LYONS, LESLIE J. (b. 1961) Professor of Chemistry. A.B., 1983, Colgate University; Ph.D., 1987, University of Wisconsin - Madison; Postdoctoral Fellow, 1987-1989, Northwestern University; Visiting Research Fellow, 1995-1996, University of North Carolina - Chapel Hill; 2002-2003, University of Oregon; 2009, Monash University (Clayton, Victoria, Australia).
ANALYTICAL CHEMISTRY. Electrochemical techniques, ionic conducting polymeric and liquid materials, and materials characterization of electrolytes for lithium battery applications. (641) 269-3159.
LYONS@GRINNELL.EDU

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 calorimenty, and FTIR spectroscopies to understand the variation in conductivity and composition we observe in the electrolytes. I intend to work with three to four students on this topic during the summer of 2014; 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 or lithium-ion 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 $s = (1/R) \times (l/A)$ where s 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 Silatronix (previously at the University of Wisconsin-Madison) who synthesize the unique silicon-containing molecules. Our earliest work looked at polysilane polymers, $[Si(R)_2]_n$, with etheric side chains and these polymer electrolytes proved to have modest ionic conductivities.[1] Then the West group synthesized poly(siloxane) polymers, $[Si(R)_2\text{-}O]_n$. 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 4.5×10^{-4} Scm^{-1}.[4]

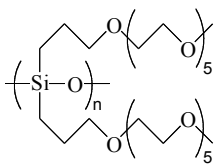


Figure 1. A disubstituted oligo(ethylene oxide) polysiloxane polymer electrolyte host.

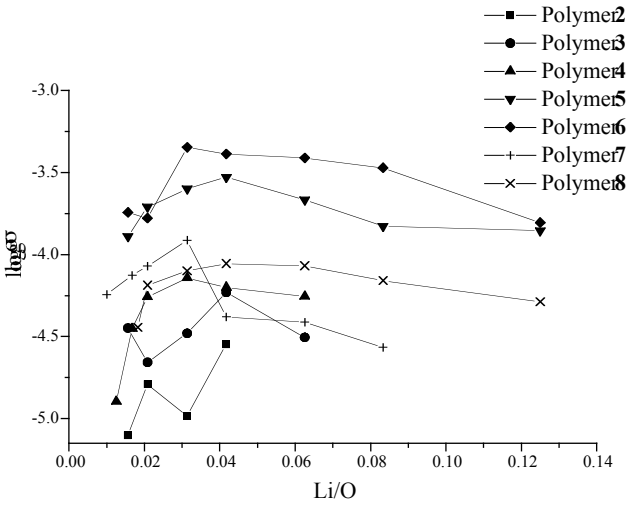


Figure 2. Ionic conductivities as a function of doping level and side chain ether length for disubstituted polysiloxanes.

Subsequently, polysiloxane polymer hosts with branched and crown ether side chains were examined and these families of electrolytes also have high ionic conductivities.[5] Investigations into more fluid electrolytes[6] and free-standing gel electrolytes[7] 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-oliogo(ethylene oxide) molecules such as the structure shown below in Figure 3.[8] Electrolytes of these hosts and LiTFSA have the highest ionic conductivities yet measured in our group (Figure 4).

