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Mixed Ionic and Electronic Conductivity in Polymers

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Our aim in this portion of the research is to prepare new electroactive films with high ion mobility, and to characterize the transport properties of these materials. The classic conducting polymers, polyacetylene, polythiophene, and polypyrrole have dense structures that prevent rapid redox switching because of the low diffusivity of ions. Our objective is to modify the latter two polymers with pendant polyethers, which should greatly improve ion transport. Five monomers have been synthesized:

*OEEM = $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$

Films of (1) and (5) have been galvanostatically polymerized in an electrochemical cell that facilitates characterization by electrochemical methods including cyclic voltammetry and complex impedance. Thin films ($\leq 0.2 \mu\text{m}$) have been found to be smooth while films $\leq 1 \mu\text{m}$ are rough and have a cauliflower appearance. The CV of (5) shows the system is reversible with a cathodic peak at 0.4V and an anodic peak at 0.55V vs Ag/AgCl. These results demonstrate the feasibility of our approach. We are now in a position to carry out quantitative measurement of ion transport in these systems.

Our research on another class of mixed conductors, polyiodide-containing polymers has progressed significantly, with the completion of a detailed study

of the temperature dependence of ionic conductivity above and below the glass transition temperature of the host organic polymer. Our previous work indicated that one component of the conductivity in these materials is an ion relay along the polyiodide chain. The recent conductivity measurements indicate that around the glass transition temperature there is little coupling of the dynamics of the organic polymer with charge transport by this iodide ion relay mechanism. This result is in marked contrast with the accepted mechanism for motion of ions in polymers, wherein polymer segmental motion is essential for significant ion transport.

The general problem of charge transport in concentrated solution involves high densities of coulomb charge interactions. If the mixed electronic/ionic problem is addressed, even in the simple incoherent limit in which electron transfer occurs by hopping, the polarization of the local electron hopping site by the overall potential must be calculated self consistently using, say, a mediated shell model picture. We have begun code development for molecular dynamics simulation of the mixed ionic/electronic conduction problem, based on use of a general dynamics code that uses Ewald methods for an exact solution of the electrostatic problem with periodic boundaries.

The code development is still continuing, and thus far no results are available from these simulations. We have, however, clarified and formulated the propagation algorithm to be used for the electron dynamics. It will be based on a simple master equation form, which is appropriate for hopping electrons: the hopping rate itself will scale with the (exponential) overlap of basis functions centered at the redox centers, such as the iodide center in polyiodides. We feel that this hopping formulation should permit avoiding the short time scale dynamical evolution required for proper study of the totally coupled quantum electron/ion system, and thus permit understanding of screening effects, local potentials and mixed ion conductivity in the sorts of mixed conductive mechanisms that pertain to these ion/electron polymer electrolytes.

Plans for research in 1991

Research on derivatized polythiophene and polyimidazole will focus on the measurement of transport properties along with careful monitoring of

variable such as film thickness, morphology and composition. To the extent that the variables can be separated we are interested in the mutual influence of ionic and electronic transport.

Investigations of the polyiodide-containing polymers will be designed to test our postulate that their thermopower is related to polyiodide redistribution reactions. Accordingly we plan to carry out detailed thermopower measurements and to obtain temperature-dependent Raman spectra, which provide a means of following the concentration distribution of polyiodides across a sample in a thermal gradient.

The theoretical studies of mixed electronic/ionic conductors will continue the development of efficient code for modeling these systems and testing formulations that circumvent the problem of short time-scale processes.

Recent publications.

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- 2) Doan, K.E.; Ganapathiappan, S.; Chen, K.; Ratner, M.A. and Shriver, D.F. "Single-Ion Conducting Polymer Electrolytes: Synthesis and Characterization" *Mat. Res. Soc. Symp. Proc.* **1989**, 135, p. 343-349.
- 3) Ratner, M.A. and Shriver, D.F. "Polymer Ionics" *MRS Bulletin* **1989** p. 39-51.
- 4) Ratner, M.A. and Nitzan, A. "Conductivity in Polymer Ionics" *Faraday Discuss. Chem. Soc.* **1989**, 88, p. 19-42.
- 5) zur Loye, H.C.; Heyen, B.J.; Marcy, H.O.; DeGroot, D.C., Kannewurf, C.R. and Shriver, D.F. "Dielectric Response and Conductivity of Poly(Propylene Oxide) Sodium Polyiodide Complexes" *Chemistry of Materials* in press.

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