Electrolytes - R&D for Advanced Lithium Batteries.
Interfacial Behavior of Electrolytes

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Overview

Timeline

- PI has participated in BATT program since 1998.
- 1994-1999 USABC/3M/HQ project on Li/Polymer batteries.
- FY10 Project started Oct. 1, 2009, completed December 31, 2010
- FY11 Project started October 1, 2010
  - 25% completed

Budget

- FY10 Funding - $550k
- FY11 Funding -$550k

Barriers

- low power and energy densities.
- Poor cycle and calendar life.
- high manufacturing cost.

Interactions/Collaborations

•Grant Smith/Oleg Borodin (U. of Utah) – Molecular Dynamics modeling.

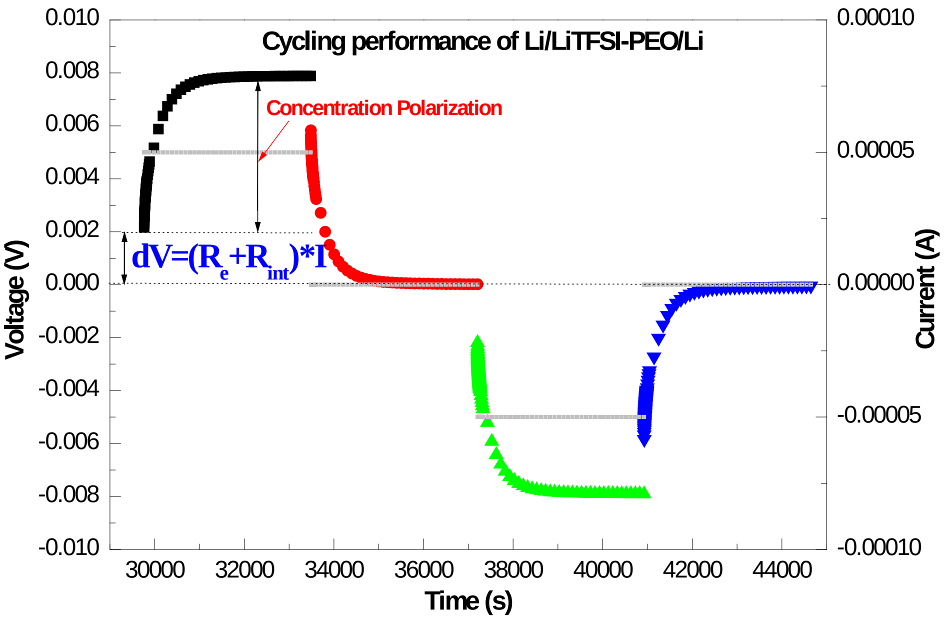
• Marshal Smart (JPL/ABR), Brett Lucht (URI) – New Electrolyte evaluation

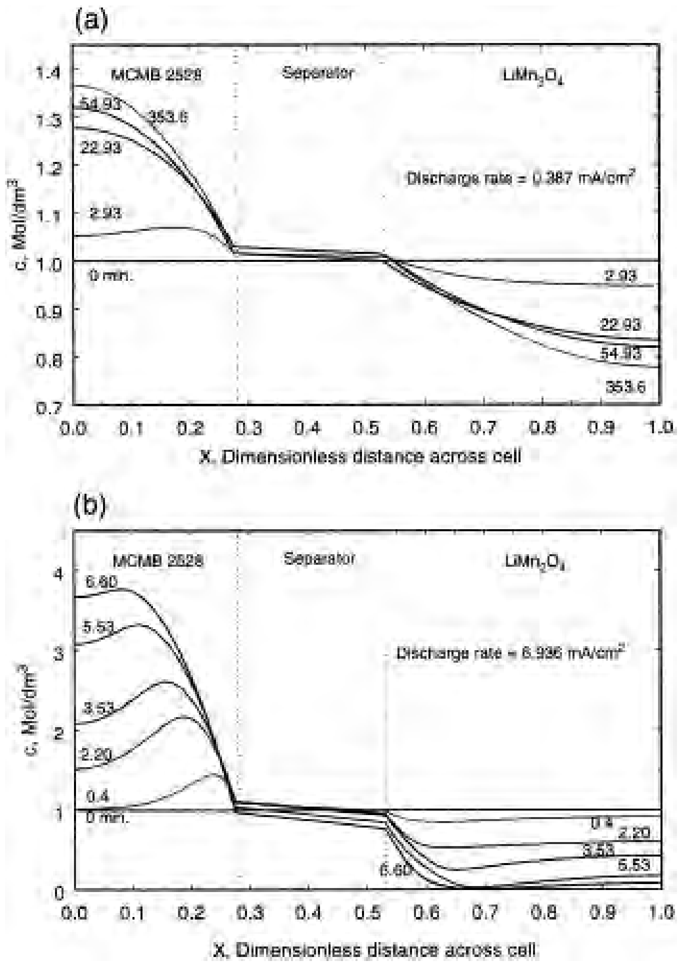
• 3M - alloy anodes.

• DOE Fuel Cell Technologies Program – New polyelectrolyte material synthesis and Applied Science Program (LANL) – composite electrode studies.

Relevance.

Impact of Interfacial vs. Bulk vs. Concentration Impedance

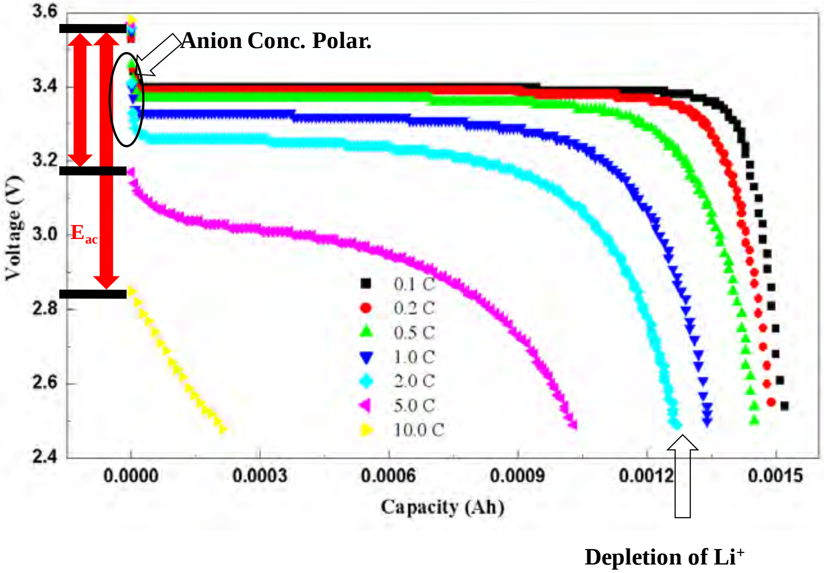




Salt concentration affects R_{int} at electrode surface & bulk conductivity.
Concentration polarization can be significantly greater than the bulk and interfacial impedances combined particularly in composite electrodes.
Remove concentration polarization by use of lithium ion single ion conducting polyelectrolytes.

Effect of Transport Properties on Li-Ion gel polymer cell, **Arora, Doyle, Gozdz, White and Newman, J. Power Sources, 88 (2000), 219-231.**

Relevance



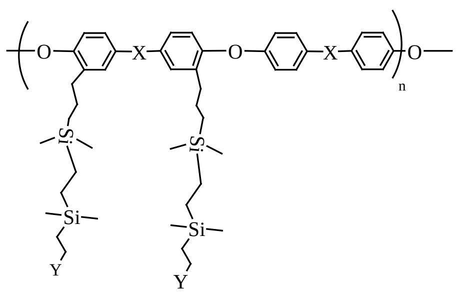
Concentration & Interfacial Polarization contribute to Capacity loss.
Single ion Conductors remove concentration polarization and allow use of thicker electrodes - fewer separators and current collectors required gives higher energy density.
Require conductivities > 10^{-4} S/cm – already achieved for gels, close for dry polymers.