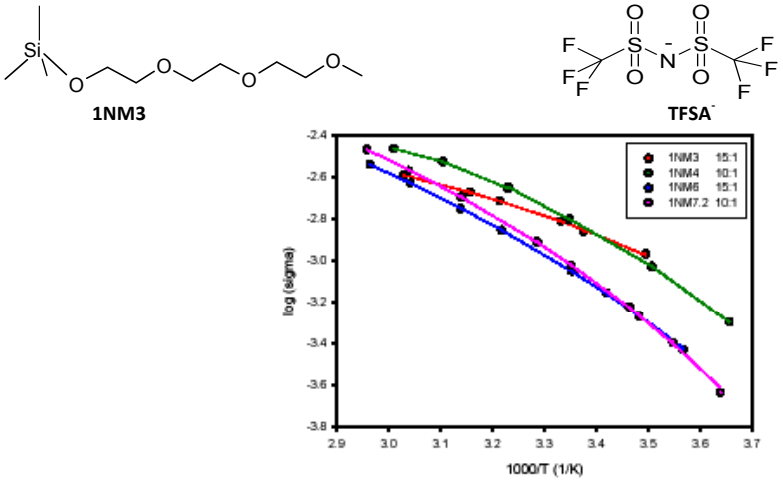


Figure 3. Variable temperature ionic conductivities of the LiTFSA doped electrolytes 1NM3, 1NM4, 1NM6, and 1NM7.2 at their optimum doping levels and the chemical structures of 1NM3 and the TFSA anion (above).

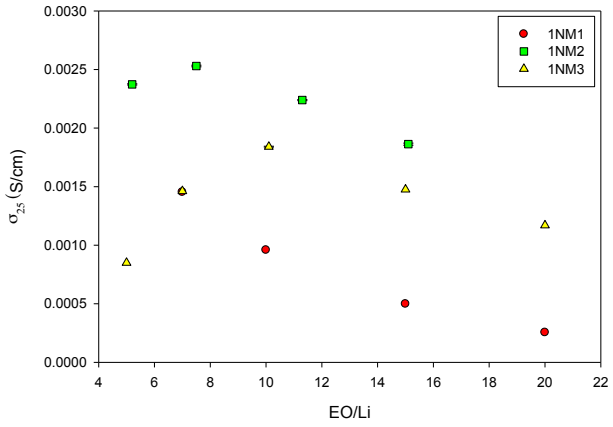


Figure 4. Ionic conductivities of the LiTFSA doped electrolytes 1NM1, 1NM2, and 1NM3 as a function of salt doping level.

These silicon-containing electrolytes are of interest to Argonne National Laboratory, Quallion Corporation in California and Silatronix in Madison who are developing prototype lithium or lithium-ion batteries. We have been collaborating for several years with their scientists who used these electrolytes in miniaturized, biological lithium batteries (BIONs).[9] 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 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 conductivites 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 cation and the anion 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 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:

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

Futhermore, ionic conductivity and diffusion measurements may be compared by a parameter called ionicity as shown below by the ratio between the molar conductivity, L, calculated from impedance measurements and the conductivity calculated from the Nernst-Einstein equation and diffusion measurements, called L_{NMR}:

$$\text{Ionicity} = L_{impedance}/L_{NMR}$$

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:

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

During the summer of 2008, Adam Kortan made progress on this problem and established that the diffusion coefficients do indeed correlate with the ionic conductivities previously measured by Jocelyn Newhouse, Chris Pretorius, and Eleni Tsivitzi (Figure 5).[11]

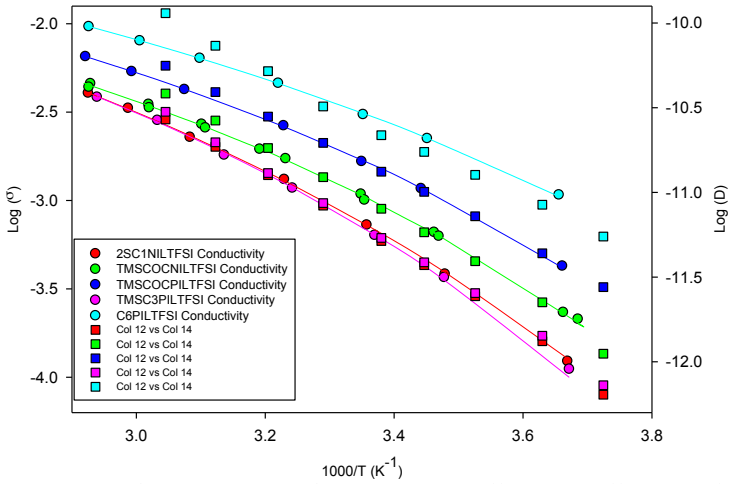


Figure 5. Ionic conductivities (lines and circles) and average diffusion coefficients of the proton (cation) and fluorine (anion) (squares) as a function of temperature for several silyl ionic liquid electrolytes.

