**MIXED IONIC-ELECTRONIC CONDUCTION AND PERCOLATION
IN POLYMER ELECTROLYTE METAL OXIDE COMPOSITES**

Final Report
Award No. DE-FG02-85ER45220

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FINAL REPORT

For any battery or electrochemical power source, it is necessary to optimize the performance of the electrolyte and the electrodes. While work on polymer solid electrolytes has advanced substantially, there are a number of very important and difficult issues involved in electrode optimization. The results from numerous experimental cells and whole-cell models (from Newman's group at Berkeley) indicate that conduction within the polymer electrolyte phase of the composite is a major limiting factor for the attainment of suitable power densities. This project is aimed at understanding and optimizing both electronic and ionic conduction properties in composite electrode structures based on polymer electrolytes.

In the synthetic phase, we studied a number of composites and nanocomposites based on a xerogel, utilizing the V_2O_5 and a polymer electrolyte. The V_2O_5 xerogel is an electronic conductor and the $(a\text{-PEO})_n\text{LiOTf}$ imparts ionic conductivity. X-ray diffraction of the composites demonstrate a V_2O_5 interlayer spacing of 13.4 Å. IR spectroscopy shows that intact V_2O_5 and $(a\text{-PEO})_n\text{LiOTf}$ are present up to 100°C, at which point a band at 1735 cm^{-1} indicates oxidation of $(a\text{-PEO})$. The water content of this composite is approximately H_2O 0.5: 1 $V_2\text{O}$ and approximately 2% of the vanadium is present at V^{+4} . The electronic conductivity is 10^{-3} S/cm at room temperature, as measured by the four-point probe method with electrodes that are blocking to Li^+ and the conductivity is activated, indicating semiconductor behavior. Thermopower measurements exhibit negative Seebeck coefficients, indicating that the electrons are the majority charge carriers. A.C. impedance measurements reveal that conductivity of the thin films are highly anisotropic. These results are discussed in publications 2 and 3, and in work to be published.

Earlier work in this project involved polyiodides, in which, again, there is mixed conduction. Polyiodide structures turn out not to be optimal, because of stability and density issues, but they were important model systems to understand how electronic percolation, as well as ionic percolation, is necessary for appropriate electrode behavior. This work is described in publication 8.

Theoretical work on the mixed conduction problem centers on the important geometric structures that are inherent in all these materials: electrons move in one regime, ions in another, but their interaction remains coulombic, and therefore long range. We have worked out the proper boundary conditions to be used in such computations, and have begun simulations using our dynamic percolation model to understand the limits in which electrons or ions will be dominant, and in which the behavior will be of ohmic or of Nernstian type. These simulations are extremely important for ion modulated electron

transfer, or ion gated electron transfer, and critical not only in electrode materials for advanced batteries, but also in organic conductors, or any other narrow band conductive material. The theoretical work on this project as been described in references 4, 5, 6 and 7, and (again) in publications currently in the write-up stage. Earlier in this project, we completed a significant effort on the dynamics of ion transport within the electrolyte subphase of the nanocomposite. We showed the clear dominance of solvent relaxation processes in deforming the ionic conduction in these electrolytes, and suggested several experimental motifs (including composite comb polymer structures to assure local effective free volume, as well as a very high (or density, rubber-like structure) to optimize conduction. Experimental work following up on these suggestions is in progress in the Shriver group.

Recent Papers Supported by DOE/ER/45220-11

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7. "Conduction in Polymers: Dynamic Disorder Transport," A. Nitzan, M.A. Ratner, *J. Phys. Chem.*, 98, 1765-1775 (1994).
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