

## Economical Membrane Identified for Zinc/Ferricyanide Battery

Charles Arnold and Roger Assink, chemists at the Organic and Electronic Materials Department, Sandia National Laboratories, recently developed a membrane that can significantly reduce the cost of the zinc/ferricyanide battery. The membrane is made from sulfonated polysulfone, a little known polymer.

The zinc/ferricyanide battery is one of several being studied as part of the U.S. Department of Energy's Exploratory Battery Technology Development & Testing (ETD) Project. The ETD Project promotes development of advanced rechargeable batteries by providing a bridge between fundamental studies of electrochemical reactions suitable for batteries and the product engineering capabilities of private industry. Development of the membrane was also partly supported by the Applied Sciences Division of Lawrence Berkeley Laboratory.

The zinc/ferricyanide battery uses zinc and sodium ferrocyanide stored in separate external reservoirs as saturated solutions in a sodium hydroxide electrolyte. As the battery is being charged or discharged, electrolyte with zinc salts is pumped into one side of a cell; electrolyte with the other active agent flows into the other side.

The commercial future of this battery has been dim because even though it performs efficiently, the only known material that worked as a membrane, a fluorinated polymer, cost about \$30/ft<sup>2</sup> representing about 50% of the battery's total cost. The sulfonated polysulfone membrane was chosen from a group of materials that would cost no more than \$5/ft<sup>2</sup>. Polysulfones are long chain polymers with very good chemical stability. Sulfonation contributes the conductive property. Polysulfones can easily be made into cellophane-like sheets; and the resulting membranes are highly conductive, semipermeable, and can withstand the extremely corrosive environment in a zinc/ferricyanide battery.

Initial performance analysis of a single zinc/ferricyanide test cell with a sulfonated polysulfone membrane showed an average energy efficiency of 77% over more than 500 two-hour-charge/two-hour-discharge cycles. The average efficiency was increased to 82% by adding more ionic sulfonate groups to the formula and using thinner films to increase conductivity. A continuous washing system was also installed to remove inorganic sodium salt buildup during polymer preparation.

Although the new membrane can significantly reduce the cost of a zinc/ferricyanide battery, this system still faces serious competition from other developing advanced technologies, especially the zinc/

bromine and sodium/sulfur systems. The ultimate acceptability of any of these batteries will be based on total life cycle costs that include initial purchase price, lifetime, operating efficiency, and maintenance.

If results with the experimental unit continue to be encouraging, the next step is to build and evaluate a multicell stack module. Other types of rechargeable batteries being studied in the ETD Project are already in or past this phase of development.

Arnold and Assink, both members of the Materials Research Society, are continuing to develop sulfonated polysulfone as a battery membrane and are studying other possible uses for the material.



B.H. Kear

## B.H. Kear Appointed Chairman of NMAB

Dr. Bernard H. Kear has been appointed chairman of the National Materials Advisory Board (NMAB) for a three-year term. The NMAB functions within the Commission on Engineering and Technical Systems of the National Research Council. The Board is concerned with the entire life cycle of materials—from their origin at the resource level through their useful application to their eventual disposal or reclamation. NMAB provides a national forum that focuses on scientific and technical problems and opportunities, on policy issues related to engineering, industrial, structural, electronic, and biomedical materials, and on the sociotechnical impact of their use. Through working groups of experts selected from academia, industry, and government, NMAB provides a mechanism to define materials problems, issues, and opportunities, to suggest possible solutions, and to stimulate appropriate action.

Kear has also recently begun a dual role at Rutgers University. He is the State of New Jersey Professor of Materials Science and Technology and also director of the new Center for Materials Synthesis. He was previously a scientific advisor with Exxon Research and Engineering Company, where he was involved in research on surface modification and the chemical synthesis of materials.

