

Interfacial Behavior of Electrolytes

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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.
- FY09 Project started Oct. 30, 2008 estimated completion June 30, 2010
- FY10 Project started October 1, 2009
 - 25% completed

Budget

- FY09 Funding - \$550k
- FY10 Funding -\$550k

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-FY10.

- 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 ($< 20 \text{ohm.cm}^2$ at RT).

FY11.

- Develop structure-function relationships for electrolyte and surface structures that can guide optimization of interfacial impedance.

FY09 Milestones– Go/No-go Decisions

Month/Year/Status	Milestone or Go/No-Go Decision
September/09/Delayed -refocused to one anode material (Graphite).	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/delayed Refocused to two cathode materials – low and high voltage	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/Completed – observed significant changes in interfacial behavior upon change of anion	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

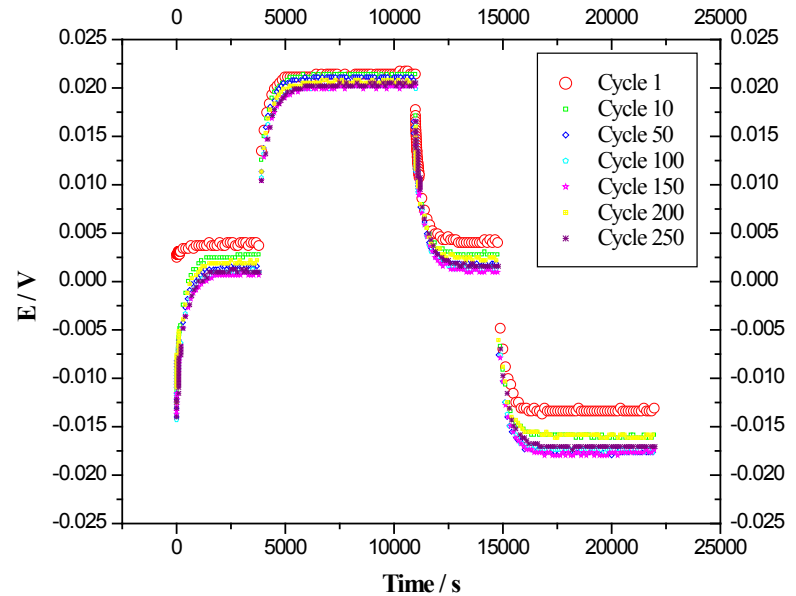
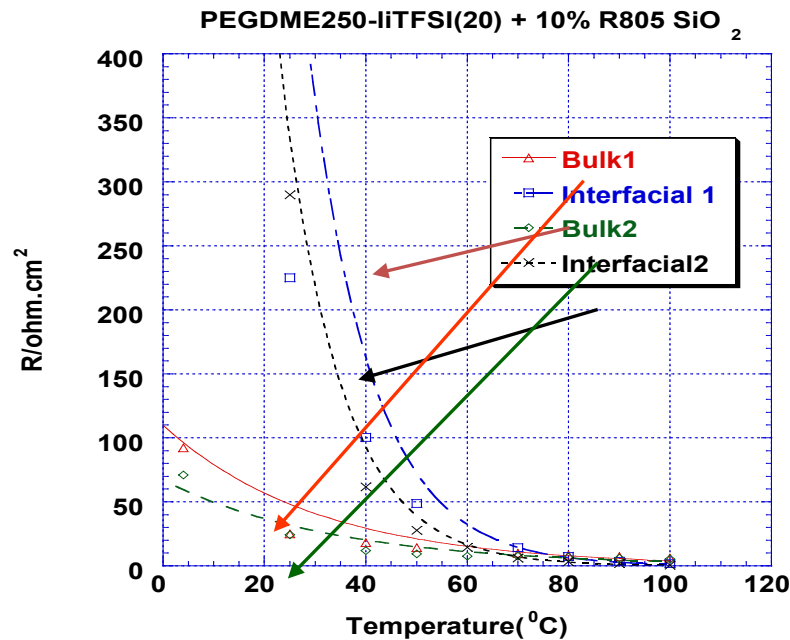
FY10 Milestones– Go/No-go Decisions

Month/Year/Status	Milestone or Go/No-Go Decision
June/10/1-2 Months behind	Demonstrate whether single-ion conductor polyelectrolytes (gel and dry polymer) prevent concentration polarization in composite cathodes and facilitate use of thicker electrodes. Go/No-Go Decision criteria: conductivity $> 10^{-4}$ S/cm and $R_{\text{int}} < 100\Omega.\text{cm}^2$ at RT.
September/10/ On Track	Determine whether single-ion conductor polyelectrolytes (gels and dry polymers) are beneficial for large volume-expansion anodes. Go/No-Go Decision criteria: Demonstrate satisfactory cycling with an expanding anode material using a single-ion conductor binder.

Approach.

Impact of Interfacial vs. Bulk vs. Concentration Impedance

Experimental Measurements on Li/Li symmetrical cells



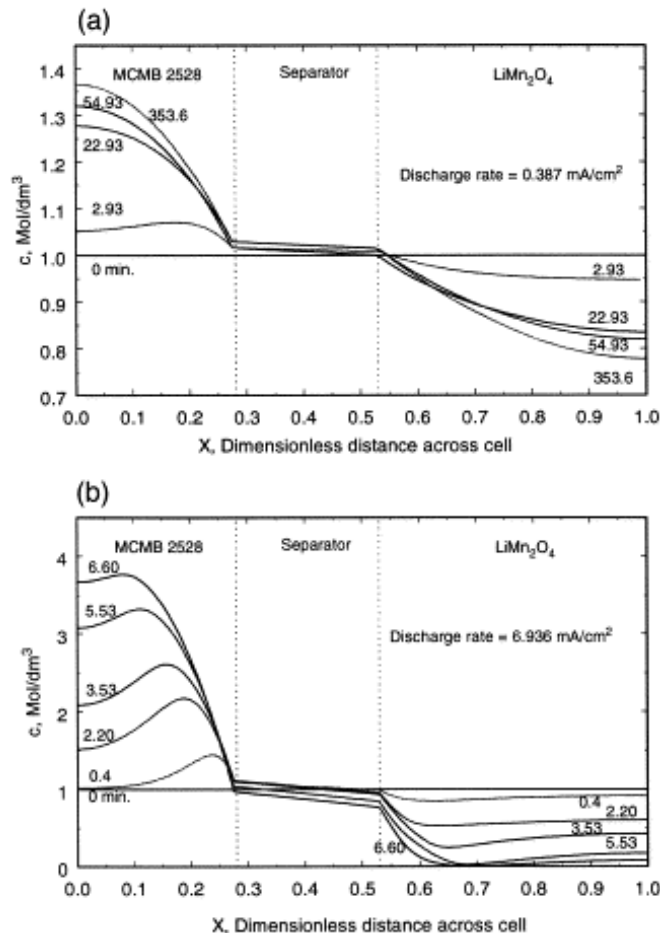
Interfacial resistance has much higher E_{act} than Bulk resistance – low temperature performance particularly sensitive.

