Solid State Ionics

Robert A. Huggins, Guest Editor

This issue of the *MRS BULLETIN* contains three articles relating to the general field that has come to be known as Solid State Ionics. The central feature of this area of science and emerging technology is the rapid transport of atomic or ionic species within solids, and the various phenomena, of both scientific and technological interest, that are related to it.

Attention to this area has grown greatly in recent years because of the rapidly increasing recognition of the possibility of a wide range of interesting technological applications. One example already widespread is the use of an oxygen-conducting solid electrolyte as the critical element in the oxygen sensors installed in the exhaust systems of almost all current automobiles to reduce deleterious emissions and improve the efficiency of the combustion process.

Work is under way in a number of other directions, including static and dynamic chemical sensors, solid state electrochemical reactors, low impedance selective atomic filters, new concepts for the direct conversion of heat to electricity by the use of sodium- or hydrogen-transporting cycles, a novel method for the low cost electrolysis of water at intermediate temperatures, batteries that can store greatly increased amounts of energy, ion exchange materials, solid state laser hosts, high efficiency fuel cells, electrochromic materials and configurations for both optical displays and "smart windows," advanced catalysts, atomic reservoirs and pumps, high temperature superconductors, and possibly solid state fusion hosts.

Despite this recent attention, however, it is worth noting that interest in solids in which ionic species can move with unusual rapidity is actually not new at all. As early as 1839, Michael Faraday[1] reported measurements on several materials that showed an unusual increase in electrical conductivity at elevated temperatures, contrary to that found in normal metals. One of these was PbF_2, and another was Ag_2S.

These two materials are now known to be representatives of the two general classes of fast ionic materials. Electronically insulating materials in which ionic transport is rapid have electrical properties comparable to those of molten salts, and thus can be employed as solid electrolytes. PbF_2 is now recognized to be an outstanding example of an anion-conducting solid electrolyte, in which electrical charge is carried primarily by the transport of fluoride ions. Ag_2S, on the other hand, is a prototypical mixed conductor, in which both ionic and electronic species can transport charge. As shown by Wagner[2] in the early 1930s, the nature of adjacent phases can influence whether charge is carried primarily by ions or by electrons in mixed conductors.

As early as 1914, Tubandt and Lorenz[3] showed that the ionic conductivity of solid electrolytes can be extremely high. For the high temperature alpha phase of AgI, it even exceeds the values observed above the melting point. Interpretation of the unusual behavior of such materials in terms of an unusually large degree of structural disorder in one of the sublattices was presented by Strock[4] in 1934 on the basis of x-ray diffraction observations. This important characteristic is also manifested by thermodynamic evidence of "sublattice melting" in a number of such materials at temperatures well below their macroscopic melting points.

The great acceleration of interest in fast ionic conductors, and especially their use as solid electrolytes, stems from observations that this is not just a high temperature phenomenon and that a number of solids can have high ionic conductivities even at ambient temperatures.[5-9] Particularly important was the work of Yao and Kummer, who showed that a number of different ionic species can exhibit rapid transport in the β-alumina structure. This led to the concept[10] of a radical approach to high performance rechargeable batteries involving liquid electrodes and a solid electrolyte, based on the reaction of sodium with sulfur by transport of sodium ions through solid ceramic materials in the β-alumina family.

Since that time there has been a great deal of progress in understanding the phenomena in the β-alumina type of materials, and in developing methods for their fabrication into practical configurations and devices. As discussed in the article by B. Dunn, G.C. Farrington, and J.O. Thomas in this issue, it is now recognized that this is not just a single compound, but a broad family of materials, with a wide range of compositions and two major structural variants.

They point out that the ability to insert a wide variety of monovalent, divalent, and trivalent guest species into one of these variants, the β'' structure, leads to interesting new possibilities. These include possibilities based on their rapid ionic transport, and also in solid state optical devices in which the local ionic environment plays a critical role.

The accompanying article by M.S. Whittingham discusses some of the interesting properties and phenomena in three classes of mixed conductors that exhibit appreciable amounts of both electronic and ionic transport.

In contrast to electronically insulating solid electrolytes (whose chemical compositions are constrained by charge balance considerations), in mixed conductors, changes in chemical composition can be balanced by changes in the electronic structure. This can give rise to a wide variety of properties, and, in some cases, the ability to vary them *in situ*.

