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**ANALYTICAL CHEMISTRY.** Electrochemical techniques, ionic conducting polymeric and liquid materials, and materials characterization of electrolytes for lithium battery applications. (641) 269-3159.  
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## I. 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 electrolytes which contain lithium salts and silicon hosts, and 2) applications of NMR, differential scanning calorimetry, and FTIR spectroscopies to understand the variation in conductivity and composition we observe in the electrolytes. I intend to work with two to three students on this topic during the summer of 2012; with 1 or 2 students working on NMR projects and 1 or 2 students doing conductivity based projects.

### A. 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  $\sigma = (l/R) \times (l/A)$  where  $\sigma$  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 and Silatronix 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.<sup>1</sup> 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.<sup>2,3</sup> 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  $4.5 \times 10^{-4} \text{ Scm}^{-1}$ .<sup>4</sup>

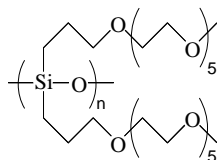


Figure 1. A disubstituted oligo(ethylene oxide) polysiloxane polymer electrolyte host.

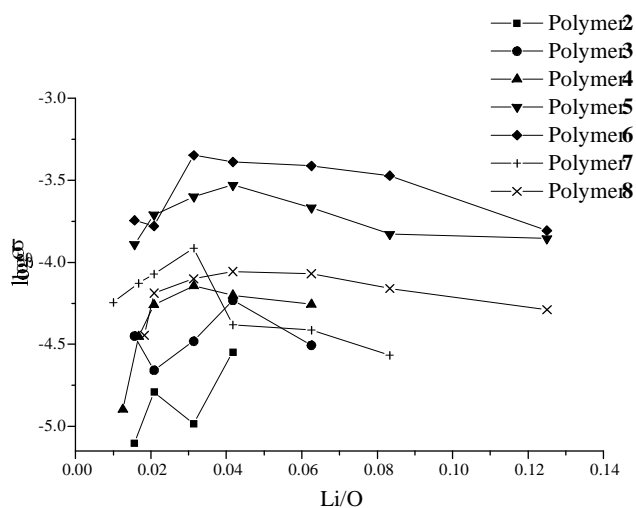


Figure 2. Ionic conductivities as a function of doping level and side chain ether length for disubstituted polysiloxanes.

Subsequently, polysiloxane polymer hosts with branched and crown ether side chains were examined and these families of electrolytes also have high ionic conductivities.<sup>5</sup> Investigations into more fluid electrolytes<sup>6</sup> and free-standing gel electrolytes<sup>7</sup> demonstrated that silicon based electrolytes have broadly promising characteristics as electrolytes.

In a continuation of study of liquid electrolytes we have explored the ionic conductivities of trimethylsilyl-oligo(ethylene oxide) molecules such as the structure shown below in Figure 3.<sup>8</sup> Electrolytes of these hosts and LiTFSA have the highest ionic conductivities yet measured in our group (Figure 4).

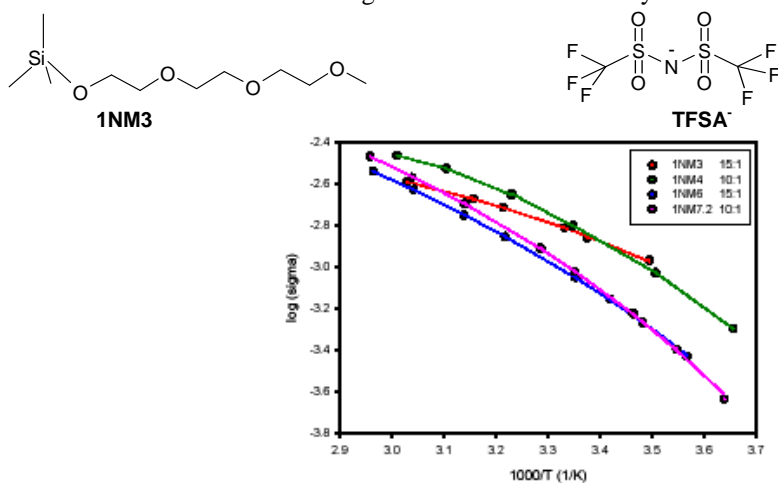


Figure 3. Variable temperature ionic conductivities of the LiTFSA doped electrolytes 1NM3, 1NM4, 1NM6, and 1NM7.2 at their optimum doping levels and the chemical structures of 1NM3 and the TFSA anion (above).

