Electrolytes - Interfacial and Bulk Properties and Stability.

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ES089

Overview

Timeline

- PI has participated in BATT program since 1998.
- 1994-1999 USABC/3M/HQ project on Li/Polymer batteries.
- FY 11-14 Project started October 1, 2010, expected completion September 2014.
  - 50% completed

Budget

- FY12 Funding - $550k
- FY13 Funding -$550k

Barriers

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

Interactions/Collaborations

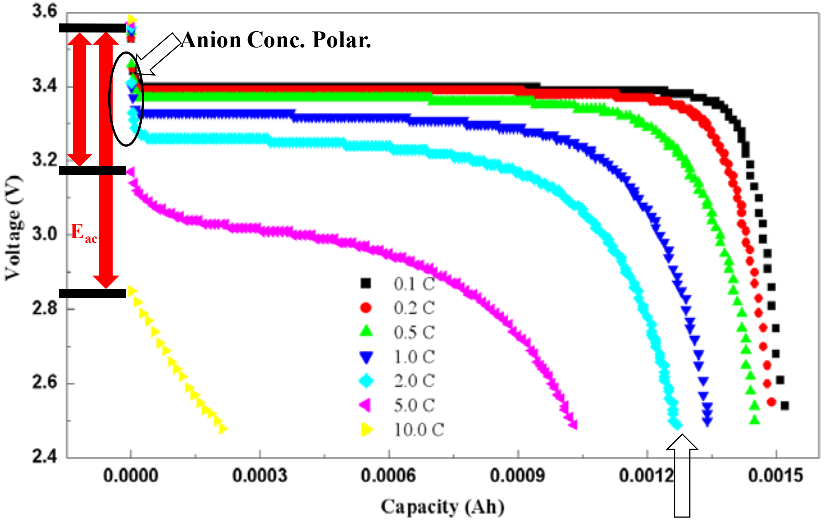
•Marshal Smart (JPL/ABR), Brett Lucht (URI) – New Electrolyte evaluation.

• DOE Fuel Cell Technologies Program – New polyelectrolyte material synthesis and Applied Science Program (LANL) Energy Frontier Research Center – GE, Stanford, Yale -composite electrode studies.

• PHI., Inc. TOF-SIMS of SEI layers.

Single Ion Conductor Electrolytes.

Relevance to Batteries and Implementation Issues.



Depletion of Li^+

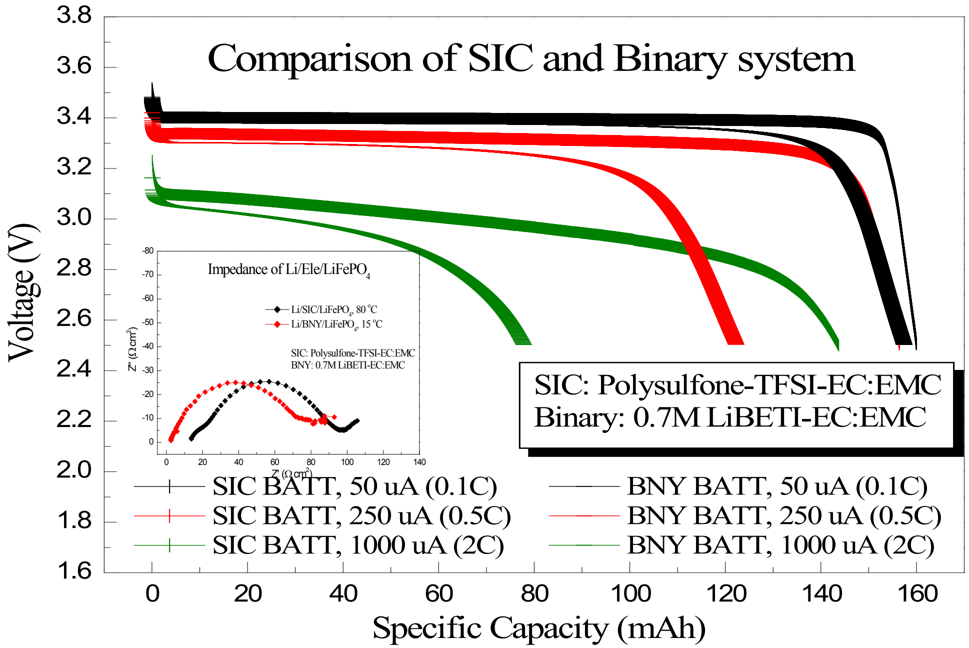
Concentration & Interfacial Polarization contribute to Capacity loss. Single ion Conductors remove concentration polarization and allow use of thicker electrodes - fewer separators and current collectors required gives higher energy density. Require conductivities > 10^{-4} S/cm – already achieved for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

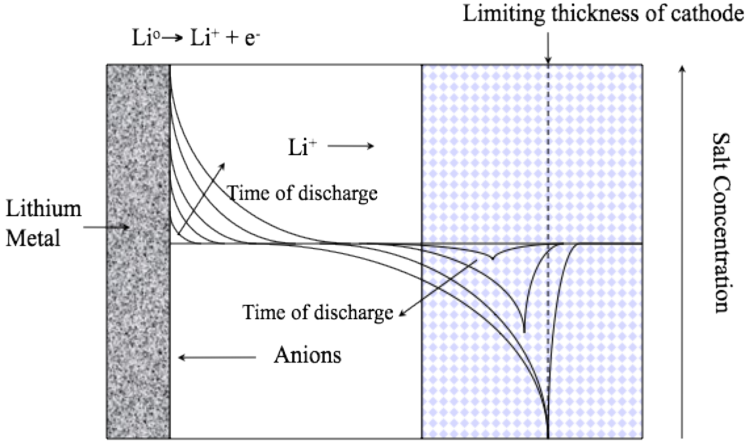
Several Roadblocks to use of SIC Materials

- Large interfacial impedances. Intrinsic electro-chemical kinetics and how it contributes to cell impedance (Energy/ power density)
- Performance/cost.
- Chemical and electrochemical stability of electrolyte materials - passivating layers (e.g. SEI) - Lifetime/performance/cost.
- Design and synthesis of single-ion conducting electrolytes to optimize transport and interfacial properties to maximize power and energy densities while minimizing life-limiting side reactions.

Relevance.

Comparison of the SIC and Binary system





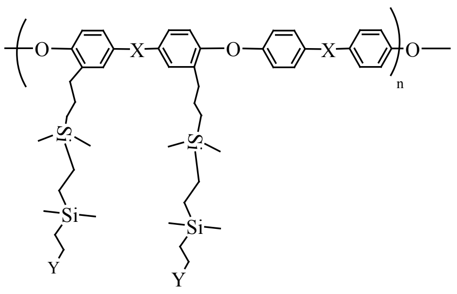
- Single ion conductor yields higher discharge capacity, particularly at high rate (nearly 2x at 2C rate).
- Experiment validates models of Newman et al.
- Cell cycling very stable at 80°C and calendar life also good at elevated temperatures – no $LiPF_6$!!!!
- **Interfacial impedance still too high (by 10X).**
  - -Reduce by modification of conducting elements in composite electrodes to increase local concentration of ions at surfaces.

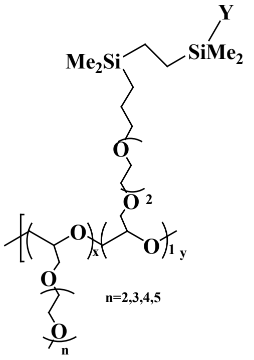
This successful demonstration of SIC performance that eliminates concentration polarization implies that cells can be built with thicker electrode thicknesses thereby reducing the penalty due to current collectors , separators, etc which leads to higher energy densities (50%) at high rates.

Interfacial impedance still too high.

Approach/Strategy

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

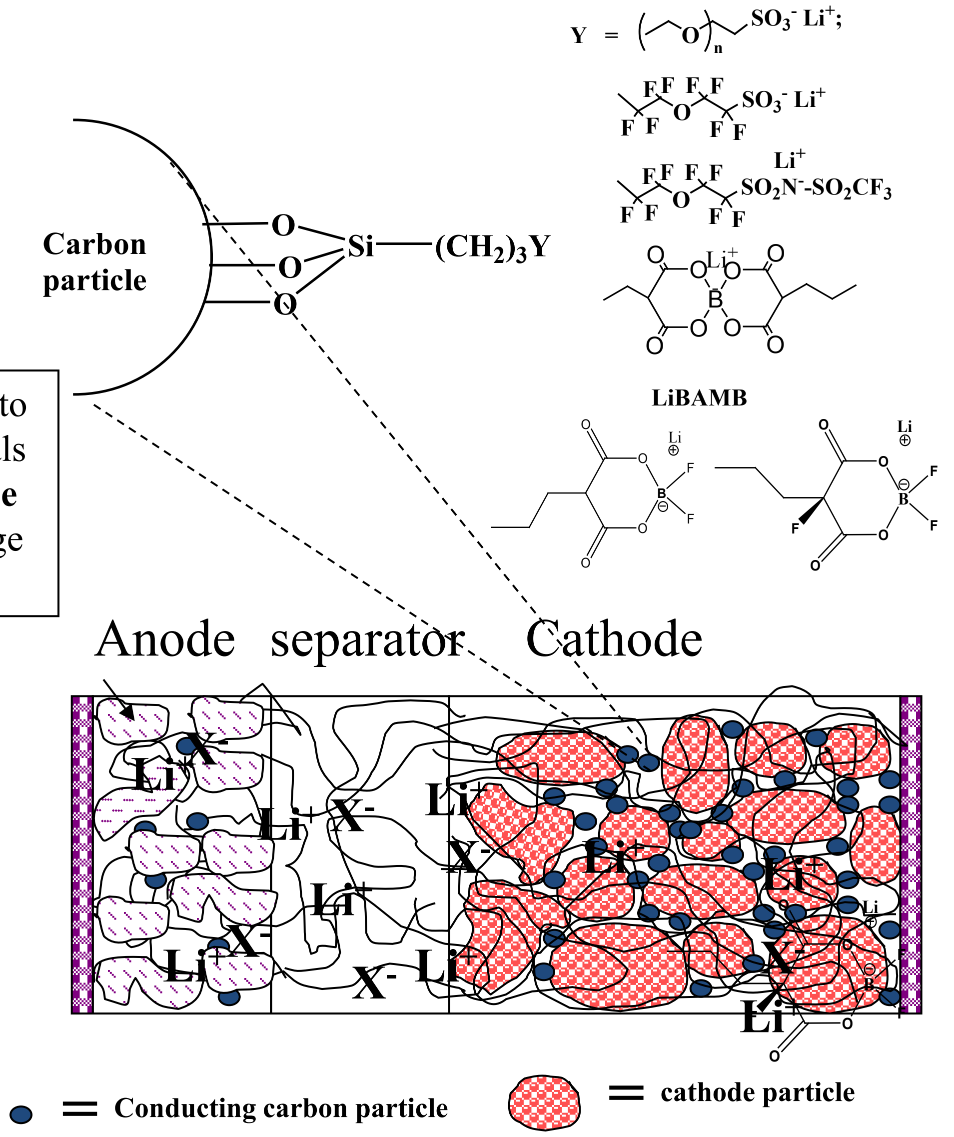




Polysulfones compatible with high positive potentials – **cathode binders**. Mechanically stiff, unable to accommodate electrode expansion.

