

# Electrolytes - R&D for Advanced Lithium Batteries. Interfacial and Bulk Properties.

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Project ID #:

**ES089**

# Overview

## Timeline

- PI has participated in BATT program since 1998.
- 1994-1999 USABC/3M/HQ project on Li/Polymer batteries.
- FY11 Project started Oct. 1, 2010, completed April 30, 2012
- FY1 Project started October 1, 2010
  - 25% completed

## Budget

- FY11 Funding - \$550k
- FY12 Funding - \$550k

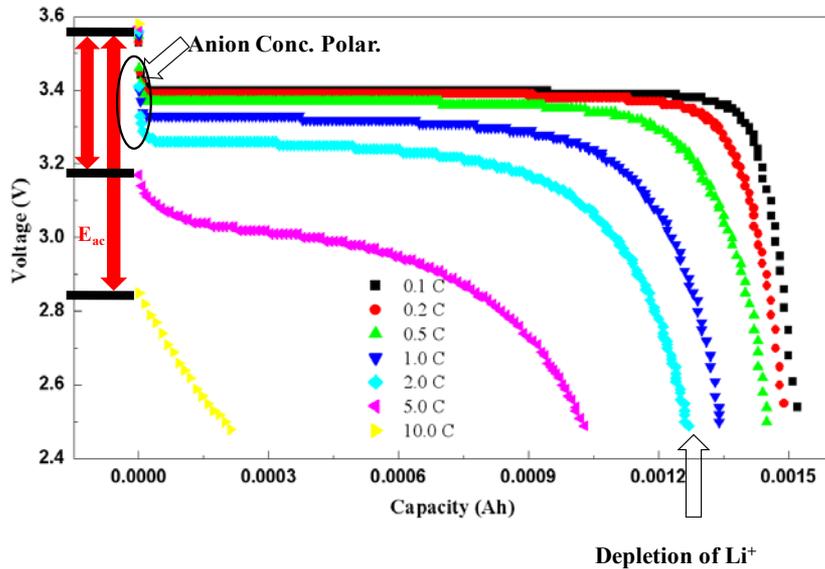
## Barriers

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

# Single Ion Conductor Electrolytes. Relevance to Batteries and Implementation Issues.



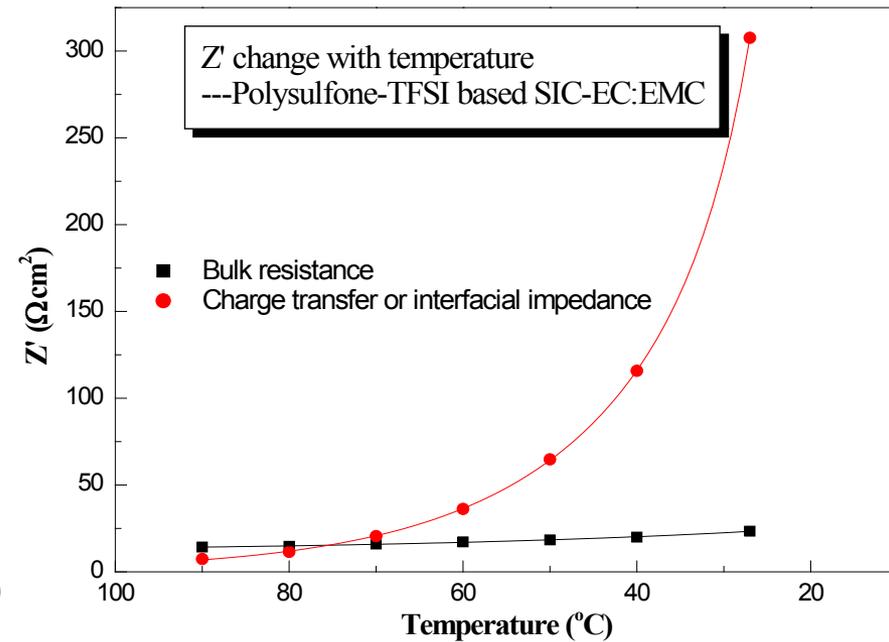
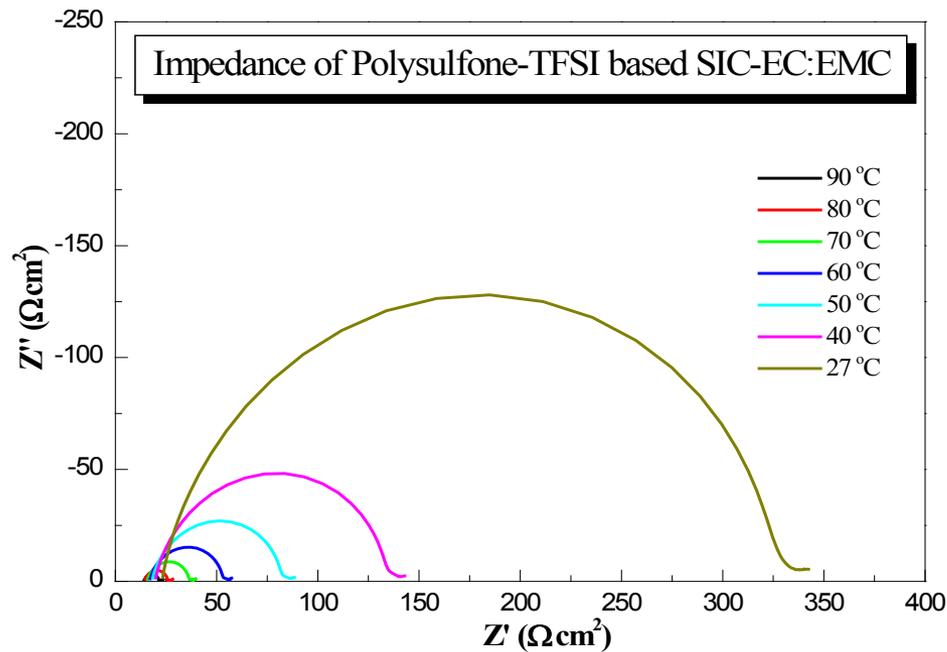
**Concentration & Interfacial Polarization contribute to Capacity loss. Single ion Conductors remove concentration polarization and allow use of thicker electrodes - fewer separators and current collectors required gives higher energy density. Require conductivities  $> 10^{-4}$  S/cm – already achieved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

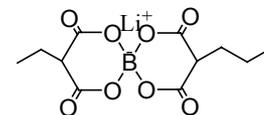
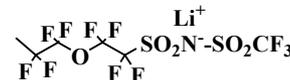
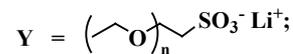
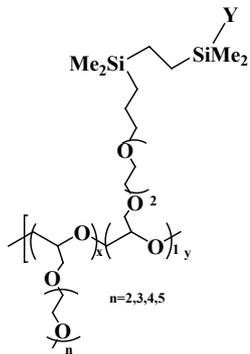
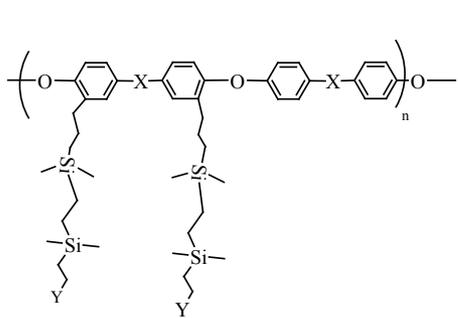
## Importance of the interfacial impedance



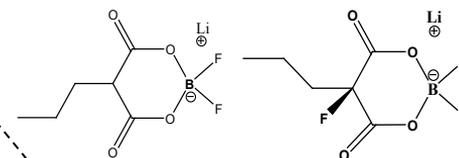
The performance of battery is determined  $R_{\text{bulk}} + R_{\text{interfacial}}$  combined, while  $R_{\text{interfacial}}$  is more sensitive to temperature.

# Approach/Strategy

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

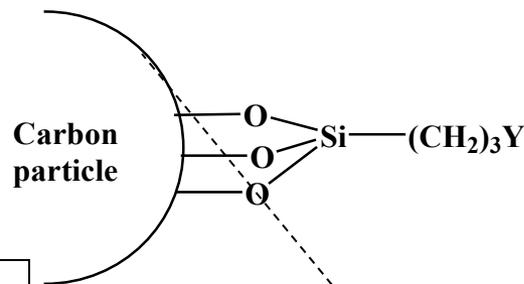


LiBAMB

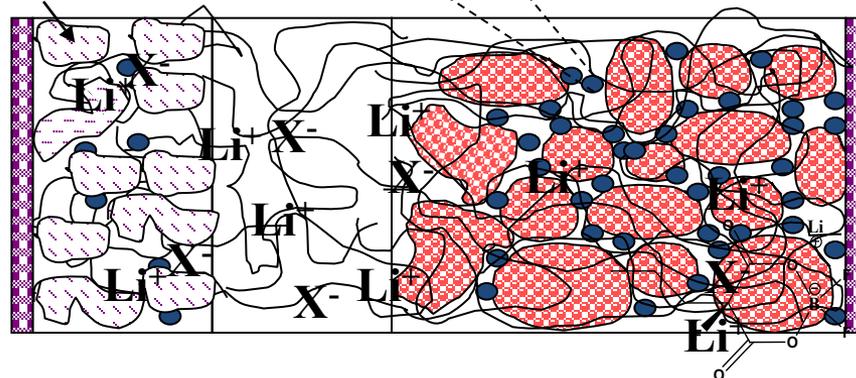


Polysulfones compatible with high positive potentials – **cathode binders**. Mechanically stiff, unable to accommodate electrode expansion.

