**MIXED IONIC AND ELECTRONIC CONDUCTIVITY
IN POLYMERS**

Progress Report

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Research Accomplishments - 1992

In the past year, we have made progress in the theory of mixed ionic and electronic conductivity in polymers. On the experimental side, we have prepared polypyrroles with pendant polyethers and studied their conductivity in the reduced state. Theoretical progress was made in the application of Monte Carlo methods to ion motion in polymers.

Progress

A. Synthesis of polypyrrole-oligoether films and complex impedance measurements.

In our last annual report, we described the synthesis and characterization of polypyrroles with oligoether groups in the 3-position of the pyrrole monomer. The aim in preparing these materials is to achieve both high ionic and electronic conductivity, and to study the mutual influence of these two processes. Electrochemical oxidation of one new substituted pyrrole, 3,6-dioxaheptyl-pyrrole-3-acetate, gave smooth polymer films on a polished platinum surface. The films were structurally characterized by SEM, STM, and profilometry, and electrochemically observed to undergo reversible oxidation at 0.3V vs Ag/AgCl. Charge transport measurements, determined by ac impedance techniques on the unoxidized film, with an electrolyte consisting of LiBF_4 and MSO_3CF_3 ($\text{M}=\text{Li}, \text{Na}, \text{K}$) in tetraethyleneglycol dimethyl ether gave $D_{\text{app}} = 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. The most likely origin of this charge transport is ionic conductivity. To determine the extent to which electronic conductivity contributes to these charge transport processes, we have measured dc conductivities with ion-blocking electrodes. The initial results indicate that ionic conductivity is at least a factor of ten greater than electronic conductivity. We are continuing to refine these experiments.

B. Development of Monte Carlo Models for Ion Transport.

In mixed electronic/ionic conductors, the first effect of the electronic conductivity on the ionic motion would be expected to be screening of the interatomic interactions, resulting in reduced ion pairing and clustering. In connection with experimental advances in the preparation and analysis of new materials, we have begun a series of experimental investigations on the role of screening, and of mixed electronic/ionic interactions, on the conduction process.

Initial work has been completed using Monte Carlo methods to discuss the role of ionic correlation effects in hopping conduction in these materials. While phenomenological and qualitative models have been used to discuss ion transport in polymer electrolytes, few microscopically quantitative attempts have been made previously. We need such microscopic results for the simple ionic case, before attacking mixed conductors.

Lattice models are not obviously appropriate for polymer electrolytes, but they can nevertheless be useful, if one interprets lattice structure as simply describing a standard tessellation of the physical space of the amorphous polymer host. Utilizing this insight, we have completed a series of Monte Carlo simulations on polymer salt complexes. We have used standard Metropolis Monte Carlo calculations to examine correlation effects, Haven ratios, hopping frequencies and static structure, as a function of temperature, in a series of models for uni-univalent salts. For example, Figure 1 shows computed pair distribution functions at equilibrium, and accumulative population statistics for two separate models. In the first model, only one ion is assumed mobile and the other is assumed frozen (this corresponds to the very low transference number for cations observed in polymer electrolytes). The second model assumes that both ions are mobile, indeed with equal jumping rates. The strong structural features, and their variations with temperature, make interesting

predictions for comparison with such experimental probes as vibrational spectroscopy, light scattering and EXAFS.

Interesting dynamical properties also follow from these simulations. For example, Figure 2 shows the time-dependence of the total ionic interaction potential surrounding a given ion. The interesting part of this decay is that it is neither single exponential nor stretched exponential, but some combination. Indeed, it indicates that there is a range of time scales that describe the effective potential felt by a hopper in a disordered electrolyte material; our dynamic percolation model, and Funke's jump relaxation model, feature two time scales. Thus the simulation indicates the reality of a second time scale, quite separate from the hopping time, that characterizes the dynamical behavior of conductivity in polymer electrolyte materials.

These calculations were done assuming true coulomb, and short-range, potentials. Because these coulomb potentials are screened only by the presence of other ions, they are missing the strong screening that comes from the mobile electron contribution. As such, these calculations serve not only to study polymer electrolytes themselves, but as the basis for the comparison with mixed electronic/ionic simulations which are to be carried out in 1993.

