicology.

Specific uses of EROC are numerous. Those that would have immediate utility include abstraction of information critical to pollution monitoring. For example, many geographical areas (especially in the western United States), could support commercial development of multiple types of industries for hydrocarbon extraction/conversion. Marker, or tracer, compounds will need to be identified so that the source of suspected pollution episodes can be inferred from monitoring data. The minimum number of types and the relative concentrations of the suite of compounds describing the unique "fingerprint" of a particular waste can be extracted from the EROC data base by means of factor analysis. Data on commonalities and unique qualities of different wastes would also be valuable for anticipating new water- and air-quality regulations that will probably evolve during construction of commercial-scale facilities; such regulations are likely because of the unique nature of the raw materials and processes that would be used by these industries.

Version β-1.0[2] of CPSS is currently available from Dr. Christian Daughton.

Other projects completed during FY 1988 include investigation of the importance of vapor-phase photochemistry in the environmental fate of nitrogen heterocycles that could be emitted to the atmosphere from the retorting of oil shale;[3] and development of a numeric model for removal of dissolved ammonia from wastewaters by use of a membrane separation technique that uses microporous polytetrafluoroethene tubes.[4]

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Studies of Animal Cell Cultures in Hollow-Fiber Reactors*

E. Fernandez, A. Mancuso, D. Clark, and H. Blanch

Normally, observations of extracellular reactor conditions allow only indirect understanding of the catalytic processes occurring inside the cell. To observe the intracellular environment directly, we have applied nuclear magnetic resonance (NMR) spectroscopy. This technique is particularly appealing because it is noninvasive, involving only static magnetic fields and radio waves. A hollow-fiber culture system/NMR probe combination has been developed which is compatible with commercially available spectrometers. This permits observation of phosphorylated and carbonaceous metabolites inside hybridoma cells.

NMR has two disadvantages relevant to studies of mammalian cells. First, it is relatively insensitive when compared to other analytical methods. As a result, previous investigators have used NMR spectroscopy to study cells at high densities to maximize the signal-to-noise ratio obtained. Second, commercial NMR sample probe

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geometries restrict the amount of apparatus that can be used to support a cellular sample. Consequently, mass transfer of nutrients and waste products has been poor, and the samples under study have generally only been stable for a few hours at a time. While such a system can provide useful qualitative metabolic information, we have been interested in exploiting the quantitative nature of NMR in steady-state and transient studies of animal cell metabolism. Our goals, therefore, have been to develop an apparatus that maintains hybridoma cells at the high densities necessary for NMR experiments and provides adequate mass transfer for nutrients and waste products, allowing us to study a stable culture for days or weeks.

We have chosen the hollow-fiber bioreactor (HFBR) for these studies because it can provide high cell densities (near those found in animal tissue) and has good mass-transfer characteristics. The culture system is designed for long-term operation, including stable temperature control ($< 0.1°C$), and has conventional probes for dissolved oxygen and pH. Dissolved oxygen and pH control are accomplished manually by mixing CO_2, N_2, and O_2. Because environmental control has been a high priority, we have abandoned use of commercial NMR probes and designed and constructed our own probes to permit greater flexibility in the design of the culture system.

The most important part of NMR probes is generally the rf coil, or "antenna," used to irradiate the sample with radio waves and receive the subsequent emitted signal. The coil must be capable of handling the high voltages used in transmission (100 V or more for short periods) and sensitive enough to detect the small voltages induced in the coil by the sample after irradiation (on the order of microvolts). In addition, to maximize the signal-to-noise ratio, we have been interested in increasing the size of the sample. We have evaluated three different coil designs for this application: the solenoid, the loop gap resonator (LGR), and the slotted tube resonator (STR). Of these, only the STR is aligned coaxially with the cylindrical NMR probe and the homogeneous portion of the static magnetic field. Thus, although we found the other two coil designs to be more sensitive (30-40% per unit volume at 15 ml), we chose the STR for reasons of convenience.

Based on these test data, we have designed and constructed NMR probes for single-resonance ^{13}C and ^{31}P NMR experiments at 9.4 tesla. We have also constructed a tunable probe capable of both ^{13}C and ^{31}P NMR. A coil tuned for the ^{1}H frequency was also included in the tunable probe to facilitate optimization of the static magnetic field based on the signal from water in the sample.