Polyethers not stable to high positive potentials (>3.6V vs. Li) - **anode binders**. Elastic. Large volume changes OK.



Anode separator Cathode



● = Conducting carbon particle

● = cathode particle

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 ( $\propto i/R_{\text{int}}$ ) depends on surface concentration.

# Approach/Strategy

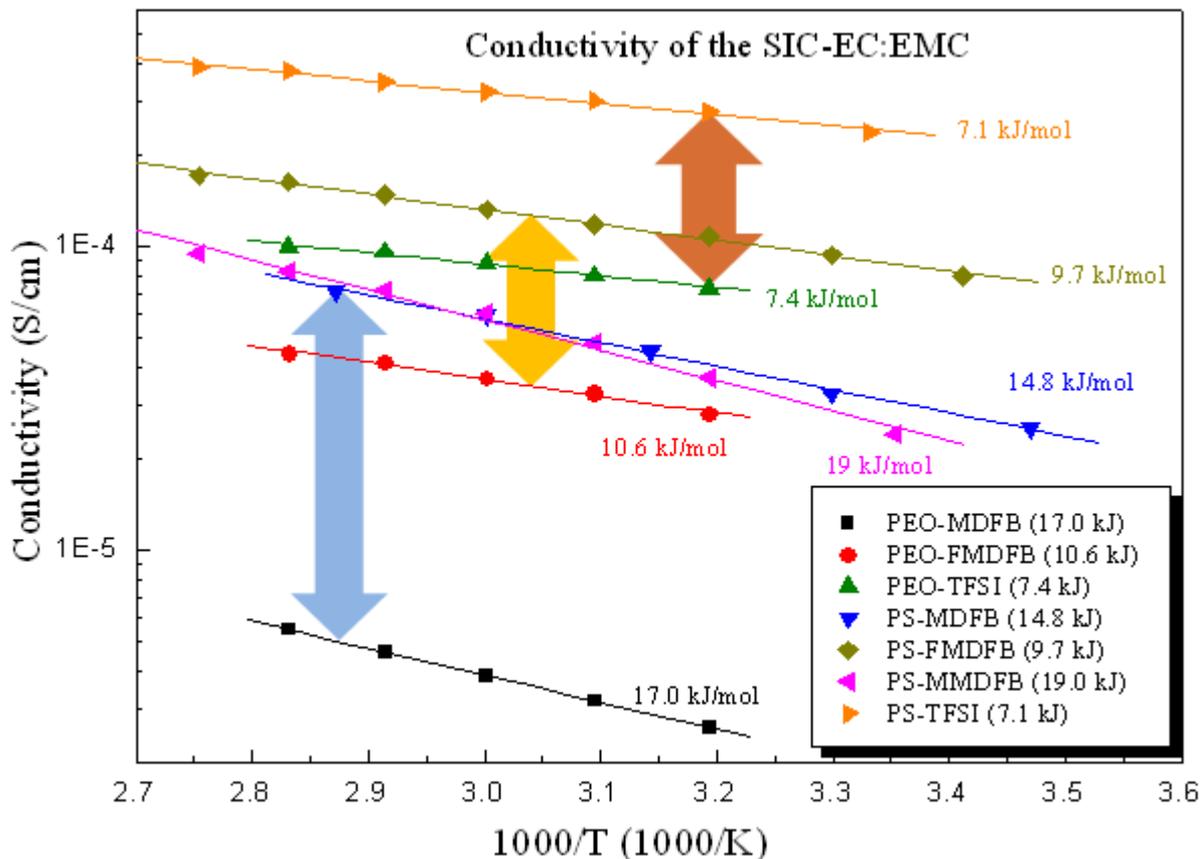
## FY 11-12 Milestones

<b>Month/Year/Status</b>	<b>Milestone</b>
<p><b>April/2011/Completed.</b> Polysulfones stable to 5V vs. Li<sup>o</sup> .</p>	<p>Determine whether available single-ion conductor polyelectrolytes function with the high voltage NiMn spinel cathodes</p>
<p><b>September/2011</b> Completed for stability. Analysis in progress.</p>	<p>Determine the stability of base-line and single-ion electrolyte to NiMn Spinel cathodes including chemical analysis of electrolyte degradation products</p>
<p><b>April/2012/ complete.</b> High surface ion concentration achieved</p>	<p>Determine the benefits of conducting element modifications on electrode performance.</p>
<p><b>September 2012/ On track.</b></p>	<p>Determine the role of electrode ink properties (e.g. viscosity, stability, etc) on electrode coating morphology and effects on electrode performance.</p>



# Technical Accomplishments and Progress.

## Conductivity of Single-ion conductor Gels vs. $1/T$



### For same backbone:

The TFSI based SIC showed much higher ionic conductor and better interfacial performance. PEO based polyelectrolyte possesses sufficient conductivity for EV use in dry form – no solvent required.

### For same salt:

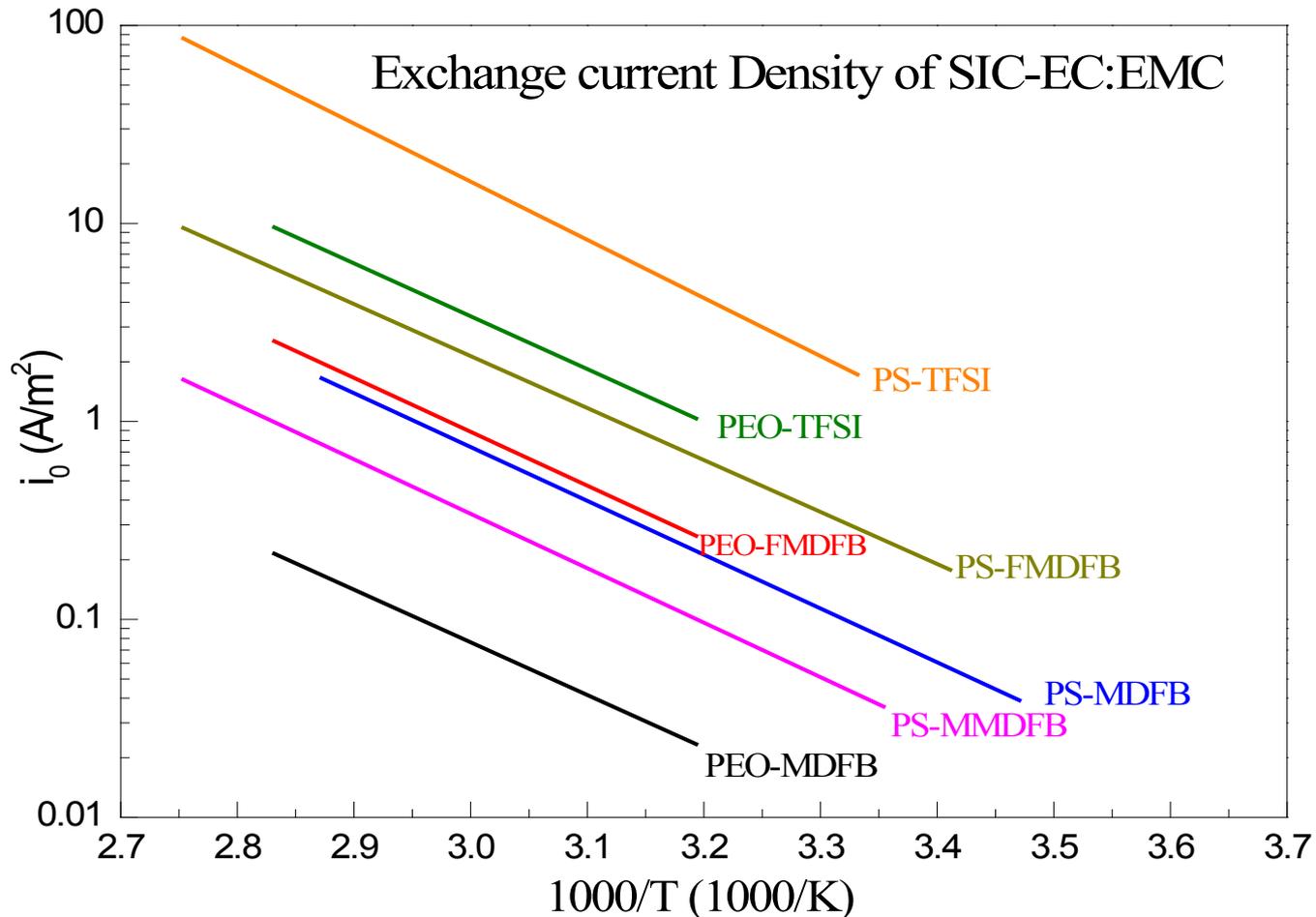
The Polysulfone based SIC also have much better electrochemical performance than PEO based SIC, results from the phase separation in which the anions dissolve into the solvent while the backbone precipitates out. Easily provides sufficient conductivity for EV use as gel.