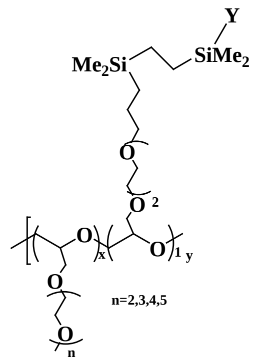
Objectives

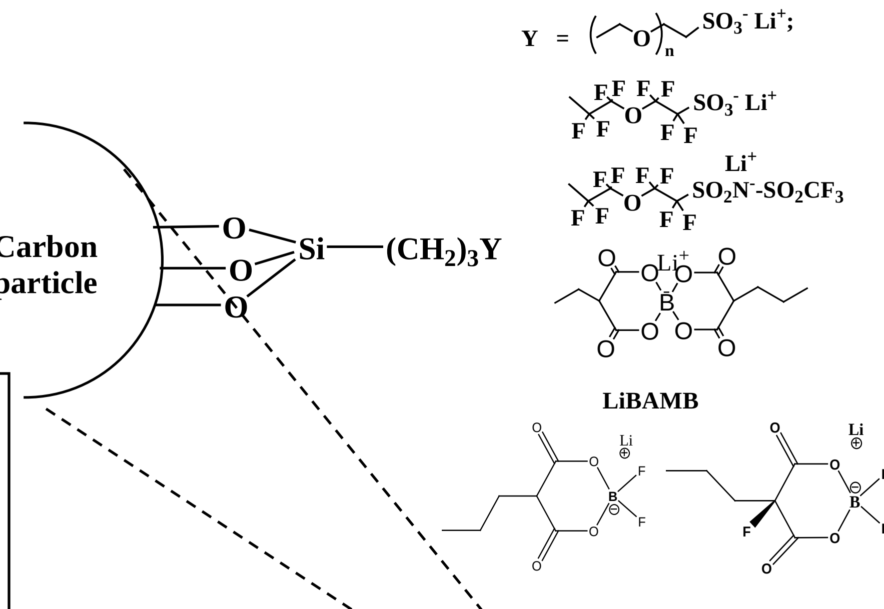
- Determine the role of electrolyte structure upon bulk transport and intrinsic electro-chemical kinetics and how it contributes to cell impedance (Energy/ power density) - Performance/cost.
- Determine chemical and electrochemical stability of electrolyte materials to allow elucidation of passivating layers (e.g. SEI) - Lifetime/performance/cost.
- Design and synthesize binary salt and single-ion conducting electrolytes to optimize transport and interfacial properties to maximize power and energy densities while minimizing life-limiting side reactions..

Approach/Strategy

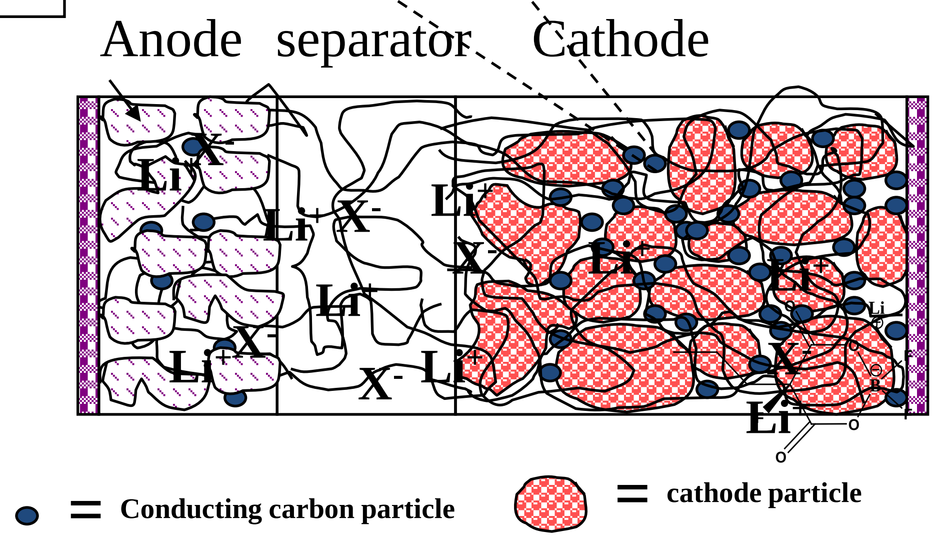
Prepare & Test polymers and surfaces that can be functionalized and tuned.







<u>Polysulfones</u> compatible with high positive potentials – **cathode binders**. Mechanically stiff, unable to accommodate electrode expansion.	<u>Polyethers</u> not stable to high positive potentials (>3.6V vs. Li) - **anode binders**. Elastic. Large volume changes OK.



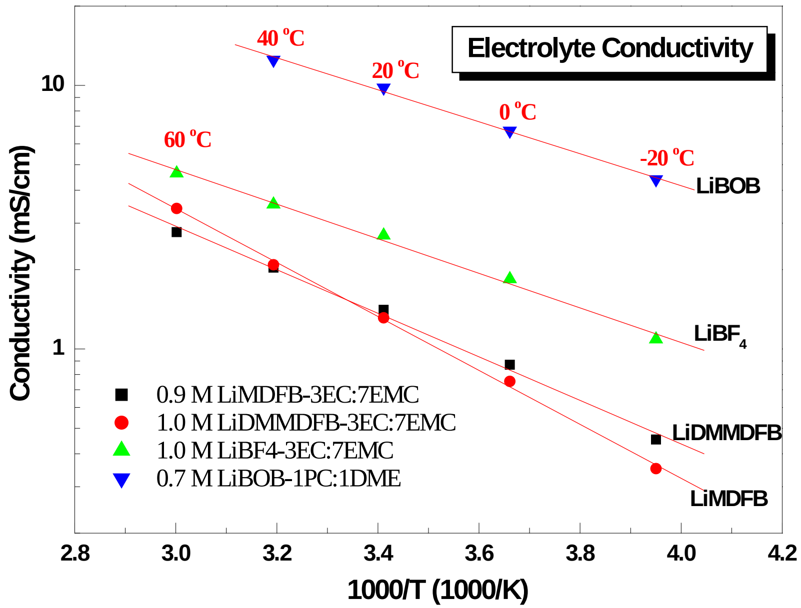
Single-ion conductor gels and binders prevent concentration polarization.
Immobilized polymers allow different salt concentrations next to the electrodes than in the bulk separator.
Functionalized conducting particles may alter electrode environment and allow control of interfacial impedance.
Exchange current density ($\propto$ i/R_{int}) depends on surface concentration.