In the summer of 2009, Mike Tylinski and Elizabeth Martin worked on parallel conductivity and diffusion NMR experiments over the same temperature range allowing calculation of ionicity and transference numbers for ten different electrolytes of the 1NM3 silyl host (Figure 6). These electrolytes have interesting trends in their ionicity and transference numbers as a function of composition and temperature.[12]

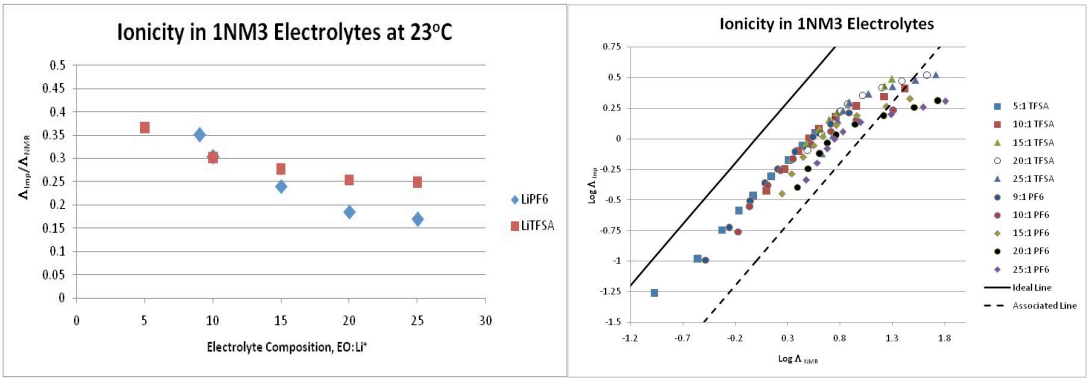
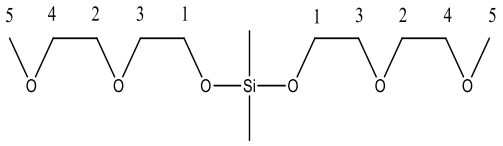


Figure 6. Ionicity for two electrolyte series as a function of composition (left) and temperature (right).

For the summers of 2011/2012 we also studied silyl molecules closely related to the 1NMx series where there are two ethylene oxide chains attached to the Si. These molecules provide more lithium cation coordinating sites than their corresponding 1NMx molecules which may prove important for device applications. One representative molecule shown below is called 1ND2:



1ND2

where the numbers identify uniquely resolvable protons in the 400 MHz ^{1}H NMR spectrum. Koua Xiong prepared a series of electrolytes based on this solvent with both the LiTFSA and LiBOB salts and Chalie Adelson and Claire Williams measured the diffusion of the solvent and ions using PFG-STE NMR as shown below:

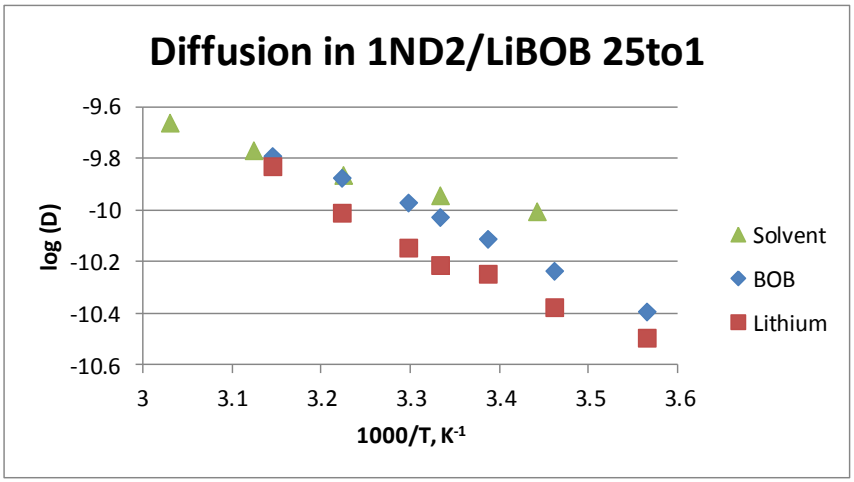


Figure 7. Arrhenius plot of the diffusion coefficients for the solvent 1ND2 (^{1}H), the BOB anion (^{11}B) and the cation (^{7}Li).

Also in 2012 Willie Barth studied mixtures of 1ND2 and 1NM2 solvents and found compositions where the LiBOB salt would dissolve as well as mixtures with enhanced ionic conductivities. In the summer of 2013 we began studies of solvent mixtures of silyl solvents and organic carbonates, and these studies will continue in the summer of 2014.

Experience

All of these research projects will introduce students to materials science, new applications of electrochemical methods, spectroscopic measurements, and computer data anaylsis. 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.

References

[1]Lyons, L.J.; Southworth, B.A.; Stam, D.; Yuan, C.-H.; West, R. *Solid State Ionics,* **1996**, *91,* 169.
[2]Hooper, R.; Lyons, L.J.; Moline, D.; West, R. *Organometallics,* **1999**, *17,* 3249.
[3]Mapes, M.K; Schumacher, D.; Lyons, L.J.; Moline, D.; Hooper, R.; West, R. *Poly. Preprints,* **2000**, *41(1)*, 401.
[4]Hooper, R.; Lyons, L.J.; Mapes, M.K; Schumacher, D.; Moline, D.; West, R. *Macromolecules,* **2001**, *34,* 931-936.
[5]Hooper, R.; Lyons, L. J.; Moline, D.; West, R. *Silicon Chemistry,* **2002**, *1,* 121.
[6] Jin, J. J. ;Lyons, L. J.; Wang, Q; West R. *Polymer Preprints,* **2003**, *44* , 1148.
[7] Zhang, Z.; Sherlock, D.; West, R.; West, R.; Amine, K.; Lyons, L. J. *Macromolecules,* **2003**, *36,* 9176.
[8] a) Harring, S.; *Straughan, M.; *Taggart, J.; Lyons, L. J.; Zhang, Z. C.; and West, R. *PMSE Preprints,* **2006**, *94,* 567. b) Lingzhi Zhang; Zhengcheng Zhang; Scott Harring; Megan Straughan; Rachel Butorac; Zonghai Chen; Leslie Lyons; Khalil Amine and Robert West, *Journal of Materials Chemistry, 2008, 18, 3713-3717*.

[9]Amine, K. *Argonne National Laboratory Report R-17: Implantable, Rechargeable Microbatteries for BION™ Microstimulators* http://www.anl.gov/OPA/factsheets/r17-02.htm, August, 2002.
[10]Harring, S.; *Straughan, M.; Mobley, T. A.; Lyons, L. J.; Zhang, Z. C.; and West, R. *PMSE Preprints,* **2006**, *94,* 541.
[11] Newhouse, Jocelyn; Lyons, Leslie J.; Pretorius, Chris; and Tsivitzi, Eleni; "Conductivity and Capacitance Measurements of Silicon-Containing Ionic Liquids for Energy Storage Devices," Symposium Q: Ionic Liquids in Materials Synthesis and Application, Materials Research Society, Spring National Meeting, San Francisco, CA, Mar. 26, 2008, oral presentation Q6.2.
[12] Lyons, Leslie J. "Silyl Electrolytes for Lithium Battery Applications," Seminar to the Chemistry Department at Monash University, Clayton, Victoria, Australia, Nov. 2, 2009.