Interfacial Behavior of Electrolytes

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May 21, 2009

Project ID #
es_39_kerr

Overview

Timeline

- PI has participated in BATT program since 1998.
- 1994-1999 USABC/3M/HQ project on Li/Polymer batteries.
- FY08 Project started Oct. 30, 2007 estimated completion June 30, 2009
- FY09 Project started October 1, 2008
    - 35% completed

Budget

- FY08 Funding - $390k
- FY09 Funding - $550k
- FY10 Funding - TBD

Barriers

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

Interactions/Collaborations

•M.M.Doeff, R. Kostecki, V. Battaglia, John Newman(LBNL) – electrodes, surface analysis, cell building, electrochemical system modeling.

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

•Leif Christensen (3M) - alloy anodes

•Daniel Abraham (ANL) – electrodes, ABR contact

•Karim Zhagib (HQ) – electrodes, Ionic Liquids

Objectives

FY09.

- Determine the role of electrolyte structure upon the intrinsic electrochemical kinetics and how it contributes to the interfacial impedance.

- Determine how bulk and electrode reactions of electrolytes contribute to impedance growth and lead to battery failure.

FY08.

- Investigate the feasibility of pre-forming SEI layers on both anodes and cathodes by use of electrolyte additives, chemical modification of the electrode particles and coating with single-ion conductor polymers.

- Determine whether the interfacial impedance of single-ion conductors can be reduced to practical values (< 20ohm.cm^2 at RT).

- Evaluate the use of very high rate polymer electrodes and redox active binders.

Milestones FY08

| Month/Year/Status	Milestone or Go/No-Go Decision
September/08/ Delayed. Likely completion June 09	Determine the feasibility of pre-forming electrode SEI layers using additives, chemical modifications and single-ion conductor polymer coatings. **Go/No-Go Decision Criteria:** No significant effect on interfacial behavior can be ascribed to the presence of the additive or the procedures
September/08/ Delayed. Likely completion September 09	Complete the evaluation of the impedance characteristics of single ion conductor electrolytes and binders at composite electrodes. **Go/No-Go Decision Criteria:** Interfacial impedance remains above 100 ohm.cm^2 at operating conditions.

FY09 Milestones– Go/No-go Decisions

Month/Year/Status	Milestone or Go/No-Go Decision
September/09/ On track	Complete evaluation of the interfacial behavior of at least three anode materials. **Go/No-Go Decision criteria:** significant differences observed in interfacial impedances with different electrode materials.
September/09/ On Track	Complete evaluation of the interfacial behavior of three cathode materials. **Go/No-Go Decision criteria:** significant differences observed in interfacial impedances with different electrode materials.
September/09/ Likely to slip to FY10	Determine the contribution to the interfacial impedance of the SEI layers versus intrinsic electrode kinetics. **Go/No-Go Decision criteria:** significant differences observed in interfacial behavior upon changing electrolyte composition

Purpose of the Work.

Impact of Interfacial vs. Bulk Impedance

Experimental Measurements
on Li/Li symmetrical cells

PEGDME250-liTFSI(20) + 10% R805 SiO$_2$
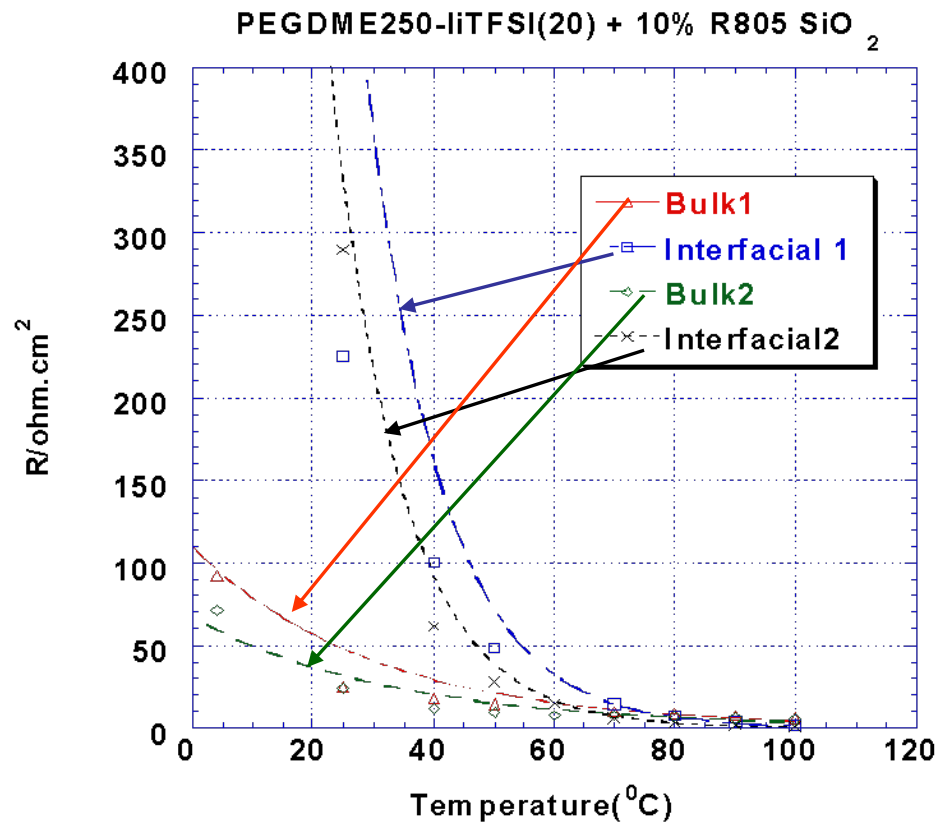
Approach

- A physical organic chemistry approach is taken to electrolyte design, where the molecular structure is varied to provide insight into the processes that may affect the performance of the battery.
  - Transport properties, electrochemical kinetics, electrode side-reactions, thermal stability of the bulk material, interfacial behavior.
  - This involves model compounds as well as new synthesis of materials to test hypotheses which may explain battery behavior.
    - Different solvents and salts, including polymer gels.
    - Electrode materials with different reaction potentials.
    - Single-ion conductor Polyelectrolyte gels.
    - Functionalized surfaces for electrode components.
- Collaborate with surface analysis groups to identify side reaction products and reactive intermediates by combination of spectroscopy and product distribution analysis,
- Collaborate with MD and electrochemical systems modeling groups to provide experimental data.
- Deliver promising materials to cell testing group.

