Electrochemical and Spectroscopic Studies of Polymer Electrolytes

My group explores the properties of ion conducting polymeric and liquid materials. We combine synthetic studies with electrochemical and spectroscopic methods to understand the unusual ion conducting properties of mixtures of polymers and salts. Work in my group is in two areas: 1) conductivity studies of solid and liquid polymer electrolytes which contain divalent salts or silicon hosts, and 2) applications of differential scanning calorimetry and FTIR and NMR spectroscopies to understand the variation in conductivity and composition we observe in the polysiloxane electrolytes. I intend to work with two students; most likely each student will work on some conductivity studies and also on some aspect of physical characterization.

I. Conductivity Studies of Silicon Polymers

There is a clear link between the maximum conductivity of polymer electrolytes, the composition of the complex, and the microstructure of the salt incorporated among the polymer chains. The goal of this project is to study the effect of composition on the ionic conductivity of polymer salt complexes which use silicon polymers as the polymeric solvent.

The preparation of the polymer salt complexes is straightforward but must be carried out in the absence of moisture since the presence of water will irreproducibly alter the structure and conductivity of the polymer salt complexes. The desired stoichiometric ratios of the polymer and salt are codissolved in an appropriate solvent on a Schlenk line, stirred together to form a homogeneous solution, and then the solvent is removed by evacuation. For this particular investigation, lithium salts will be used because of their applicability to lithium batteries. The bulk ionic conductivity of the polymer salt complexes will be measured by impedance spectroscopy. Impedance spectroscopy measures the alternating current resistance (the impedance) of a sample as a function of frequency. The measured resistance allows the bulk conductivity to be calculated from the equation $\sigma = \frac{1}{R} \times \frac{l}{A}$ where $\sigma$ is the conductivity, $R$ is the resistance and $l/A$ is the geometric factor for the experimental cell arrangement used.

Recently, we have been collaborating with Robert West and his group at the University of Wisconsin-Madison to study silicon polymers as hosts for polymer electrolytes. Our earliest work looked at polysilane polymers, $[\text{Si}(\text{R})_2]_n$, with etheric side chains and these polymer electrolytes proved to have modest ionic conductivities. More recently the West group has synthesized poly(siloxane) polymers, $[\text{Si}(\text{R})_2-\text{O}]_n$, which we are currently studying. Polymer electrolytes of some disubstituted linear ethoxy poly(siloxane) polymers doped with the lithium bis(trifluoromethylsulfonyl) imide have very high ionic conductivities. In a systematic study of side chain length (see Figures 1 and 2 below) we have reported a very high ionic conductivity for a polymer electrolyte of $4.5 \times 10^{-4}$ S cm$^{-1}$.4

![Figure 1. A disubstituted oligo(ethylene oxide) polysiloxane polymer electrolyte host.](image)

Subsequently, polysiloxane polymer hosts with branched and crown ether side chains were examined and these families of electrolytes also have high ionic conductivities. More recent work has gone in two directions: less viscous liquid siloxanes and siloxanes incorporated into free-standing gels. Polymethylsiloxane polymers with an oligo(ethylene glycol) methyl ether side chain are lower molecular weight hosts and liquids. The doped electrolytes have ionic conductivities between $10^{-5}$ S cm$^{-1}$ and $10^{-4}$ S cm$^{-1}$. A solid polysiloxane electrolyte can be formed by synthesizing polymethylhydrosiloxane (PMHS) partly substituted with oligo(ethylene glycol) methyl ether. This precursor can be cross-linked with $\alpha,\omega$-diallyl poly(ethylene glycol) to form a conductive gel as shown in Figure 3.

These siloxane electrolytes are of interest to Argonne National Laboratory and Quallion Corporation in California who are developing prototype lithium batteries. We have been collaborating for several years with their scientists who plan to use the siloxane electrolytes in miniaturized, biological lithium batteries. Performance tests are in progress and show promise.

II. Spectroscopic Studies

Recent installation of a differential scanning calorimeter (DSC), FTIR spectrometer, and the 400 MHz NMR give us improved tools to examine the chemical environments of the polysiloxane polymer electrolytes in much more detail. From the DSC we can measure the glass transition temperature, $T_g$, of the siloxane hosts and electrolytes. High conductivities often correlate with low glass transition temperatures. The new FTIR can access the near IR region between 5000 and 10 000 cm$^{-1}$ which affords us the opportunity to examine the vibrational modes of the salts in the polysiloxane polymer electrolytes. Perturbations of the vibrational modes are typical of ion-ion interactions and may explain the optimum conductivities we observe in the doped polysiloxanes. Lithium and fluorine NMR studies on the polysiloxanes would allow us to determine the contributions to ionic conductivities from the anion and the cation diffusion, respectively.
Since our ionic conductivity measurements are bulk, total conductivities we would like to separate out the lithium portion of the conductivity since that will ultimately be most important in lithium based devices.

**Experience**

All of these research projects will introduce students to materials science, new applications of electrochemical methods, spectroscopic measurements and computer data analysis. These research areas are not often encountered by undergraduates, although they are quite important areas of current research. The electrochemical techniques and other characterization techniques will be taught over the course of the project. Work on NMR spectroscopy will require completion of organic chemistry.

**References**