$10^{-4}$  S/cm is sufficient for EV applications (Newman et al.)

# Technical Accomplishments and Progress.

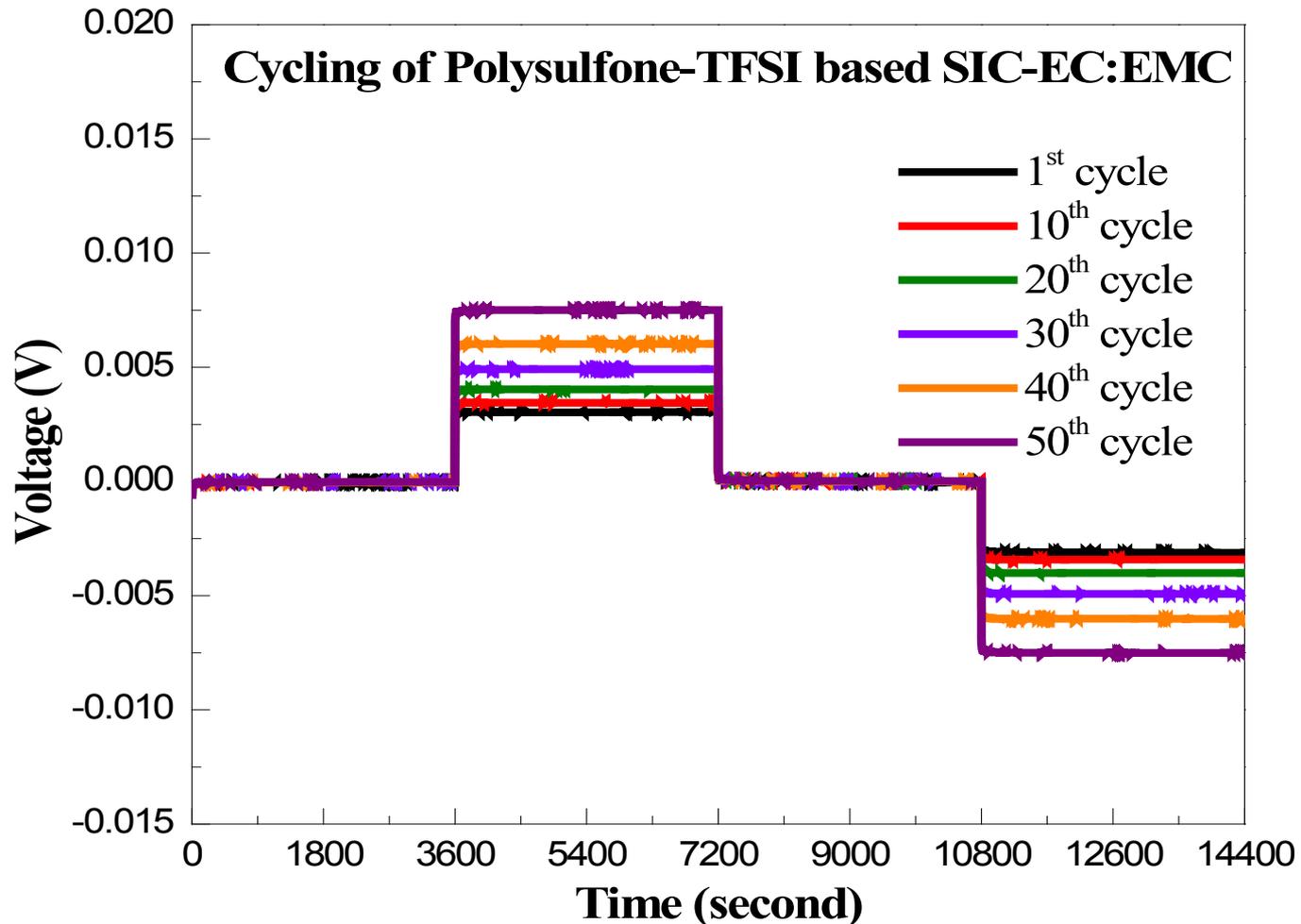
## Exchange Current Density as Function of Temperature

Indicates Activation Barrier is Same for all Anions but  
Concentration of Active Lithium ions are different.



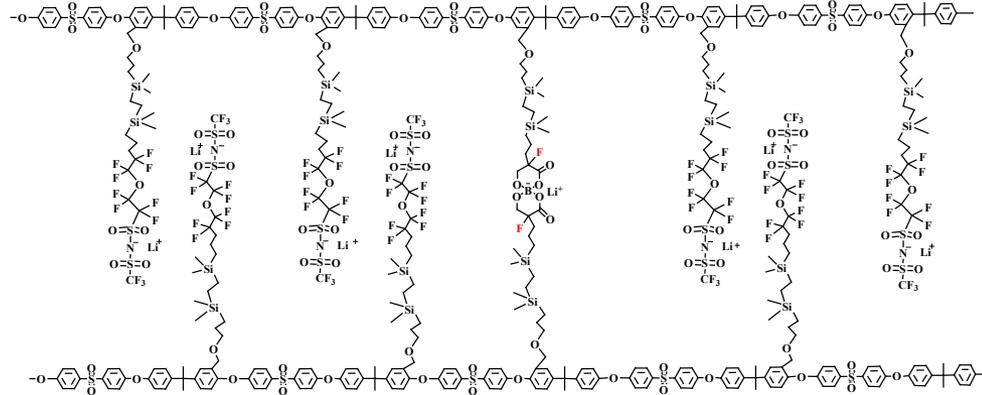
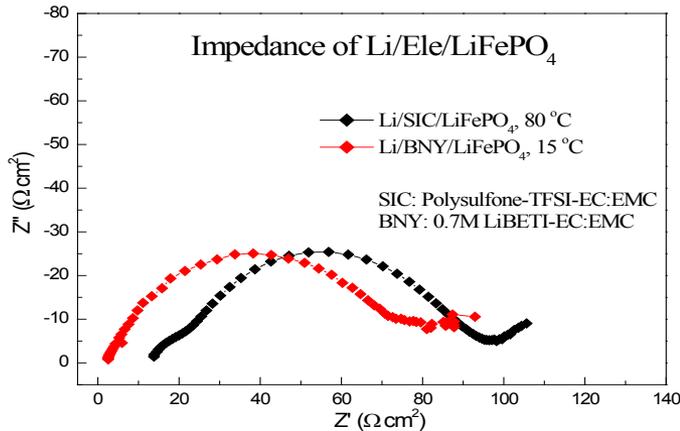
# Technical Accomplishments and Progress.

Lithium-Lithium Cycling exhibits no Concentration Polarization and no Dendrites



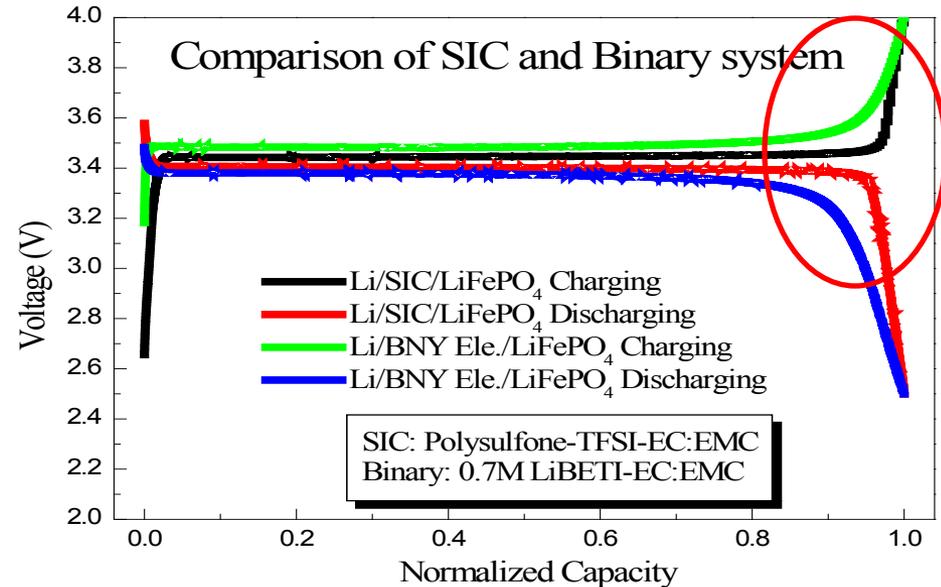
# Technical Accomplishments and Progress.