Technical Accomplishments
Selection and Preparation of Materials

- **Electrodes**
  - Anodes
    - MCMB graphite
      - Most negative potential
    - $Si_{57}Al_{28}Fe_9Ti_6$ alloy
    - Li Titanate
      - Least negative potential
  - Cathodes
    - $Li_{1.1}Ni_{1/3}Co_{1/3}Mn_{1/3}O_{2+y}$
      - Most positive potential
    - $LiMn_2O_4$
      - Manganese dissolution
    - $LiFePO_4$
      - Least positive potential

- **Electrolytes**
  - **EC-EMC (3:7v/v) + 1.0M Salt ($LiPF_6$, LiTFSI)**
    - (can be either Wet or Dry); Dry < 0ppm in KFT
    - TFSI used as control for PF_6
    - The electrolytes prepared are stored in ambient ($\sim$28-30°C) or preheated and aged at 50°C.
  - PC, GBL + salts
  - Polymer Gels
    - Polyethers, polysulphones, hydrocarbon block copolymers (e.g.Kraton) with PC, EC/EMC, GBL + salts.
  - Single-ion conductor polymer gels.
    - Fix anions to polymers (HFCIT)

Technical Accomplishments
Stability of Electrolytes

Karl-Fisher Titrations

Water content **(W_0)** of selected electrolyte solutions over time.
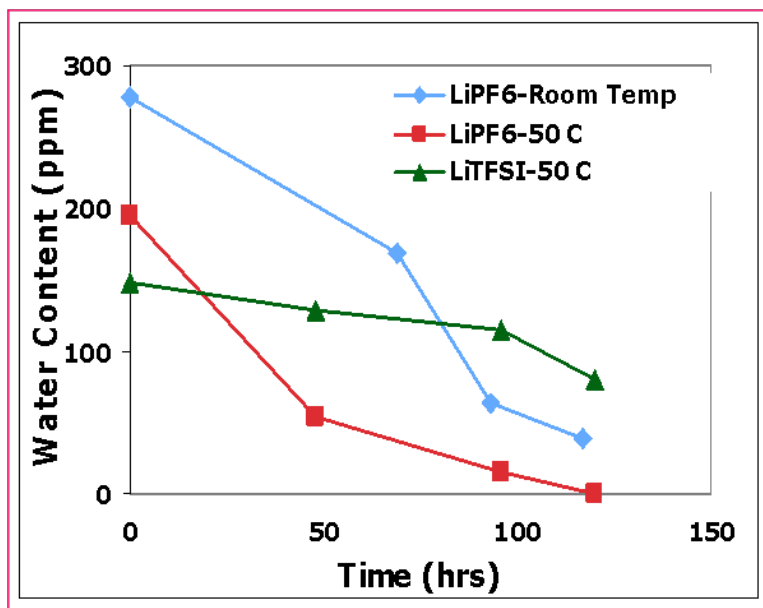
The temperature refers to that at which the solutions were stored throughout the time period
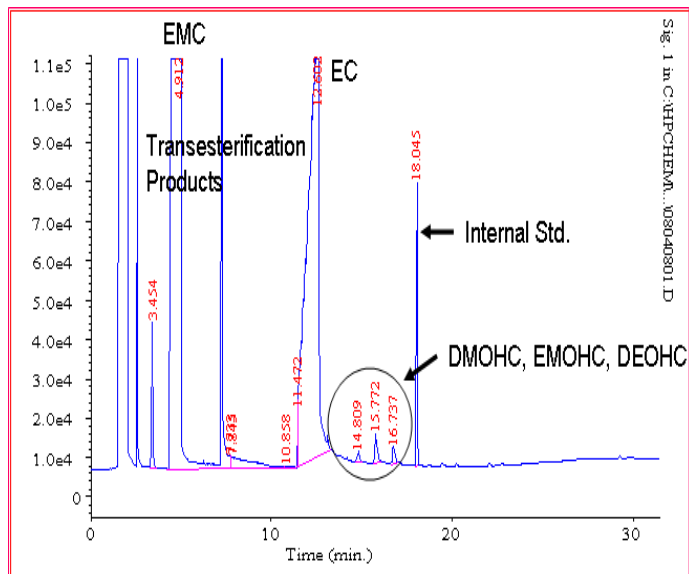
Viscosity Measurements
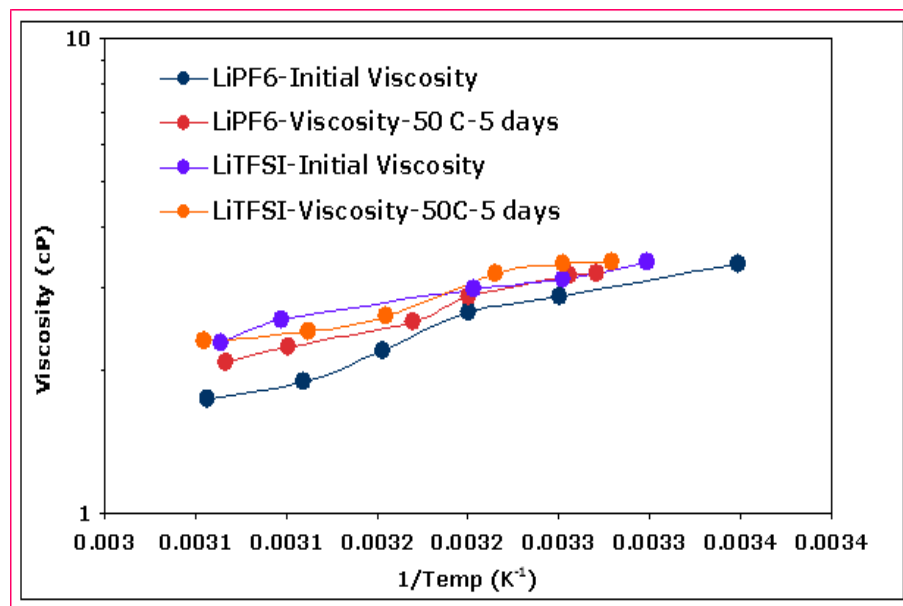
Observed increase in viscosity ~ 10 – 15% over the time period of test particularly for $LiPF_6$ electrolyte

Technical Accomplishments
Chemical Analysis- Product Distribution

Gas Chromatography

GC of LiPF$_6$ wet solution heated at 50˚C for 96hrs.

Transesterification Products:

dimethyl carbonate and diethyl carbonate Further **mixed products:** DMOHC (dimethyl-2,5-dioxahexane carboxylate), EMOHC (ethyl methyl-2,5-dioxahexane carboxylate), and DEOHC (diethyl-2,5-dioxahexane carboxylate)

Gel Permeation Chromatography.

Shows formation of high M.Wt. material (50k) after 48hr at 50°C followed by a decrease to ~4k after 144hr at 50°C.