What is the source of the interfacial impedance?
Intrinsic electrochemical rates or SEI formation?

Concentration polarization can be significantly greater than bulk and interfacial impedance 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.



Simulated salt concentration profiles across the thin cell during galvanostatic discharge at the (a) C/6 rate (0.387 mA/cm²). (b) 3C rate (6.936 mA/cm²). The separator region is set off by dashed lines. Times since the beginning of discharge are given in minutes

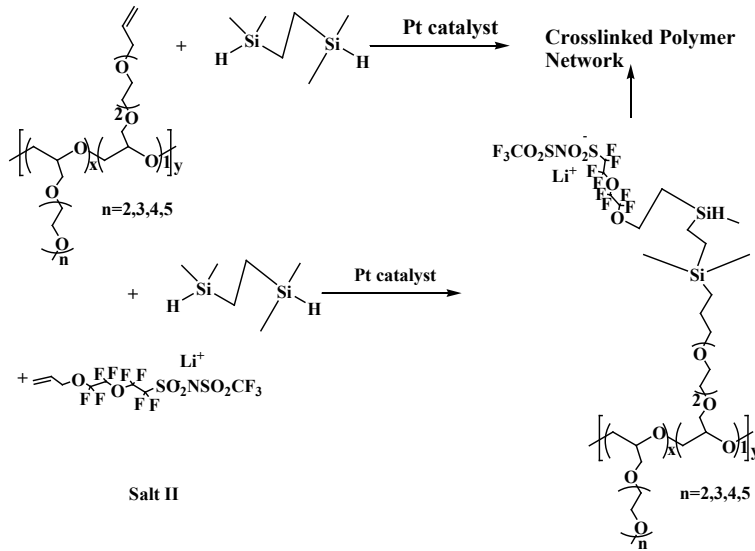
Single-ion Conductor Electrolytes Prevent Concentration Polarization

- Binary salt systems suffer from concentration polarization which results in salt precipitation in the discharging anode and salt depletion in the cathode
- Limits the thickness of the composite electrodes and the charge/discharge rates - limits energy and power density of the battery and limits charging rates.
- Immobilization of the anion prevents concentration polarization.
- Need bulk conductivity $> 10^{-4}$ S/cm
- Need interfacial impedance $< 20 \Omega \cdot \text{cm}^2$

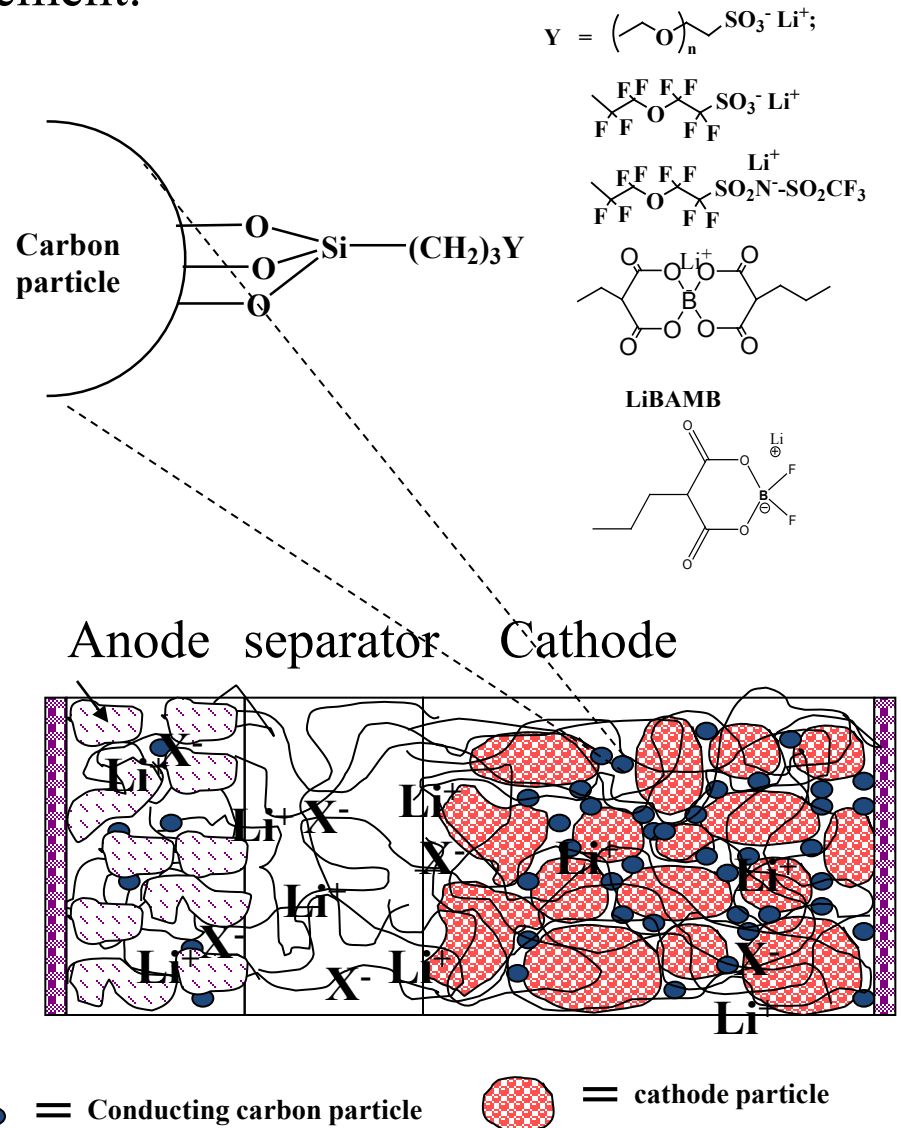
Previous non-BATT work has demonstrated adequate bulk conductivity but huge interfacial impedances. What is the source of the impedance & how can it be reduced?

Approach

Prepare polymers and surfaces that can be functionalized and tuned to the requirement.