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



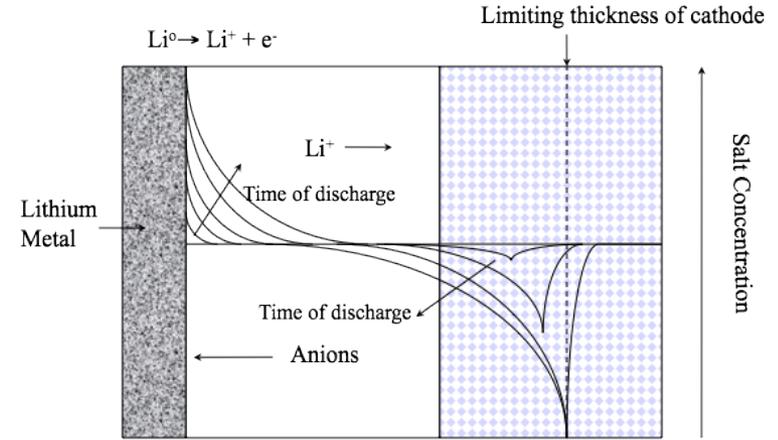
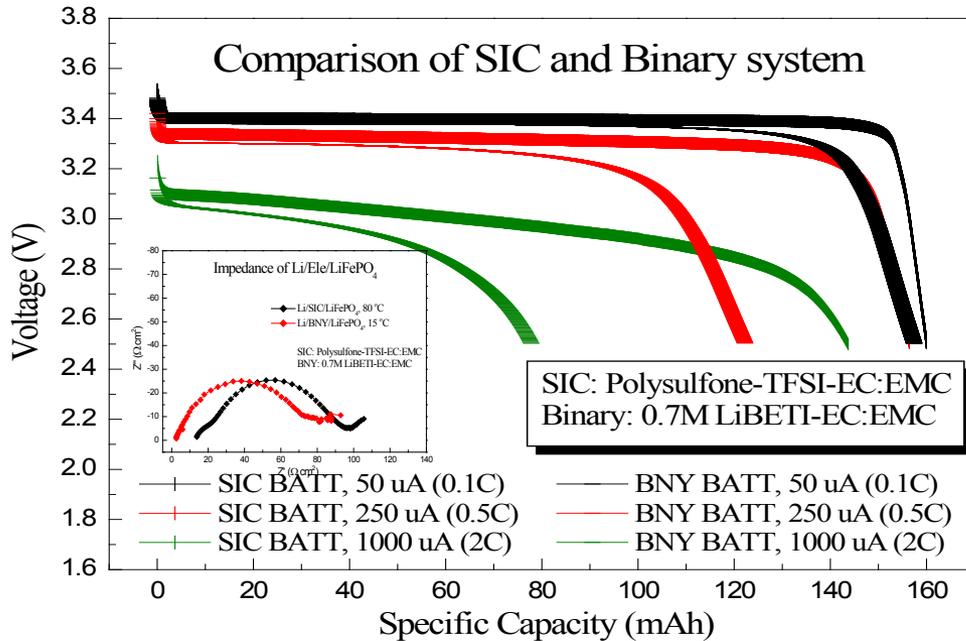
The full SIC battery based on Li/SIC/LiFePO<sub>4</sub> showed an impedance in the normal range as binary electrolyte system.

- 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<sub>4</sub> is firstly fully charged/discharged; more driving force needed to push Li<sup>+</sup> deeper into the electrode.



# Technical Accomplishments and Progress.

## Comparison of the SIC and Binary system

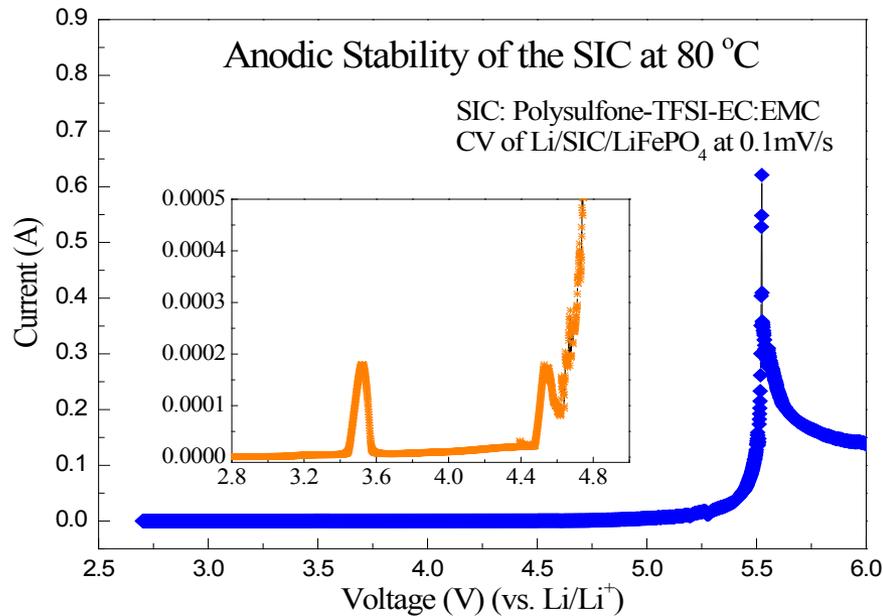


- Single ion conductor yields higher discharge capacity, particularly at high rate (nearly 2x at 2C rate).
- Experiment validates models of Newman et al.
- Cell cycling very stable at 80°C and calendar life also good at elevated temperatures – no LiPF<sub>6</sub> !!!!
- Interfacial impedance still too high (by 10X).
  - Reduce by modification of conducting elements in composite electrodes to increase local concentration of ions at surfaces.

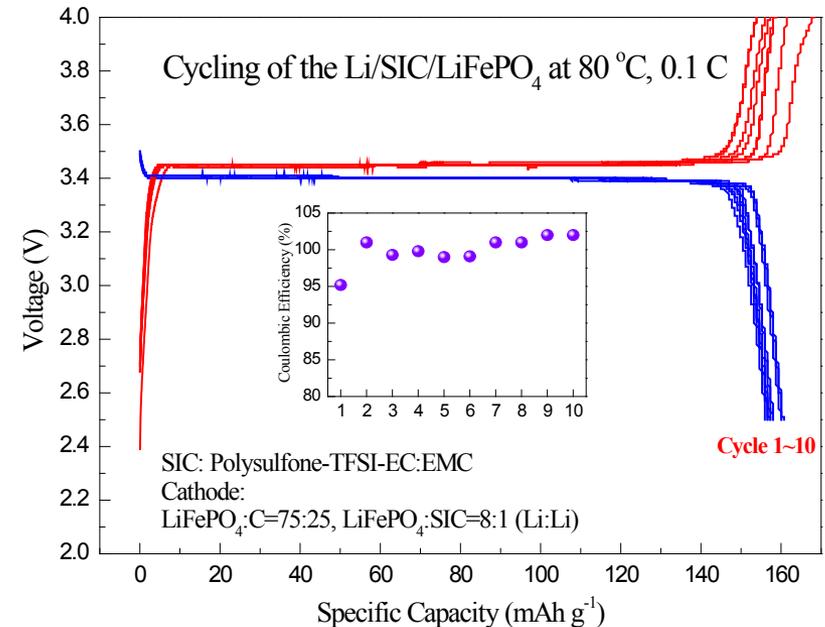
This successful demonstration of SIC performance that eliminates concentration polarization implies that cells can be built with thicker electrode thicknesses thereby reducing the penalty due to current collectors, separators, etc which leads to higher energy densities (50%) at high rates.

# Technical Accomplishments and Progress.

## Stability of SIC Gels to High Voltage, High Temperature and Cycling



SIC Gel is stable to 5.0 Volts according to CV & confirmed by chronopotentiometry.

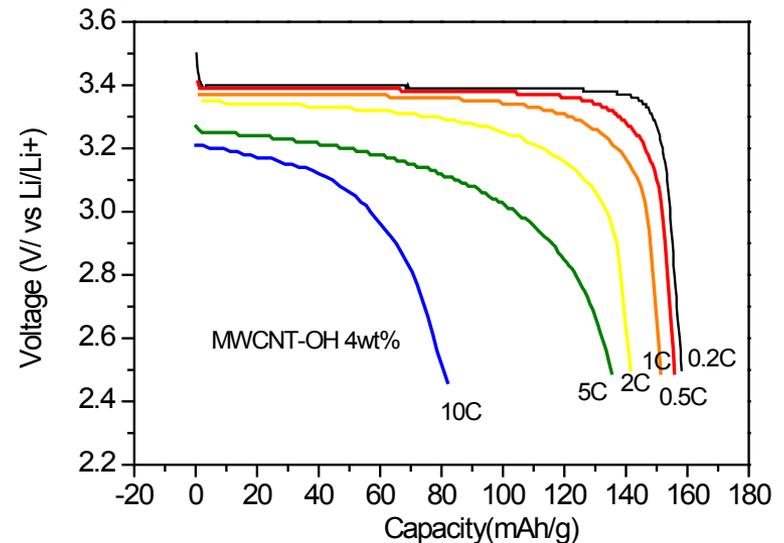
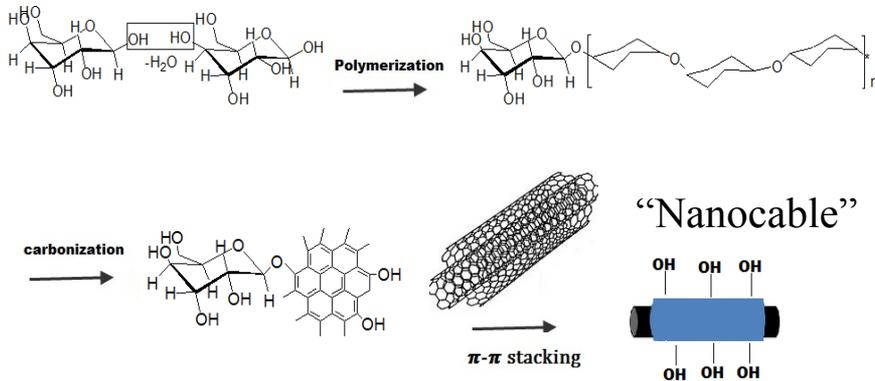


Cell cycling is stable after initial beak-in for hundreds of cycles.