Capillary Electrophoresis
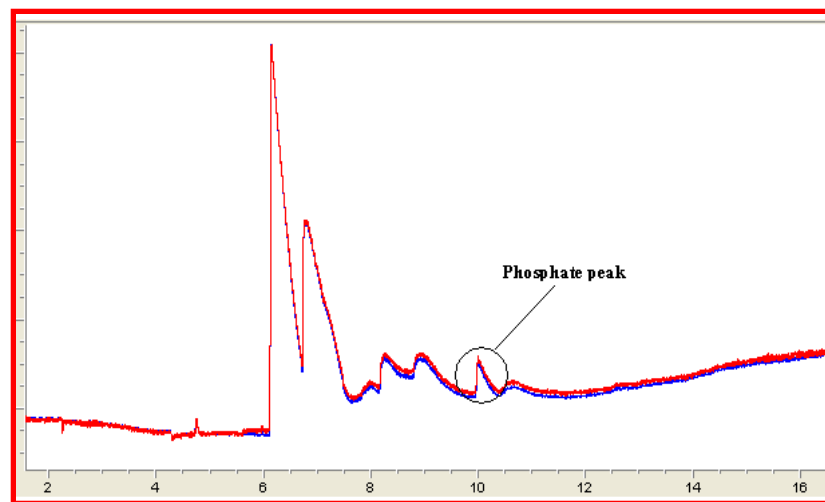
CE data from a wet LiPF6 electrolyte solution after heating at 50˚C for 144hrs.

Probable Reaction Mechanisms

$$LiPF_6 (s) \leftrightarrow PF_5 (g) + LiF (s)$$
$$PF_5 + H_2O \rightarrow POF_3 + 2HF$$

These reactions can be stopped by addition of LiF to the electrolyte and by deposition of LiF on surfaces

EC
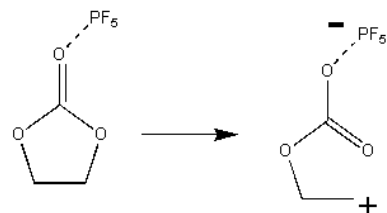
(1)
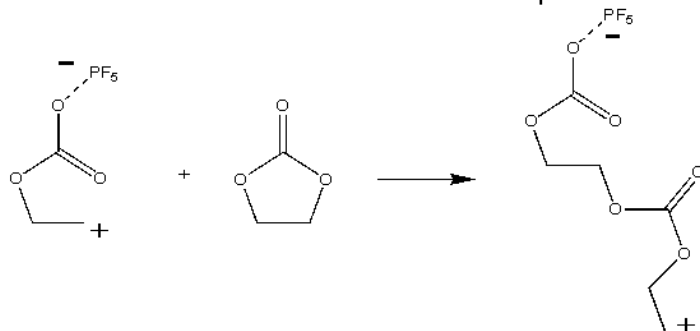
Oligo-ether Carbonates **(2)**

Oligo-ether Carbonate
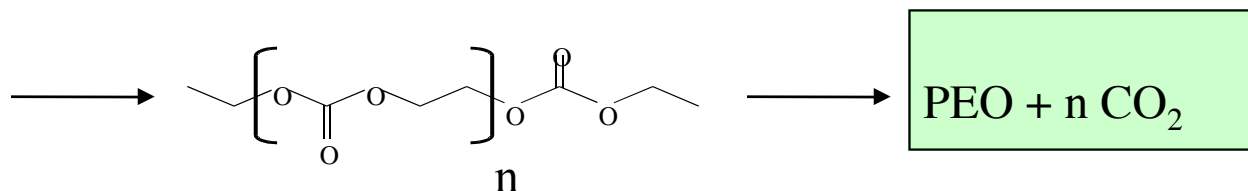
$$PEO + n\ CO_2$$ **(3)**

Gas (CO_2) is evolved after the electrolytes are heated.
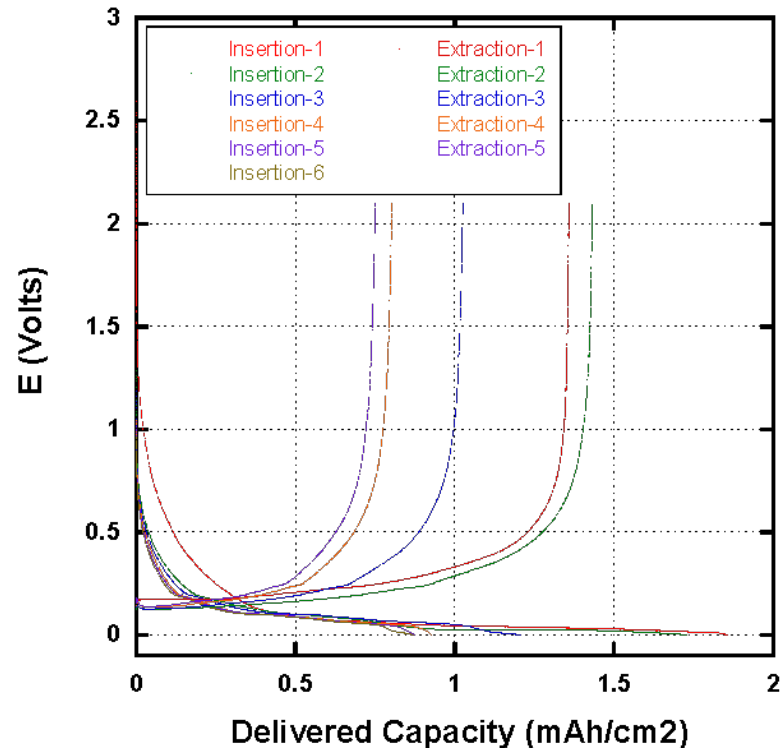PEO reacts further with PF_5 and produces organophosphates which finally decompose to Lithium Phosphate.