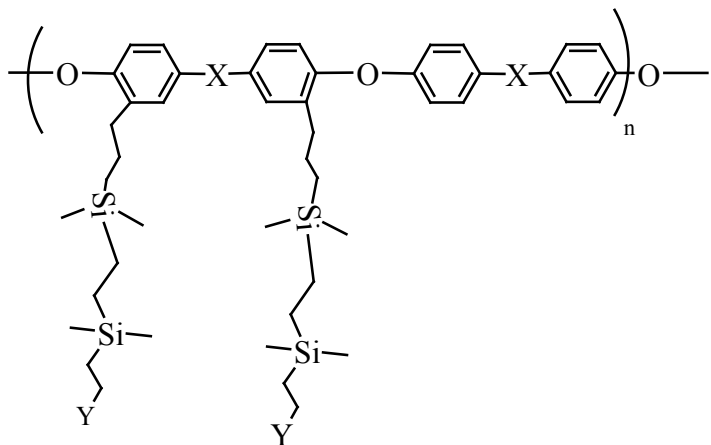


Single-ion conductor gels and binders prevent concentration polarization. Immobilized polymers allow different salt concentrations next to the electrodes than in the bulk separator. Functionalized conducting particles may alter electrode environment and allow control of interfacial impedance. Exchange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



Approach

Classes of Polyelectrolyte Single Ion Conductors

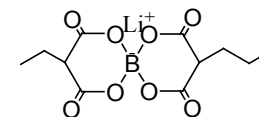
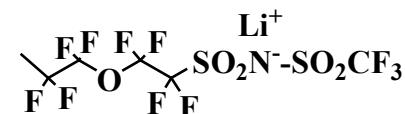
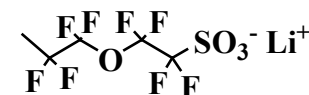
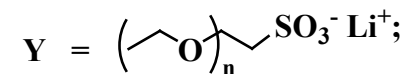


Polyelectrolyte materials compatible with high positive voltages if Y is perfluorinated. Not so stable at negative potentials.

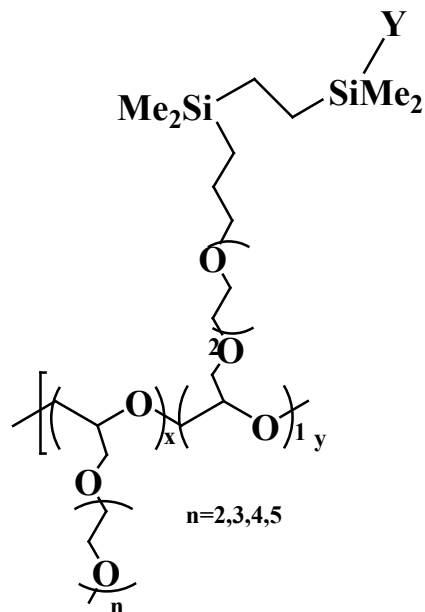
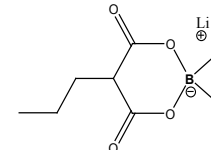
Stiff materials that Phase separate with carbonate solvents - good for interfacial impedance.

Need modification to accommodate volume changes.

– **cathode binders.**



LiBAMB



Polyether polyelectrolytes compatible with very negative electrodes but not stable to high positive potentials (>3.6V vs. Li).

Flexible and elastic mechanical properties that can accommodate large volume changes.

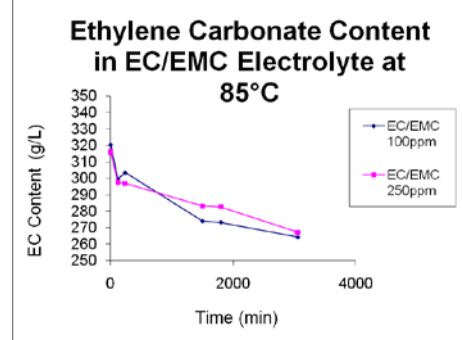
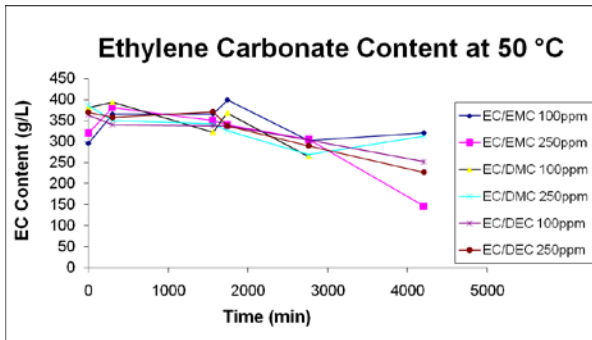
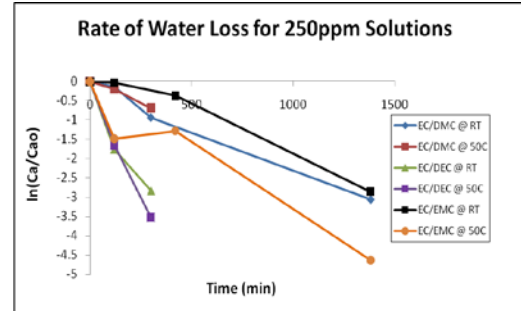
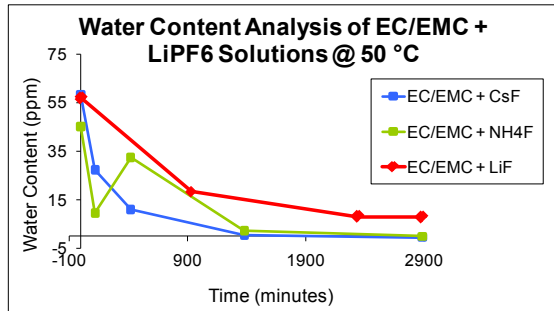
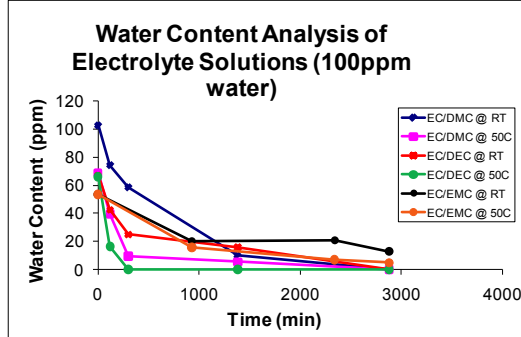
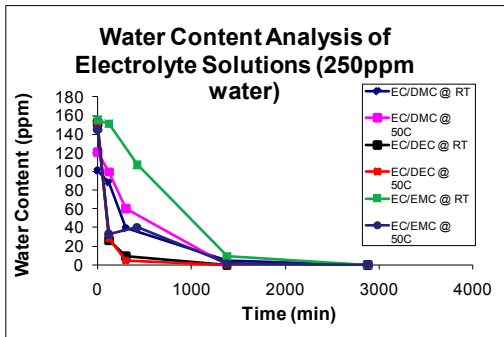
– **anode binders**

Approach

- Interfacial impedance – a difficult problem.
 - How much is intrinsic kinetics – exchange currents
 - What affects the kinetics? – salt concentration, anion dissociation and mobility, solvent, electrolyte viscosity, surface functionalities, presence of side reaction products – the SEI layer?
 - How much is due to the presence of the SEI layer?
 - Products from side reactions of electrochemical processes.
 - Products from inherent instability of the electrolyte components – hydrolysis (water content) acid-base reactions.

