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**NEUTRON AND X-RAY SCATTERING EXPERIMENTS
ON LITHIUM POLYMER ELECTROLYTES***

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Invited presentation workshop on Advanced Non-Aqueous Battery Technology Research and Development, Hunt Valley, Maryland, October 15-17, 1997.

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• OBJECTIVE

We are carrying out structural, dynamical and transport measurements of lithium polymer electrolytes, in order to provide information needed to improve the performance of secondary lithium battery systems. Microscopically, they behave as liquids under conditions of practical interest. Development of batteries based on these materials has focused on rechargeable systems with intercalation/insertion cathodes and lithium or lithium-containing materials as anodes. The electrolytes are generally composites of a polyethylene oxide (PEO) or another modified polyether and a salt such as LiClO_4 , LiAsF_6 or LiCF_3SO_3 .

Research on electrolyte materials for lithium batteries has focused on synthesis, characterization, and development of practical devices (1). Some characterization work has been carried out to determine the properties of the ion-polymer and ion-ion interactions, principally through spectroscopic, thermodynamic and transport measurements. It is generally believed that ionic conduction is a property of the amorphous phase of these materials. It is also believed that ion association, ion-polymer interactions and local relaxations of the polymer strongly influence the ionic mobility. However, much about the nature of the charge carriers, the ion association processes, and the ion-polymer interactions and the role that these play in the ionic conductivity of the electrolytes remains unknown (2,3).

• APPROACH

We have initiated a combined

experimental and theoretical study of the structure and dynamics of lithium polymer electrolytes. We plan to investigate the effects of the polymer host on ion solvation and the attendant effects of ion pairing, which affect the ionic transport in these systems. Questions that arise in this connection involve:

- a) the configuration of the migrating ions relative to the polymer matrix and/or to the counter ions (i.e., contact ion pairing).
- b) identification of the migrating ions (not always apparent from macroscopic transport measurement) and the time and distance scales of the local jumps involved in the migration process.

This experimental work is carried out in conjunction with theoretical studies by Curtiss *et al.* involving electronic structure calculations using *ab initio* molecular orbital theory, and with molecular dynamics (MD) simulations being carried out by Halley and co-workers.

• ACCOMPLISHMENTS

To provide a reference point for the lithium polymer studies, the structure of pure PEO was investigated by neutron scattering in both semi-crystalline and liquid state (4). Time-of-flight neutron diffraction measurements were performed using the Glass, Liquids and Amorphous Materials Diffractometer (GLAD) facility at the Intense Pulsed Neutron Source (IPNS), Argonne. Due to the large incoherent scattering cross-section of hydrogen, only fully deuterated polymer was used.

The results were compared to the *ab initio* molecular orbital calculations of Curtiss *et al.*, based on different unit chain configurations, and to the MD simulations

(5). These were based on polymerization of a previous model of flexible dimethyl ether monomers, found to be in good agreement with the experimental data for the monomer liquid (6). Polymerization was achieved through a succession of processes in which two monomer units were joined when their ends came close together and their end hydrogen atoms eliminated. A polydisperse sample was produced in this way, yielding partial radial distribution functions for the O and C atoms. H atoms were not explicitly taken into account.

To compare the MD results with the present data, the H atoms had to be incorporated into the simulated structure. One approximation is to place OH₂ structural units at the O positions allowing for the H's to move about central positions in order to reflect the peak broadening seen in the liquid structure. The distribution function $g(r)$ obtained in this way compared with the experimental data for liquid PEO at 90°C in Fig. 1. It is seen that the structure obtained from the simulation is considerable more ordered than the actual polymer: even though the first peak in the real-space distribution function $G(r)$ is in fact too relaxed in the simulation result, all the remaining features are too pronounced. The simulation clearly needs to allow for a more relaxed C-C and C-O backbone. Since the potentials used give satisfactory results for the monomer liquid (6), the disagreement probably lies in the polymerization process, which may not allow sufficient time for the chains to shorten and assume more flexible bond orientations.

• FUTURE DIRECTIONS

The next step in the experimental program will be to study the effect of adding lithium salts, starting with LiClO₄, to the polymer. Initial studies at GLAD with ⁶Li and ⁷Li isotope substitution indicate relatively small changes in the

structure and conformation of the polymer itself, but a rather well defined Li-O and Li-C/Li-O environment. They will also be compared with the *ab initio* molecular orbital calculations of Curtiss *et al.* and MD simulations which have already been carried out on the salt-in-polymer system (7) with pair potentials based on *ab initio* quantum chemical calculations (8). Following these structural measurements, dynamical studies of Li⁺ ion conduction at the microscopic level will be carried out with quasielastic neutron scattering.

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