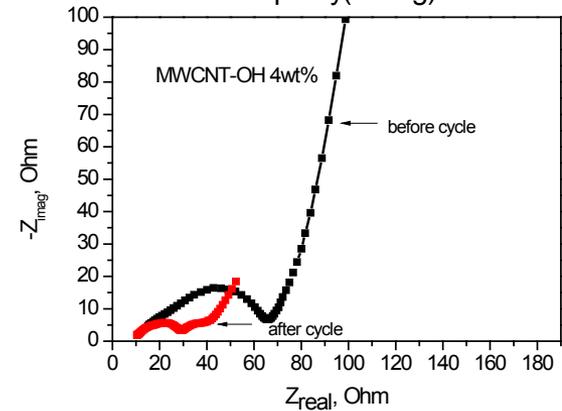
Note the electrolyte is stable at 80°C since the SIC contains no Lewis Acid Salts. (e.g. PF<sub>6</sub><sup>-</sup>)

# Technical Accomplishments and Progress

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



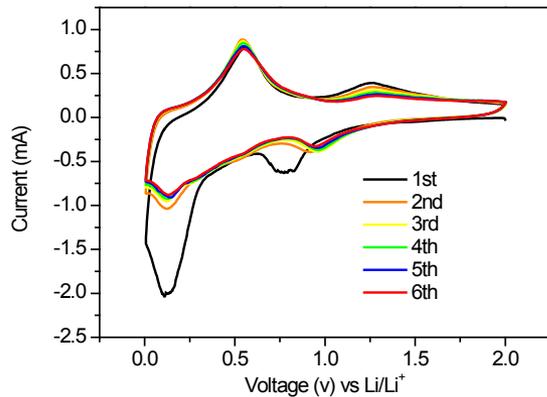
- MWCNT's are modified by polymerization of Glucose on the surface followed by carbonaization at high temperature to give hydroxylated surface.
- Hydroxyl groups will be used to attach anions.
- Hydroxylated nanotubes give improved performance of cathodes (Capacity, rate capability) similar to MWCNT's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



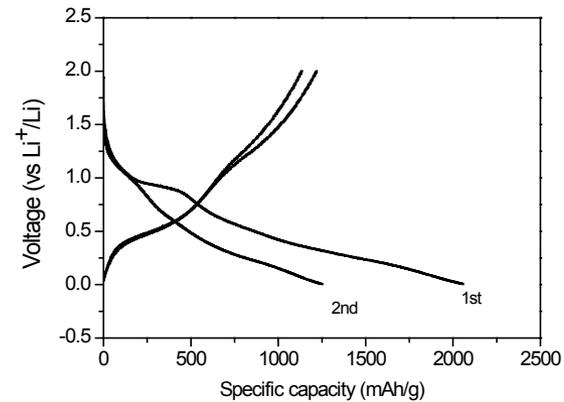
Discharge performance of Li-LiFePO<sub>4</sub> cells (EC, EMC-LiPF<sub>6</sub> electrolyte) at RT (above) and EIS Nyquist plot before and after cycling (below).

# Technical Accomplishments and Progress

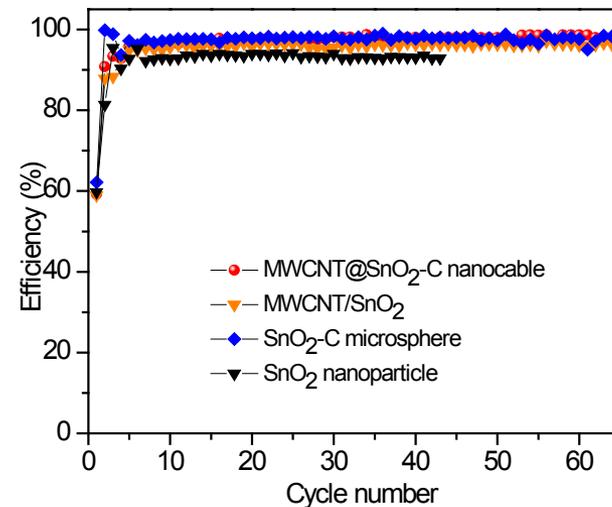
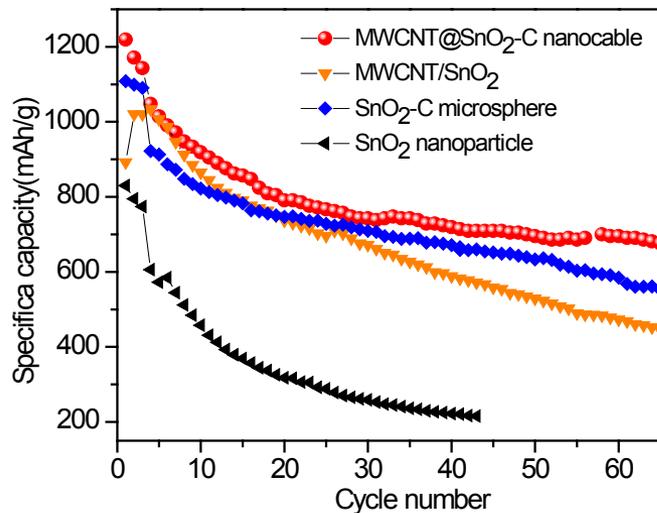
## Modified Carbons with SnO<sub>2</sub> electrodes



Cyclic voltammograms of electrode MWCNT@SnO<sub>2</sub>-C at a scan rate of 0.1 mVs<sup>-1</sup>



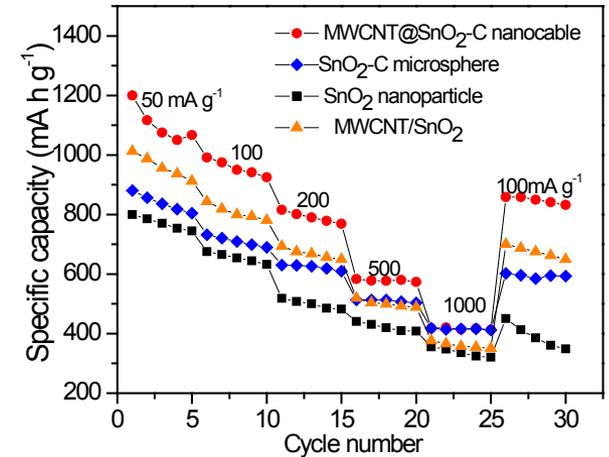
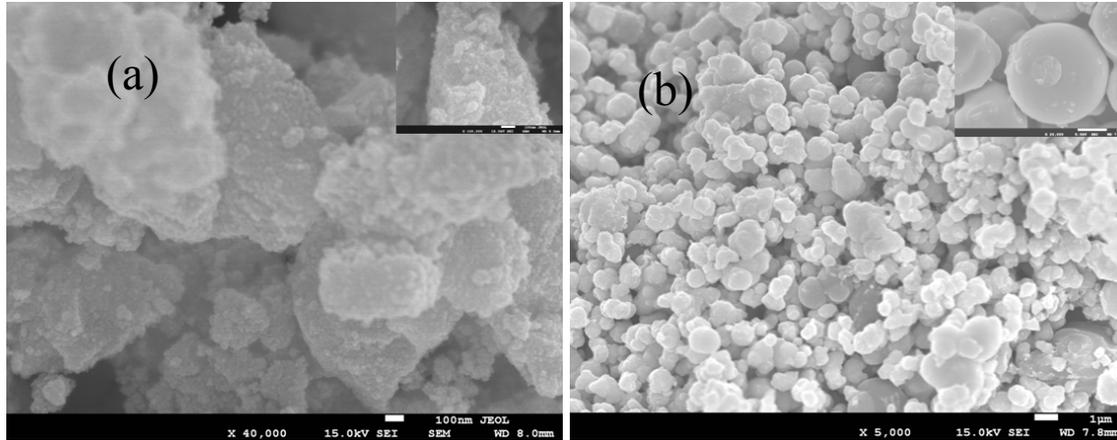
The charge-discharge curve for the first two cycles