Technical Accomplishments

Capacity Fading of Graphite Anodes (Gen 3)

- Dry Electrolyte

Li/EC:EMC (3:7v/v) + 1.0M LiTFSI/Gen3(-) Cell
wc = 0 ppm; 0 < V < 2.1; I = 0.1mA/cm^2
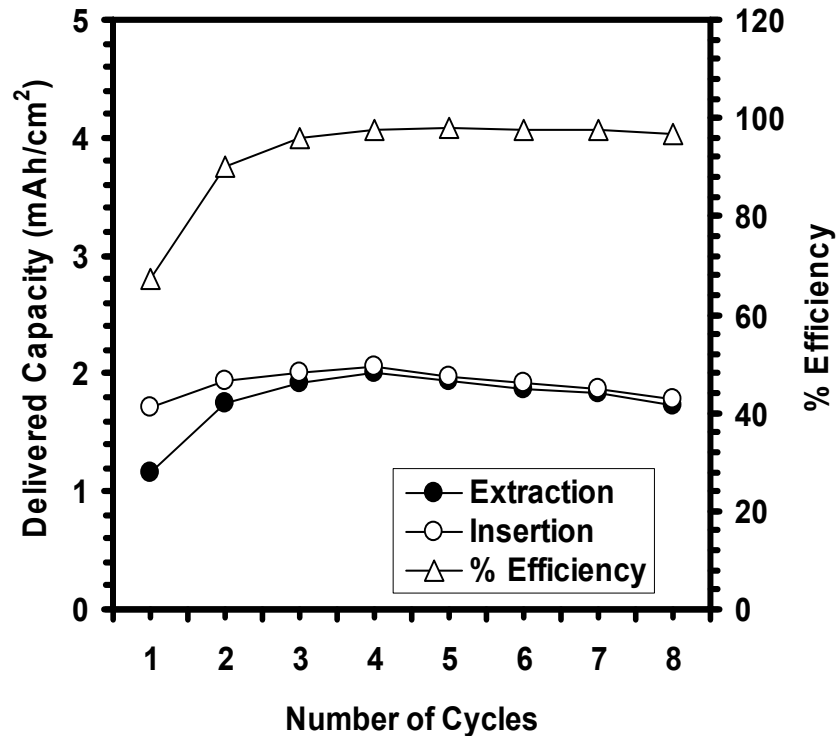
Galvanostatic (I = 0.1mA/cm^2) Li-ion Insertion/Extraction in a
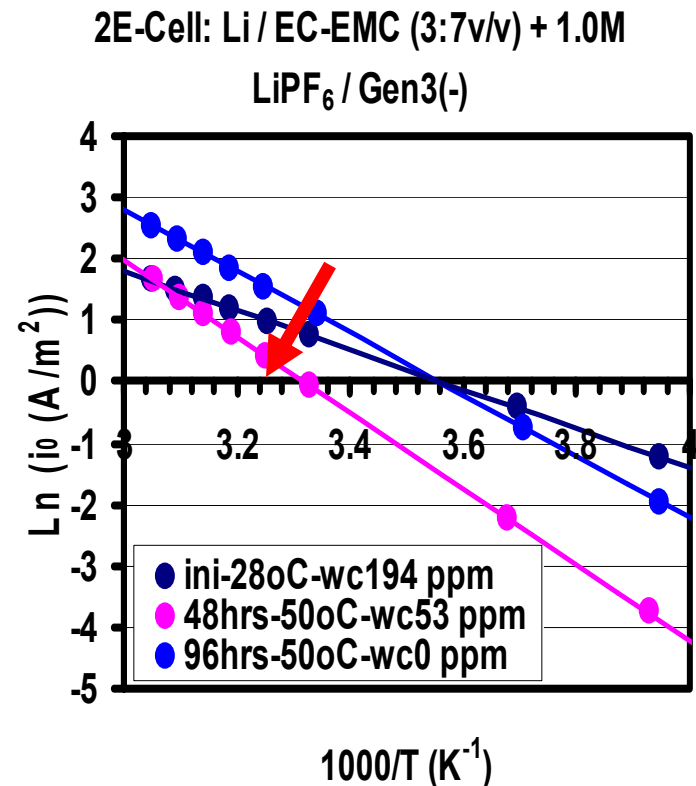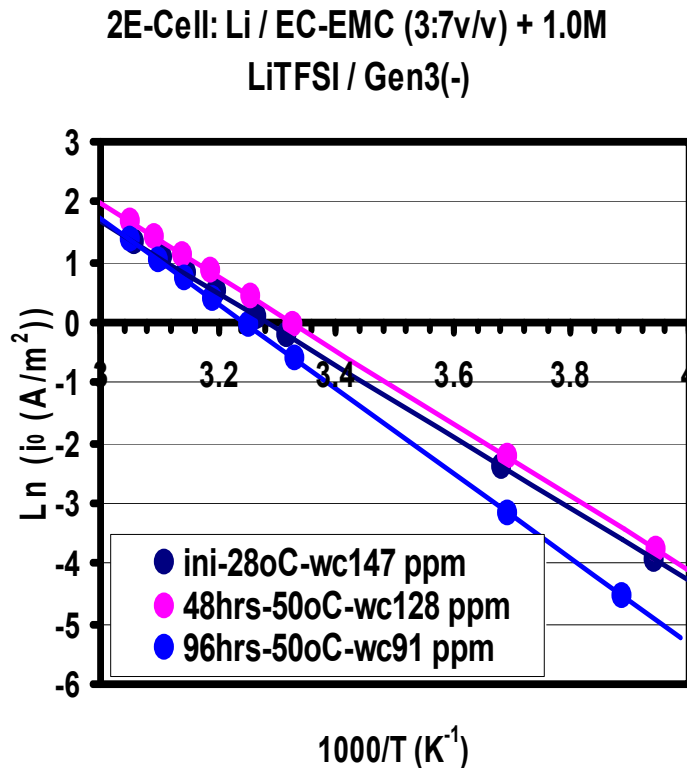Li/EC:EMC (3:7v/v) + 1M LiTFSI (ini, RT)/Gen3(-) Cell; wc ~ 147ppm

- Wet Electrolyte

Wet electrolyte fades more rapidly

Technical Accomplishments

Exchange Current Density from Temperature Step Impedance Measurements (2-electrode cell)

Arrhenius plots and comparison of activation energy

2E-Cell: Li / EC-EMC (3:7v/v) + 1.0M LiTFSI / Gen3(-)

- ini-28oC-wc147 ppm
- 48hrs-50oC-wc128 ppm
- 96hrs-50oC-wc91 ppm

1000/T (K^{-1})

2E-Cell: Li / EC-EMC (3:7v/v) + 1.0M LiPF$_6$ / Gen3(-)

- ini-28oC-wc194 ppm
- 48hrs-50oC-wc53 ppm
- 96hrs-50oC-wc0 ppm

1000/T (K^{-1})