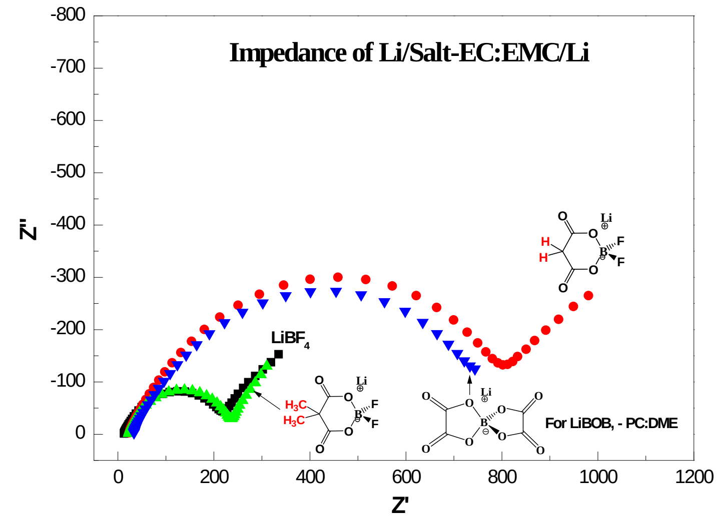
Approach/Strategy
FY 10-11 Milestones

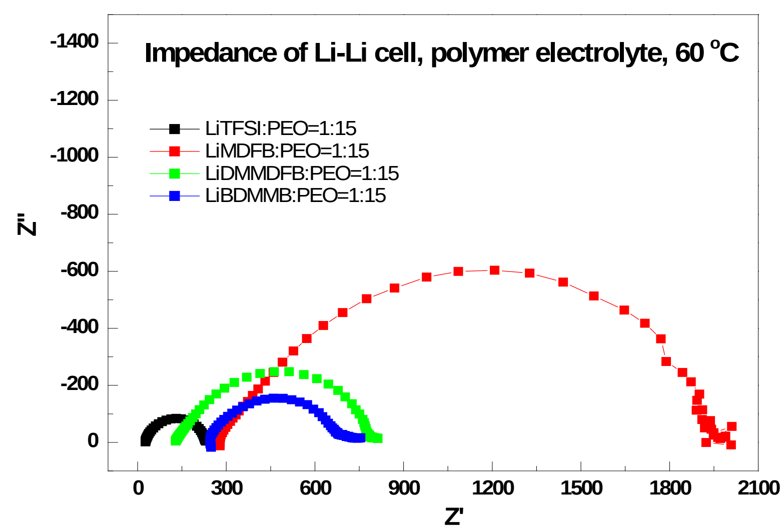
Month/Year/Status	Milestone
February/ 2011/ Completed. Delay due supply of material and complications in composite fabrication.	Demonstrate whether single-ion conductor polyelectrolytes (gel and dry polymer) prevent concentration polarization in composite cathodes and facilitate thicker electrodes.
April/2011/Delay due to supply of material	Determine whether single-ion conductor polyelectrolyte (gels and dry polymers) are beneficial for large volume-expansion anodes.
April/2011/3 months behind	Determine whether available single-ion conductor polyelectrolytes function with the high voltage NiMn spinel cathodes
September/2011/ On track	Determine the stability of base-line and single-ion electrolyte to NiMn Spinel cathodes including chemical analysis of electrolyte degradation products.

Technical Accomplishments and Progress

Electrolyte conductivity & Interfacial behavior of lithium salts with lithium metal







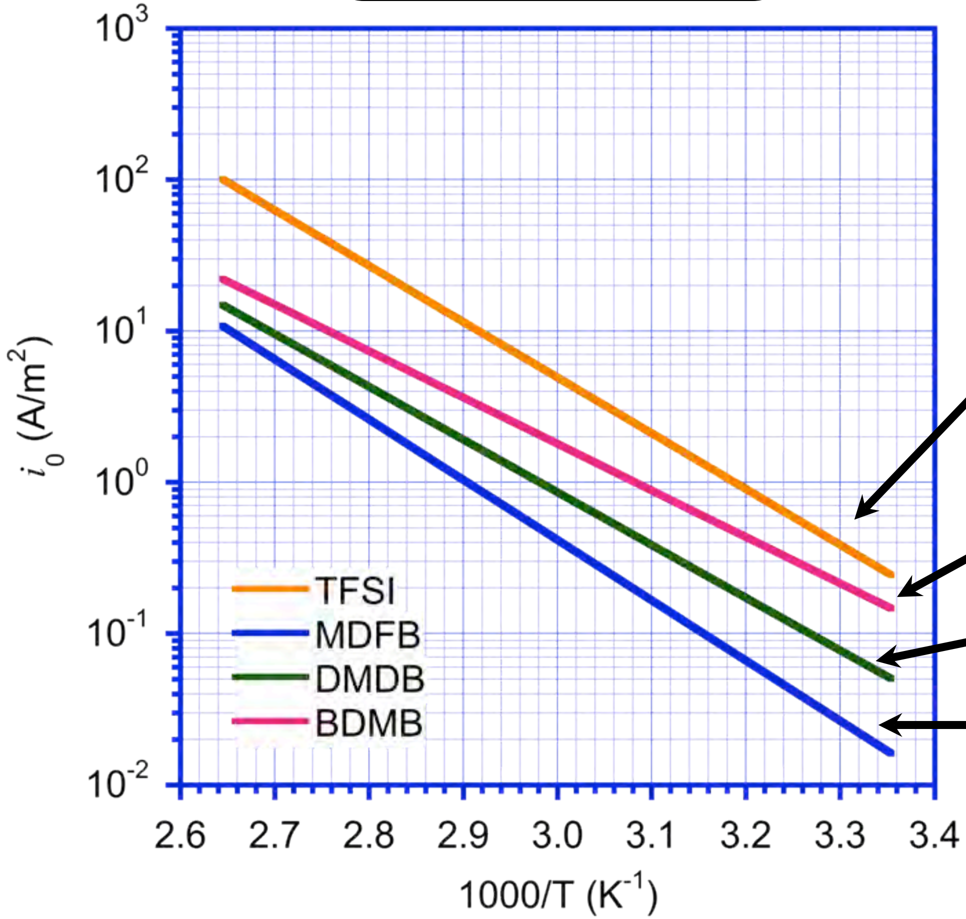
- LiBOB has the highest conductivity, 1 order higher than the 6-membered ring salts, LiMDFB.
- LiMDFB displayed a significant larger impedance, due to the acidic proton
- Replace the acidic protons can to large extent decrease the impedance/reactivity of the salt with Li.

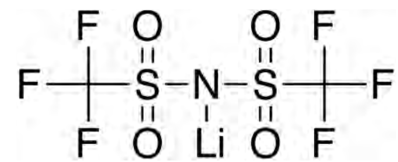
Technical Accomplishments and Progress

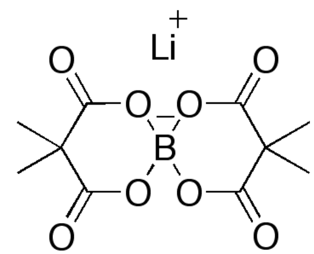
Exchange Current Density

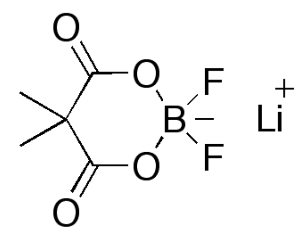
Exchange current densities quantify the rates of lithium deposition at the electrode/electrolyte interface and are determined from the charge transfer resistance measured by impedance spectroscopy.

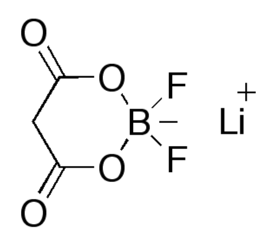
$$i_0 = \frac{RK_0}{z_+ F A_s} \exp\left(\frac{K_1}{T}\right)$$





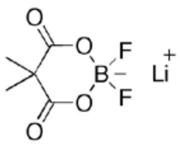


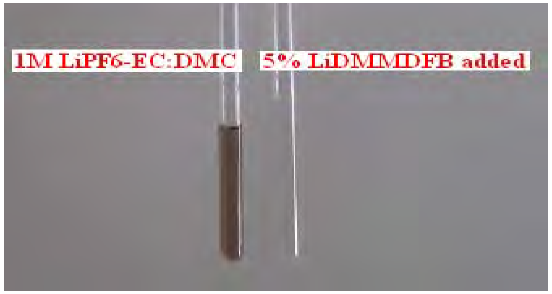




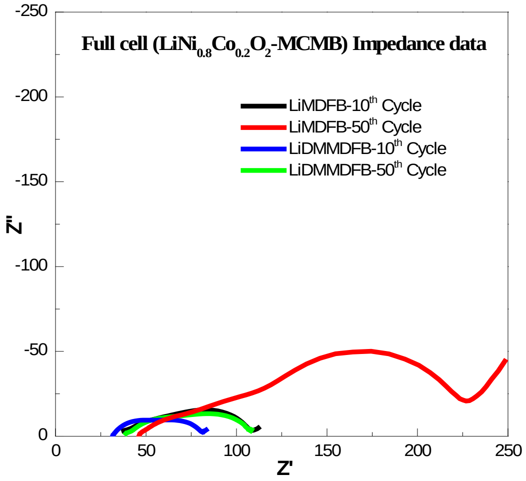
Technical Accomplishments and Progress

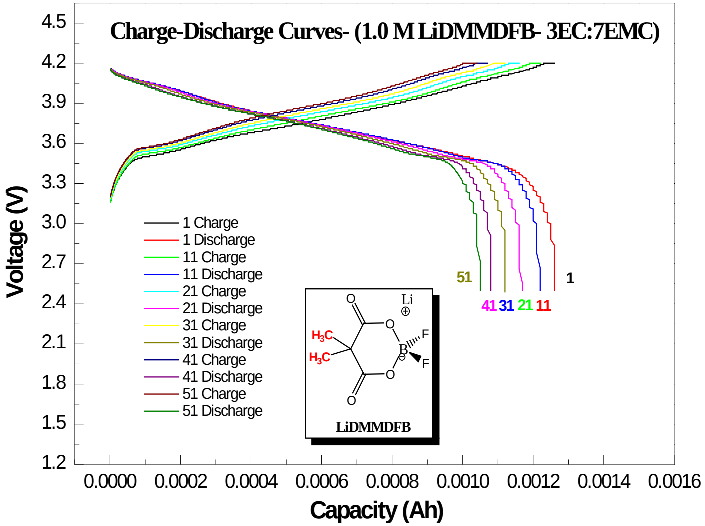
Salts as additives for Stabilization of Electrolytes