One of the more obvious applications for such materials is as reversible reservoirs for atomic species such as hydrogen, lithium, sodium, and oxygen. This has led to their use as electrodes in new types of advanced batteries, and for the solid state storage of hydrogen.

Such materials can have extremely high rates of chemical diffusion, in some cases (e.g., Ag_2S at about 200°C) exhibiting diffusion coefficients comparable to those typically found in gases.[11] This makes some of these materials interesting as catalysts for several important reactions. Others can be used as fuel cell electrodes or selective atomic filters. One use of palladium alloys as filters for hydrogen purification is briefly discussed in Whittingham's article.

The ability to tailor properties by controlling the identity and concentration of mobile species inserted into a relatively static host crystal lattice can be especially interesting. One example is the so-called 1-2-3 phase of mixed-conducting copper oxide bronze superconductors. It is now recognized that its electronic transport properties are particularly sensitive to the oxygen stoichiometry, which can be established by controlling the oxygen activity and temperature during synthesis and preparation.

There are numerous other potential applications of mixed conductors. Particularly interesting is the possibility of varying the composition-dependent properties of many solids *in situ* by varying simple electrical parameters. One such direction being pursued is based on the ability to change the optical properties of some mixed-conducting transition metal oxide bronzes reversibly at ambient temperatures *in situ*. This leads to the possibility of electrochromic devices when such materials are used with liquid (or preferably solid) electrolytes in electrochemical configurations. Whittingham also discusses some materials of this type.

The third article in this issue, by M.A. Ratner and D.F. Shriver, covers polymer ionics. While many materials typically thought of as fast ionic or mixed conductors are inorganic and crystalline, it has been recognized for the last 15 years that rapid ionic transport can also be found in several families of polymeric materials containing dissolved salts. These materials, in which the polymer generally can be considered a solvent for mobile ionic species, are getting a good deal of attention as potential solid electrolytes for practical devices and systems.

As discussed in Ratner and Shriver's thorough article, both the structural and dynamic aspects of the host polymer greatly influence the ionic transport mechanisms in such materials. Thus some phenomena and properties are quite different from those found in organic crystalline solids, and one must think in terms of theoretical models somewhat different from those normally considered for transport in crystalline environments.

In addition, Ratner and Shriver point out examples of polymeric mixed conductors. The concept of using polymeric electrodes in electrochemical configurations as new types of batteries, sensors, and electrochromic configurations has received much visibility in recent years.

On March 23, 1989, Martin Fleischmann and Stanley Pons announced they had observed the evolution of appreciable quantities of excess heat when using an electrochemical cell to insert deuterium into palladium. They also reported that they could not explain their experimental results by any known chemical reaction, and proposed that they were the result of some hitherto unknown nuclear reaction involving the fusion of deuterium inside the palladium.

This announcement and the related paper (submitted March 13 to the *Journal of Electroanalytical Chemistry* and published in its April 10, 1989 issue) containing the proposal that a fusion reaction might take place inside a solid at ambient temperature — hence the term "cold fusion" — was so far removed from the conventional paradigm in fusion physics that it immediately elicited both incredulity and, in some quarters, scorn.

Great attention has been given to these issues in both the scientific community and the public press. There has been a rush to perform experiments to see whether the reported observations can be repeated, and whether the hypothesis that they are related to some type of fusion reaction can be confirmed.

Somewhat over two months later, as this is being written, it is increasingly obvious that something unusual is happening in the deuterium-hydrogen system, but the jury is still out regarding many details and the question of mechanism. A number of laboratories have reported observing thermal effects, some have detected low level neutron fluxes, and a few have found tritium. On the other hand, many others have not yet been able to conduct experiments that show such effects, and have reported negative results.

The hydrogen-palladium system is a well-known example of one type of fast mixed conductor, as pointed out in Whittingham's article. So is the analogous deuterium-palladium system. There has been a great deal of research on both of these over many years, and much is known about the insertion of protons and deuterons into them, both electrochemically and by controlling external pressure under relatively normal experimental conditions.

The major deviation from prior work in the Fleischmann-Pons experiments is the use of much more extreme electrochemical parameters so that the deuterium activity at the electrolyte-palladium interface is many orders of magnitude greater than is typically employed. Interpreted by some as imposing an extremely high virtual deuterium pressure, this provides the possibility of a noncommitant large influence on the stoichiometry and related properties.