Wet LiPF$_6$ electrolyte shows lower E$_{act}$ and best low temperature performance.
Driest LiPF$_6$ electrolyte shows best performance above 0°C.
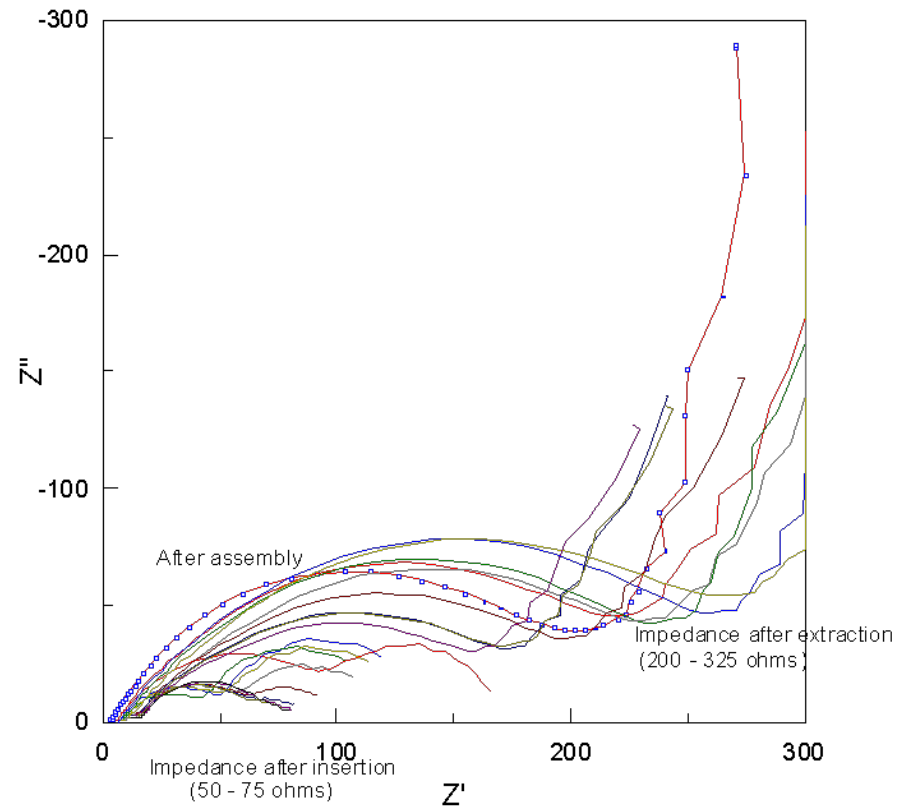Wet LiTFSI electrolyte generally poorer than LiPF$_6$ electrolyte.

Technical Accomplishments

Impedance measurements on 3 Electrode-systems while cycling Gen 3 cathode.
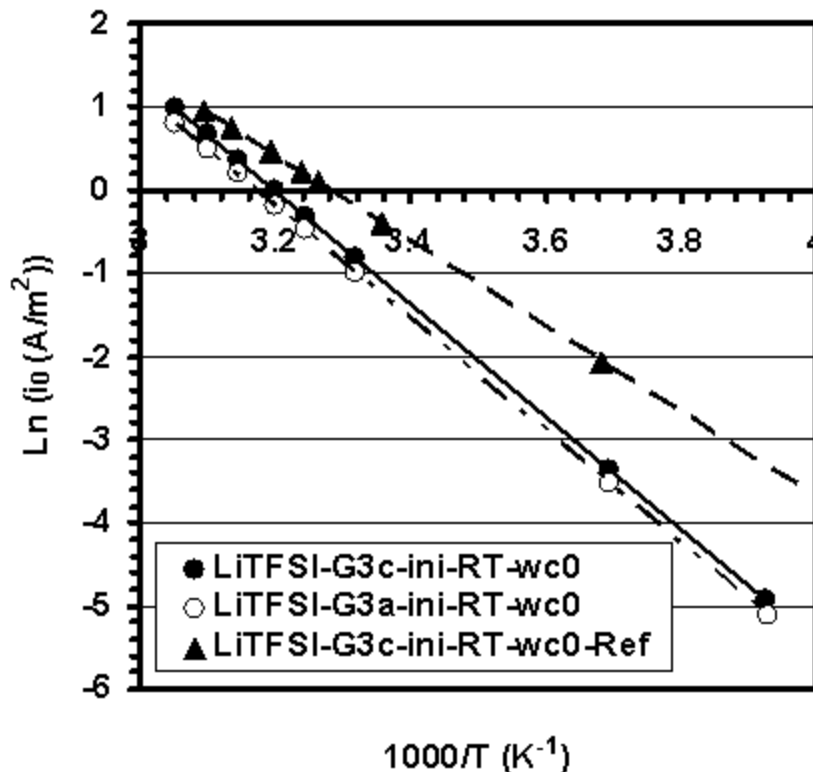
LiTFSI-122308-3E-G3c-0hrs-RT-wc0-Ref
4.1>V>2.0
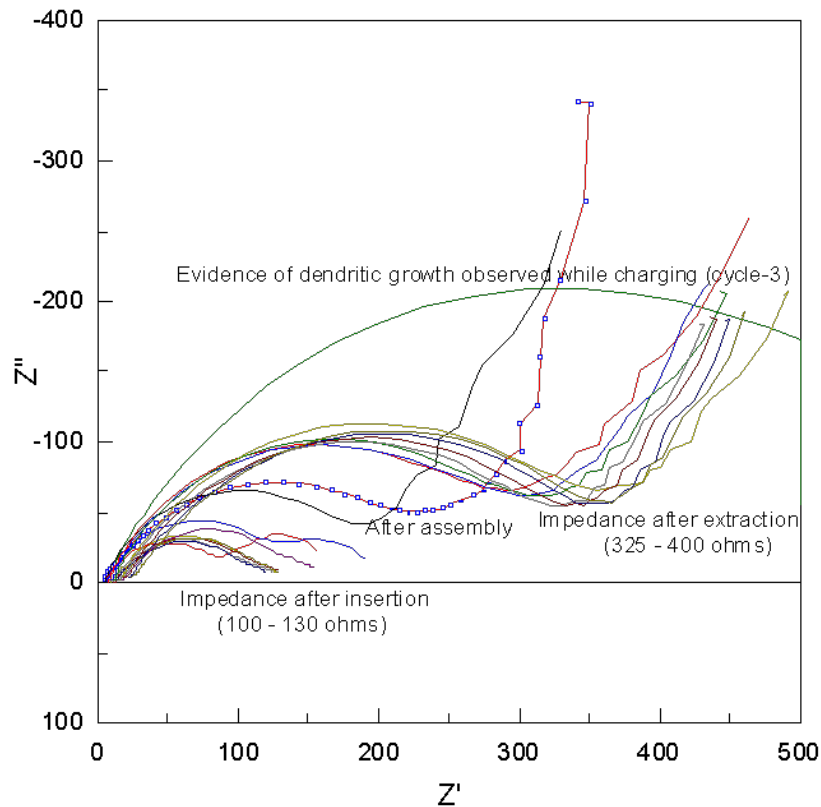
LiPF$_6$-122308-3E-G3c-0hrs-RT-wc0-Ref
4.1>V>2.0

Technical Accomplishments.
## Exchange current density from 2- and 3-electrode cells.