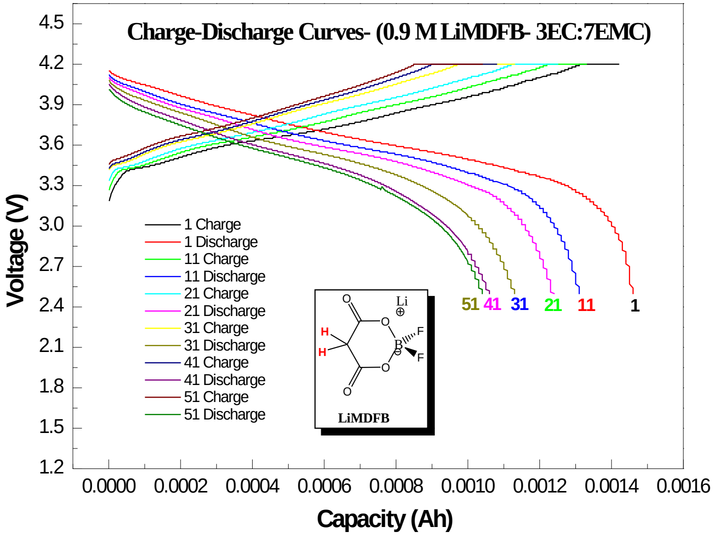




EC:DMC $LiPF_6$ electrolytes heated in sealed nmr tube at 80° C for three weeks.



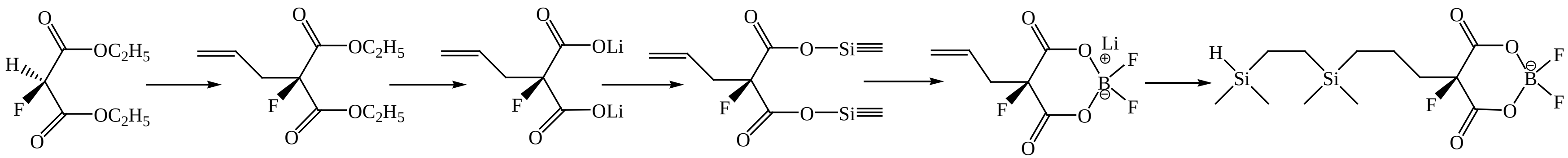


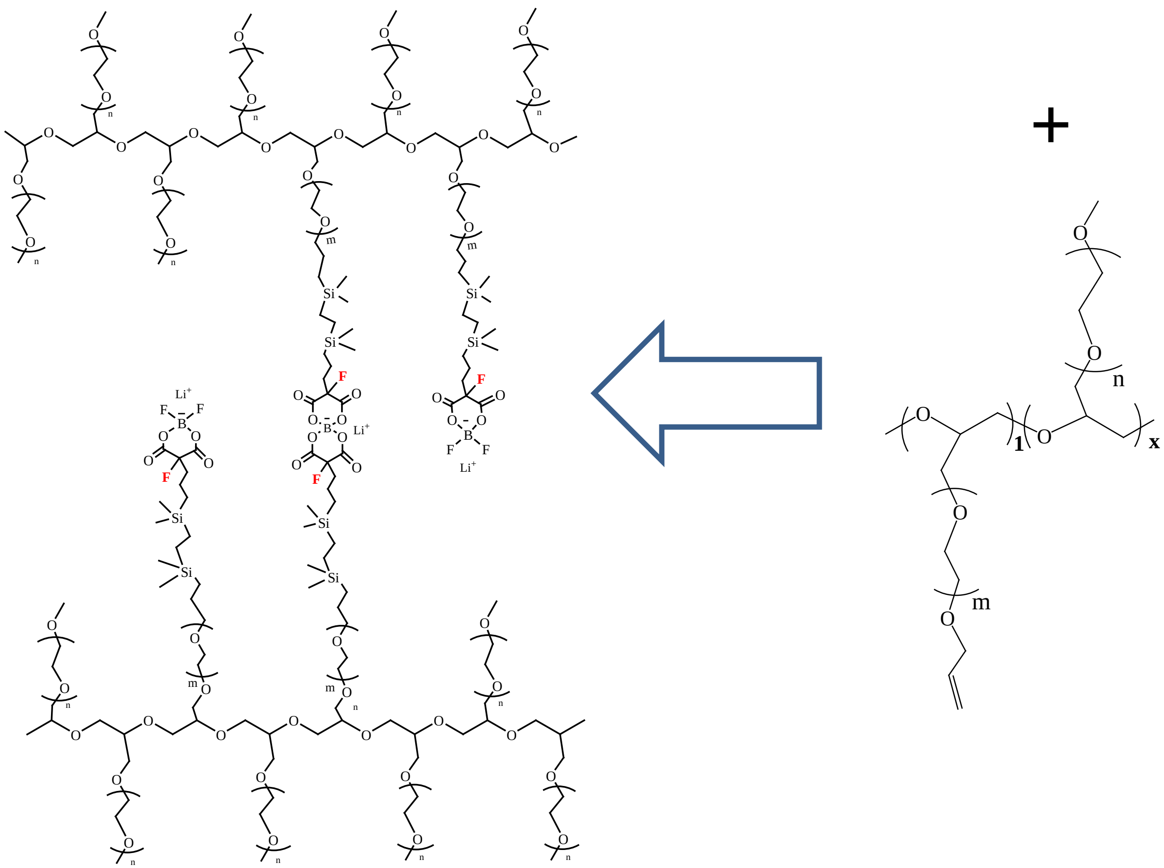


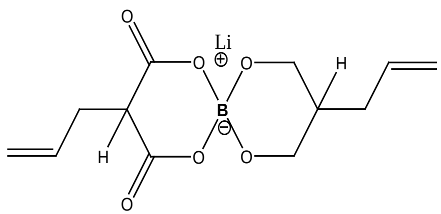
Presently under evaluation by JPL (Marshal Smart) as electrolyte additive in MCMB-$LiNi_xCo_{1-x}O_2$ Cells

Technical Accomplishments and Progress

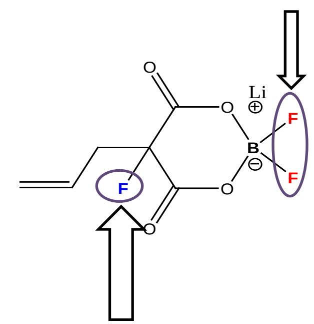
Preparation of Single Ion Conductors (Modified)