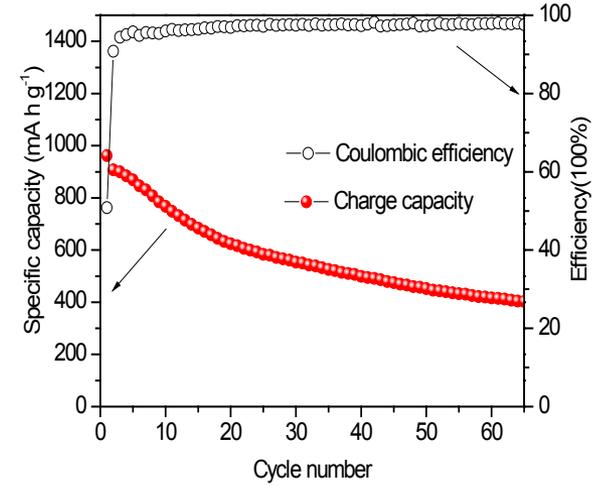
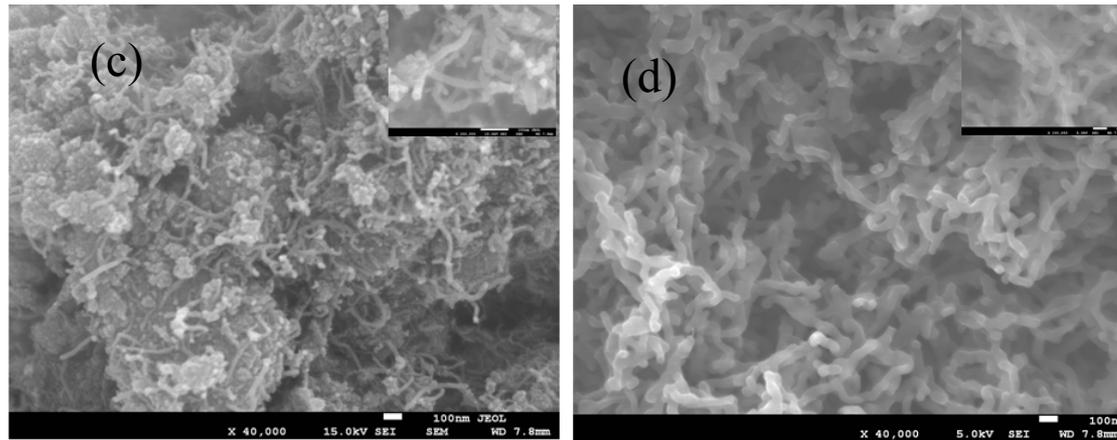
Cycling performance and coulombic efficiency of SnO<sub>2</sub> based anodes at a current density of 100 mA g<sup>-1</sup>.

# Technical Accomplishments and Progress

## Comparison of Nanocable performance with other Carbons



Rate capability of SnO<sub>2</sub> anodes.



SEM images of (a) SnO<sub>2</sub> nanoparticles, (b) SnO<sub>2</sub>-C microspheres, (c) MWCNT/SnO<sub>2</sub> composite and (d) MWCNT@C nanocables. Insets are the higher magnification of SEM images.

Cycling performance and coulombic efficiency of MWCNT@SnO<sub>2</sub>-C anode at current density of 1300 mA g<sup>-1</sup>.

# Collaborations.

- SIC materials are relevant for Li Metal Dendrite suppression – ILRP. (ANL and LBNL collaborators).
- Close collaboration with Grant Smith (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, PHI,)
- Need sources of reproducible electrode materials (Zhagib, ANL, 3M, other industrial collaborators).
- 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).

# 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 using nanocable method.
- 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

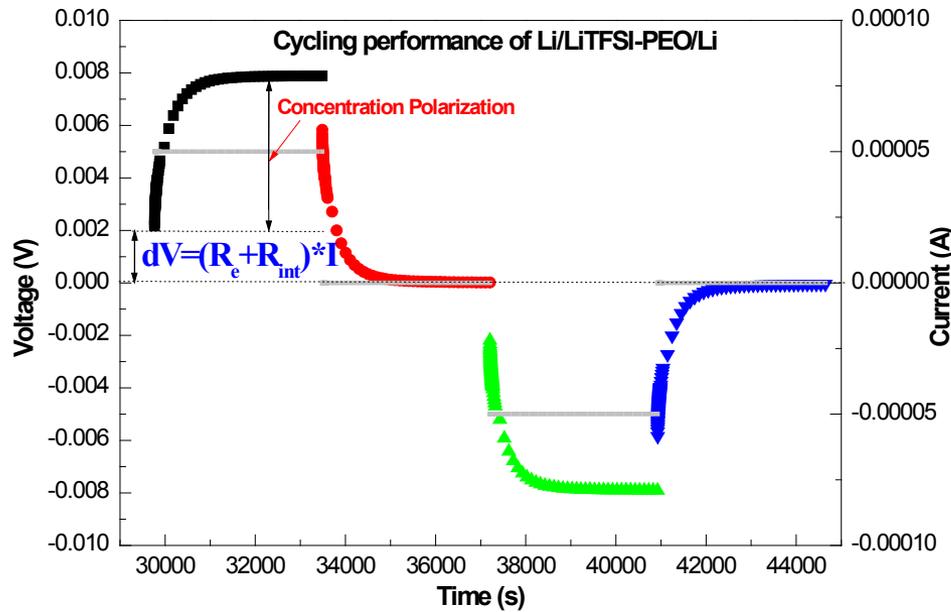
- Electrochemical characterization of polyelectrolyte SIC's.
  - Li metal cells: impedance, lithium cycling.
    - Effects of variable equivalent weight layers on impedance and dendrite growth.
  - Composite Electrodes.
    - Cathodes. Focus on Low voltage materials ( $\text{LiFePO}_4$  if available) for polyether materials. Reduce interfacial impedance enough to build completely dry (no solvents), solid-state cells.
    - Cathodes.  $\text{LiCoO}_x$  and  $\text{LiMn}_2\text{O}_4$  for polysulfone materials. Characterize composite electrodes thermally, mechanically and electrochemically. Particular emphasis on electrode kinetics and electrode thickness behavior –thicker electrodes.
    - Anodes. Graphite: 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 for characterization of SEI layers.

# 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. Capacities at high rates are doubled due to this and thicker electrodes are possible which will lead to increased energy and power densities.
- Modification of the electrode surfaces alters the surface concentration of ions. It is apparent that improvement of performance is due to better distribution of conducting additives in the composite electrodes.
- 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.

# **TECHNICAL BACK-UP SLIDES**

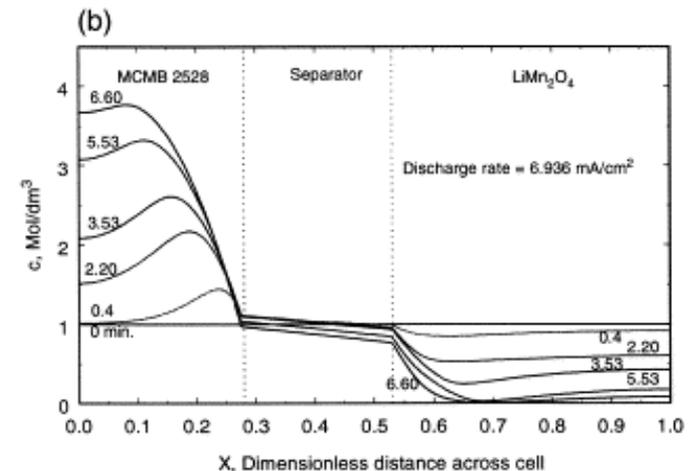
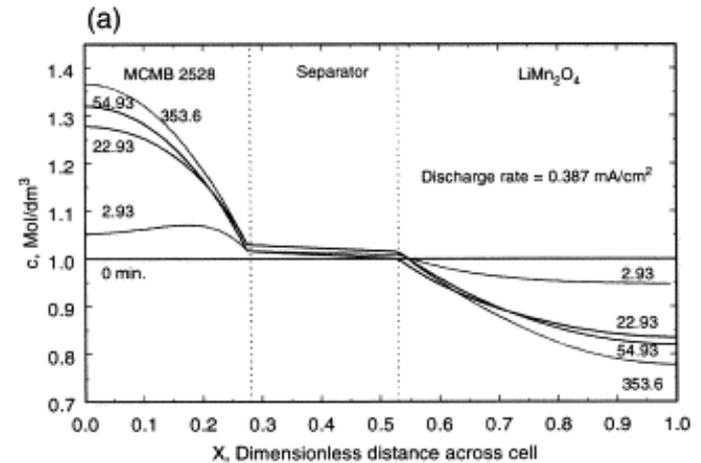
# Impact of Interfacial vs. Bulk vs. Concentration Impedance



Salt concentration affects  $R_{int}$  at electrode surface & bulk conductivity.