plots for two- and three- electrode cells derived from the interfacial impedance measurements

- Two-electrode measurements are identical – impedance dominated by the Lithium metal interface.
- Gen 3 cathode shows lower E_{act} than Li metal for LiTFSI electrolytes.
- Three-electrode cells are mandatory for study of the interfacial behavior.
- Presence of Li metal, even as a reference electrode and especially as a counter electrode will change the electrolyte conditions by scavenging moisture and other contaminants and/or additives.
- Need engineering help to devise better cells and reference electrodes (e.g. ATD reference)
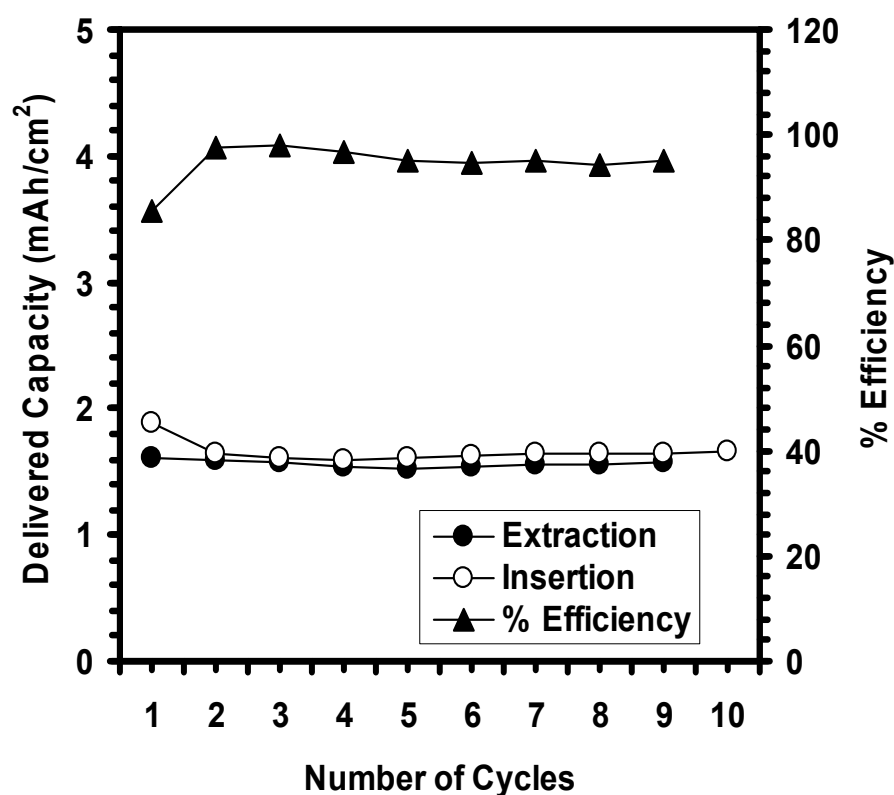
Technical Accomplishments

Galvanostatic cycling of three electrode systems

LiTFSI-122308-3E-G3c-0hrs-RT-wc0-Ref
4.1>V>2.0
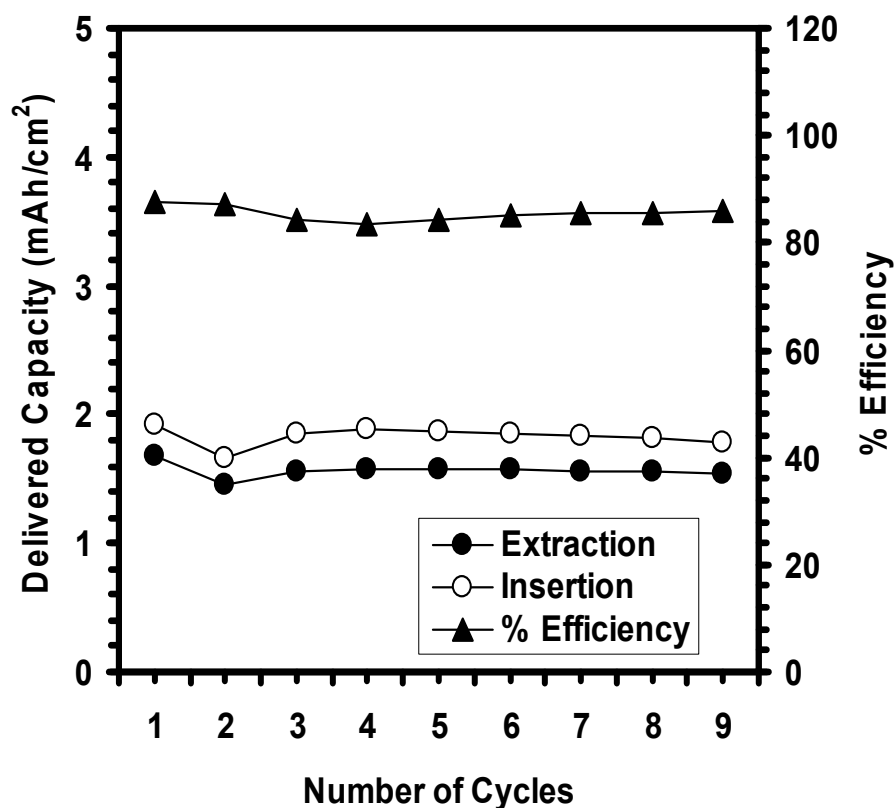
LiPF$_6$-122308-3E-G3c-0hrs-RT-wc0-Ref
4.1>V>2.0

Very stable performance with dry electrolyte. TFSI inefficiency suspected to be due to dendrite growth on the Li metal counter electrode

Other Electrolyte Systems for Study of Interfacial Behavior

- Gamma-butyrolactone (GBL), PC, Ionic Liquids for high voltage systems.

- Ethers (PEGDME250, 500 etc.) – low voltage.

- Polymer Gels.

- Single ion conductor gels and dry polymers.

  - Prevent concentration polarization allowing better electrode utilization and hence higher energy density.