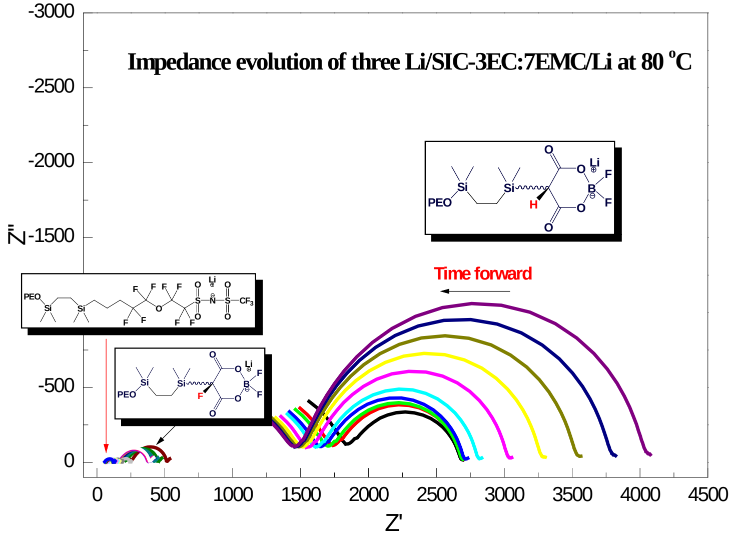
Increased conductivity



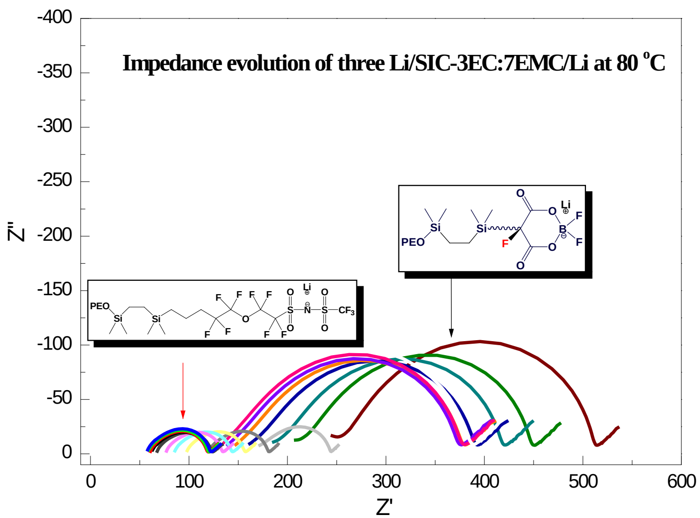
Interfacial stability

Technical Accomplishments and Progress

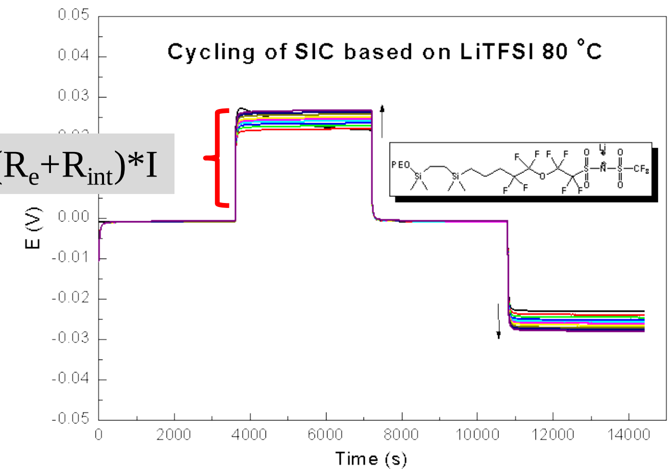
Interfacial Impedance and Cycling Behavior at Lithium Metal



- All SIC showed decreased R_e (R_{bulk}) as time evolved due to the wetting/contact procedure.
- H-MDFB based SIC showed increased R_{int} as time evolved, due to the reactivity of the salt itself.
- F-MDFB and TFSI based SIC showed a stable interfacial resistance (R_{int}) as time evolved.