Polyethers 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 (∞ i/R_{int}) depends on surface concentration.



● = **Conducting carbon particle**

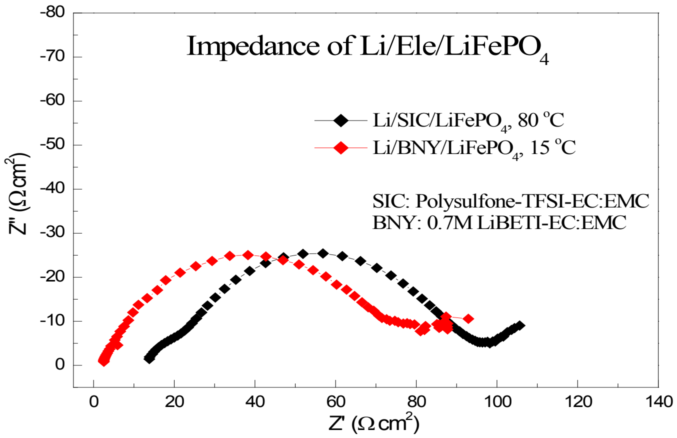
= **cathode particle**

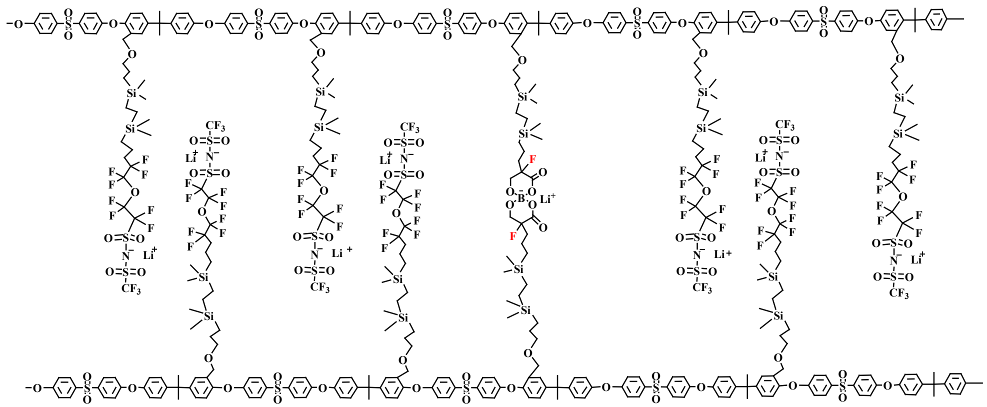
Approach/Strategy
FY 12-13 Milestones

Month/Year/Status	**Milestone**
April/2012/ complete. High surface ion concentration achieved.	Determine the benefits of conducting element modifications on electrode performance.
September 2012/In progress	Determine the role of electrode ink properties (e.g. viscosity, stability, etc) on electrode coating morphology and effects on electrode performance.
April 2013. Delayed pending interfacial impedance reduction.	Complete construction and test of three different thicknesses of composite cathode electrode cells using gel electrolyte.
September 2013. On track provided reduced interfacial impedance is achieved.	Construct and test single-ion conductor solid state cells with no free solvents and composite anodes and cathodes

Technical Accomplishments and Progress.

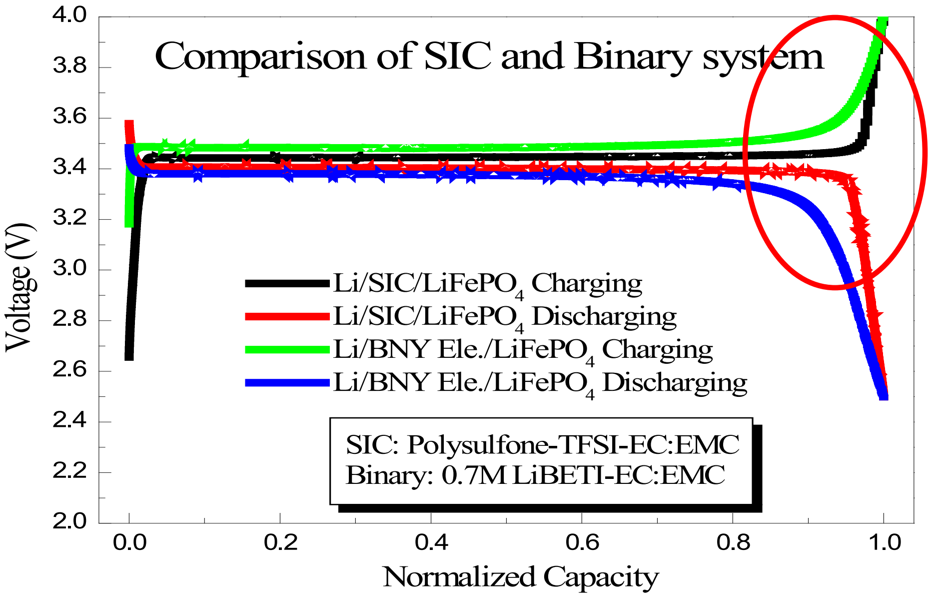
Comparison of Single ion Conductor(SIC) behavior with Binary salt electrolyte





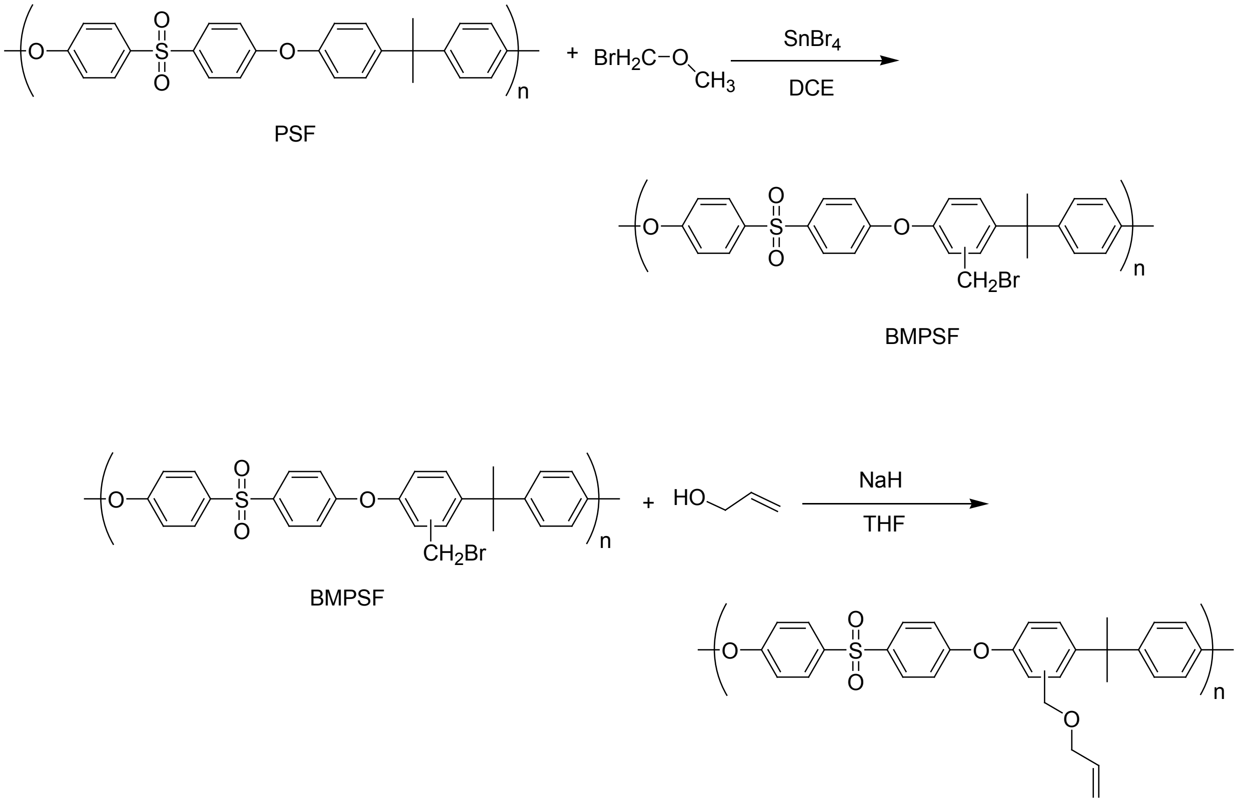
The full SIC battery based on Li/SIC/LiFePO$_4$ showed an impedance in the normal range as binary electrolyte system.