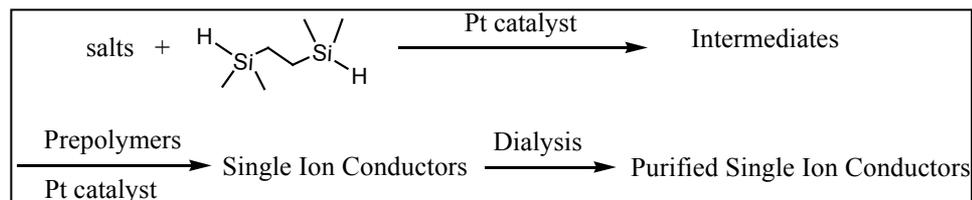
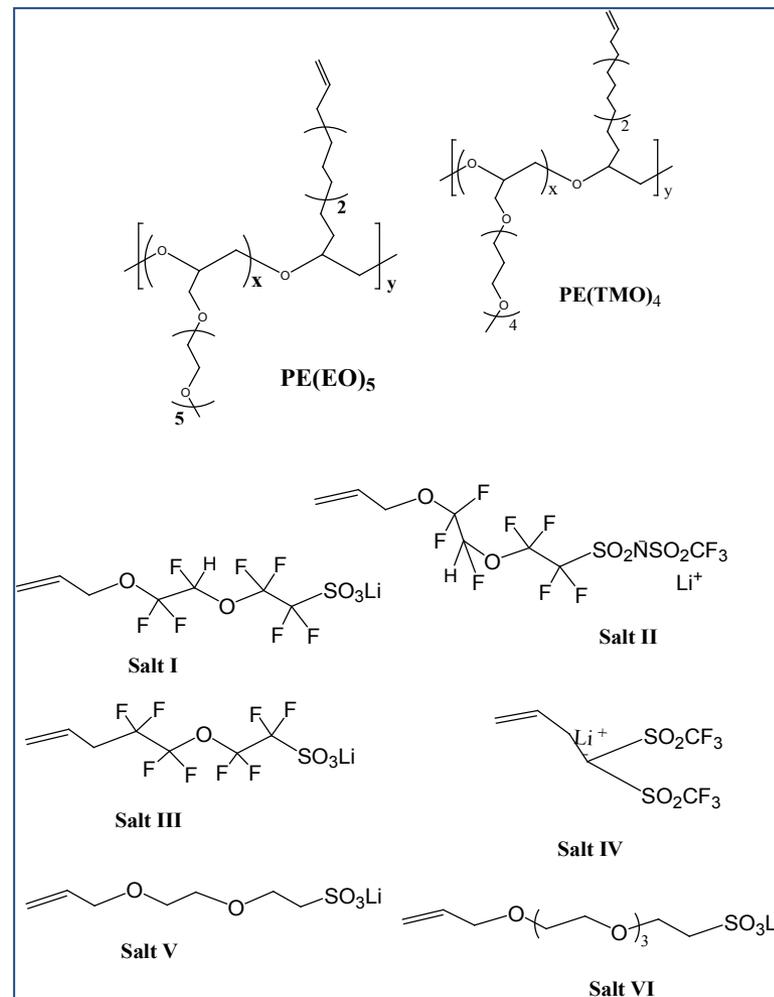
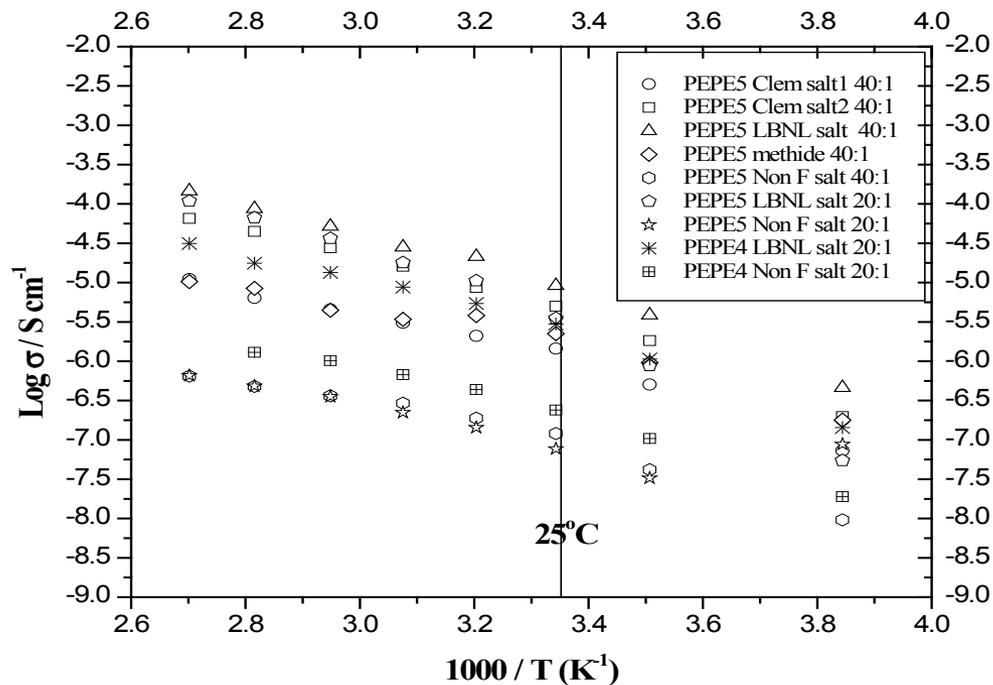
Concentration polarization can be significantly greater than the bulk and interfacial impedances combined particularly in composite electrodes.

Remove concentration polarization by use of lithium ion single ion conducting polyelectrolytes.



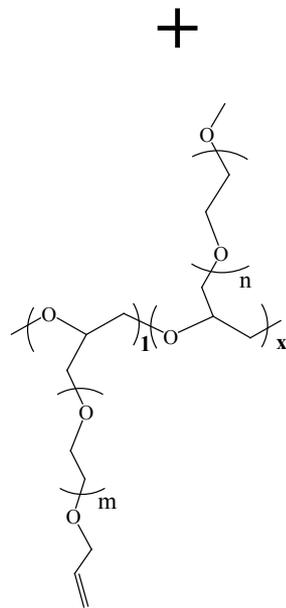
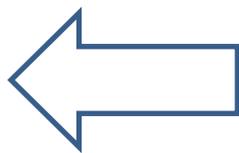
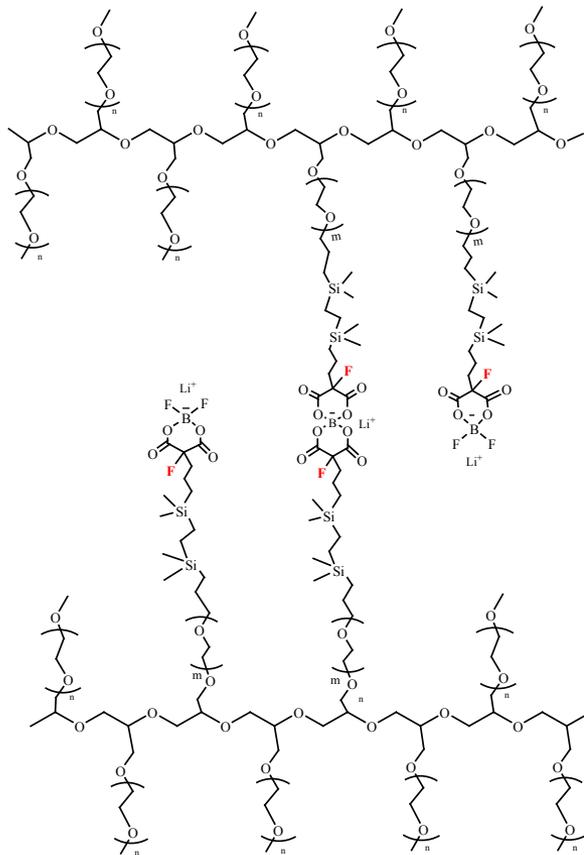
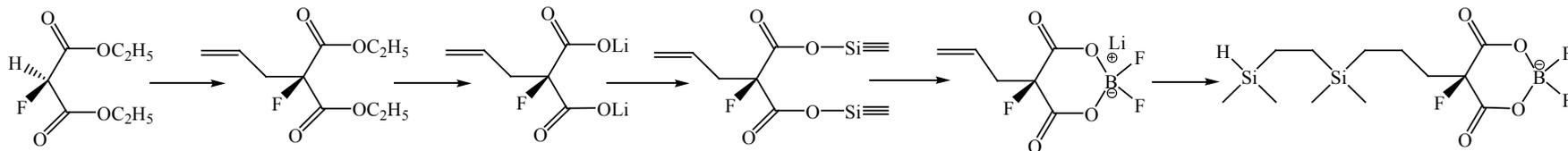
**Effect of Transport Properties on Li-Ion gel polymer cell, Arora, Doyle, Gozdz, White and Newman, J. Power Sources, 88 (2000), 219-231.**