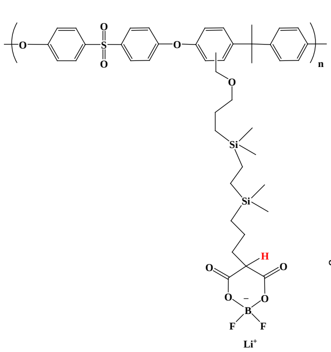


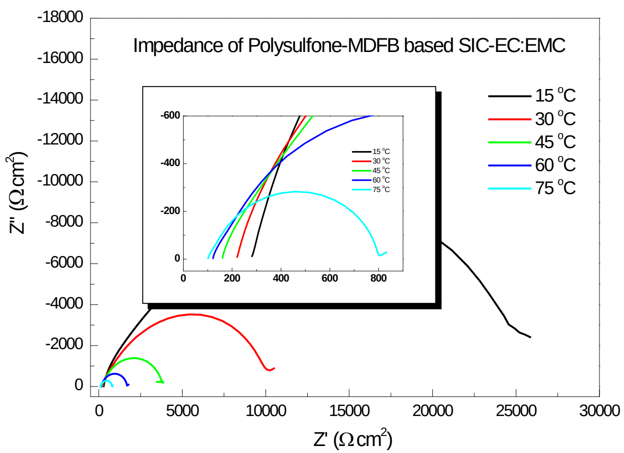
$E_{ac}=(R_e+R_{int})*I$

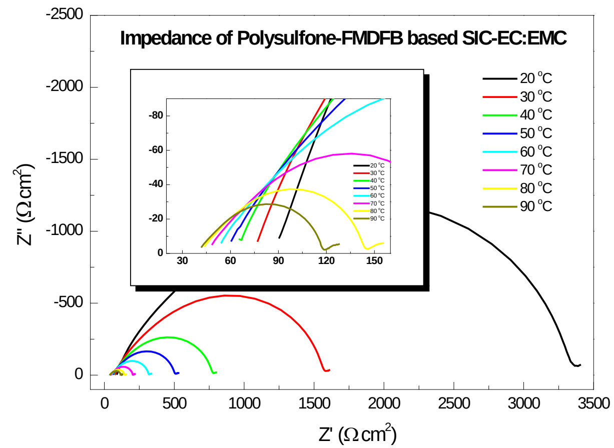


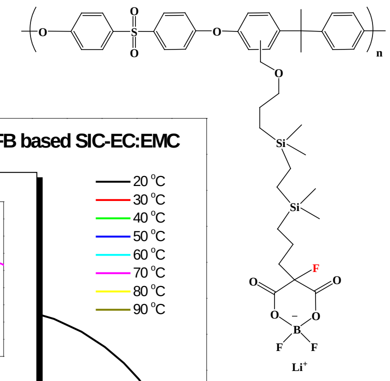
Technical Accomplishments and Progress

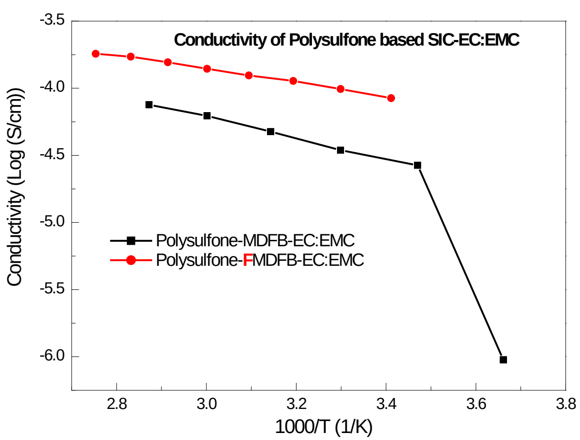
Polysulfone backbones

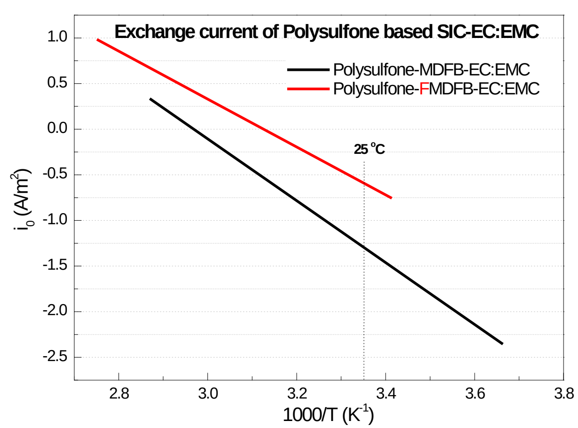


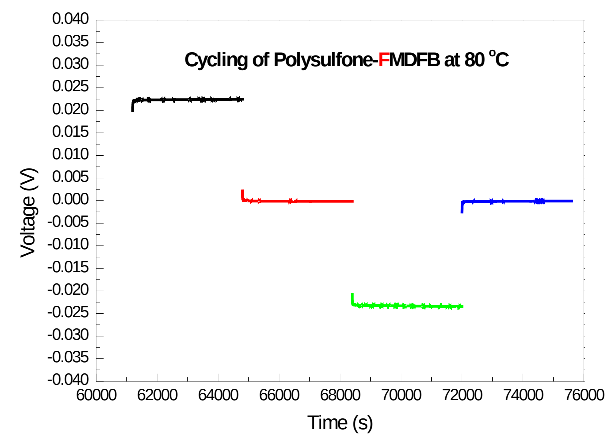








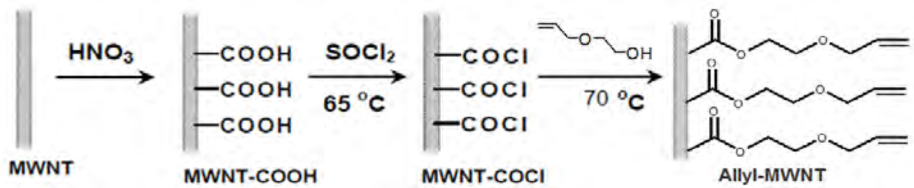




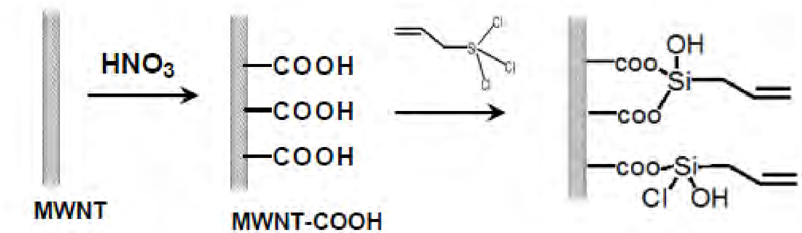
Impedance, conductivity and cycling behavior dependent upon concentration of anions.
Optimized concentration for bulk conductivity not necessarily ideal for interfacial properties.

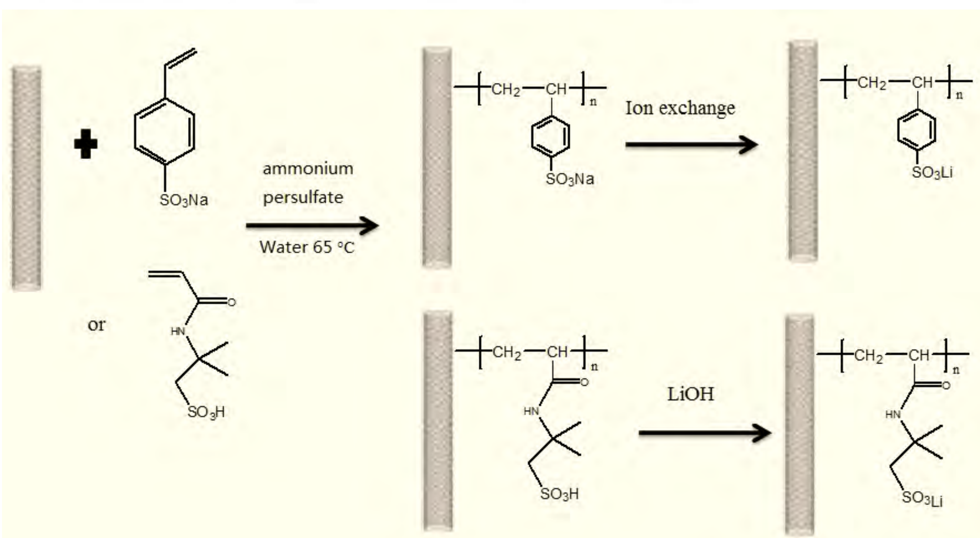
Technical Accomplishments and Progress

Modification of Carbon Additives (MWNT) to control surface ion concentration in composite electrodes.



FTIR and TGA demonstrates functionalization of the Multi-walled Carbon Nanotubes (MWNT). Next step to add anions fails due to reactivity





PSSLi

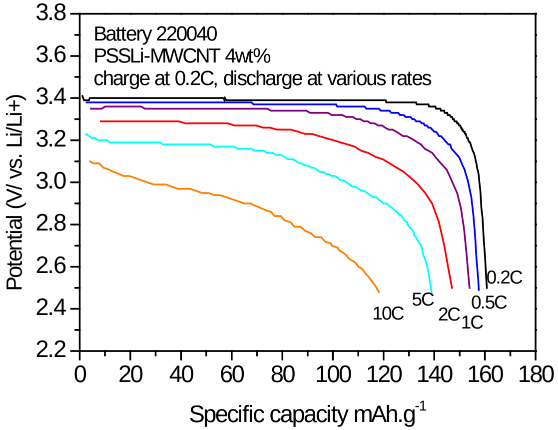
Method also applied successfully to carbon black.

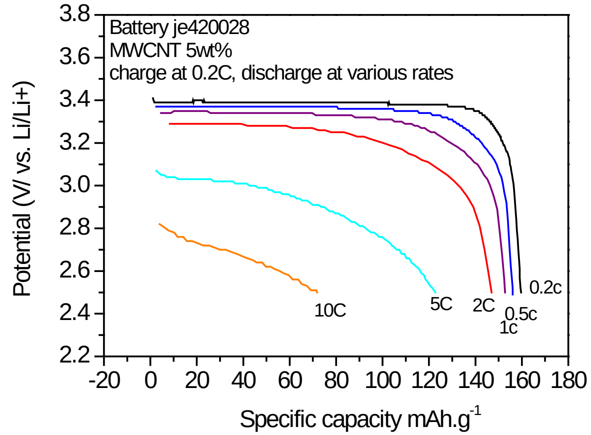
PAMPSLi

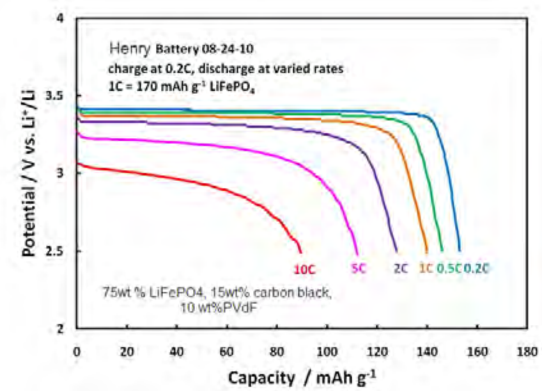
Technical Accomplishments and Progress

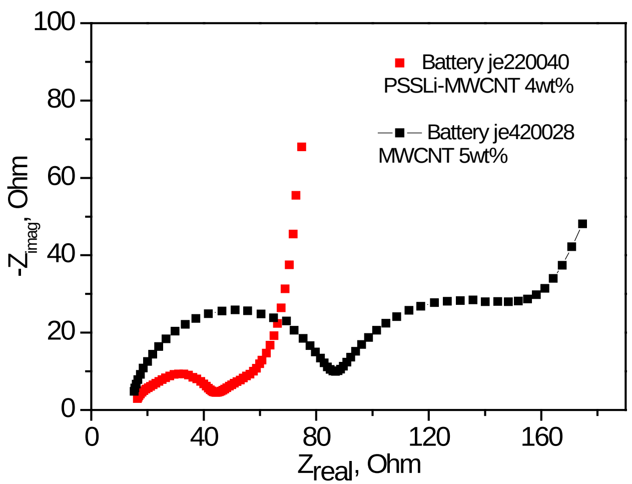
Effect of Modified Conductive Additives on Composite Electrode Performance