By mounting the HFBR inside this last probe, we have been able to observe phosphorylated metabolites in hybridoma cells online. To date, we have examined the cells under three different conditions: *a)* during an interruption of medium flow (effectively a rapid starvation of oxygen); *b)* before, during, and after a glucose step change; and *c)* over several hours, under varied oxygen levels. Examination of these NMR data suggests that most energy in these cells is derived from oxidative phosphorylation rather than from glycolysis.

We have also performed a preliminary steady-state ^{13}C NMR experiment in which the glucose in the feed was changed from naturally abundant glucose to glucose labeled with ^{13}C in the C-1 position. This experiment showed lactate, alanine, and some unidentified compounds.

Future research topics are examined in the following paragraphs.

CONTINUOUS MEASUREMENT OF P:O RATIO

To measure an apparent P:O ratio, we plan to use NMR techniques to measure the rate of ATP hydrolysis and/or formation and conventional methods to measure the oxygen uptake rate. If the cells are deriving most of their energy from oxidative phosphorylation, this number should be near three. Anything over this number would represent a significant contribution to energy production by other pathways (*e.g.*, glycolysis).

MEASUREMENT OF GLYCOLYTIC RATE

By performing ^{13}C NMR experiments involving ^{13}C-labeled glucose, we expect to obtain a glycolytic rate by monitoring lactate production from glucose as well as glucose consumption rate. This data would complement measurement of the P:O ratio.

STEADY-STATE ^{13}C EXPERIMENTS

We would like to examine the relationship between glutamine, glucose, and oxygen by performing experiments utilizing ^{13}C-labeled glutamine or glucose to monitor the formation of intermediates and products of their metabolism under different concentration ranges of these nutrients. We are interested in examining the dependence of energy production, waste product formation, and antibody formation under various conditions.

Separations by Reversible Chemical Association*

C.J. King, A.S. Kertes, J. Tamada, D. Arenson, A. Garcia, L. Poole, J. Starr, W. Rixey, and M. Ng

Reversible chemical association, or complexation, is an attractive method for recovery of carboxylic acids, alcohols, glycols and related substances from the dilute solutions resulting from manufacture by fermentation of biomass. We have focused upon extraction and sorption processes.

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EXTRACTION OF CARBOXYLIC ACIDS

We have measured equilibria for extraction of acetic, succinic, malonic, lactic, maleic and fumaric acids from aqueous solution by Alamine 336 (Henkel Corp.; tri-C8 to C10 amine) in several diluents, including heptane, methyl isobutyl ketone (MiBK), chloroform, methylene chloride, and nitrobenzene. The association constant for the complex depends upon the acidity of the acid and the chemical nature of the diluent. Tendencies for overloading (more than one acid extracted per amine) are also strongly affected by the chemical nature of the diluent. In light of spectroscopic measurements and comparable results from prior studies, we have interpreted our results through mass-action-law modeling. We have obtained and interpreted exploratory data underlying regeneration of amine extracts by four different methods: *a)* back-extraction into water following a change in temperature; *b)* back-extraction into water following a change in diluent composition (can be combined with *a*); *c)* precipitation of a low-solubility acid (*e.g.*, fumaric) following evaporation of diluent and/or temperature change; *d)* back-extraction into an aqueous solution of a volatile tertiary amine, followed by concentration and decomposition of the trialkylammonium carboxylate to produce the product acid and the light amine for recycling.

Future research will explore more deeply the various methods of regeneration and will investigate alcohol and phenol diluents and competitive equilibria in the presence of multiple acids.

SORPTION OF CARBOXYLIC ACIDS

We have used various functionalized basic polymeric sorbents to measure and interpret equilibria for uptakes of acetic acid and water from aqueous solution. We have also measured and interpreted equilibria for leaching of sorbed acetic acid by solvents having various degrees of basicity. Most basic sorbents are difficult to regenerate; however, we have demonstrated the feasibilities of regenerating Dowex MWA-1 tertiary amine resin (Dow Chemical Co.) by hot-air stripping, regenerating Aurozez polybenzimidazole resin (Celanese Chemical Co.) by leaching with successively less polar solvents, and regenerating polyvinylpyridine sorbents by leaching with common solvents.

EXTRACTION OF ALCOHOLS AND GLYCOLS

We have found that phenols interact more strongly with alcohols than do other common solvents. In studies of extraction of ethanol and the four butanol isomers by m-cresol in various diluents, we have shown that specific 1:1 alcohol:cresol complexes are formed.