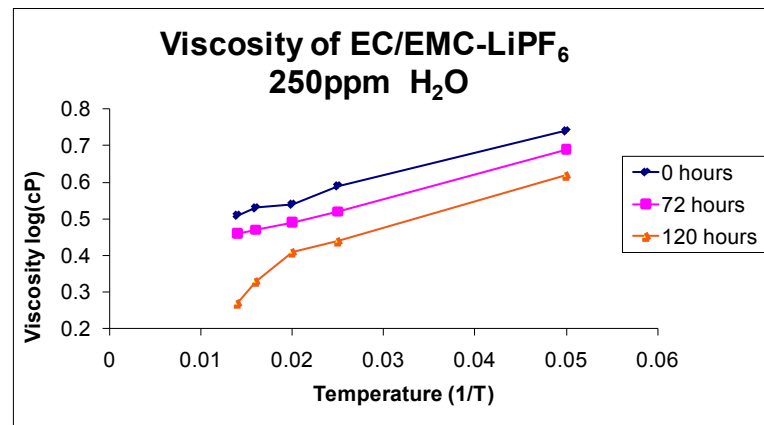
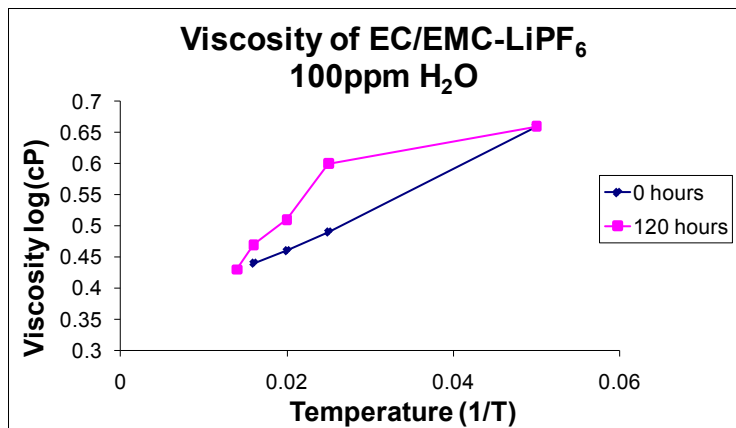
Inherent Instability of Electrolytes.

Stability of Typical Li Ion Electrolyte Components

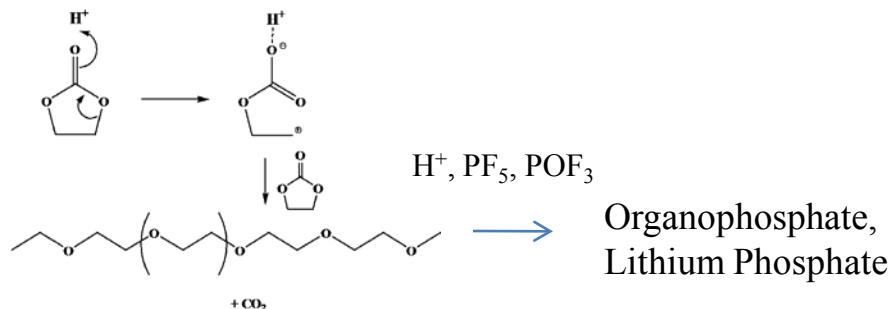


- EC/DEC electrolyte solutions lost water at the fastest rate.
- The data fits an exponential curve which suggests that the rate of water loss is first order.
- Heating the samples increased the rate of water loss but the addition of CsF and NH₄F had no observable effect although LiF has a small effect.
- Rate of water loss increases with temperature.
- This data is consistent with:
- $\text{H}_2\text{O} + \text{PF}_5 \rightarrow 2\text{HF} + \text{POF}_3$
- LiF competes with H₂O to react with PF₅ but is less active.

Reactivity of Carbonate Solvents



Viscosity of electrolytes increases then decreases particularly in presence of water. Consistent with ring-opening polymerization followed by acid-catalyzed cleavage of ether polymers to yield small molecule fragments that can deposit on electrodes to form the SEI **and increase impedance.**



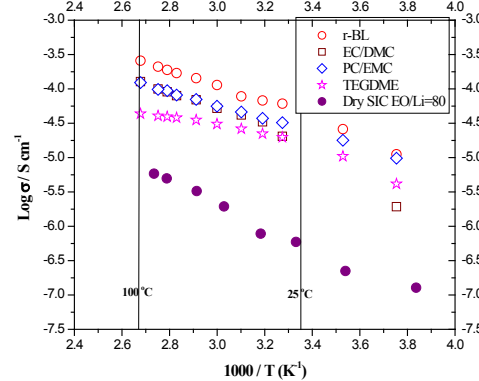
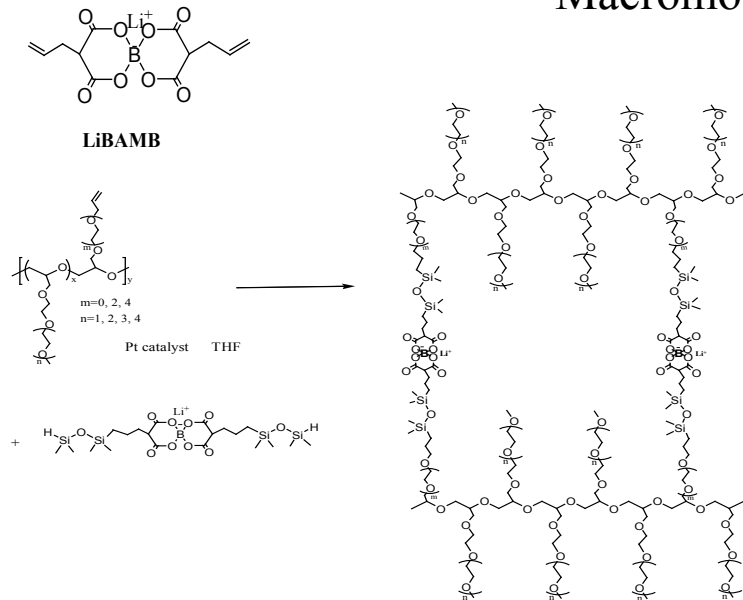
Control experiments using LiTFSI in place of LiPF₆ also showed consumption of water, although at a slower rate. Measurement of water content of EC/EMC with no salt showed consumption of water.

Water causes hydrolysis of carbonate solvents to give carboxylic acids and alcohols. Carbonate solvents need to be replaced for long life.

