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MIXED IONIC AND ELECTRONIC CONDUCTIVITY
IN POLYMERS

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Progress Report

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Abstract

The conductivity of iodine-containing polymers was investigated and conductivity along polyiodide chains is implicated by the concentration dependence of the conductivity data and spectroscopic measurements. On the theoretical side, entropy based models were developed to describe ion motion in polymers.

Progress

Our primary focus in the experimental program has been on the nature of polyiodide-containing polymer electrolytes. These interesting materials exhibit ohmic behavior associated with polyiodides and nonohmic behavior associated with the transport of cations and simple anions, in a polar host polymer. The two host polymers receiving most of our attention were MEEP, $\langle \text{NP}(\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4(\text{CH}_3)_2)_n \rangle$, and atactic PPO, $\langle \text{CH}(\text{CH}_3)-\text{CH}_2\text{O} \rangle_n$. One major accomplishment was to map the conductivity surface for the ternary system, $\text{MEEP}_x\text{NaI}-y\text{I}_2$. This surface has a ridge in the conductivity corresponding to intermediate concentrations of NaI, emphasizing the central role of I_n^- formation in the electronic conductivity. Far infrared and Raman spectra substantiate the presence of polyiodides in these materials. In the course of these conductivity studies we discovered how to circumvent problems with electrode corrosion, which have interfered with previous measurements. We found that polyiodides result from the interaction of I_2 with polyethers; apparently redox disproportionation of I_2 is responsible for this polyiodide generation. Currently, we are studying the nature of this reaction.

In another branch of our experimental research, we have initiated synthetic work on polypyrroles and polythiophenes with pendant polyether groups. When doped with alkali metals, these materials should exhibit mixed ionic and electronic conductivity.

The primary theoretical emphasis in this part year has been on the nature of ion pair

formation. When mixed conductivity occurs, one major effect of the electronic carriers on the ions should be screening of the coulomb attraction, resulting in reduced formation of ion pairs and increased ionic conductivity. The ultimate challenge in this regard is development of a full frequency and wave vector dependent dielectric function, a project that we intend to begin in 1990. The dependencies of ion pair formation, however, should be the same in mixed conductors and in complex electrolytes. Important spectroscopic work by Torell and by us have indicated that the importance of ion pairing in fact increases with temperature; this observation is quite different from earlier reports from several groups in Grenoble. It is also consistent with the observation by Greenbaum that "salting out" occurs with increased temperature in various (PPO) electrolytes. Theoretical understanding of this increased formation with temperature seems similar to the problem of lower consolute temperatures in the classical physical chemistry of solutions.

We developed an entropy-based model to explain this behavior. Essentially, the entropy cost for breaking up an ion pair is positive in most cases, since the free ions, particularly the cation, will complex with the electrolyte and thus reduce very substantially the configurational entropy. Utilizing a simple lattice model, we have been able to predict both the change in ion pair formation with temperature and conditions under which ion pairs will in fact, either decrease or increase with increasing temperature. We feel that this is an important effort, since ion pair formation can substantially reduce overall conductivity in these materials.

DOE Supported Publications 1989:

"Synthesis, Characterization, and Electrical Response of Phosphazene Polyelectrolytes", S. Ganapathiappan, K. Chen and D. F. Shriver, *JACS*, 111, 4091 (1989).

"Polymeric Electrolytes and Polyelectrolytes: Salt Concentration and Domain Effects on Conductivity", M. A. Ratner, S. D. Druger and A. Nitzan, *Mat. Res. Soc. Symp. Proc.*, 135, 13 (1989).

"Fluctuations, Structure Factors and Correlations: Ionic Transport in Framework Electrolytes", M. A. Ratner and Y. Boughaleb, in Laskar and Chandra, eds., *Superionic Solids and Solid Electrolytes: Recent Trends*, Academic Press: 515 (1989).

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