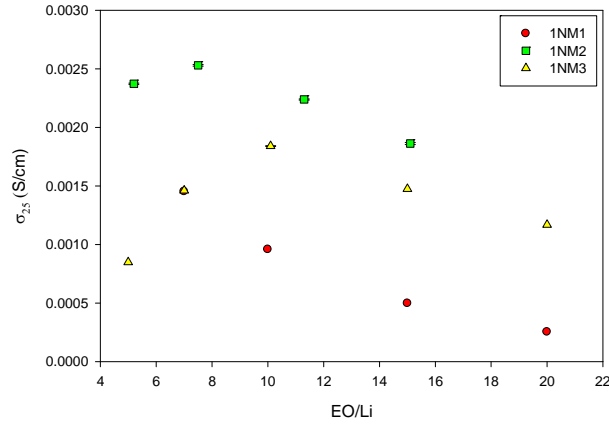


Figure 4. Ionic conductivities of the LiTfSA doped electrolytes 1NM1, 1NM2, and 1NM3 as a function of salt doping level.

These silicon-containing electrolytes are of interest to Argonne National Laboratory and Quallion Corporation in California and Silatronix in Madison who are developing prototype lithium batteries. We have been collaborating for several years with their scientists who used these electrolytes in miniaturized, biological lithium batteries (BIONs).<sup>9</sup> Performance tests have shown promising results leading to a R&D 100 award in 2005. More recent applications are geared toward batteries for hybrid electric vehicles.

## B. Spectroscopic Studies

Another research area goal is to use spectroscopic methods and/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  $\text{cm}^{-1}$  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 or boron NMR studies on the electrolytes 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.<sup>10</sup> Since our ionic conductivity measurements are bulk, total conductivities we would like to separate out the lithium portion of the conductivity since that ultimately will be most important in lithium based electronic devices. Our bulk conductivity can be related to cation and anion diffusion by the Nernst-Einstein equation:

$$\Lambda_{\text{NMR}} = \frac{Ne^2}{kT} (D_{\text{cation}} + D_{\text{anion}})$$

Furthermore, ionic conductivity and diffusion measurements may be compared by a parameter called ionicity as shown below by the ratio between the molar conductivity,  $\Lambda$ , calculated from impedance measurements and the conductivity calculated from the Nernst-Einstein equation and diffusion measurements, called  $\Lambda_{\text{NMR}}$ :

$$\text{Ionicity: } \Lambda_{\text{impedance}} / \Lambda_{\text{NMR}}$$

In addition, by measuring both the diffusion coefficient,  $D$ , for the anion and cation we can calculate transference numbers which represent the portion of the charge carried by either the cation or anion:

$$t_+ = \frac{D_{\text{cation}}}{D_{\text{cation}} + D_{\text{anion}}} \quad t_- = \frac{D_{\text{anion}}}{D_{\text{cation}} + D_{\text{anion}}}$$



where the numbers identify uniquely resolvable protons in the 400 MHz NMR spectrum. Koua Xiong prepared a series of electrolytes based on this solvent with both the LiTFSA and LiBOB salts and Chalie Adelson measured the diffusion of the solvent and ions using PFG-STE NMR as shown below:

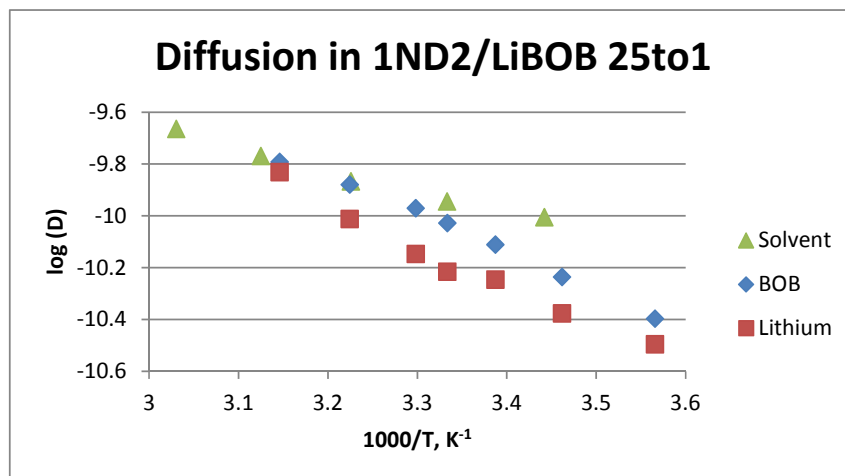


Figure 7. Arrhenius plot of the diffusion coefficients for the solvent 1ND2 (<sup>1</sup>H), the BOB anion (<sup>11</sup>B) and the cation (<sup>7</sup>Li).

### 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 210. Work on NMR spectroscopy projects will require completion of organic chemistry.

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