Whether or not these unusual observations are due to some sort of fusion process in these materials, the chance is good that this activity will lead to a significant increase in both understanding and interest in mixed conductors of this general type.

In recent years, solid state ionics has received somewhat more attention in other countries than in the United States, and the seventh in a biennial series of International Conferences on Solid State Ionics will be held in Hakone, Japan in November 1989. The previous two were held in Lake Tahoe, California in 1985, and Garmisch-Partenkirchen, West Germany in 1987.

An indication however, of the increasing interest in this area by the U.S. materials research community was the inclusion of a symposium on solid state ionics at the 1988 Fall Meeting of the Materials Research Society. The proceedings of this meeting are now available.[12] In addition, the second of what may well become a continuing series of Gordon Conferences on this subject was held this summer.

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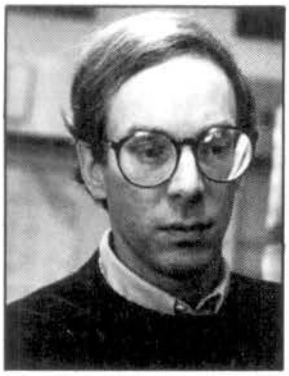
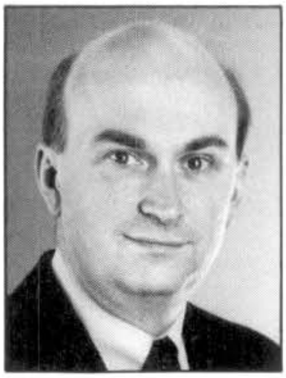
R.A. Huggins



B. Dunn



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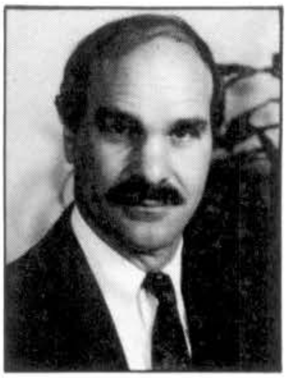
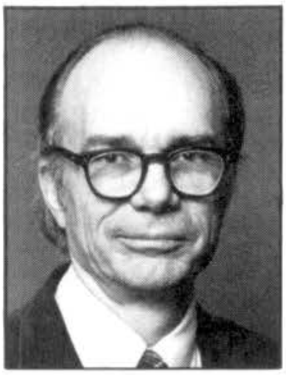
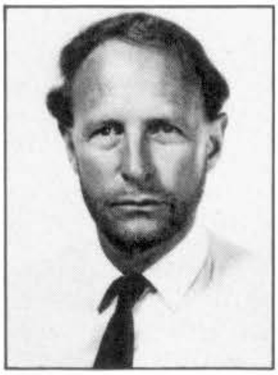


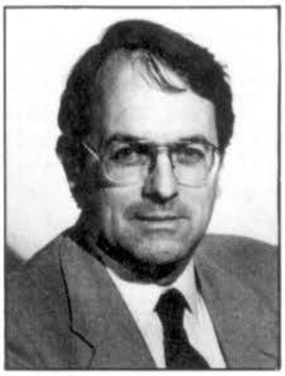
M. Ratner



D.F. Shriver



J.O. Thomas



M.S. Whittingham

Robert A. Huggins, Guest Editor for this issue of the *MRS BULLETIN*, is a professor in the Department of Materials Science and Engineering at Stanford University, California. After receiving degrees in physics and metallurgy from Amherst College and the Massachusetts Institute of Technology, he served as an instructor at MIT before joining the Stanford faculty in 1954. He was director of Stanford's Center for Materials Research from its initiation in 1961 until 1977. Huggins' research has spanned studies of imperfections in crystals, solid state kinetics, magnetism, mechanical behavior of solids, crystal growth, and solid state electrochemistry. He has recently focused on solid state ionic phenomena involving solid electrolytes and mixed ionic-electronic conducting materials containing atomic or ionic species with unusually high mobility, as well as their use in novel battery and fuel cell systems, electrochromic optical devices, sensors, and in enhanced heterogeneous catalysis. Of particular interest to Huggins now is hydrogen transport and hydride formation in metals, alloys, and intermetallic compounds. Huggins is currently an MRS councillor and president of the International Society for Solid State Ionics.