Li/1M $LiPF_6$-EC:DMC (1:2)/Li $FePO_4$

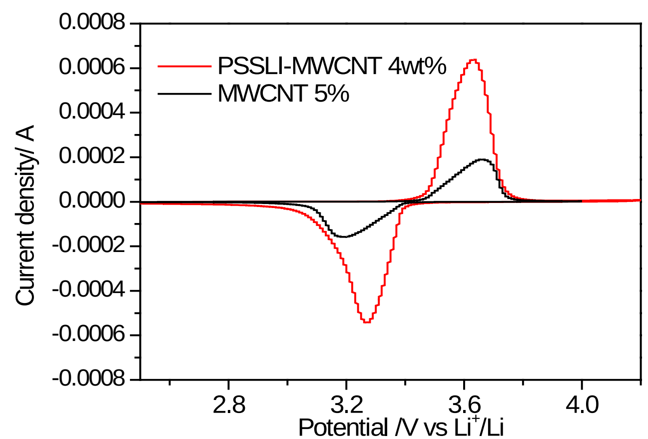








AC impedance of LiFePO4 electrode with different conductive additives

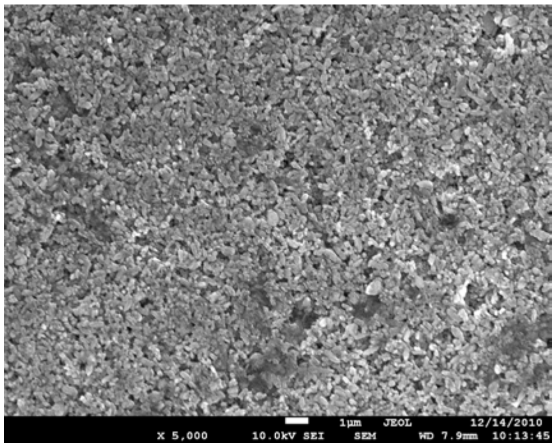


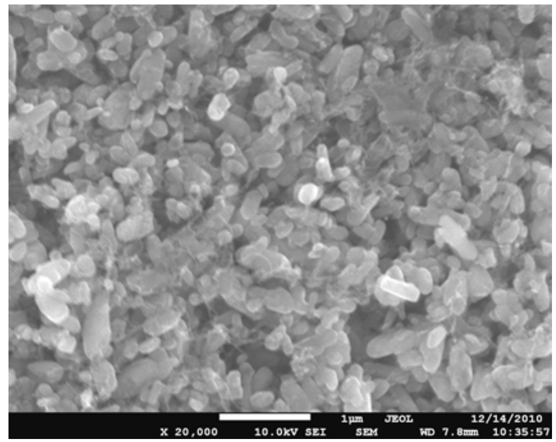
Cyclic voltammetry profiles of Cathodes at 0.2 mV/s

Technical Accomplishments and Progress

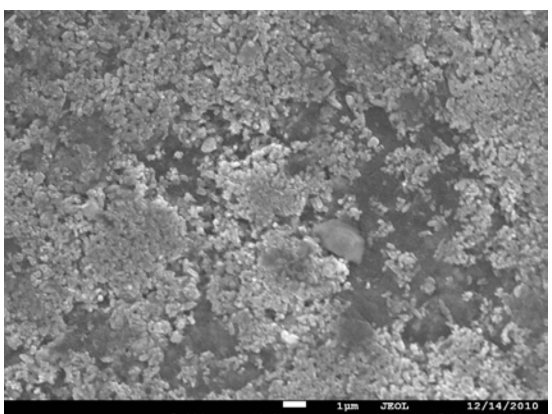
Microscopy of Composite Cathodes

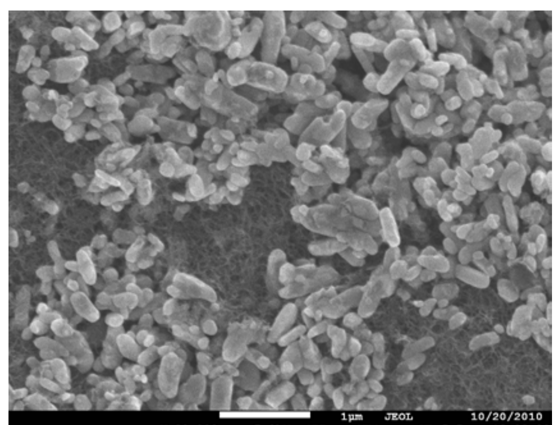
Improved performance with modified carbons appears to be due to better dispersion of conductive additives.





SEM images of $LiFePO_4$/ PSSLi-MWCNTs composite cathode



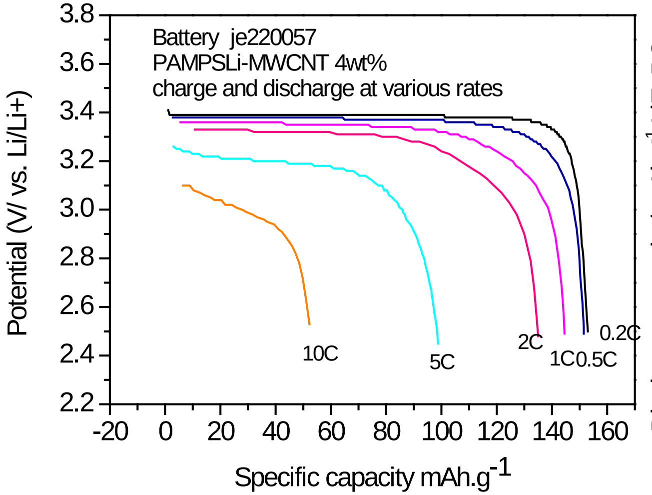


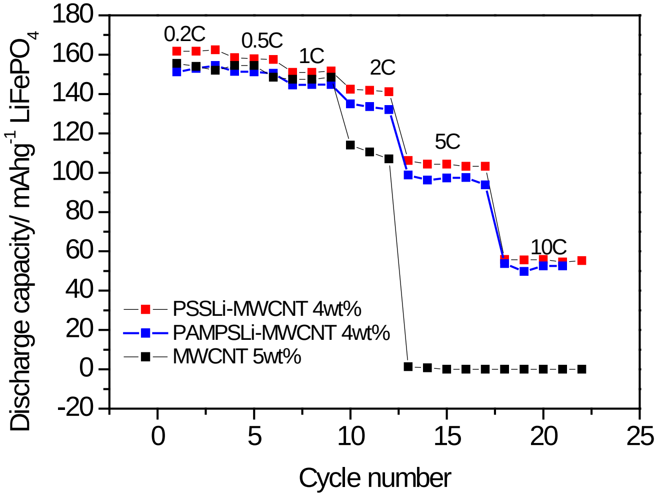
SEM images of $LiFePO_4$/MWCNTs composite cathode