# PEP(EO)<sub>x</sub>-based Ionomers

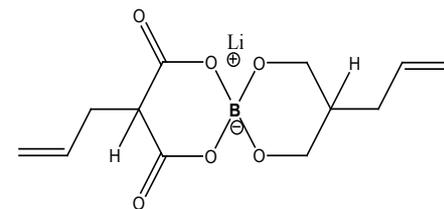


# Technical Accomplishments and Progress

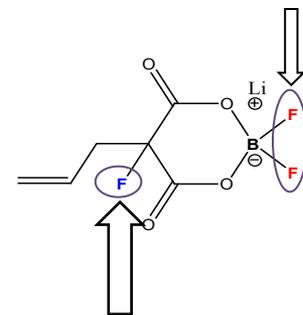
## Preparation of Single Ion Conductors (Modified)



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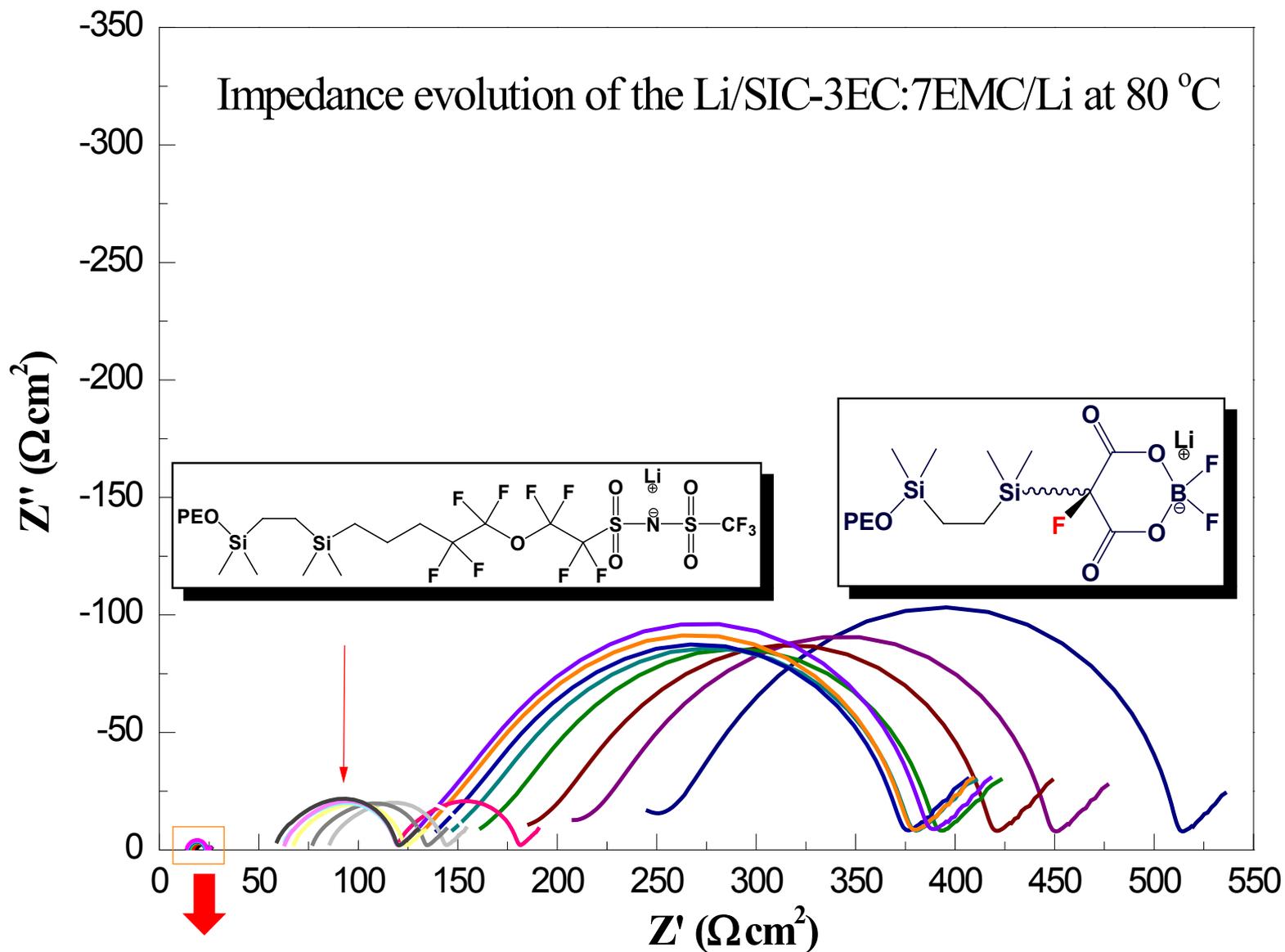


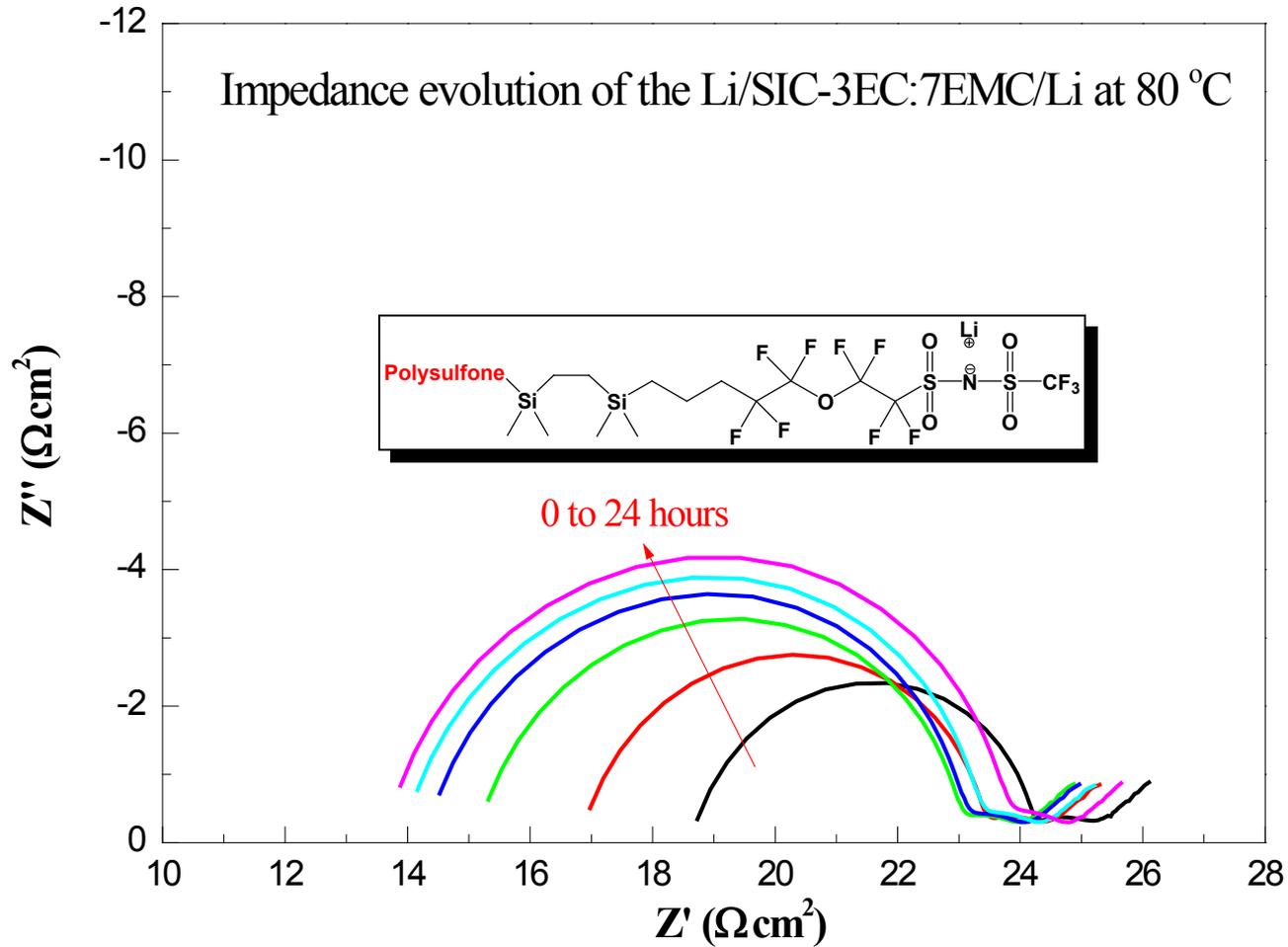
**Increased conductivity**



**Interfacial stability**

# Impedance evolution of the Li/SIC-3EC:7EMC/Li at 80 °C





- The best single ion conductor impedance on Lithium metal.
- Sulfone is reactive with lithium