  - Unable to use due to very large impedance at Li metal and in a composite cathode.
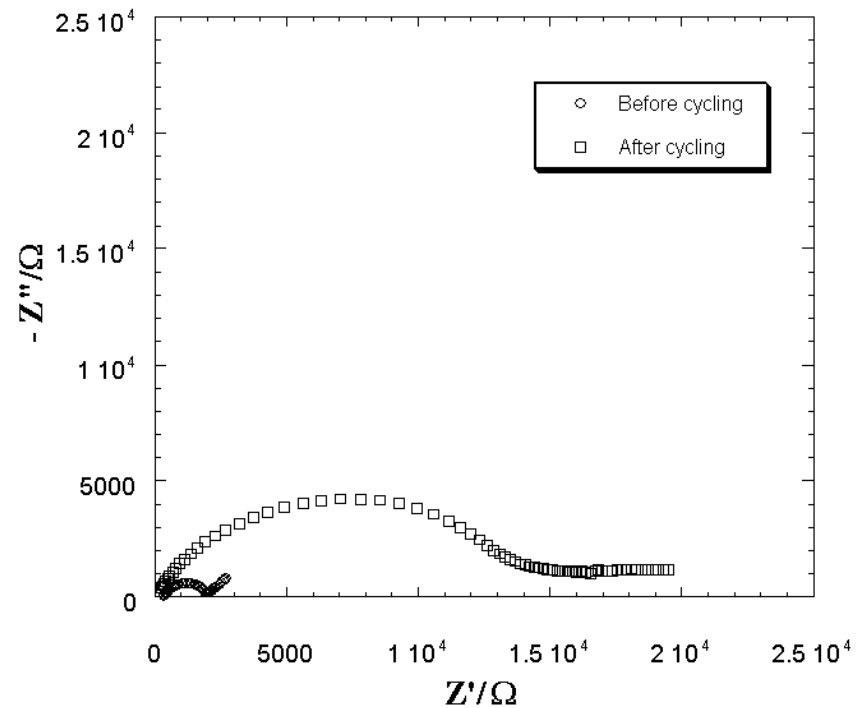
Single-ion Conductors

Possess adequate bulk transport but enormous interfacial impedance. What is the source of this?
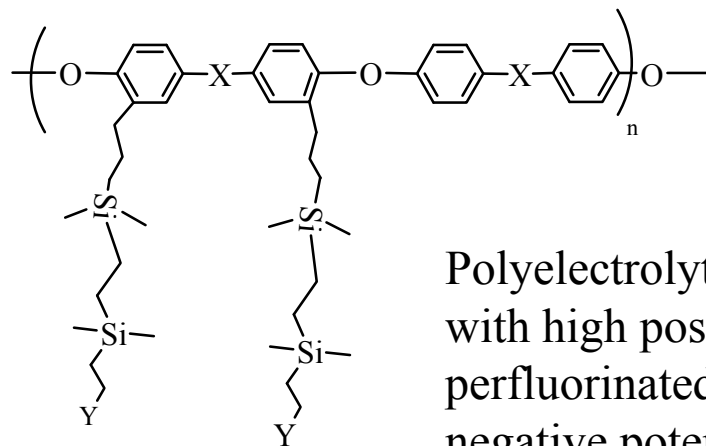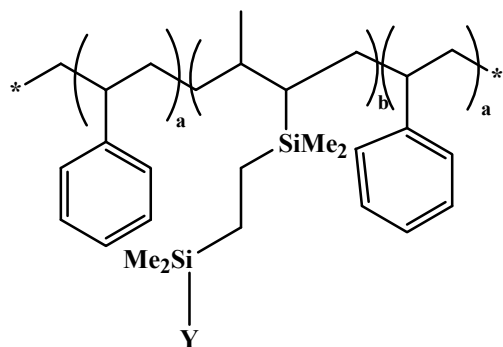
Ionic Conductivity
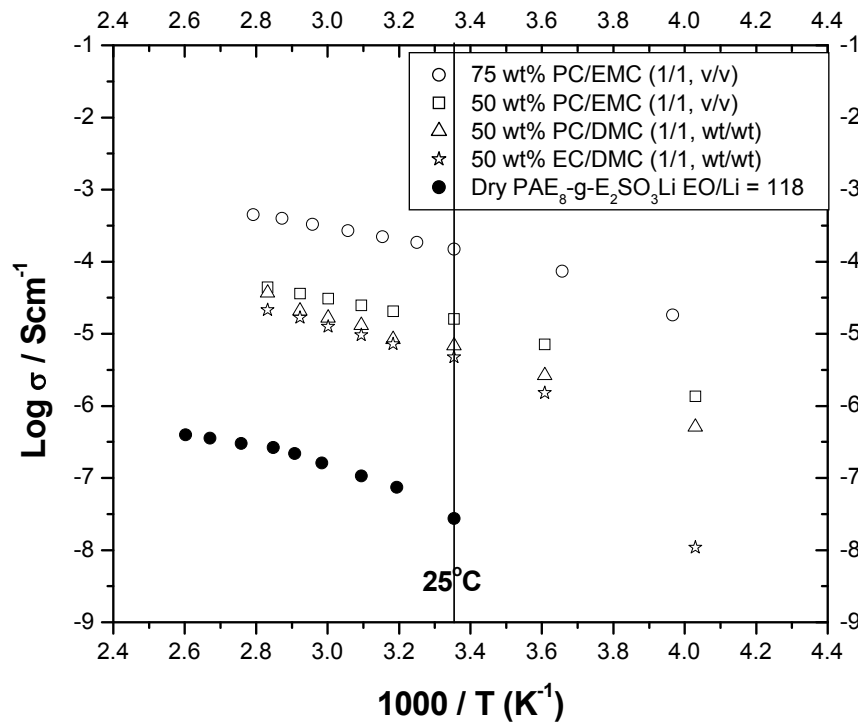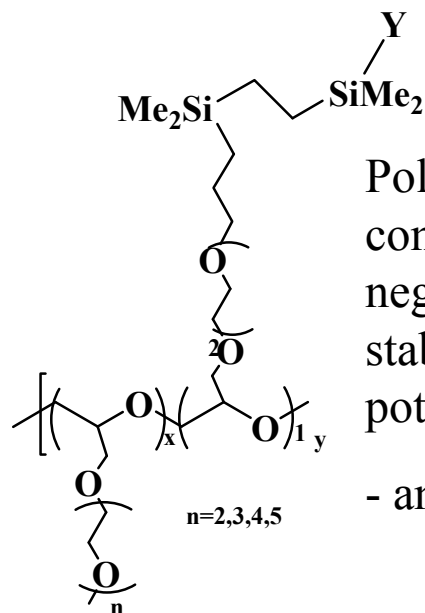
Interfacial Impedance at Lithium

