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### Liquid and Solid State NMR Investigations of Electrolytes for Beyond Lithium Ion Applications

Nuclear magnetic resonance (NMR) has been productively employed to investigate ion transport and solvation in Li ion battery electrolytes. NMR is a unique method of probing local structure and dynamics in a wide variety of materials owing to the short range nature of the interactions that produce spectral features and govern relaxation behavior. Among its advantages are elemental (nuclear) specificity and its reliably quantitative nature in that the integrated intensity of a particular spectral component is directly proportional to the number of nuclei in the corresponding material phase. Modern day NMR has grown into an enormously diverse array of sophisticated experimental techniques in studies ranging from complex biochemical systems in the solution phase to a wide selection of solid-state compounds, with often negligible overlap in methodology. As a counterexample of the increasing divergence between the liquids and solids NMR communities, we present here several recent or ongoing NMR investigations of lithium battery materials, utilizing both liquid state and solid state NMR. Future electrochemical power sources require new electrolytes to adapt to disruptive changes in the basic working chemistry, such as moving from Li ion to Na ion, or to Li metal electrodes. We highlight three recent collaborative activities on electrolytes in our group (i) glyme-based electrolytes for Li-S and Na ion batteries; (ii) Li<sub>3</sub>PS<sub>4</sub> solid electrolyte (iii) non-polyether polymer electrolyte for Li-metal batteries.

DEPARTMENT OF  
CHEMICAL & BIOMEDICAL  
ENGINEERING

GRADUATE SEMINAR  
SERIES

Where:

Aero-Propulsion,  
Mechatronics and Energy  
Building (AME) 106

When:

Friday, April 13<sup>th</sup>, 2018 at  
11:00am

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## *Abstract Continued*

A series of Li electrolytes made with glymes of variable length (mono, di, tri, tetra, and higher) has been synthesized by collaborators (Jusef Hassoun, Lorenzo Carbone) at the University of Ferrara, Italy. Natural abundance  $^{17}\text{O}$  NMR is found to be an exquisitely sensitive probe of the total charge on the solvent as well as anion oxygens, and thus provides useful information on solvent-ion and ion-ion association. Though these electrolytes show promise for use in Li metal and Li-S batteries, NMR measurements reveal a significant degree of ion association. Results are also presented for the corresponding Na electrolytes, as well as for (time permitting) binary carbonate solvent mixtures for Na ion batteries in collaboration with the U.S. Army Research Lab (Kang Xu, et.al.)

In the solid electrolyte realm, in collaboration with Chengdu Liang, et.al., (formerly of Oak Ridge National Lab), we investigated the phase evolution of nanoporous  $\beta$ - $\text{Li}_3\text{PS}_4$  prepared by wet chemical synthesis and subsequent thermal treatment by  $^7\text{Li}$  and  $^{31}\text{P}$  magic angle spinning NMR. The  $\beta$  phase exhibits ionic conductivity over two orders of magnitude higher than that of the corresponding bulk crystalline compound,  $\gamma$ - $\text{Li}_3\text{PS}_4$ .

Ionic Materials, Inc. (Mike Zimmerman, Randy Leising, et.al.) has invented a novel polymer electrolyte with extremely high ionic conductivity over a range of temperatures, even surpassing that of a commercial porous separator containing the standard liquid carbonate-based electrolyte at room temperature. This solid polymer can be reliably extruded into very thin films, is non-flammable, has attractive mechanical properties for lithium dendrite suppression, is electrochemically stable against Li, and is compatible with a variety of different anodes and cathodes. The polymer electrolyte is based on an inexpensive semicrystalline commercially available polymer such as polyether ether ketone or polyphenylene sulfide and Li salts familiar to the battery and polymer electrolyte communities. The ionic transport mechanism is unlike that which characterizes the PEO salt complexes – that is ion mobility is completely decoupled from polymer host motion, as verified by differential scanning calorimetry and NMR. In fact NMR pulsed gradient measurements reveal Li self-diffusion coefficients at room temperature that the highest in any known solid.

**Bio:** Dr. Steve Greenbaum is a Professor of Physics at Hunter College (CUNY), Executive Officer of the PhD Program in Physics at the CUNY Graduate Center, and a Fellow of the American Physical Society. Dr. Greenbaum earned his PhD in Physics from Brown University. He was an NRC Postdoc at the Naval Research Laboratory in Washington, DC, and spent sabbatical years as a Fulbright Scholar at the Weizmann Institute of Science and Senior Research Fellow at the Jet Propulsion Laboratory. He has held Visiting Professorships at Stony Brook University, Rutgers University, Tel Aviv University, University of Paris-Sud, University of Padova, and University of Rome Sapienza. Dr. Greenbaum's research involves spectroscopic studies of disordered solids by magnetic resonance and synchrotron x-ray absorption, most recently on materials for electrochemical energy storage and conversion (i.e. batteries and fuel cells). He has authored or co-authored over 250 peer reviewed publications and given over 50 invited talks at national or international conferences, and received the NSF-sponsored 2002 Presidential Award for Excellence in Science, Mathematics, and Engineering Mentoring. Dr. Greenbaum served, 2014-15, as one of eleven Jefferson Science Fellows as senior Science and Technology advisors to the U.S. State Department.