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FAST PROTONIC CONDUCTING SOLID ELECTROLYTES(U)
NORTHWESTERN UNIV EVANSTON IL M A RATNER ET AL 1987
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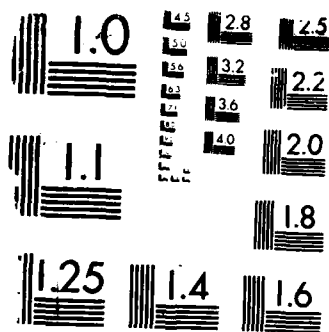
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MICROCOPY RESOLUTION TEST CHART

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Theoretical and experimental research on glassy and crystalline solid electrolytes materials has been pursued. In lithium aluminum silicate we found that the presence of disorder in the aluminosilicate framework can exert substantial effects on the conductivity of the lithium ion; in particular the activation energy for ionic motion is substantially lower in the glassy phase than in the crystalline one, despite the greater disorder in the glass. This was explained in terms of reduced effects of interionic correlation in the disordered material compared to the rigidly alternating crystal. This substantial reduction in the localizing effects of ionic correlations should be operative in all glasses, and may account for enhancements of conductivity in stoichiometric glass compositions at relatively low temperatures. Complex impedance spectroscopy, magnetic resonance, vibrational spectroscopy and differential anomalous scattering techniques have been used to study local

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structures in silver selenide-germanium selenide glasses. The data seem to show the coexistence of well-defined local order with typical glassy randomness.

Diffusion measurements on both uranyl phosphate and beta alumina protonic electrolytes were completed using nuclear magnetic resonance spectroscopy. The results strongly suggest that the simple for the Grotthus mechanism is not operative here.

A detailed study of the transport properties of the proton conducting hydrogen-uranyl-periodate-water glasses was made. The protonic conductivity and diffusivity are dependent on the partial pressure of water vapor in the surrounding atmospheric are photosensitive.

A theoretical dynamic percolation model was developed, which describes proton hopping in a dynamically disordered lattice. Some general theorems were proven relating dc conductivity to that in the static case. The model has also been applied to polymer electrolytes, where there is the additional reorientation of the local polymer chain segments.

A series of studies on the general issue of correlated motion in framework solid electrolytes was completed and three important conclusions were made. First, the structures of the mobile-ion array and of the framework lattice will determine the dc conduction. Second, corrections to this qualitative picture due to interionic correlation effects can be quite well approximated using the homogeneous approximation or one-component plasma. Thirdly, dynamical large-amplitude motions in the host lattice can produce entirely different mechanisms of dynamic percolation type.

Reynolds

Final Technical Report

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Summary of Completed Research

Theoretical and experimental research on two classes of solid electrolyte materials has been pursued. In the area of glassy solid electrolytes, we have measured and interpreted data on conduction in both glassy and crystalline LiAlSiO_4 . In this material, we find that the presence of disorder in the aluminosilicate framework can exert substantial effects on the conductivity of the Li^+ ion; in particular, the activation energy for ionic motion is substantially lower in the glassy phase than in the crystalline one, despite the greater disorder in the glass. This can be explained quite readily in terms of reduced effects of interionic correlation in the disordered material compared to the rigidly alternating crystal (Publication 4). This substantial reduction in the localizing effects of ionic correlations should be operative in all glasses, and may account for enhancements of conductivity in stoichiometric glass compositions at relatively low temperatures.

Analysis of X-ray and vibrational data obtained for the glassy LiAlSiO_4 has permitted discussion of the nature of the structural disorder in the glass (Publication 10). We find that the empirical Loewenstein rule, which requires strict alternation of Al and Si sites in aluminosilicate crystals, is substantially relaxed in the glass. Upon devitrification, the alternative structure reasserts itself. It is this framework disorder that is largely responsible for the reduction in correlation induced ion localization and consequent higher conductivity in these materials.

We have begun extensive study of the structure of a series of vitreous electrolytes based on $\text{Ag}_2\text{Se}-\text{GeSe}_2$ materials, using complex impedance spectroscopy, magnetic resonance, vibrational spectroscopy and differential anomalous scattering (DAS) techniques; we believe this to be the first application of DAS, a technique for obtaining local structures in the form

of partial radial distribution functions, to solid electrolytes. While still incompletely analyzed, the data seem to show quite clearly the coexistence of well-defined local order with typical glassy randomness on a distance scale of 3-5 coordination shells. There is also some evidence for heterogeneous regions, such as have been invoked very recently (1987) by Ingram to explain the mixed alkali effect in glasses.

Protonic solid electrolytes are of major interest as fuel cell materials. We have completed a series of diffusion measurements, using pulsed-field-gradient nuclear magnetic resonance spectroscopy, on both uranyl phosphate and θ " alumina protonic electrolytes. (Publication 3) These are, to our knowledge, the first diffusion measurements made on these substances, and they strongly suggest that the simple form of Grotthus mechanism, with rotational motions "renewing" the lattice for a series of proton jumps, is not operative here. Dielectric loss measurements show that there is a substantially higher activation energy for dielectric loss than for conductivity. Since dielectric loss should be sensitive to the rotational motions, these measurements suggest that rotation is not the rate-determining step.