Technical Accomplishments
## Polyelectrolyte Single Ion Conductors Prepared

Polyelectrolyte materials compatible with high positive voltages if Y is perfluorinated. Not so stable at negative potentials – cathode binders.
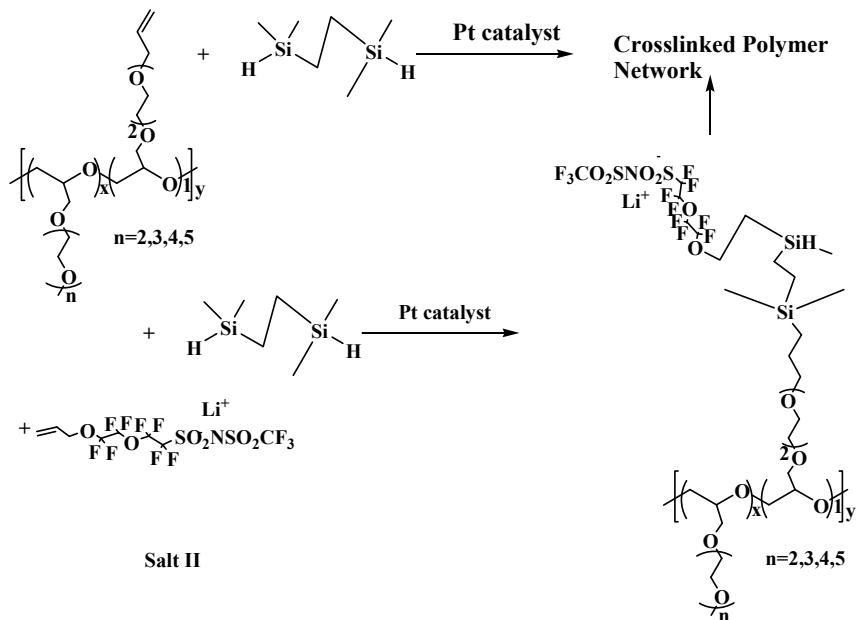
Polyether polyelectrolytes compatible with very negative electrodes but not stable to high positive potentials (>3.6V vs. Li)

- anode binders

n=2,3,4,5

$Y =$ ... $SO_3^- Li^+$;

... $SO_3^- Li^+$
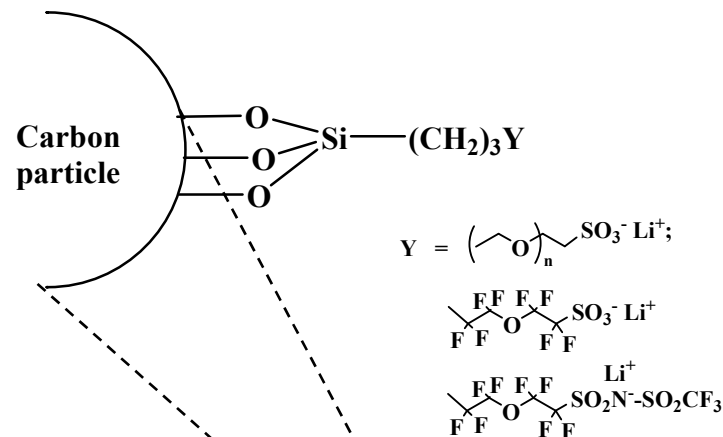
... Li^+ $SO_2N^- - SO_2CF_3$
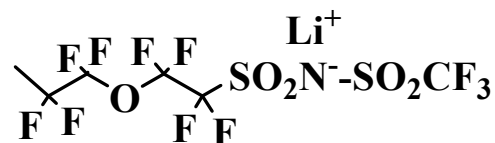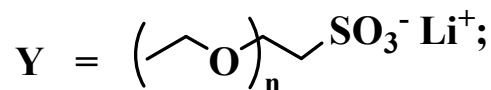
Synthesis
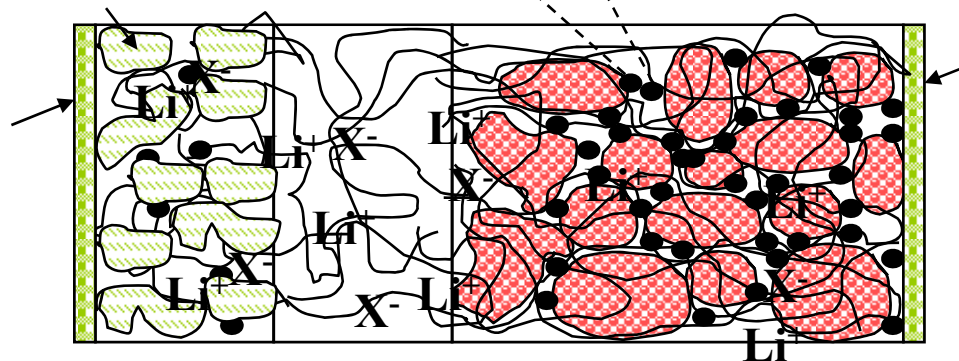
Grafting strategy allows attachment of many Acid groups to Polymers and Surfaces (USP 6,956,083, USP 7,101,643)

Single-ion conductor gels and binders prevent concentration polarization. Functionalized conducting particles may alter electrode environment and allow control of interfacial impedance

Anode separator Cathode

● = **Conducting carbon particle**   ▨ = **cathode particle**

Future Work

- Complete synthesis and characterization of Single-ion Conductor polymers and surface-functionalized conducting carbons. Complete delayed FY08 Milestones.

- Characterize base-line Gen 3 electrodes with three-electrode cells that contain no lithium metal with:
  - EC/EMC(LiPF$_6$) & EC/EMC (LiTFSI) w/o polymer gel matrix.
  - LiTFSI and LiPF$_6$ with Pyrrolidinium ionic liquids
  - Single-ion conductor polymer gels (various solvent systems).

- Evaluate interfacial behavior of anode and cathode materials in three-electrode cells using same range of electrolytes as above. Complete first two FY09 Milestones.

- Use newly installed HPLC/ & CE/Mass spectrometer system to identify side reaction products and collaborate with surface analysis groups to characterize the surface layers that constitute the SEI Layer. Attempt to estimate the contribution of these products to the interfacial impedance.

- Collaborate with new BATT sub-contractors in the electrolyte and additive areas.

Summary

- Resistive losses due interfacial phenomena are generally more important than bulk transport resistance and limit lithium ion battery performance and lifetime.

- Interfacial resistance can be due to intrinsic electrode kinetics and changes in the electrode surface due to electrochemical side reactions or intrinsic instability of the bulk electrolyte. Studies with well controlled electrolyte and different electrodes are designed to separate kinetics from SEI effects.

- Impurities such as moisture can accelerate deleterious reactions. Fundamental studies of how this affects interfacial behavior lead to better understanding and design of better surfaces, electrolyte and additives.

- Three-electrode cell systems that do not contain lithium metal are recommended for interfacial studies.

- Single-ion conductor polymer gels are being prepared to study the source of the high impedance with these materials. Combined with studies of ionic liquid electrolytes as well as commonly used carbonate electrolytes, it is hoped that a molecular basis of interfacial impedance can be formed which may be amenable to MD modeling (U. of Utah).