Kear's diverse background includes degrees in metallurgy; studies of the effects of long-range ordering on the plastic

properties of crystals; investigations of the relationships of structure, properties, and processing in superalloys; participation in the development of single-crystal turbine blade technology; and a position where he spearheaded the development of laser surface modification of materials. Kear has published extensively and has been awarded 23 patents on various aspects of materials processing and optimization. He was awarded the Mathewson Gold Medal by The Metallurgical Society of AIME in 1971 and the Howe Medal by the American Society for Metals in 1970. He is a member of TMS-AIME, a Fellow of ASM, and is active in the Materials Research Society. Kear was a Councillor for MRS from 1982 to 1985, a meeting co-chair for 1983 MRS Annual Meeting, and a co-editor of *Rapidly Solidified Metastable Materials* (Vol. 3, MRS Symposia Proceedings series). Currently, he is co-chair of Symposium V on Multi-component Ultrafine Microstructures at the 1986 MRS Fall Meeting.

## Zirconia-Based Process Toughens Glass-Ceramics

Keith Keefer and Terry Michalske, scientists in the Ceramics Development Division at Sandia National Laboratories, have developed an inexpensive process that increases the strength and toughness of glass-ceramics and improves their corrosion resistance.

The use of zirconia in two forms and for two distinctly different purposes led to the improved performance—crystalline zirconia helps strength and toughness; uncrystallized zirconia aids corrosion resistance. The tetragonal-to-monoclinic zirconia crystal change has been used to toughen ceramics for about 10 years, but it has never been used for this purpose in glass-ceramics.

Glass-ceramics made by this new process may be particularly useful when formed into fibers that strengthen composite materials. The resulting glass-ceramic resists attack by aqueous alkalis because of the uncrystallized zirconia that remains in the matrix. "It's this trait that may prove to be the most useful," says Keefer. "Glass fibers now used to reinforce concrete tend to corrode rapidly in wet concrete, greatly reducing their strength. The fibers of zirconia-toughened glass-ceramics would not have this problem."

The patented processing technique produces unstable tetragonal zirconia crystals in a glass-ceramic. These crystals experience a spontaneous "martensitic" phase transformation to monoclinic crystals when a crack passes nearby. Monoclinic crystals, larger and less symmetrical than tetragonal ones, essentially close the crack, making it harder for the crack to grow. Research

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shows that glass-ceramic toughness can double when about 10% of the zirconia it contains crystallizes.

Typical compositions, on a weight basis, of glass-ceramics suitable for zirconia phase transformation toughening are 61-65% network-forming oxide, (silica, boria, alumina, or a combination), 10-15% network-modifying oxide (oxides of sodium, potassium, rubidium, calcium, and lithium, or a combination), and 21-28% zirconia.

To make a glass-ceramic using the new technique, researchers first heat powdered ingredients to a homogeneous melt at temperatures below 1700°C. (This permits objects to be shaped while the glass is still molten.) At this temperature, noncrystalline zirconia is dissolved in the molten mass. As the melt cools, tetragonal zirconia crystals precipitate out of the solution. To keep enough of them in the tetragonal phase, the melt must either harden to a glass above 900°C, or undergo a carefully controlled heat treatment so that the tetragonal crystals formed at 1200°C do not redissolve and reprecipitate in the monoclinic phase.

"The process yields tetragonal crystals of such a large size that they are not stabilized by surface energy effects," says Keefer. "Because of this instability, they transform to the monoclinic form under mechanical stress, an action that toughens the glass."

Examination of zirconia-toughened glass-ceramics at the Stanford Synchrotron Radiation Laboratory confirmed that toughness is proportional to the amount of zirconia transformed to monoclinic crystals. It also showed that the transformed crystal zone is limited to crystals that actually touch a crack. "That is why small tetragonal crystals do not increase toughness as much as large ones," Keefer says. "With large crystals, much more material is transformed." Keefer is a member of the Materials Research Society.