Future research will address extraction of glycols, use of sorbents with phenolic groups, other functional groups effective for complexing of alcohols and phenols, and the possibility of recovery of glycols through adductive crystallization.

NON-WET ADSORBENTS

Sufficiently non-polar polymeric adsorbents, such as styrene-divinylbenzene and pyrolyzed sulfonated styrene-divinylbenzene copolymers, are not wetted by dilute aqueous solutions. In the non-wet state, such adsorbents take up solutes of moderate and high volatility at substantial rates. They provide advantages of low concomitant water uptake and an ability to fractionate among solutes on the basis of volatility. Measurements of adsorption of acetic and propionic acids, ethanol, and 1,3-butanediol have demonstrated that the rate limit is Knudsen diffusion through pores, and that performance of fixed-bed adsorbers can be rationalized through that concept.

Future work will explore the use of these non-wet adsorbents at higher temperatures, which should give economically attractive uptake rates for glycols.

Ultrasensitive Laser Spectroscopy*

R.E. Russo, J.D. Spear, and R.J. Silva

Photothermal laser spectroscopic techniques were developed for ultrasensitive optical absorption measurements of rare-earth and actinide solutions. The techniques developed and compared in FY88 were photothermal deflection (PDS) and thermal lensing (TLS) spectroscopies. For PDS and TLS, we investigated using modulated continuous-wave (cw) and pulsed laser excitation sources.

Optical absorption by the modulated or pulsed excitation laser and subsequent non-radiative relaxation (heating) induce a refractive index gradient in the sample solution. For TLS, a probe laser propagating collinear to the excitation laser will be defocused by the induced refractive index gradient. A pinhole and photodiode are used to measure the change in probe-beam intensity due to defocusing, which is related to the optical absorption. For PDS, the excitation and probe beams cross. The refractive index gradient causes a deflection of the probe beam. A lateral position sensor measures the deflection, the magnitude of which is related to the sample's absorption coefficient. PDS probes the maximum gradient of the refractive index whereas TLS probes its curvature.

For FY 1988 cw work at LBL, we employed an argon-ion pumped dye laser, using rhodamine 6G dye to excite the 575 nm transition of N^{3+} (molar absorptivity = 6.9 L/mole cm). We developed a dual-beam differential arrangement for both the PDS and TLS systems. Dye laser power normally used was 50 mW at 575 nm. Using both cw PDS and TLS, we can regularly measure Nd

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down to 3 x 10^{-6} molar. The signal-to-noise ratio at this concentration is ~10 for PDS and 18 for TLS. The TLS system appears to be slightly more sensitive, although further work is needed to optimize both systems and obtain an accurate comparison.

At LLNL, both PDS and TLS were developed using the pulsed Nd:YAG pumped dye laser. For Nd^{3+} (at λ = 521 nm, molar absorptivity = 4.7 L/mole cm), we measured a concentration of 3 x 10^{-6} M in 0.001 M HCl, with a signal-to-noise ratio of ~65. The detection limit (S/N = 3) is therefore calculated to be 1.4 x 10^{-7} M. This detection limit is the best obtained for any of our techniques, including photoacoustic spectroscopy (PAS). In addition, the PDS detection limit reported above was obtained using only 0.75 mJ/pulse, compared to the 2 mJ/pulse normally employed for PAS. Therefore, the absorptivity (cm^{-1}) for Nd using pulsed PDS (1 mJ/pulse) would be ~4 x 10^{-7}, a better value than those reported in the literature for comparable techniques. A lower pulse energy was required using PDS and TLS because the beam is tightly focused, compared to PAS, and the resultant high power density causes ablation of the sample cell. Also, the PDS data seem to be affected by long-term drift. We can average longer with the PDS and TLS techniques, compared to PAS, but the spectrum becomes influenced by long-term drift. At this time, it is not known where the drift originates.

We have preliminary results for pulsed TLS. Although we can easily measure 1 x 10^{-5} M, the spectrum is strongly influenced by the spectrum of the dye laser itself. In TLS, the excitation and probe beams overlap (collinear). A bandpass filter is used to pass the HeNe laser to the photodiode but not the excitation dye laser. However, because of the high peak power of the dye laser, a small amount of excitation light leaks through the filter and is measured by the photodiode. A more effective filter or use of a crossing configuration would permit an accurate detection limit for Nd using pulsed TLS.

