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Ionic Transport in Electrochemical Media
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This project was a molecular dynamics study of the relevant issues associated with the structure and transport of lithium in polymer electrolytes such as polyethylene oxide(PEO) . In close collaboration with quantum chemist Larry Curtiss and neutron scatterers David Lee Price and Marie-Louise Saboungi at Argonne, we used molecular dynamics to study the local structure and dynamics and ion transport in the polymer. The studies elucidated the mechanism of Li transport in PEO, revealing that the rate limiting step is extremely sensitive to the magnitude of the torsion forces in the backbone of the polymer. Because the torsion forces are difficult to manipulate chemically, this makes it easier to understand why improving the conductivity of PEO based electrolytes has proven to be very difficult. We studied the transport properties of cations in ionic liquids as possible additives to polymer membranes for batteries and fuel cells and found preliminary indications that the transport is enhanced near phase separation in acid-ionic liquid mixtures.

This project addressed a long standing problem of inadequate lithium conductivity in polyethylene oxide based membranes for lithium-polymer batteries by studying the mechanism of lithium transport in amorphous polyethylene oxide. We developed a molecular dynamics model for the amorphous polymer [1,2]and verified its validity by comparison with elastic neutron scattering experiments done at Argonne [3]. Because the molecular dynamics model uses the united atom model, we adopted a representation of the hydrogen positions (actually deuterium in the experiment) to make the comparison. We placed hydrogen scatterers in the appropriate tetrahedral positions around the united atom carbon positions. We used two statistical distributions of the hydrogen positions. In the first, described in reference 3 , we used a spherically symmetric distribution around classical positions. Later[2], we derived an appropriate , nonspherically symmetric distribution from quantum mechanical first principles. Other computational innovations in these simulations included production of the simulation sample by digital 'polymerization'. In studies of barriers to lithium transport in the model of polyethylene oxide, we published a report[4] of relaxed barrier distributions, consistent with both first principles calculations and experiment.

Using recently developed potentials for perchlorate interaction with polyethylene oxide we carried out a study of lithium perchlorate ion pairing in amorphous polyethylene oxide[5] The results showed that there are two minima in the potential of mean force between the lithium and perchlorate ions. One of these, at a lithium-chlorine separation of a little more than 3 Å corresponds approximately to the predicted distance of a stable lithium perchlorate dimer in vacuum. However, the calculated potential of mean force indicates a very significant component of entropic binding in the pair at this separation in the amorphous polymer. Such an

effect has been observed in polymer electrolytes [6] and Marc Ratner and colleagues [7] suggested qualitatively that the effect was an entropic one. The second minimum in the potential of mean force for the lithium-perchlorate ion pair in amorphous polyethylene oxide occurs just above 6 Åand is associated with a fully six-fold oxygen coordinated lithium ion bound to the perchlorate. There is little or no entropic component to the binding free energy of this second pair state.

In the later years of the project we used the molecular dynamics model for lithium salts in amorphous polyethylene oxide to study the mechanism of lithium transport. We accumulated a large amount of data on lithium transport events in our using an adaptation of the 'parallel replica method', due to Voter [8–11] . In these studies we established that Li transport occurs in the amorphous polymer by occasional transfer of lithium ions from one solvating oxygen cage to another as the polymer rearranges its configurations on a time scale set by its 'crank-shaft' dynamics which are controlled by the torsion forces in the PEO backbone. When the polymer configuration is favorable, the lithium transfer occurs very rapidly (on picosecond scales) so the rate limiting dynamical step is the polymer rearrangement which is much slower (nanoseconds). This qualitative insight is in agreement with results by the Curtiss group on smaller clusters, with earlier, qualitative models by M. Ratner and coworkersi[12] and with independent simulation by Borodin and Smith[13]and others. However, this insight has unfortunately not led to design of improved polymer electrolytes, mainly because it is difficult to find polymers which effectively reduce the torsion forces in the polymer backbone.

In the last year of the project, we studied transport of cations, particularly protons, in ionic liquids, because ionic liquid additives have been proposed as a solution to transport problems in membranes of both batteries[14] and fuel cells[15]. Extending a previous collaboration with 3M, we showed that mixtures of 1-ethyl-3-methylimidazolium (EMI)- bis(triflouromethylsulfonyl) imide (TFSI) and the acid H-TFSI appear to exhibit maximum proton conductivity when the mixture has a concentration near the concentration at which the acid and ionic liquid phase separate[15]. We have also done some preliminary work on lithium cations in ionic liquids, with more direct application to the battery problem in mind.

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