- SIC: Sharp increase/drop in voltage when fully charging/discharging
- Binary: Slowly increase/drop in voltage when close to fully charging /discharging; outer layer of LiFePO$_4$ is firstly fully charged/discharged; more driving force needed to push Li$^+$ deeper into the electrode.



Technical Accomplishments and Progress

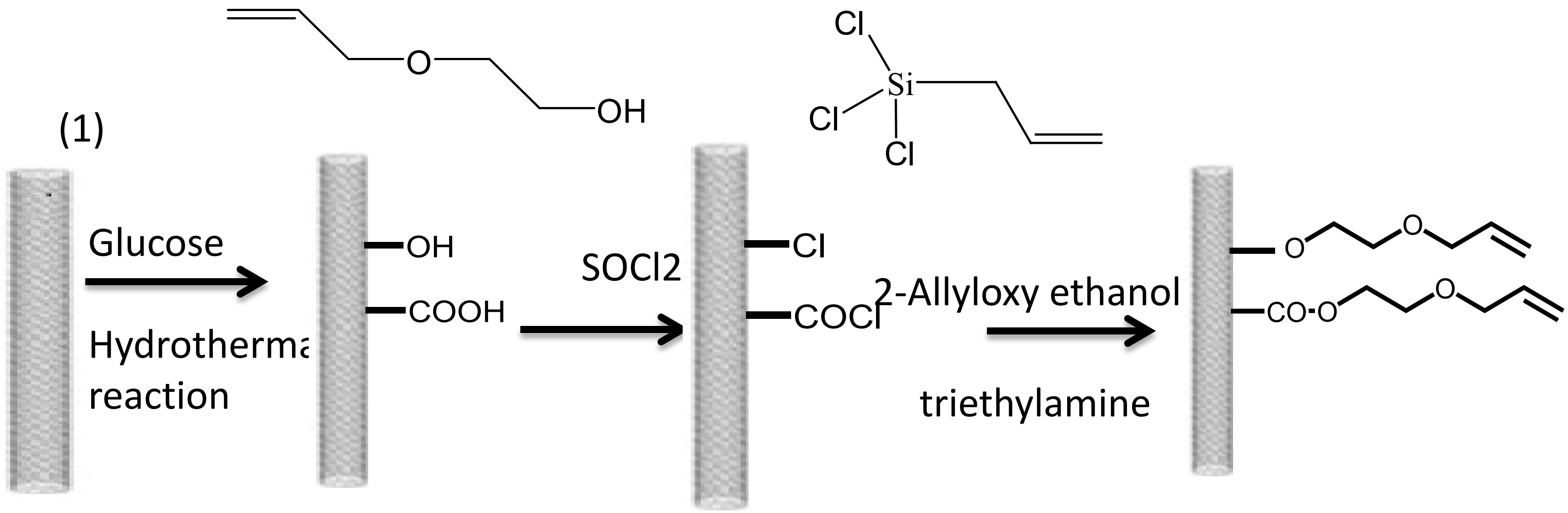
Modification of Commercial Polysulfone (Udel)



Technical Accomplishments and Progress

Attach allyl groups to MWCNT

(1)



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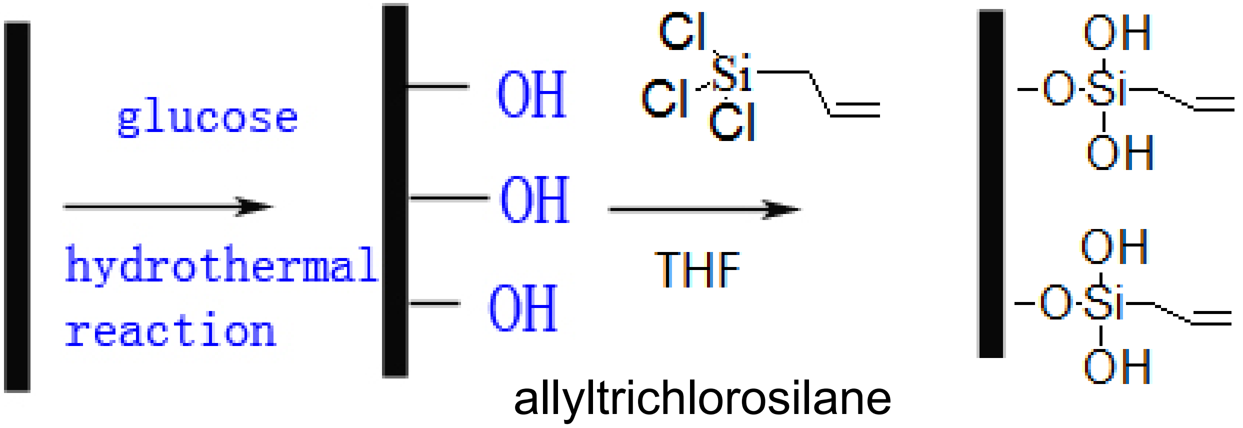
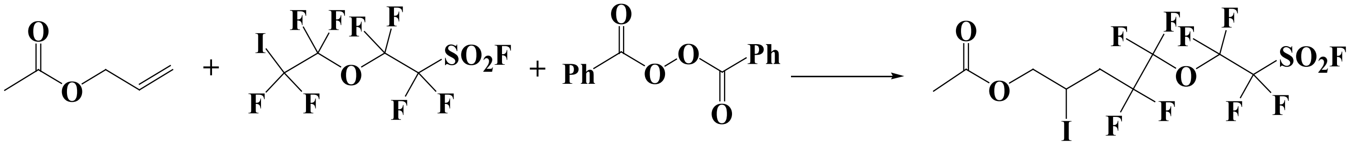
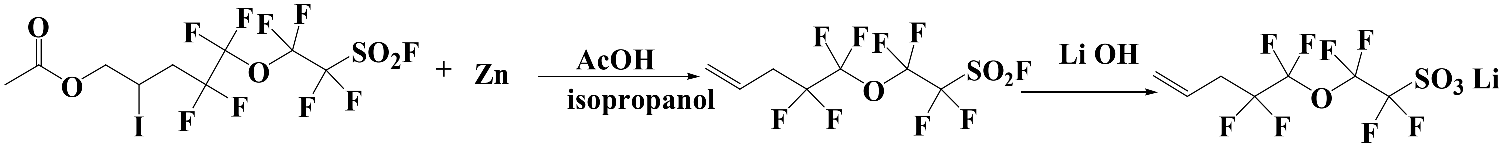


Technical Accomplishments and Progress.

Synthesis of Ionic fragments



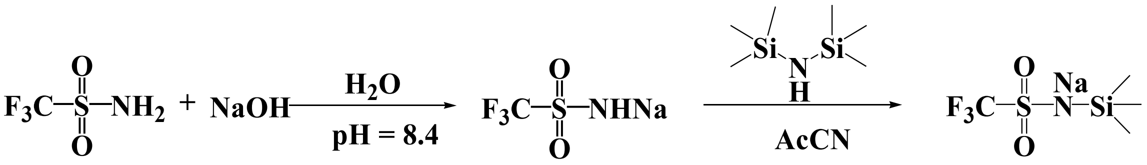
(II)



(II)

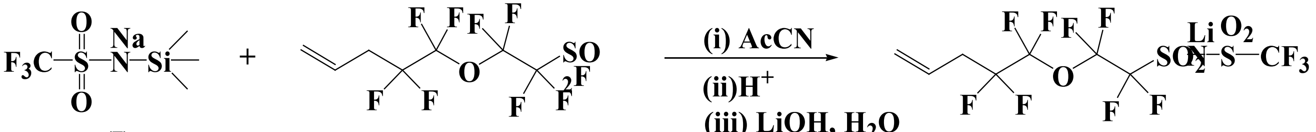
(III)

Triflate fragment



(I)

Imide fragment



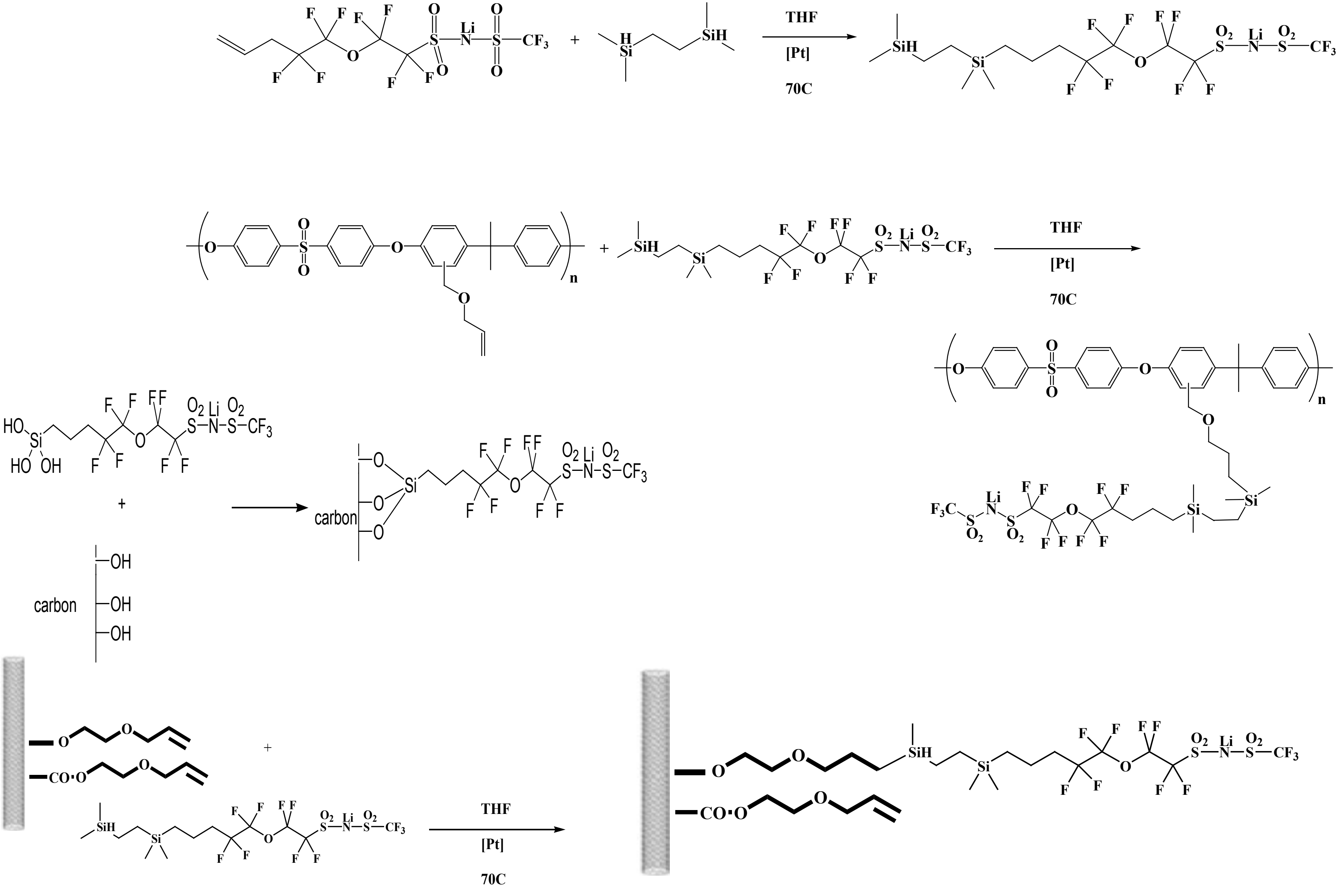
(I)