During FY 1989, the sensitivity of TLS will be improved by using a better blocking filter to eliminate the excitation wavelength from the detector photodiode. These photothermal techniques will be employed to measure complexation constants for actinides in various aqueous solutions.

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Pulsed Laser Ablation for Thin-Film High-Temperature Superconductors*

R. Russo and B. Olsen†

This project involved study and development of pulsed laser ablation for making thin-film high-temperature superconductors. Laser ablation involves non-thermodynamic, shock-wave processes that occur from the interaction of a short-pulsed, high-energy laser focused on a solid material surface. Material with the exact stoichiometry as the target can be removed. The ablated material is collected on a substrate placed in close proximity to the ablation plume. We have used this technology to produce superconducting thin films of $YBa_2Cu_3O_{7-\gamma}$.

During FY 1988, a pulsed laser ablation system was designed and constructed as a joint effort between the Lawrence Berkeley Laboratory (LBL) and the Lawrence Livermore National Laboratory (LLNL). The system is housed at LLNL because of the availability of an excimer laser. A vacuum chamber was constructed containing several feedthroughs, a filament heater, and optical ports. The chamber accommodates four separate bulk targets and substrates simultaneously. With these capabilities, we can deposit multilayered films from different materials and can deposit several films consecutively without exposing the chamber to the environment.

A pulsed high-energy excimer laser was used because its characteristic ultraviolet wavelength contributes to a photophysical interaction with less thermal evaporation involved in the material removal processes than would be the case using infrared lasers. The laser can deliver up to 1.5 J per pulse at 308 nm. We use 750 mJ per pulse and lightly focus the beam to obtain 1.5 J/cm^2 energy density on the targets. Strontium titanate substrates, placed 1.5 cm from the bulk target, were used to collect the ablated vapor. With these conditions, we achieved a deposition rate of ~5 Å per pulse (repetition rate of one pulse per second). The laser ablation approach maintains excellent control of the material's stoichiometry with these condi-

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tions; the elemental composition ratio in the film matched that in the bulk target. Analytical techniques of x-ray fluorescence, Auger spectroscopy, Rutherford spectroscopy, and atomic emission spectroscopy were used to compare the elemental composition ratio of the bulk and thin-film samples.

The figure shows resistance *vs* temperature for one of our YBCO films. The film is ~2 μm thick on a 5 x 5 mm^2 strontium titanate substrate. The film was annealed over a ten-hour period with a maximum temperature of 850°C. The onset of superconductivity occurred at 92°K with zero resistance reached at 72°K. Resistance was measured with a standard four-point probe technique.

During FY 1989, an improved laser ablation system will be constructed at LBL. This system will provide the capability for depositing multi-layered, thin-film configurations and for depositing films in a reactive, secondary plasma environment. We plan to deposit superconducting films from materials containing bismuth and thallium, and to produce films that are superconducting as deposited, *i.e.*, without post annealing.

Interactions with industry will be initiated to determine their needs in this field and to explore possible collaborative efforts.

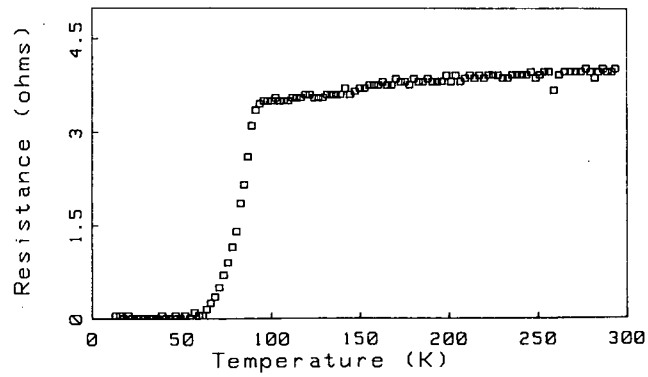

FIGURE. Plot of resistance *vs* temperature for a YBCO film. The film is ~2 μm thick on a 5 x 5 mm^2 strontium titanate substrate. The film was annealed over a ten-hour period with a maximum temperature of 850°C. The onset of superconductivity occurred at 92°K, with zero resistance reached at 72°K. The resistance was measured using a standard four-point probe technique (XBL 8812-4093).

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