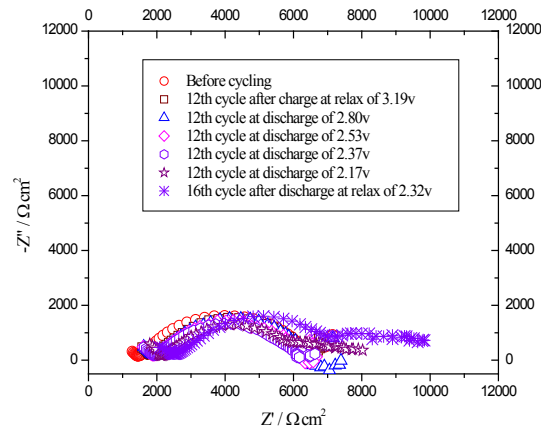
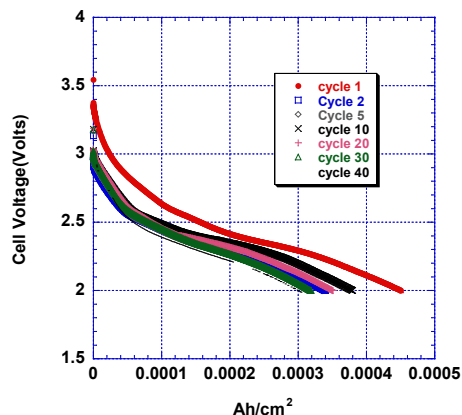
Network Single Ion Conductor

Salt (LiBAMB) Cross-links Polymer

Macromolecules (2006) 39, 362-371



Conductivity of gel system meets EV requirement (10^{-4} S/cm at RT). GBL solvent best. Conductivity of dry polyelectrolyte too low.



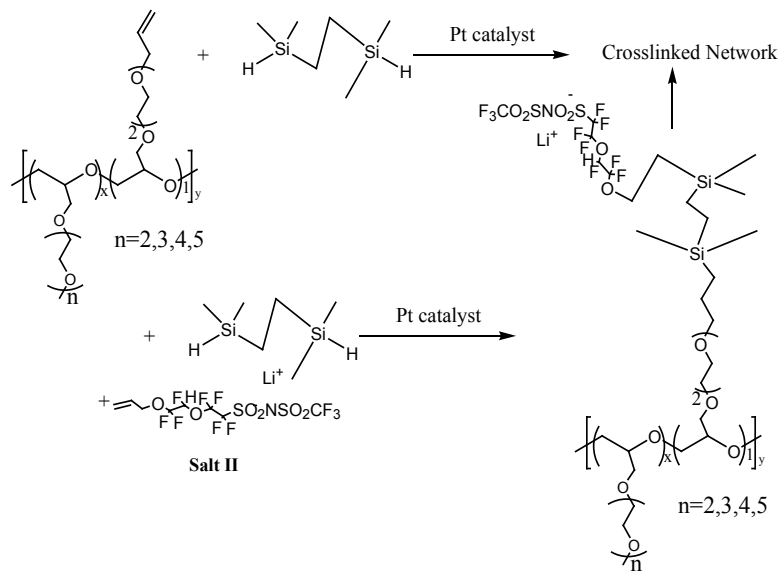
Full cell cycling with single ion conductor gelled with PC/EMC as separator/electrolyte and cathode binder/electrolyte. Rate is limited by large interfacial impedance of Cathode. Capacity retention is good at low rates and better than binary salt system.

Cathode: 30% V_6O_{13} , 58% SIC (EO/Li=40), 10% carbon black, 2% brij

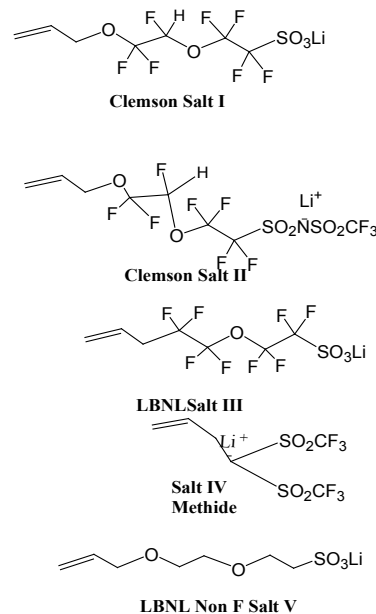
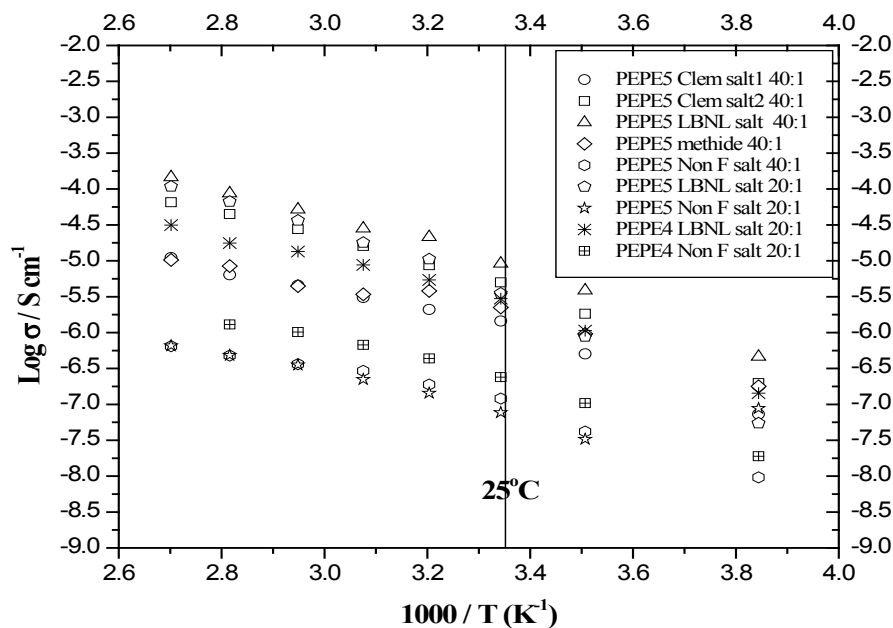
$I_c = I_d = 25 \mu\text{A cm}^{-2}$ Cut-Off Voltage: 2.0 - 3.25V, $T = 25^\circ\text{C}$

What is the source of the impedance?