(III)

(IV)

Technical Accomplishments and Progress.

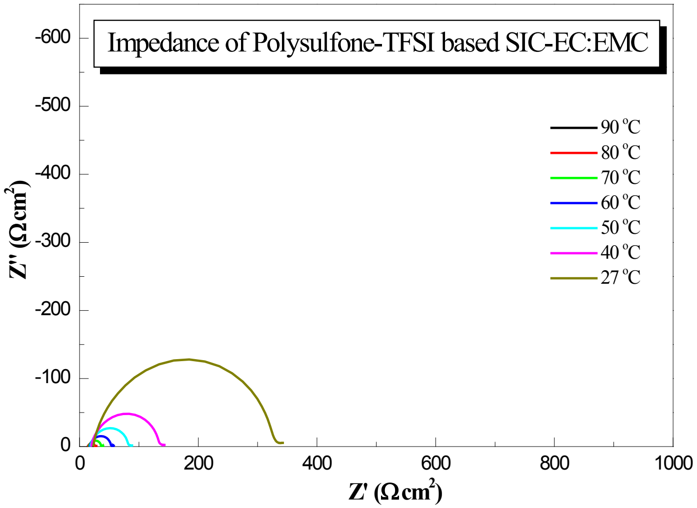
Attachment of ions to Polymers and Carbons

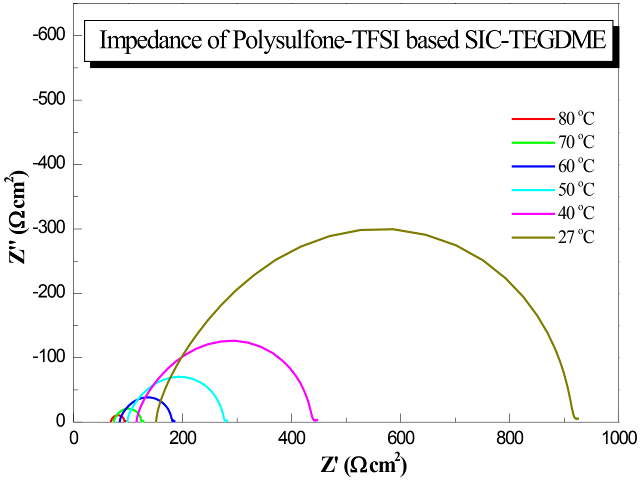


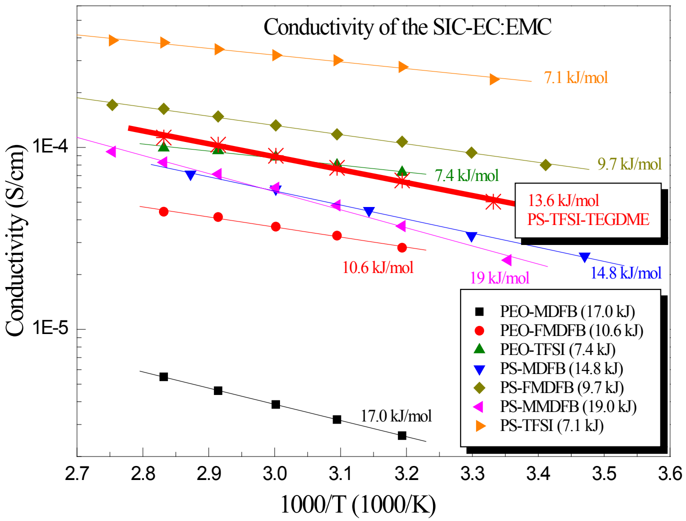
Technical Accomplishments and Progress.

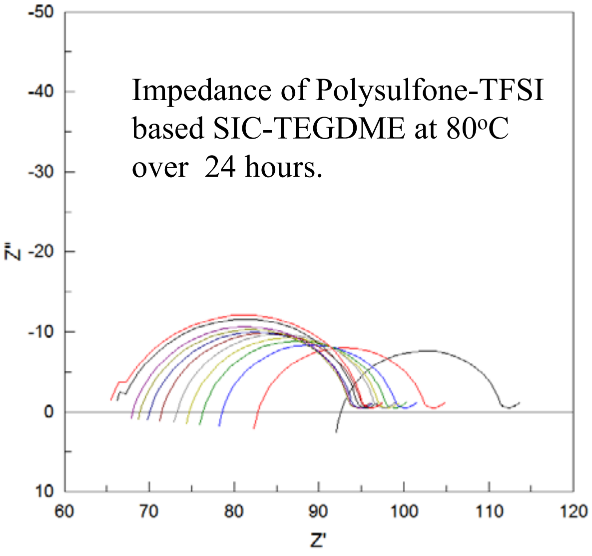
Anode Reactivity of SIC with Different Solvents.

Li/Li Symmetrical cells


Impedance of Polysulfone-TFSI based SIC-EC:EMC


Impedance of Polysulfone-TFSI based SIC-TEGDME


Conductivity of the SIC-EC:EMC

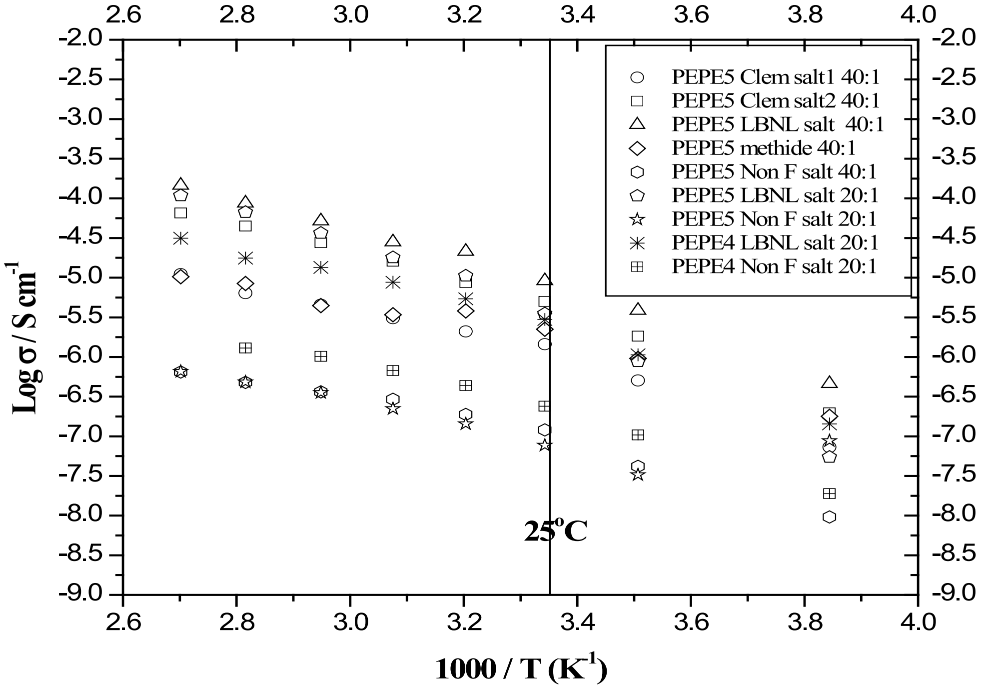

Impedance of Polysulfone-TFSI based SIC-TEGDME at 80°C over 24 hours.