## ORNL Tests Superconducting Magnets for Fusion Research

Full-scale testing of six 45-ton superconducting magnets has begun at Oak Ridge National Laboratory's (ORNL's) International Fusion Superconducting Magnet Test Facility. The array of three U.S.-built and three foreign-built electromagnetic coils produced a magnetic field of 8 Tesla and allowed successful tests of one of the coils at its design values of magnetic field and current. These tests have been a major objective of ORNL's fusion energy program since the inception of the multinational collaboration more than 10 years ago.

The test magnets, about one third to one half the size of those that will be needed for operating fusion power reactors, were designed and built by industrial teams

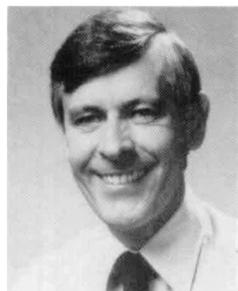
under the terms of an agreement arranged by the International Energy Agency. Four partners are included: the United States (through the U.S. Department of Energy), Japan, Switzerland, and the European Atomic Energy Community (EURATOM).

In the United States, magnets were produced by General Dynamics-Convair Division, Westinghouse Electric Corporation, and General Electric Company. The other three magnets were produced by Hitachi for the Japan Atomic Energy Research Institute; by Siemens AG for the Nuclear Research Center, Karlsruhe, West Germany (for EURATOM); and by Brown Boveri & Company, Ltd., for the Swiss Institute for Nuclear Research.

Although the six test magnets are externally similar, their internal designs reflect each team's independent ideas on how best to achieve the required performance specifications. Each country has access to all magnet test data.

## G. Kostorz Directs Institute of Applied Physics

Prof. Dr. Gernot Kostorz has terminated his two-year term as dean of the faculty of materials science and engineering at the Swiss Federal Institute of Technology (Eidgenössische Technische Hochschule or ETH) in Zurich. Hans Böhni is the new dean beginning October 1986. Kostorz, a member of the Materials Research Society, will continue as director of the Institute of Applied Physics of the ETH.



A. Wolfenden

## A. Wolfenden Receives Doctor of Science Degree

Alan Wolfenden, Halliburton Professor of Mechanical Engineering at Texas A&M University was one of two recipients of the advanced degree of Doctor of Science from the University of Liverpool (England). The degree, awarded to candidates who have distinguished themselves by their published contributions to science, was conferred at ceremonies in Liverpool on July 11, 1986. Wolfenden has published over 100 articles on such topics as electron microscopy, plastic deformation, measurements of elastic modulus, and damping. His articles have been published in *Acta Metallurgica* and *Journal of Materials Science*. Wolfenden, a

member of the Materials Research Society, is editor of the *Journal of Testing and Evaluation* published by the American Society for Testing and Materials.



F.W. Saris

## F.W. Saris Named Director of FOM-Institute

Frans W. Saris was named director of the FOM-Institute for Atomic and Molecular Physics in Amsterdam, the Netherlands, effective July 1, 1986. The FOM-Institute in Amsterdam belongs to the Foundation for Fundamental Research on Matter, which is part of the Netherlands Organization for Advancement of Pure Research. The research program of the FOM-Institute includes atomic and molecular physics, surface and materials science, and plasma physics.

Saris has been a member of the FOM staff since 1964. In 1973 he became group leader of surface science, and in 1978 deputy director. He has been adjunct-professor at the University of Utrecht since 1980. Currently, Saris serves on the editorial board of *Materials Science Reports*, *Nuclear Instruments and Methods*, *Materials Letters*, and *Vacuum*. He has published 60 journal articles in atomic physics and more than 100 articles in surface and materials science.

He has been a visiting scientist at CRNL (Canada), Kansas State University, IBM Research Center, Cornell University, and Beijing Normal University. In 1974 he was awarded the Röntgen-plakette, in 1975 the Röntgenprice, and in 1986 he shared the Jacob Kistemaker Prize with Dr. Friso van der Veen for their work on ion beam crystallography. Saris is a member of the Böhmsche Society and the Materials Research Society.



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