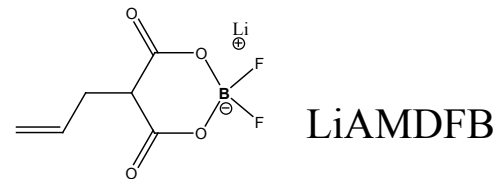
Comb Polyelectrolytes



Comb structures are more mobile as the anion is singly tethered and does not cross-link the polymer. Separate Cross-links are introduced to provide mechanical strength that does not impact conductivity so much. Conductivities of dry polyelectrolytes are Shown and are close to EV performance needs at RT for these non-optimized systems. Theory (Ratner) predicts best conductivity at $\text{EO:Li}^+ \sim 40:1$. N



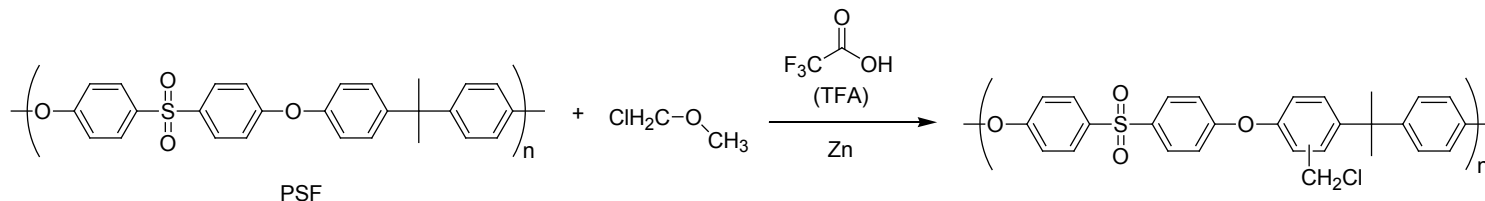
Different salts have been attached to investigate the effect of structure. The side chain and the backbone structure have been varied and a new salt has been prepared that contains less fluorine.



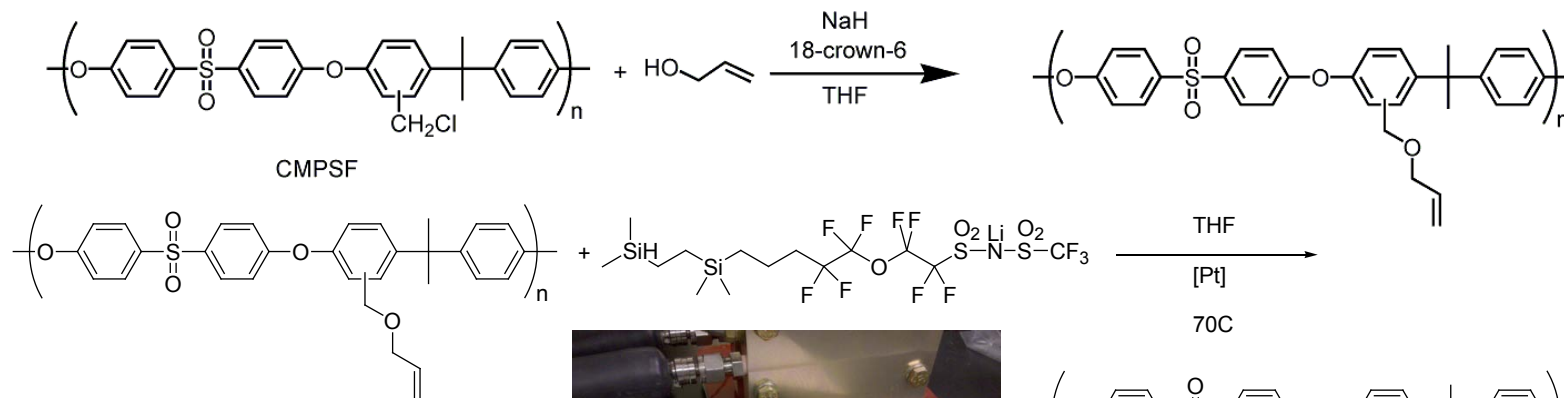
Backbone Variation

Commercial Polysulfone Polymer Modification

- Chloromethylation via an electrophilic substitution

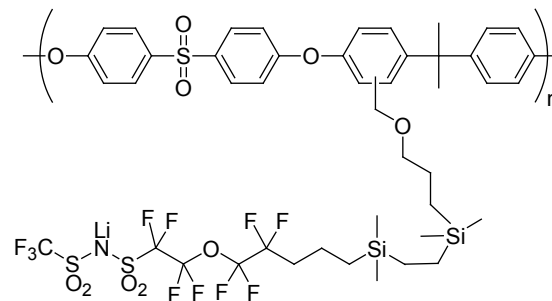


- The polymer was functionalized via ether linkages with allyl groups

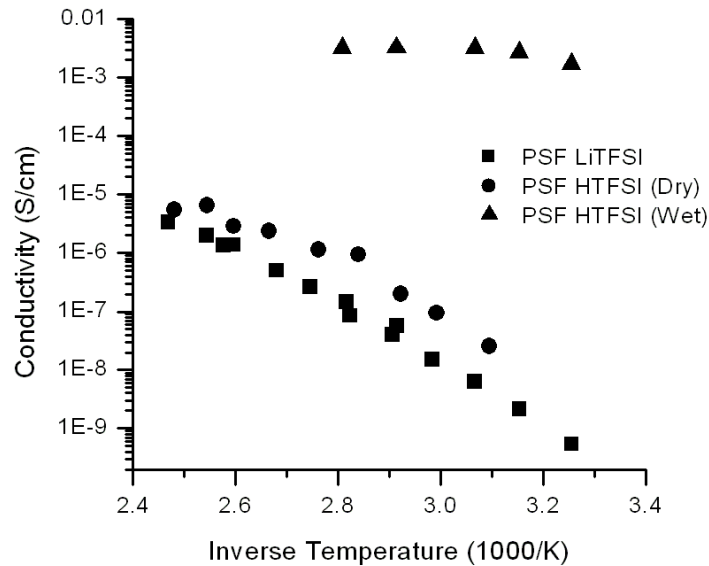
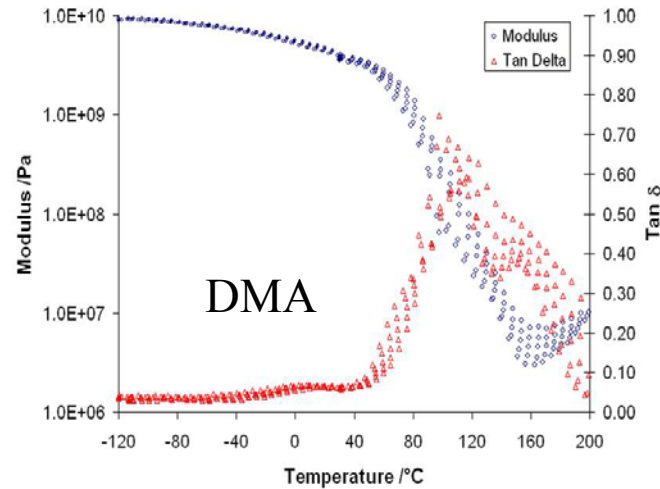
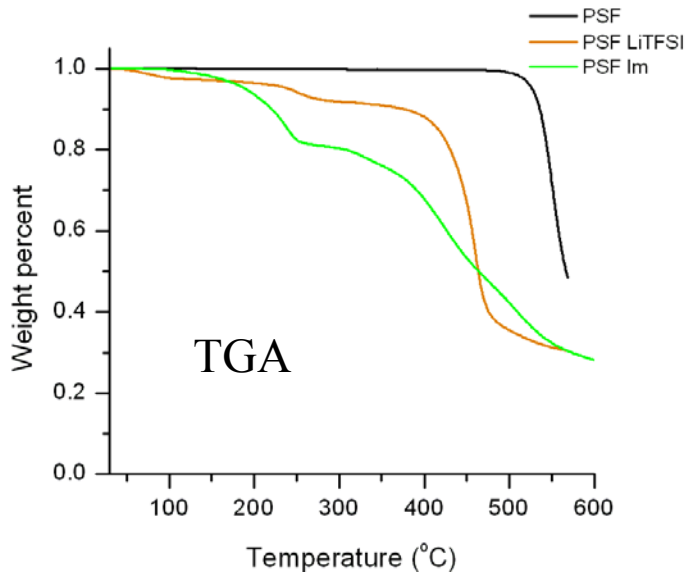