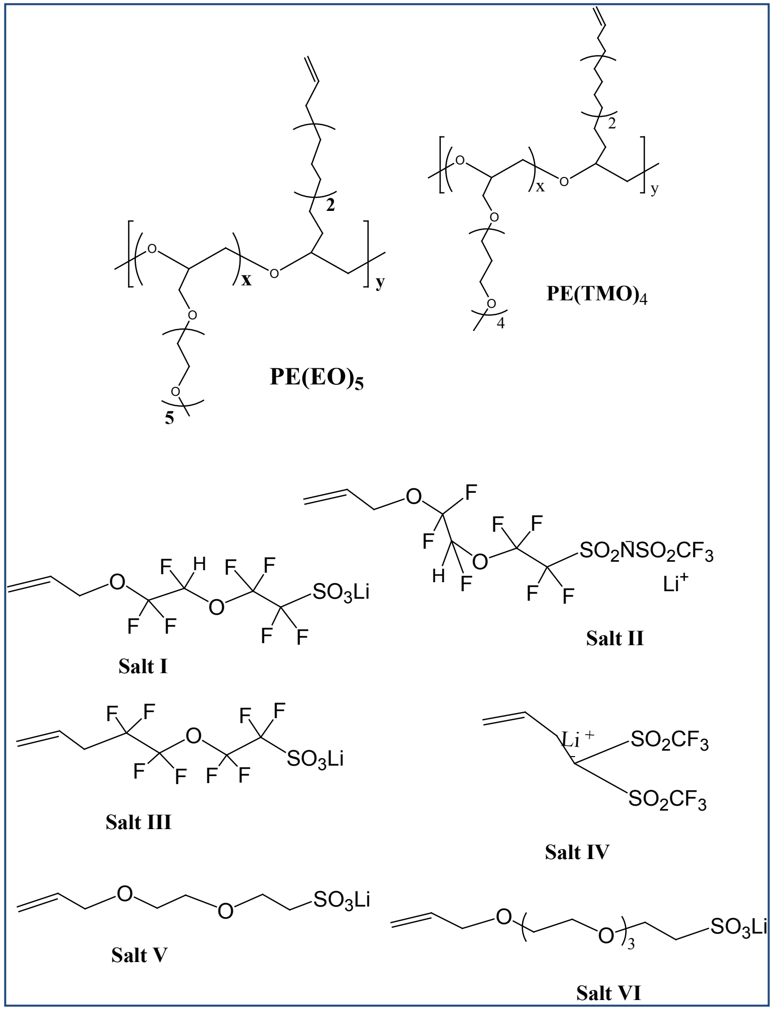
Ether solvents have higher interfacial impedance at Li metal than carbonates.

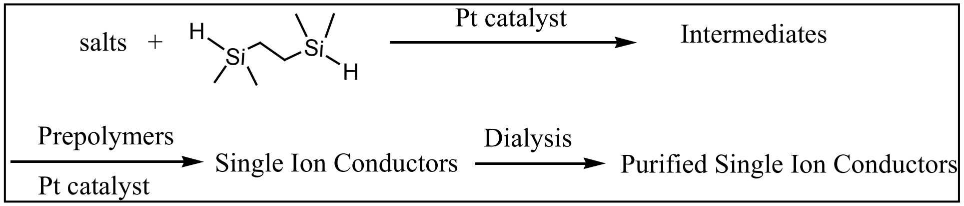
Ether solvents have lower conductivity and higher E_{act} than carbonates.

Ether solvents exhibit stability at 80°C.

PEP(EO)$_x$-based Ionomers



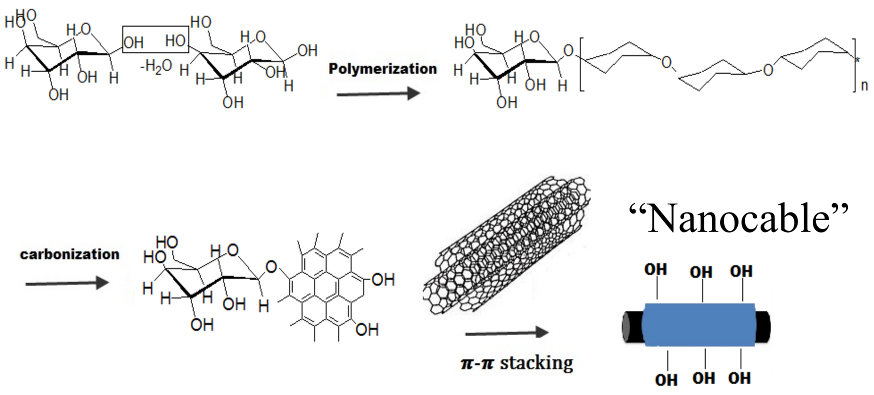



salts + $\xrightarrow{\text{Pt catalyst}}$ Intermediates

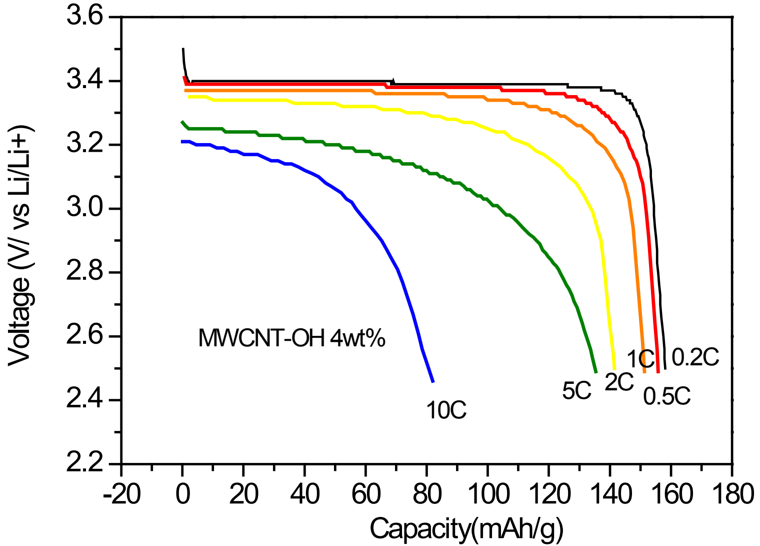
$\xrightarrow[\text{Pt catalyst}]{\text{Prepolymers}}$ Single Ion Conductors $\xrightarrow{\text{Dialysis}}$ Purified Single Ion Conductors

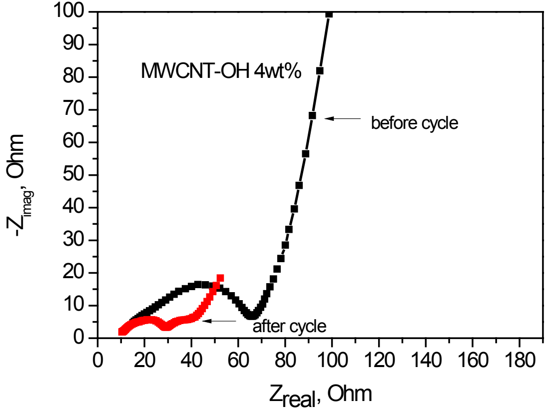
Technical Accomplishments and Progress

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



- •MWCNT's are modified by polymerization of Glucose on the surface followed by carbonaization at high temperature to give hydroxylated surface.
- •Hydroxyl groups will be used to attach anions.
- •Hydroxylated nanotubes give improved performance of cathodes (Capacity, rate capability) similar to MWCNT's modified by sulfonated polystyrenes (see FY2011 presentation).
- • Performance indicates functionalization of carbons leads to better dispersion of carbon.





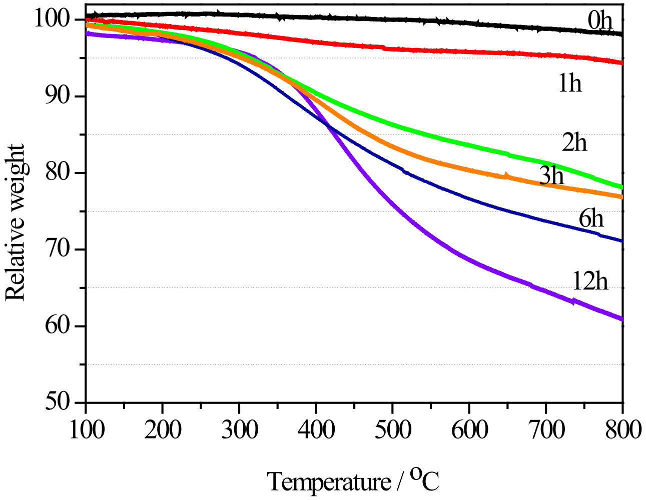
Discharge performance of Li-LiFePO$_4$ cells (EC, EMC-LiPF$_6$ electrolyte) at RT (above) and EIS Nyquist plot before and after cycling (below).

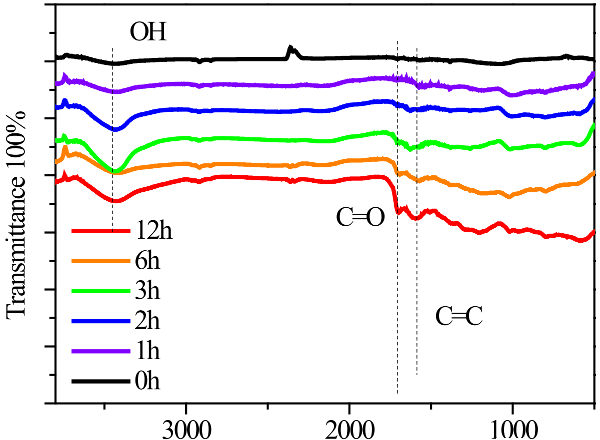
Technical Accomplishments and Progress

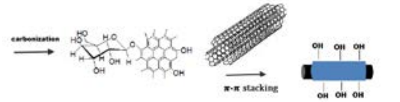
Characterization of Surface Modification