Bruce Dunn is professor of materials science at the University of California, Los Angeles. His principal research interests are in the synthesis of ceramics and inorganic solids and the characterization of their electrical and optical properties. His research interests in solid electrolytes and the β-aluminas span many years, from when he was a staff scientist at the General Electric R&D Center working on the sodium/sulfur battery and the electrochemical behavior of high temperature interfaces. He presently serves as chairman of the Department of Materials Science at UCLA.

Gregory C. Farrington is professor of materials science and engineering and chemical engineering at the University of Pennsylvania, Philadelphia, where he has been on the faculty since 1979. From 1985-1987 he served as chairman of the Department of Materials Science and Engineering and is currently director of the Laboratory for Research on the Structure of Matter. He earned a BS in chemistry from Clarkson University and a PhD in chemistry from Harvard. In 1984 he was awarded a DPhil (honorary) by the University of Uppsala, Sweden, in recognition of his research in solid state chemistry and electrochemistry. From 1972 to 1979, Farrington was a member of the research staff of the General Electric Research and Development Center in Schenectady, NY. His principal research interests are in electrochemistry, solid state chemistry, and polymer chemistry. He has been awarded 27 patents.

Mark Ratner is a professor in the Department of Chemistry at Northwestern University. His research interests include transport processes in molecular materials, including theoretical study of ionic conductivity, electronic conductivity, nonlinear optical response, and fracture processes. A theoretical chemist whose work is closely linked with experiment, his research efforts also include the dynamics of molecular and cluster systems, mean-field methods for description of enharmonic species, and electron and ion transport in biological materials. His degrees are from Harvard and Northwestern.

Duward F. Shriver is Morrison Professor of Chemistry at Northwestern University. He received his bachelor's degree from the University of California, Berkeley in 1958 and his PhD from the University of Michigan in 1961. He joined the chemistry faculty at Northwestern University in 1961, where he is a member of the Materials Research Center and the Catalysis Center. His research interest in preparative and physical inorganic chemistry have led his research group to synthesize and characterize new inorganic and polymeric electrolytes, as well as mixed ionic-electronic conductors.

John Oswald Thomas was recently appointed professor of solid state electrochemistry at Uppsala University, Sweden. After receiving his bachelor's degree in physics from Oxford University in 1965, he received a PhD in crystallography from London University in 1969, and then moved to a postdoctoral position at Uppsala, where he has remained since. His research interests have spanned experimental and theoretical studies of hydrogen-bonded systems, the development of the Rietveld x-ray powder refinement method and, more recently, structural and molecular dynamics studies of solid mobile-ion systems. His latest interest has been real-time studies of solid-state electrochemical processes by diffraction methods.

M. Stanley Whittingham is professor of materials chemistry and director of the Materials Research Center at the State University of New York at Binghamton. He was formerly with the Corporate Research Laboratories of Exxon Research and Schlumberger. He obtained his MA and DPhil in organic chemistry from Oxford University, and then spent four years at the Center for Materials Research at Stanford University. His research has focused on the synthesis, characterization and properties of nonstoichiometric inorganic compounds with emphasis on ambient temperature reactions, solid state electrochemistry and ion transport properties. His group discovered the ambient temperature lithium intercalation batteries. He has chaired many international and national meetings, including the 11th International Symposium on the Reactivity of Solids held in Princeton in 1988. Whittingham is the principal editor of *Solid State Ionics*. ☐

Letters to the Editor

Dear Editor,

Encouraged by your interest in readers' opinions and by emphasizing the Society's interdisciplinary approach, I wish to take up a special materials question.

Dental amalgam for filling carious teeth has been a matter of controversy for a long time. However, it has not been unambiguously shown that the amounts of mercury released by corrosion and wear are either neglectable or unacceptable from a biological point of view.

After years of interest in the issue, it is my opinion that the matter is suffering from lack of interdisciplinary approach. At the same time, there are a few questions with equally distinct interdisciplinary character as the question of dental amalgams, touching on fields such as metallurgy, electrochemistry/corrosion, mechanical properties, wear, analytical chemistry, toxicology, biology and biocompatibility, and medicine, e.g., neurology and immunology.

One of the reasons of the prolonged use of dental amalgams has been lack of attractive and better new dental materials. Thus, development of new materials with good properties at acceptable cost would make the use of mercury alloys for implants superfluous. The issue might perhaps be a challenge for MRS.

With best regards,

Jaro Pleva
Hagfors, Sweden