Research Plans - 1993

A. Experimental

Two issues will be addressed in the next year: (1) The extent of ionic versus electronic conductivity in reduced polypyrrole-oligoether films, and (2) Ion and electronic transport in oxidized polypyrrole-oligoether films.

As described in the Research Accomplishments section, we have employed low-

frequency complex dielectric measurements to determine charge transport in our newly prepared polypyrrole-oligoether films. In the next year we plan to carry out more incisive studies of the relative electronic vs ionic transport in these materials, using a polarization cell with provision for precise control of the redox state of the polymer. Simple cells have been used so far and a new cell design is in progress.

Our major thrust in the next year will be to explore ionic conductivity in the partially oxidized film where electronic conductivity is substantial. For low levels of oxidation the above-mentioned polarization cell will be of some use, but in the more highly electronically conducting fully oxidized films, an entirely new strategy will be needed to differentiate ionic and electronic conductivity. Our plan is to follow the transport of ^7Li and ^{19}F associated with SO_3CF_3^- in these materials by the use of solid state pulsed field gradient NMR spectroscopy. In the coming year, we should complete the equipment-building phase for this experiment and start data collection.

B. Theory.

Electronic and ionic transport occur on completely different time scales. The Born-Oppenheimer separation, based on the mass disparity between electrons and ions, suggests that to a very good approximation motion of the ions occurs in the averaged fields of the electrons, and motion of the electronics in the instantaneous field of the ions. This strongly suggests that, in modelling dynamics of response in the conductive systems, a time scale separation can be used based on the Born-Oppenheimer description.

We will begin this year on a very challenging but very important study of the mutual conductivity of electrons and ions in mixed conductors. It will be based on the use of methods very similar to the Car-Parinello picture for molecular dynamics with electronic motion included. More explicitly, we will represent the potential acting on the nuclei as an

instantaneous average of the electronic wave function. The electronic wave function itself will be represented (for the description of systems such as the salt complexes of functionalized polythiophenes or polypyrroles) in terms of a tight binding model with repulsions, such as a Hubbard model or a Hubbard model with extended repulsions. By computing the electronic wave function at an instantaneous nuclear geometry, and then computing the electron density from that wave function to yield an effective interaction potential for the nuclear motion, we will be able to study the mutually dependent time evolution of electronic and ionic functions. By completing such a simulation with different concentrations of electrons and ions, we should be able to characterize precisely how the presence of delocalized electrons changes the interionic potentials, and therefore, the ionic conductivity. While ionic conductivity as enhanced by several orders of magnitudes due to electronic screening has been suggested several times in the ionic conductivity literature, the experiments are themselves inconclusive. We feel that these self consistent dynamical models will be very instructive for understanding the mechanisms of mixed electronic and ionic conductivity in mixed conductive polymers.

DOE Supported publications.

1. H.-C. zur Loye, B. J. Heyen, H. O. Marcy, D. C. DeGroot, C. R. Kannewurf and D. F. Shriver, Dielectric Response and Conductivity of Poly(propylene oxide) Sodium Polyiodide Complexes. Discussion of Charge Transfer by an Ion Relay Mechanism, *Chem. Mater.*, **2**, 603 (1990).
2. M. A. Ratner, Review Article: Polymer Solid Electrolytes: Charge Transport Mechanisms, *Materials Forum*, **15**, 1-15 (1991).
3. M. A. Ratner and A. Nitzan, Polymer Electrolytes: Hopping, Domain Structures and Frequency-Dependent Conductivity, *Mat. Res. Soc. Symp. Proc.*, Vol. 210, 109 (1991).
4. B. J. Heyen, C. Adamson McConnachie and D. F. Shriver, Synthesis and Ion Diffusion Measurements of 3-Substituted Polypyrroles, paper in preparation.
5. Ionic Conductivity in Poly(diethylene glycol-carbonate)/Sodium Triflate Complexes, M. Forsyth, D. R. MacFarlane, D. F. Shriver and M. A. Ratner, paper in preparation.

6. M. Forsyth, D. F. Shriver, M. A. Ratner, D. C. DeGroot and C. R. Kannewurf, Conductivity Percolation in Polyiodide/Polymer Complexes, paper in preparation.

DOE Supported Personnel.

Christine Adamson (Graduate Student).
Tina Hoover (Graduate Student).
Bruce Heyen (Graduate Student-Ph.D. 1992).

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