Modified polymer forms good films.

Structure contains few ether bonds so is stable to high voltage cathodes.



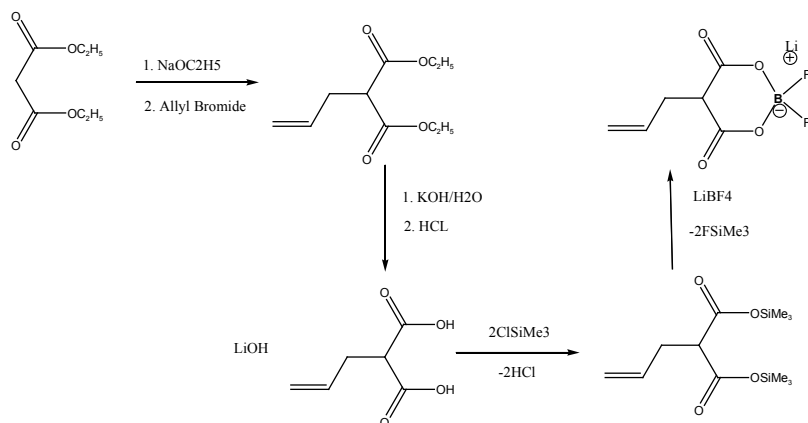
Characterization



Conductivity

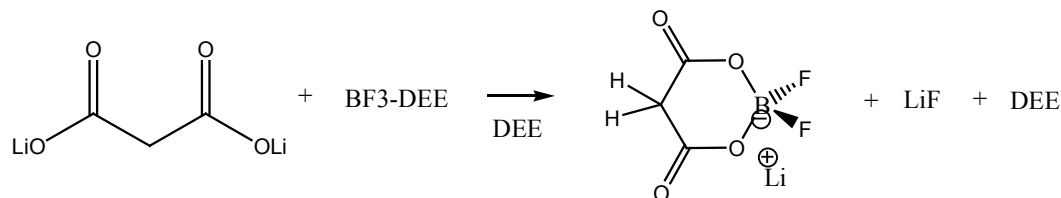
TGA shows thermally stable polymer (PSF LiTFSI). DMA (Dynamic mechanical analysis) shows a strong material with thermal transitions at $\sim 0^{\circ}\text{C}$ and 100°C . Conductivity of lithium form is similar to protic form in dry state and the conductivity is poor since there is no solvent present to dissociate the cations. Addition of solvent results in a large increase in conductivity. Conductivity and mechanical measurements are under way on gels prepared with organic solvents such as carbonates and GBL.

Preparation of LiAMDFB



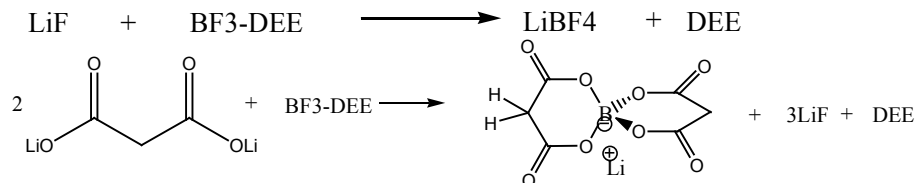
Attach to polymer backbones.
(presently under way)

First synthesise of Lithium Malonate Difluoro Borate (LiMDFB) to check conductivity of anions in solution:

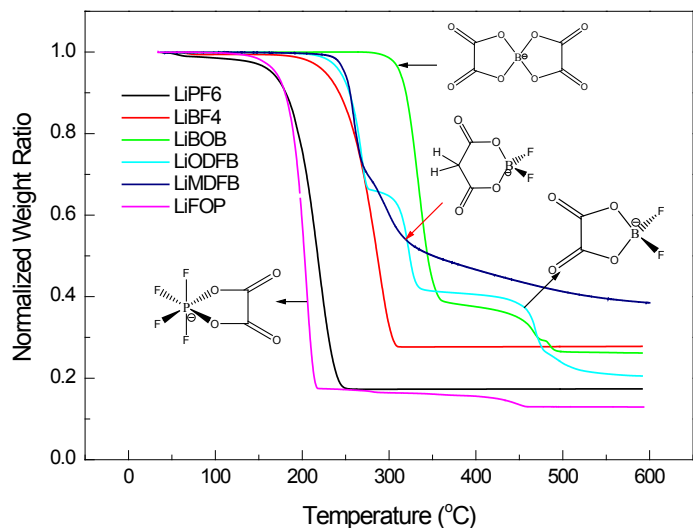


Side reactions

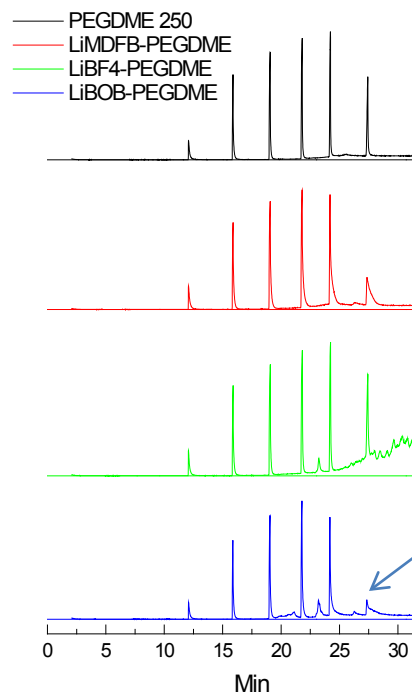
Desired salt obtained by recrystallization



Stability of Salts

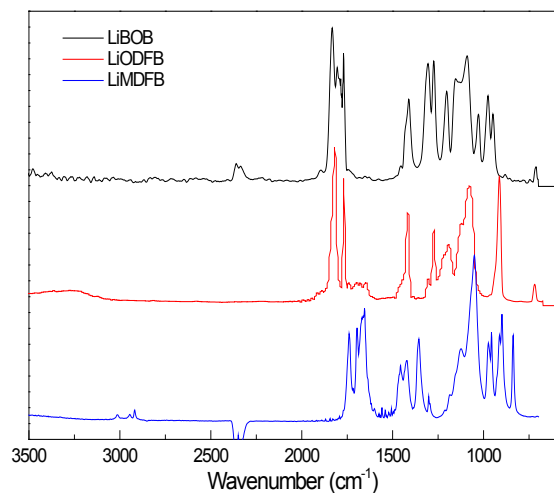


TGA comparison. LiMDFB shows good stability. Note the instability of phosphorus-based salts.