Some very preliminary work done by Howe and Shilton ten years ago on the hydrogen-uranyl-periodate-water system revealed the possibility of fast proton conduction in glasses of the general composition $H_{5n-2}UO_2(10_6)_n \cdot mH_2O$ with $1.0 \leq n \leq 1.5$ and $m = 3$ or 5 . We have made a careful and detailed study of the transport properties of these proton conducting glasses and found that they exhibit values of proton conductivity and pulsed field gradient NMR diffusivity which rank them among the best of the solid proton conductors investigated to date. Another interesting observation made during our

investigation was that both the protonic conductivity and diffusivity are strongly dependent on the partial pressure of water vapor in the surrounding atmosphere. Moreover, the impedance of these glasses was found to be photo-sensitive and to decrease in magnitude when they were exposed to a sudden intense flux of light. It has been known for some time that photoexcitation of UO_2^{2+} ions in water solutions abstracts hydrogen from the water molecules and that subsequent reactions produce protons and hydronium ions. We postulate that an excitation process of the UO_2^+ in our glass, similar to this, is, indeed, responsible for increasing the concentration of protonic carriers in our glass specimens when they are exposed to light and that this increase in protonic concentration is responsible for the observed decreases in specimen impedance.

Theoretical work on the protonic materials has been based on a dynamic percolation model, which describes proton hopping in a dynamically disordered lattice, with the dynamic disorder arising from local rotations of the network. We have been able to prove some general theorems relating dc conductivity to that in the static (rotation-free) case (Publications 1,2), and to derive some interesting results about the nature of the threshold region for ionic motion as the completeness of the protonic net as well as the rate of hindered rotations about hydrogen bonds, varies (Publication 11).

The dynamic percolation model is useful for description of conductivity in any solid electrolyte in which diffusion occurs due to two separate processes. In H-bonded protonic electrolytes, the Grotthus type mechanism would involve hops and local rotations as these two sorts of motion. In polymeric electrolytes, including some of the newest proton-conducting solid electrolytes being studied in Grenoble, the two steps are carrier hopping

and reorientation of the local polymer chain segments. We have investigated the application of dynamic percolation to these polymer species in some detail, and have shown how the macroscopically based free volume model relates to the dynamic percolation (Publication 5); essentially, the renewal time characterizing the evolution of the percolation geometry is fixed by the amount of free volume. Limitations of the free-volume idea, especially kinetic limitations, have also been stressed (Publications 5,12).

We have also completed a series of studies on the general issue of correlated motion in framework solid electrolytes, focusing particularly on the relationship between the static and dynamic structure and the conductivity. We find a very good qualitative relationship with the local effective potential arising from the bare potential plus the average of interionic repulsions. This effective potential determines the dc conduction very well in cases of a strong-damping. (Publications 6,7,12) In the weak damping regions, relevant at lower temperatures, there remain very substantial dynamical correlations, and the activation energy for conduction differs from that fixed by the effective local potential.

We find that the liquid structure function $s(\vec{q})$ and dynamical structure function $s(\vec{q},\omega)$ are themselves very sensitive to interionic correlation effects. In particular, Publication 8 studies the 8" alumina materials using a hopping model, and shows that the short-range and long-range order parameters, within the ordered region of the phase diagram, will be very sensitive to interionic repulsions; previous studies using related methods predicted incorrect phase boundary effects, because of the very slow formation of ordered domains upon cooling from the disordered phase. Publications 9 and 13 extend this investigation to the consideration of a dynamical model, including inertial as well as hopping motions. We find that the so-called homogeneous approximation, in which the pair distribution function is

approximated by its value for a homogeneous melt, in general will not give quantitatively accurate results for the structure function, though its qualitative predictions are correct.

Overall, our theoretical studies point to three important conclusions about these framework-type solid electrolyte systems. First, the structures of the mobile-ion array and of the framework lattice will determine, to good qualitative accuracy, the dc conduction. Second, that corrections to this qualitative picture due to interionic correlation effects can be quite well approximated using the homogeneous approximation, or one-component plasma. Thirdly, dynamical large-amplitude motions in the host lattice can produce entirely different mechanisms of dynamic percolation type, mechanisms in which, as in adiabatic electron-transfer reactions, the overall conduction is fixed entirely by host dynamics, with the mobile ions simply following on a fast, experimentally-irrelevant time scale. For these systems, including protonic polymer electrolytes, work to increase the fast-ion conductivity should focus on improvement of the renewal rate, or rate of host dynamical change, rather than on ion hopping.

Our experimental work on the protonic materials strongly suggests that a simple Grotthus mechanism for motion in the S" structures is incorrect; the independence of the diffusion rate to partial deuteration, and the striking difference between activation energies for dielectric relaxation and conduction, imply, respectively, that neither proton hopping nor neutral molecule rotations are the rate-limiting step. This might argue in favor of a so-called "vehicle" mechanism, in which the proton is carried

through the lattice by formation of larger, polarizable entities such as H_3O^+ or NH_3^+ .

The experimental work on glasses, like the theory, stresses the close relationship of mobile-ion structure to conduction. The relaxation of interionic correlation by framework disorder rationalizes the otherwise puzzling high conductivity for stoichiometric compositions as well as the lowered activation energy for glassy, as opposed to crystalline, conductors. The strong implications for preparing higher conductivity materials is to take advantage of the framework disorder offered by glasses while, at the same time, avoiding Mott-type trapping by charge compensators. Glasses with low optical basicity and "soft" anions, such as sulfides or selenides, would seem ideal candidates.

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