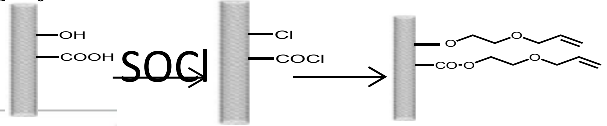
TGA

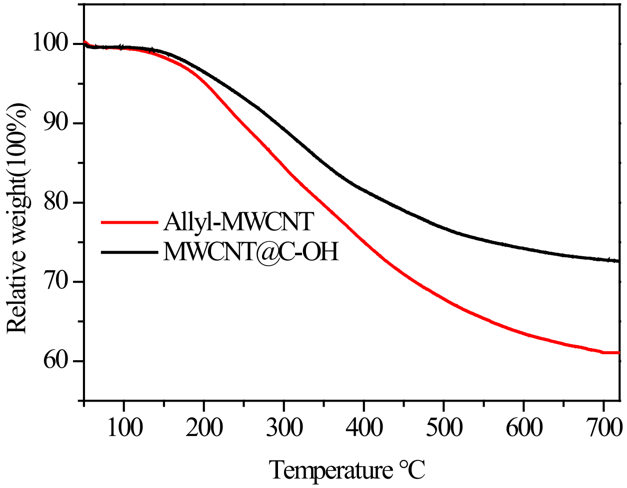
FTIR

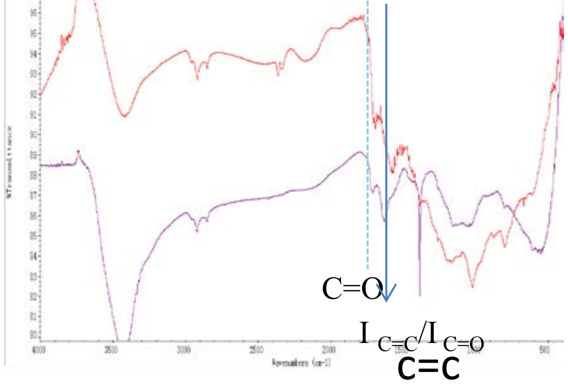






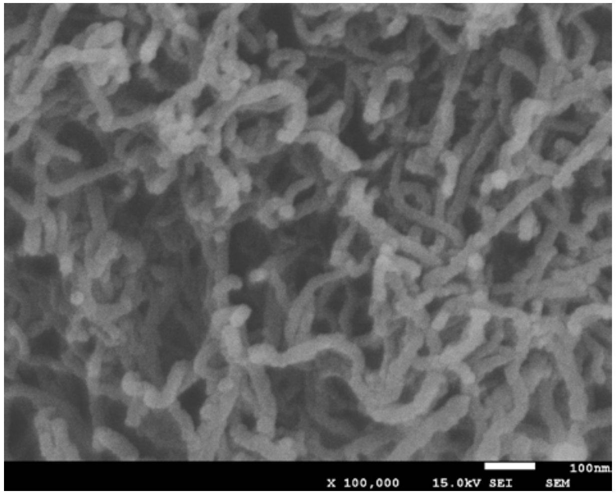


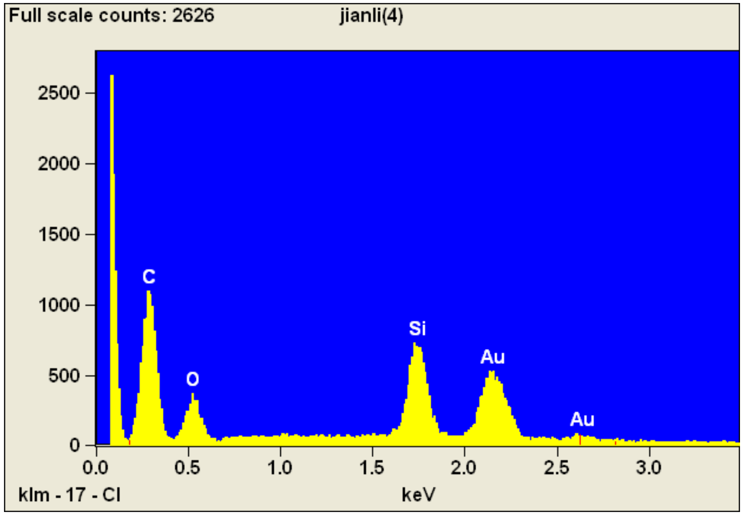




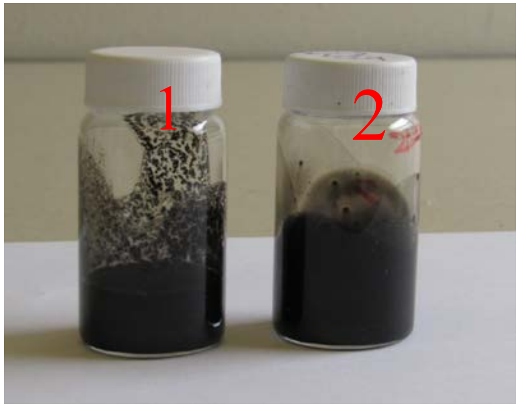
Technical Accomplishments and Progress

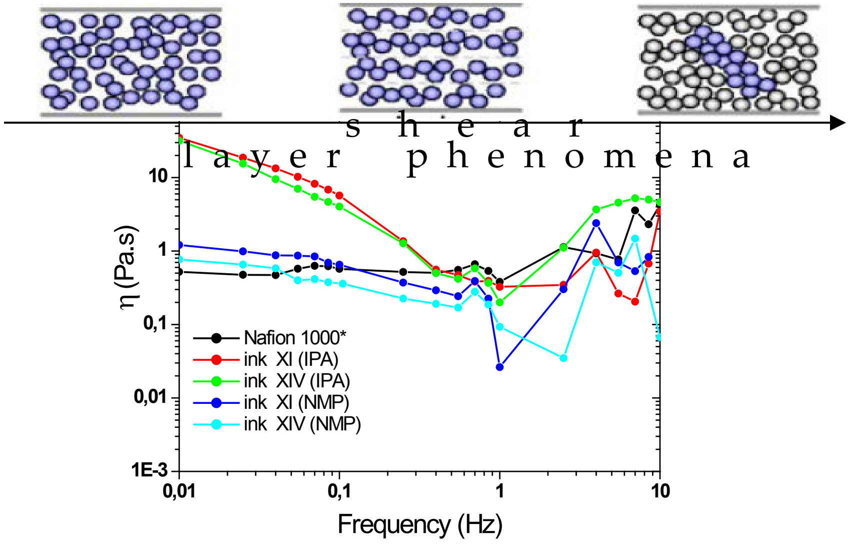
SEM images and EDX map of allyl-si-MWCNT





Electrode ink characterization



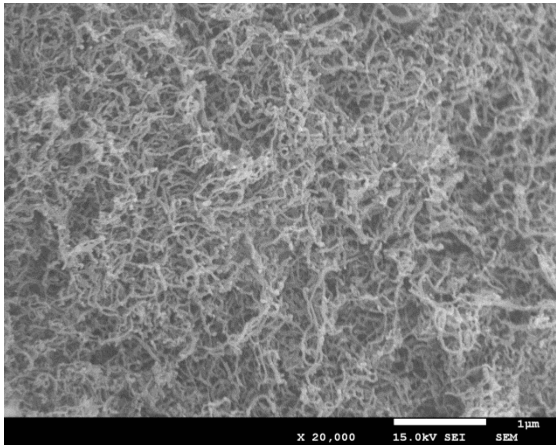


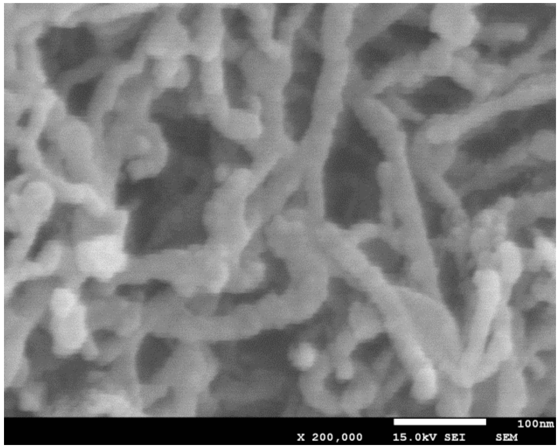
inital stress THINNING — reorganization of the particles — hydrodynamic clusters formation THICKENING

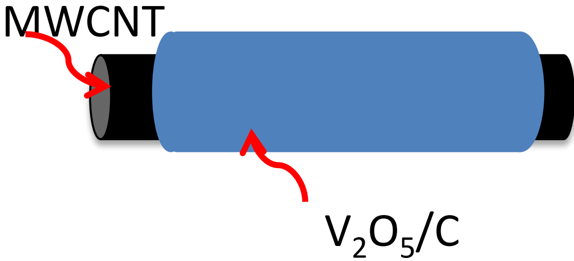
shear layer phenomena

Technical Accomplishments and Progress

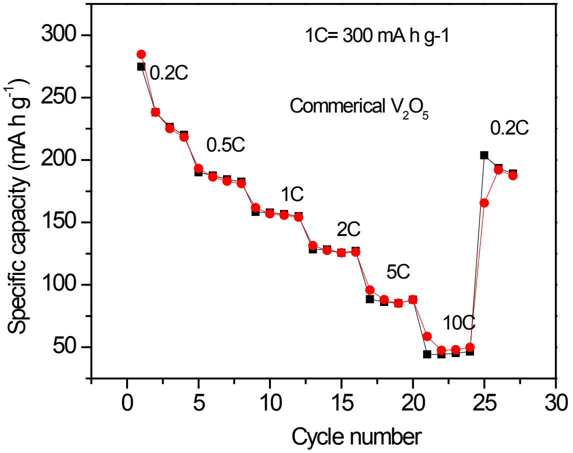
MWCNT@V_2O_5-C coaxial nanocable prepared with Glucose Hydrothermal method.

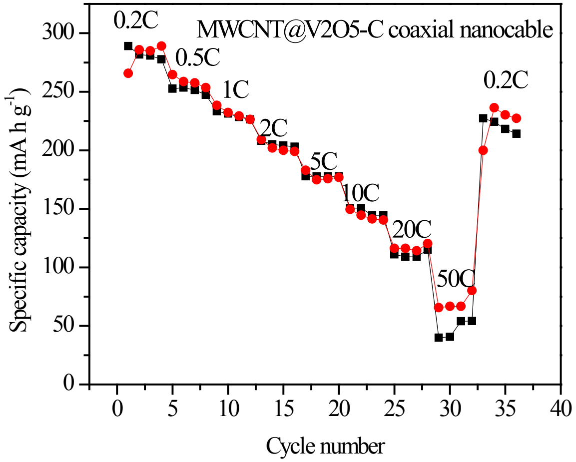




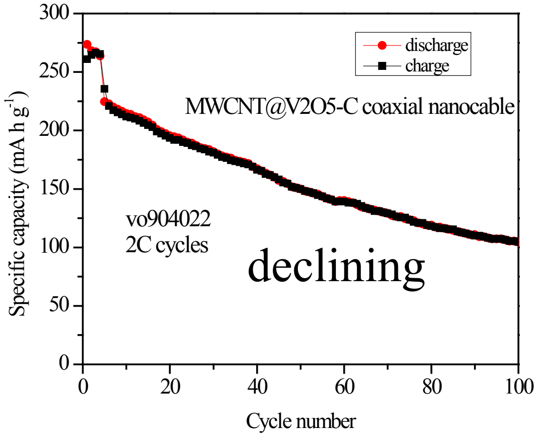


The rate performance





Cycling performance



Collaborations.

