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Electrochemical and Spectroscopic Studies of Silicon-Containing Electrolytes

My group explores the properties of ion conducting polymeric and liquid materials. We employ electrochemical and spectroscopic methods to understand the unusual ion conducting properties of mixtures of organic molecules which incorporate the element silicon and salts. Work in my group is in two areas: 1) ionic conductivity studies of solid and liquid polymer electrolytes which contain lithium salts and 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 electrolytes. I intend to work with two to three students during the summer of 2008; most likely each student will work on some conductivity studies and also on some aspect of physical measurements.

I. Conductivity Studies of Silicon and Lithium Electrolytes

There is a clear link between the maximum conductivity of electrolytes, the composition of the mixture of the organic solvent and the doping salt, and the microstructure of the salt incorporated among the solvent molecules. One goal of this project is to study the effect of composition on the ionic conductivity of electrolytes which use silicon based molecules as the solvent and lithium salts as the doping ions so these electrolytes can be employed in lithium batteries and supercapacitors.

The preparation of the electrolytes 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 electrolytes. The desired stoichiometric ratios of the organic liquid and the lithium salt are combined in a dry box and handled under argon or in sealed containers. The bulk ionic conductivity of the electrolytes is 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 $\sigma = (1/R) \times (l/A)$ where σ is the conductivity, R is the resistance and l/A is the geometric factor for the experimental cell arrangement used.

In this project we have been collaborating with Robert West and his group at the University of Wisconsin-Madison who synthesize the unique silicon-containing molecules. 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.¹ Then the West group synthesized poly(siloxane) polymers, $[\text{Si}(\text{R})_2\text{-O}]_n$. Polymer electrolytes of some disubstituted linear ethoxy poly(siloxane) polymers doped with the lithium bis(trifluoromethylsulfonyl) imide, LiTFSI, salt have very high ionic conductivities.^{2,3} 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 $4.5 \times 10^{-4} \text{ Scm}^{-1}$.⁴

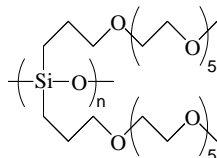


Figure 1. A disubstituted oligo(ethylene oxide) polysiloxane polymer electrolyte host.

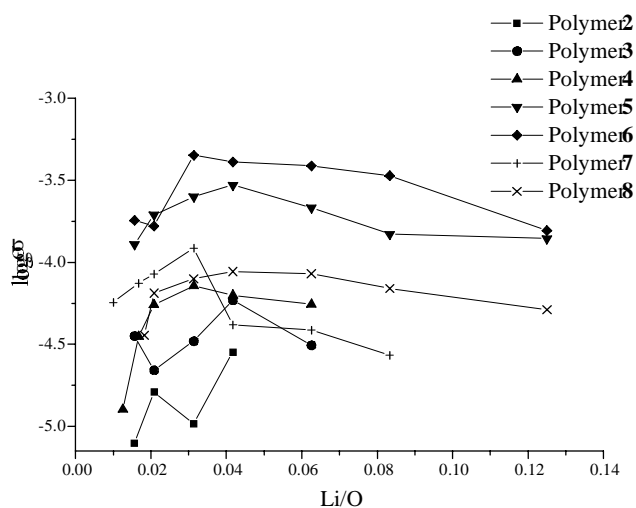


Figure 2. Ionic conductivities as a function of doping level and side chain ether length for disubstituted polysiloxanes.

Subsequently, polysiloxane polymer hosts with branched and crown ether side chains were examined and these families of electrolytes also have high ionic conductivities.⁵ More recent work has gone in several directions: less viscous, lower molecular weight liquid silicon-containing molecules 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} Scm^{-1} and 10^{-4} Scm^{-1} .⁶ 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 α,ω -diallyl poly(ethylene glycol) to form a conductive gel as shown in Figure 3.⁷

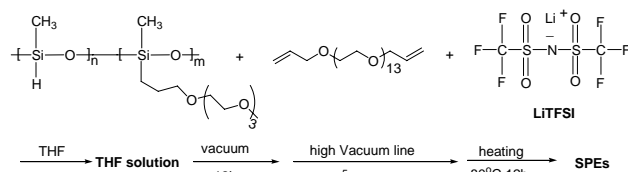
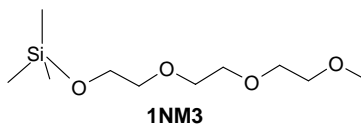


Figure 3. Synthetic procedure to prepare a cross-linked polysiloxane electrolyte film.

Most recently we have explored the ionic conductivities of trimethylsilyl-oligo(ethylene oxide) molecules such as the structure shown below in Figure 4.⁸ Electrolytes of these hosts and LiTFSI have the highest ionic conductivities yet measured in our group.



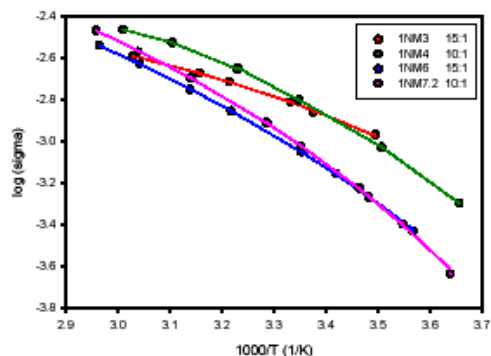


Figure 4. Variable temperature ionic conductivities of the LiTFSI doped electrolytes 1NM3, 1NM4, 1NM6, and 1NM7.2 at their optimum doping levels and the chemical structure of 1NM3 (above).

This summer we plan to continue conductivity studies of a new series of silicon and nitrogen containing electrolyte hosts such as:



With the Si and N atoms covalently bound in a charged positive ion, salts with the imide anion are ionic liquids. Ionic liquids are very interesting substances because of their high ion content, and extended liquid range. This family of new molecules has tremendous potential as electrolytes.

These silicon-containing 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 these electrolytes in miniaturized, biological lithium batteries.⁹ Performance tests are in progress and show promise.

II. Spectroscopic Studies

Another research area goal is to use spectroscopic methods or thermal methods to understand variations in conductivity at a fundamental physical level. Instruments such as the differential scanning calorimeter (DSC), FTIR spectrometer, and the 400 MHz NMR give us improved tools to examine the chemical environments of our electrolytes in much more detail. From the DSC we can measure the glass transition temperature, T_g , of the molecular solvents and then the doped electrolytes. High conductivities often correlate with low glass transition temperatures. The FTIR can access the near IR region between 5000 and 10000 cm^{-1} which affords us the opportunity to examine the vibrational modes of the salts in the electrolytes. Perturbations of the vibrational modes are typical of ion-ion interactions and may explain the optimum conductivities we observe in the doped electrolytes. Lithium and fluorine NMR studies on the electrolytes would allow us to determine the contributions to ionic conductivities from the anion and the cation diffusion, respectively. We have already been able to assign every proton chemical shift resonance for the small molecules 1NM3 and 1NM4 in preparation for DOSY and NOESY experiments.¹⁰ 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 electronic devices.

Experience

All of these research projects will introduce students to materials science, new applications of electrochemical methods, spectroscopic measurements, and computer data analysis. The electrochemical techniques and other characterization techniques will be taught over the course of the project but build on the

material in CHM 130/210. Work on NMR spectroscopy projects will require completion of organic chemistry.

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