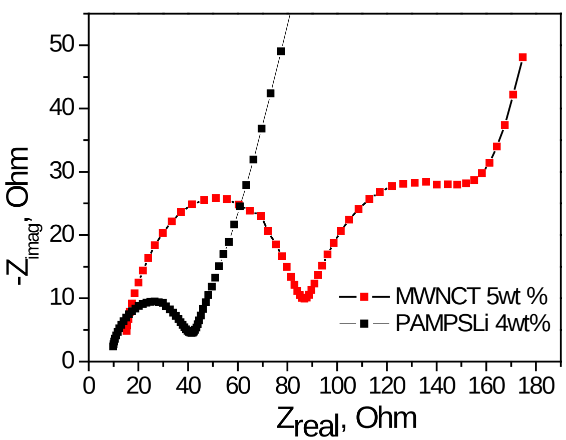
Technical Accomplishments and Progress

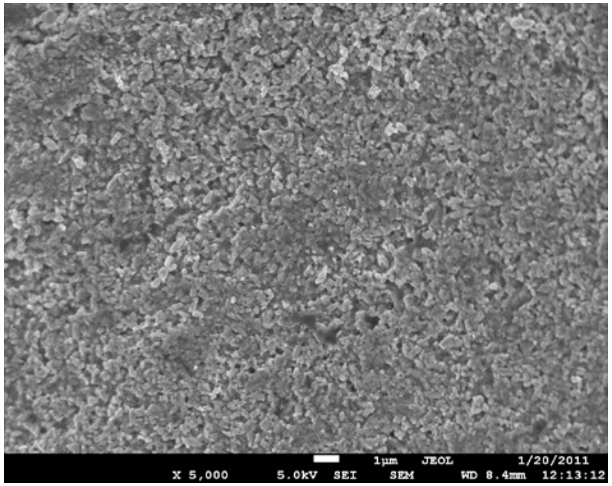
Effect of different Modifier

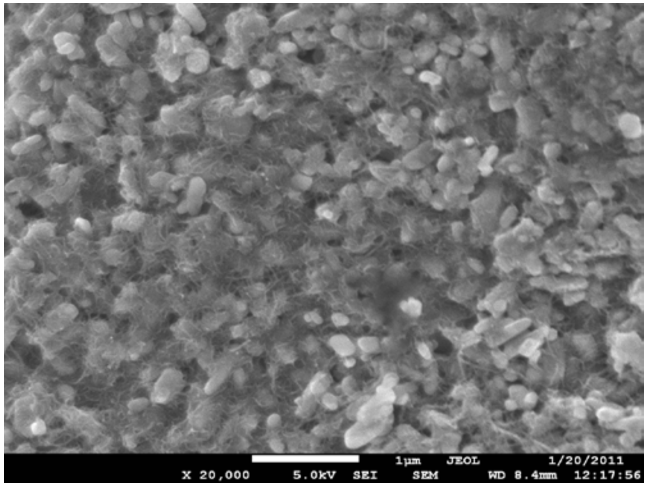
Li/1M $LiPF_6$-EC:DMC (1:2)/Li $FePO_4$







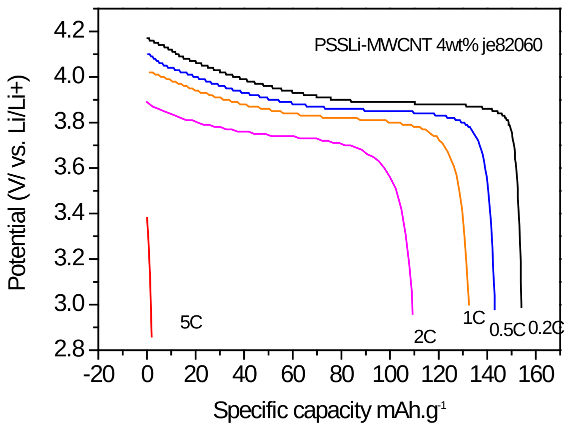


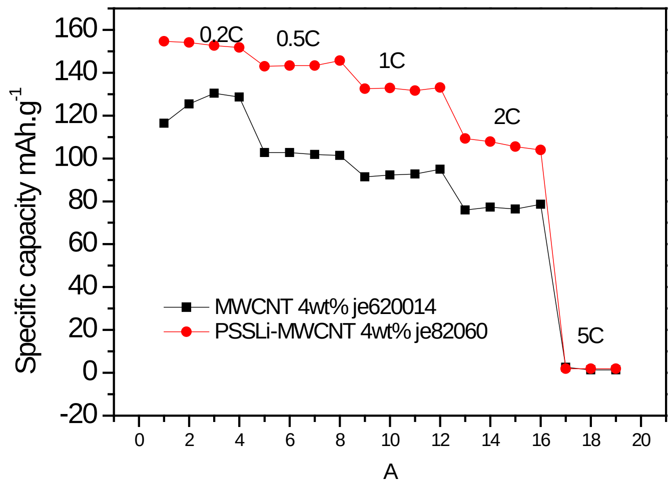


SEM images of $LiFePO_4$/ PAMPSLi-MWCNTs composite cathode

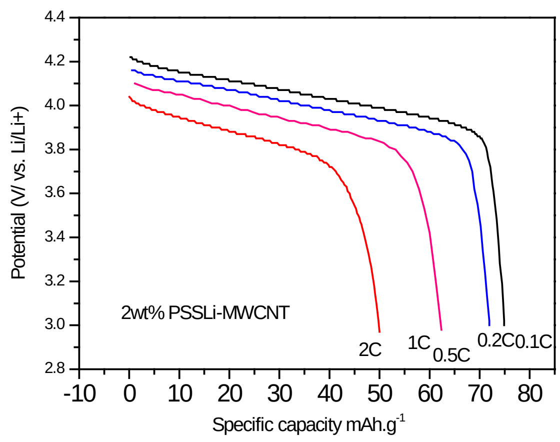
Technical Accomplishments and Progress

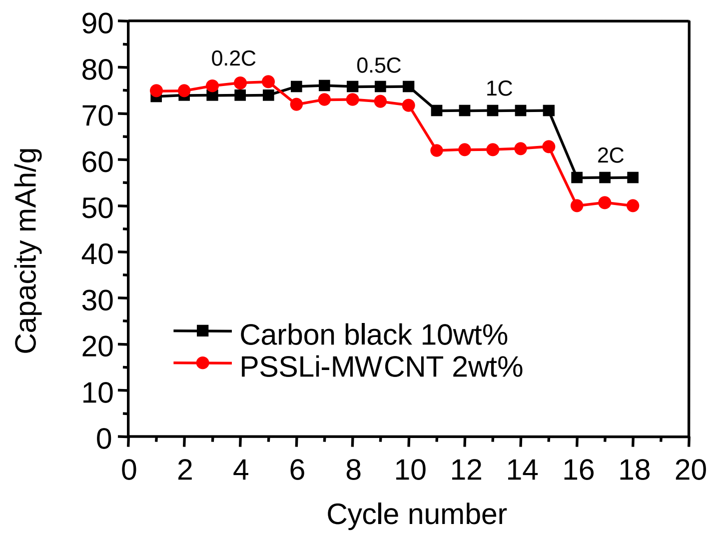
Different Cathode Materials





$LiCoO_x$





$LiMn_2O_4$

Collaborations.

- Close collaboration with Grant Smith and Oleg Borodin (U. of Utah) on MD modeling of systems for both bulk and surface charge transfer.
- Work guided by transport models of system modeling group.
- Electrolyte reactivity and surface reactions requires surface analysis collaborations (Kostecki)
- Collaborating with other electrolyte groups in ABR (Marshal Smart –JPL and Brett Lucht –URI)
- Need sources of reproducible electrode materials (Zhagib, ANL, 3M, other industrial collaborators).
- Need assistance from Cell assembly group (Battaglia, Liu) on reproducibility for celectrode preparation and testing.
- Work is heavily leveraged with Office of Fuel Cell Technologies work on preparation of polyelectrolytes and composite electrode structures for fuel cells where there is close synergy – includes close collaboration with Los Alamos National Lab (Yu Seung Kim, Christina Johnson).
- Providing samples for analysis by Dielectric Relaxation(Penn State and Neutron Scattering(NIST)

Future Work

- Continued Synthesis of polyelectrolyte materials
  - TFSI and fluoroalkylsulfonate LiMDFBanions attached to both polyether and polysulfone backbones with a range of equivalent weights (concentrations of ions).
  - Attach above anions to conducting carbons.
- Characterization of materials.
  - Thermal, mechanical and chemical testing as dry materials and gelled with organic solvents (carbonates, GBL, ethers, sulfones) .
  - Bulk conductivity, dielectric relaxation measurements (Penn State U) and Neutron relaxation (NIST)

Future Work

- Electrochemical characterization of polyelectrolytes.
  - Li metal cells: impedance, lithium cycling.
    - Effects of variable equivalent weight layers on impedance.
  - Composite Electrodes.
    - Continue exploration of modified conducting components in combination with binary salt and single-ion conductor binders.
    - Cathodes. Focus on Low voltage materials ($LiFePO_4$ if available) for polyether materials, $LiCoO_x$ and $LiMn_2O_4$ for polysulfone materials. Characterize composite electrodes thermally, mechanically and electrochemically. Particular emphasis on electrode kinetics and electrode thickness behavior .
    - Anodes. Initial emphasis on Graphite anodes. Characterize composite electrodes thermally, mechanically and electrochemically. Particular emphasis on electrode kinetics and electrode thickness behavior.
    - Expanding anodes. Collaborate with other groups investigating these materials and determine whether elimination of concentration polarization helps to resolve cycling issues.
- Continue development of chemical analysis methods

Summary

- Single ion conductor polyelectrolytes contribute to energy and power densities of lithium batteries but the previously observed interfacial impedances are too high to be practical. A variety of polyelectrolytes have been prepared with sufficient bulk conductivity for EV performance
- Synthesis and characterization of new anions has demonstrated that the anion has a major impact on the electrode kinetics and hence the interfacial impedance. The results indicate that the impedance problem is tractable.
- Modification of the electrode surfaces alters the surface concentration of ions. It is not yet clear whether improvement of performance is due to better kinetics or better distribution of conducting additives.
- Meaningful studies of interfacial behavior requires careful control of conditions to obtain reproducibility. This requires considerable collaboration.