- SIC materials are relevant for Li Metal Dendrite suppression – ILRP. (ANL and LBNL collaborators).
- Grant Smith (U. of Utah) on MD modeling of systems for both bulk and surface charge transfer.
- System modeling group.
- Electrolyte reactivity and surface reactions requires surface analysis collaborations (e.g.PHI,)
- Assistance from Cell assembly group (Battaglia, Liu) on reproducibility for electrode 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) and the Center for Electrocatalysis, Transport Phenomena, and Materials (CETM) for Innovative Energy Storage, an Energy Frontier Research Center (EFRC).

Future Work

- Continued Synthesis of polyelectrolyte materials
  - TFSI and fluoroalkylsulfonate LiMDFB anions attached to both polyether and polysulfone backbones with a range of equivalent weights (concentrations of ions).
  - Attach above anions to conducting carbons using nanocable method (In process).
- Characterization of materials.
  - Thermal, mechanical and chemical testing as dry materials and gelled with organic solvents (carbonates, GBL, ethers, sulfones) .
  - Bulk conductivity, Morphology measurements(SAXS/WAXS at LBNL ALS), dielectric relaxation measurements (Penn State U) and Neutron relaxation (NIST)

Future Work

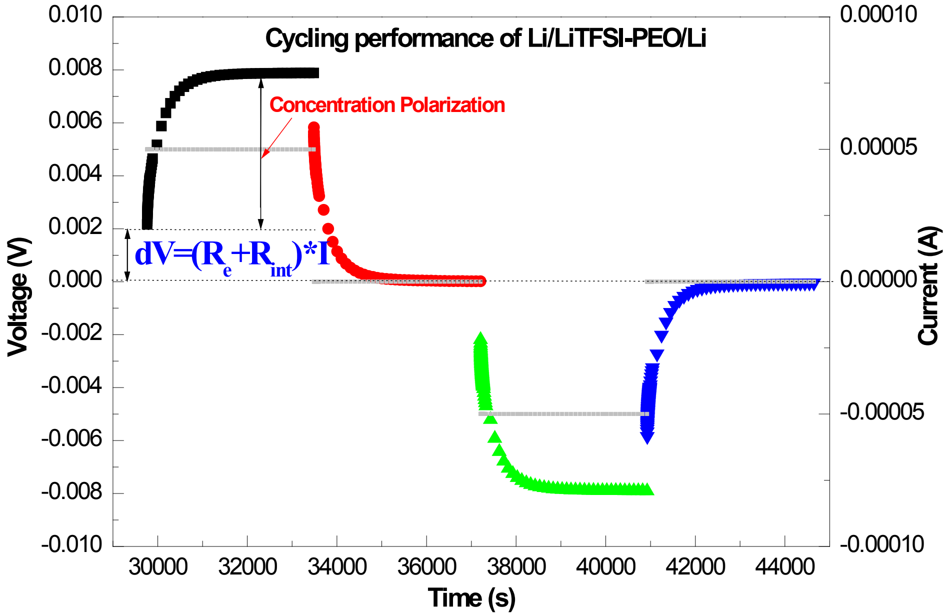
- Electrochemical characterization of polyelectrolyte SIC's.
  - Li metal cells: impedance, lithium cycling.
    - Effects of variable equivalent weight layers on impedance and dendrite growth. Work transferred to ILRP project
  - Composite Electrodes.
    - Cathodes. Focus on Low voltage materials ($LiFePO_4$ if available) for polyether materials. Reduce interfacial impedance enough to build completely dry (no solvents), solid-state cells.
    - Cathodes. $LiCoO_x$ and $LiMn_2O_4$ for polysulfone materials. Reduce interfacial impedance so that electrode thickness studies can be practical.
    - Anodes. Graphite: Characterize composite electrodes thermally, mechanically and electrochemically. Particular emphasis on electrode kinetics (Interfacial impedance) 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 for characterization of SEI layers (PHI collaboration)

Summary

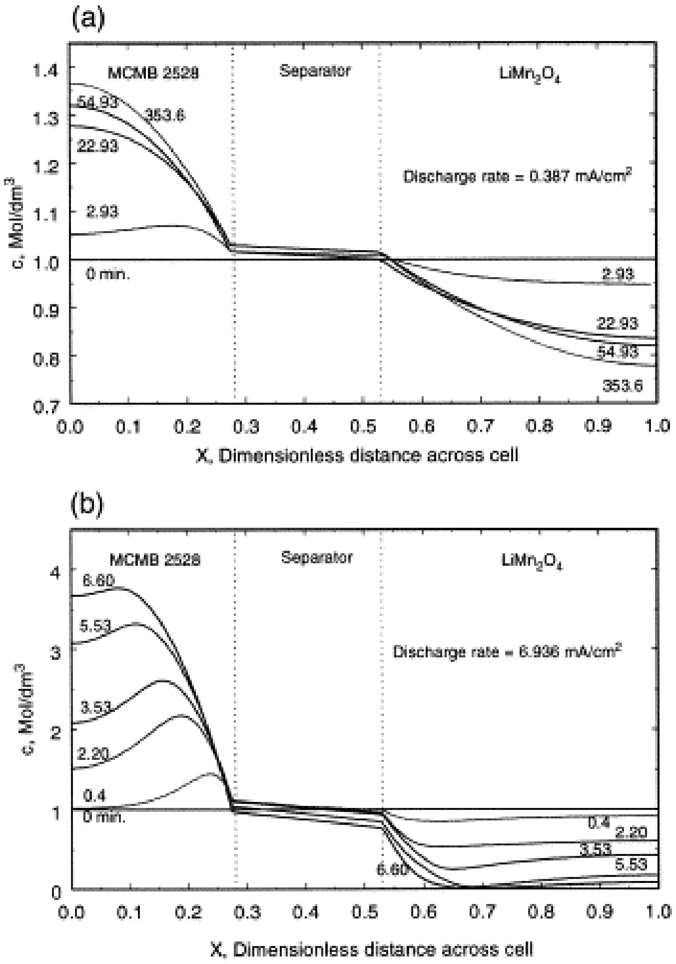
- A variety of polyelectrolytes have been prepared with sufficient bulk conductivity for EV performance both as gels with solvents and as dry polymers.
- Testing of composite electrodes with SIC gel electrolytes has demonstrated the elimination of concentration polarization. However, the interfacial impedance is still too high.
- Modification of the electrode surfaces alters the surface concentration of ions. Surface modification alters electrode ink properties.
- Improvement in the intrinsic rates of the electrochemical reactions is necessary to achieve adequate room temperature performance – this will be achieved by control of ion concentrations in the electrodes – surface modification..

TECHNICAL BACK-UP SLIDES

Impact of Interfacial vs. Bulk vs. Concentration Impedance

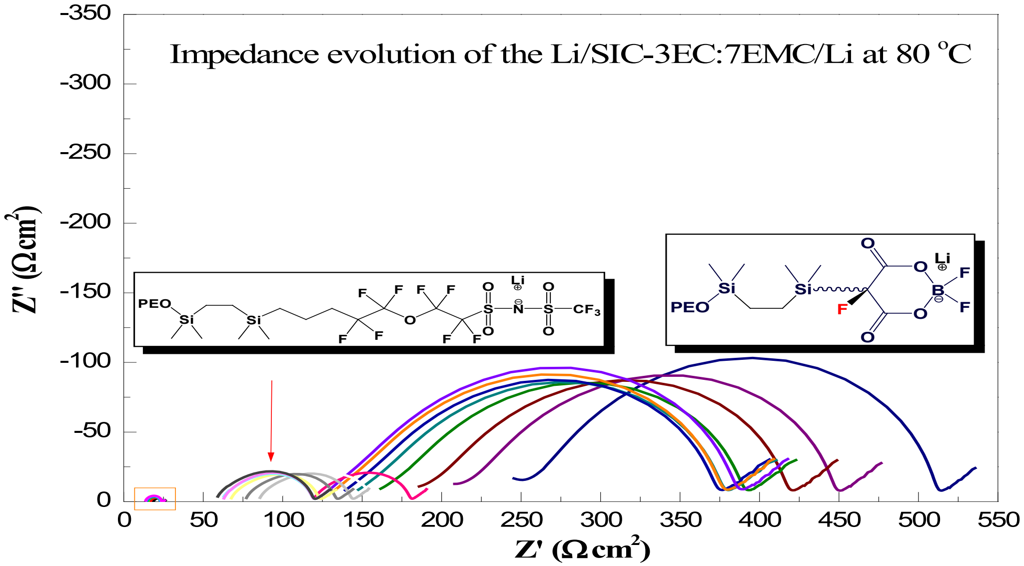


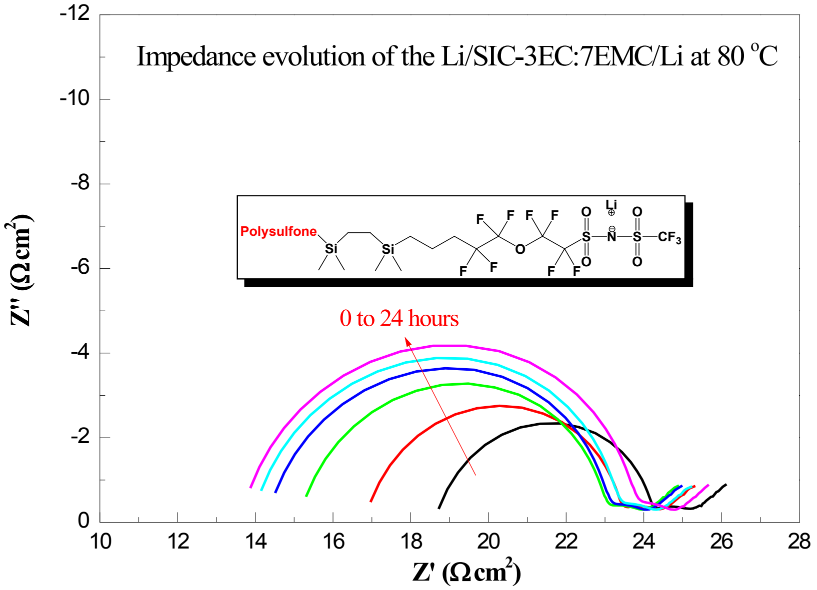
Salt concentration affects R_{int} at electrode surface & bulk conductivity.
Concentration polarization can be significantly greater than the bulk and interfacial impedances combined particularly in composite electrodes.
Remove concentration polarization by use of lithium ion single ion conducting polyelectrolytes.

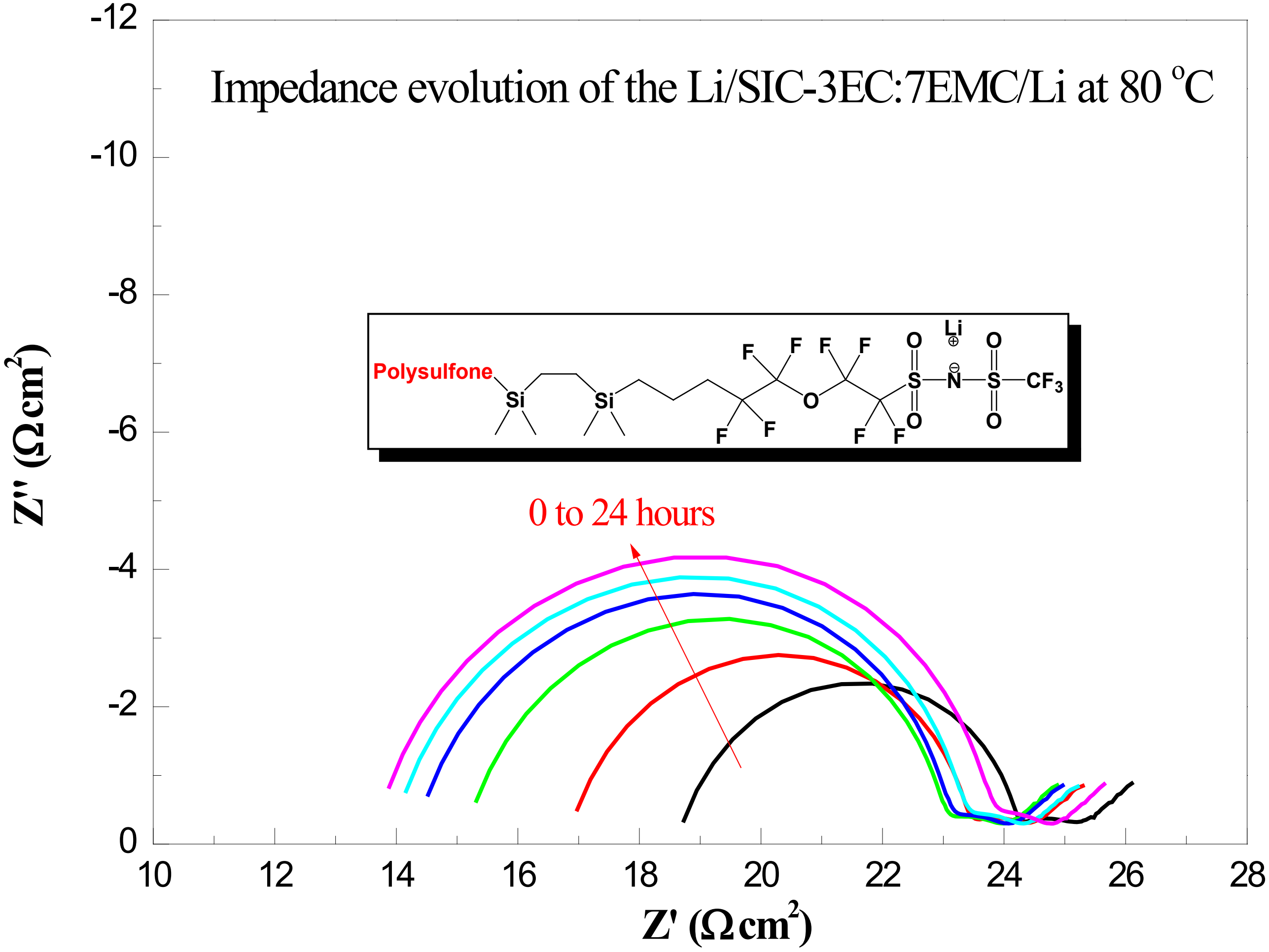


Effect of Transport Properties on Li-Ion gel polymer cell, **Arora, Doyle, Gozdz, White and Newman, J. Power Sources, 88 (2000), 219-231.**

TFSI anions perform much better than Lewis acid anions



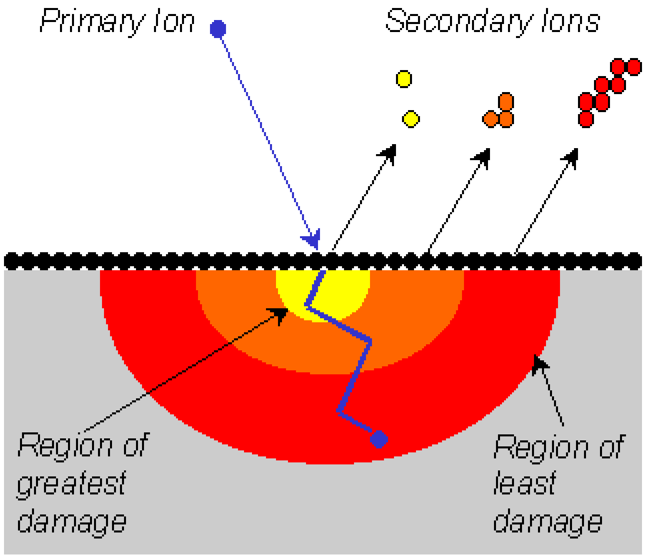




- The best single ion conductor impedance on Lithium metal.
- Carbonate solvents are reactive with lithium not the polymer

TOF-SIMS Analysis of SEI Layers

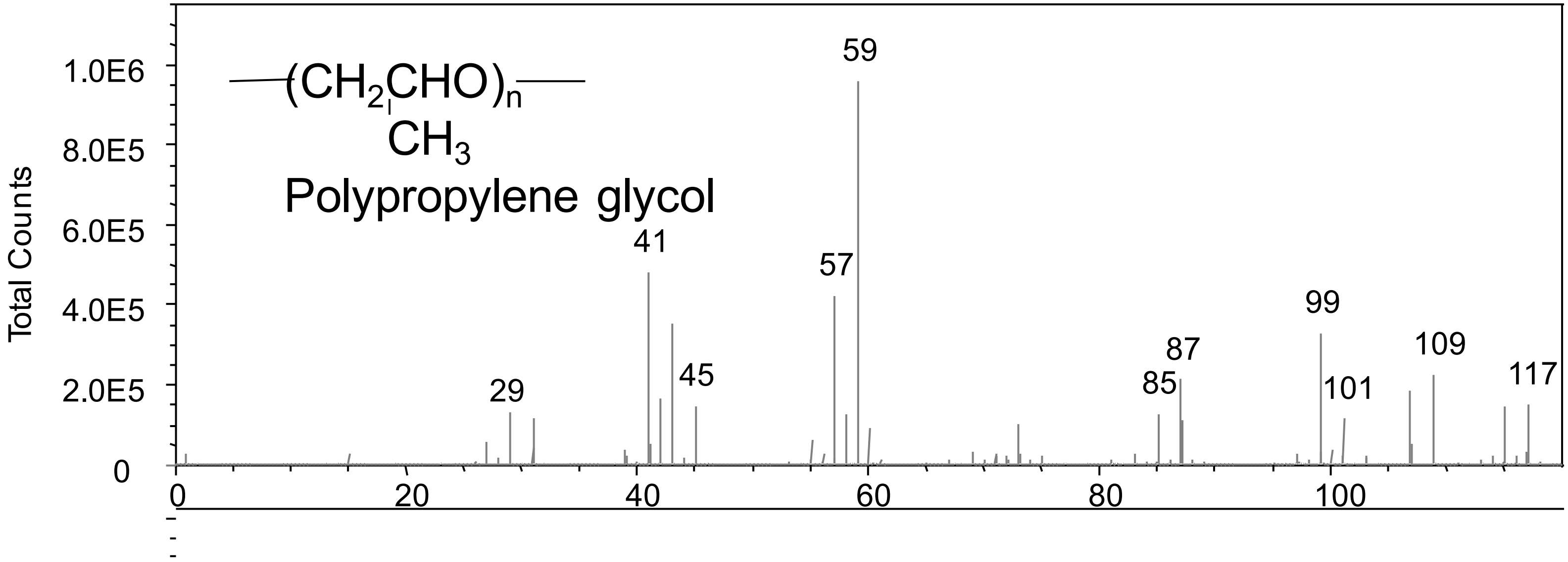
PHYSICAL ELECTRONICS
A DIVISION OF ULVAC-PHI



New method developed by PHI, Inc that uses C_{60} to sputter layers in a fashion that provides interpretable mass spectra.

The sputtering is much more gentle than with Ar^+ ions which causes less damage to the layers.

Depth profiling is possible with the C_{60} sputtering and provides good MS data through the layers.



TGA-GC/MS Analysis of Electrode layers

Decompose surface layers thermally.

ThermoGravimetric Analyzer (TGA)

Gas Transfer line

Mass Spectrometer (MS)

Gas Chromatograph (GC)