Compatibility of salts with PEGDME ether solvents. Solutions of salts in PEGDME 250 stored for one week at 30° C. All solutions show signs of reaction but LiBOB is the worst.

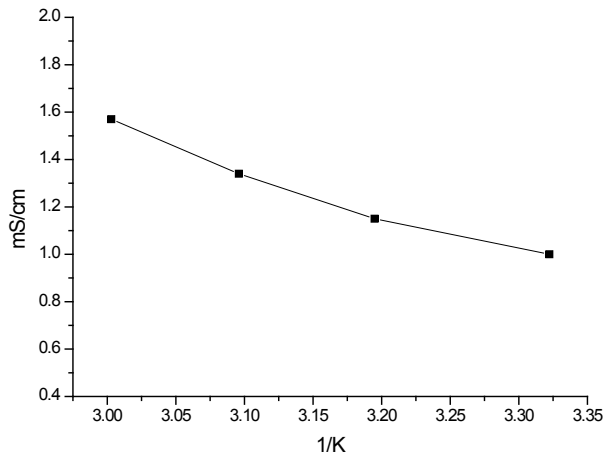
LiPF₆ reaction with PEGDME 250 is much greater. Lewis acid salts are incompatible with Ether solvents such as PEO.



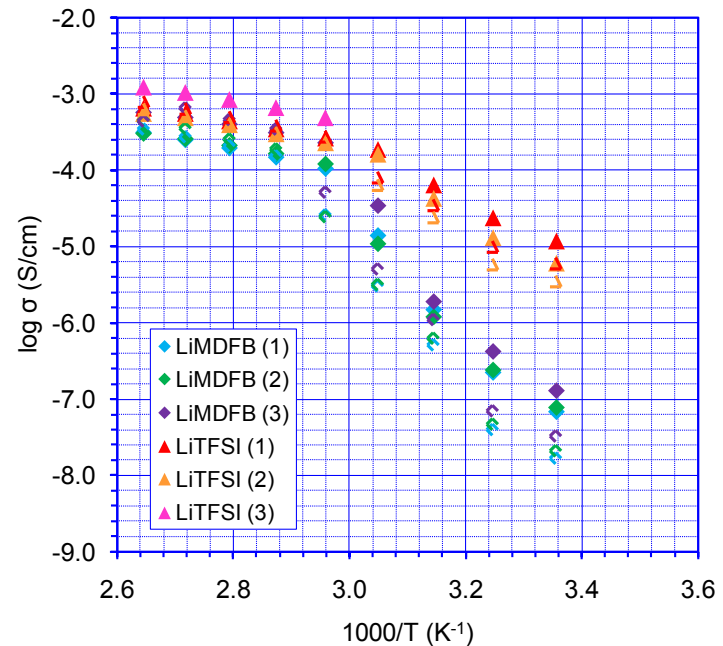
FTIR spectral comparison of salts. The C=O stretching for LiMDFB is down-shifted to 1600 ~1750 cm⁻¹, compared with LiBOB and LiODFB, due to the decrease of ring strain.

Conductivity of LiMDFB

1 M LiBF ₄ in poly(ethylene glycol) dimethyl ether (250)	1.77 mS/cm at 28C
0.7 M LiBOB in poly(ethylene glycol) dimethyl ether (250)	1.52 mS/cm at 28C
1 M LiMDFB in poly(ethylene glycol) dimethyl ether (250)	1.0 mS/cm at 28C



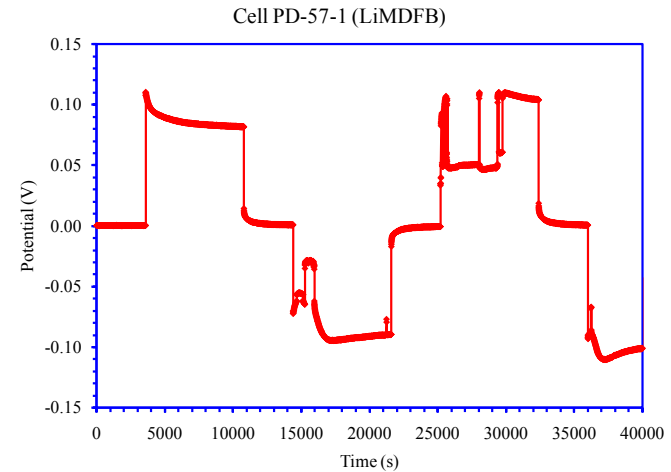
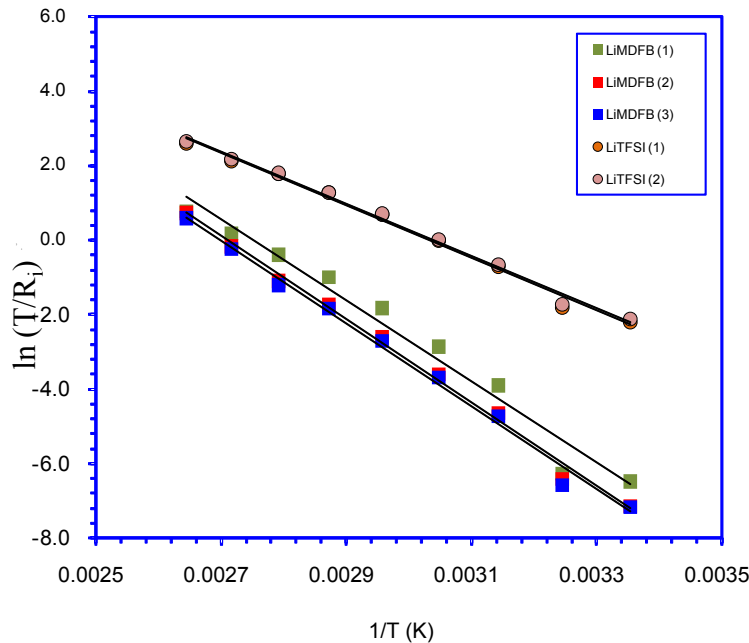
Conductivity of LiMDFB in PEGDME 250 as a function of temperature.



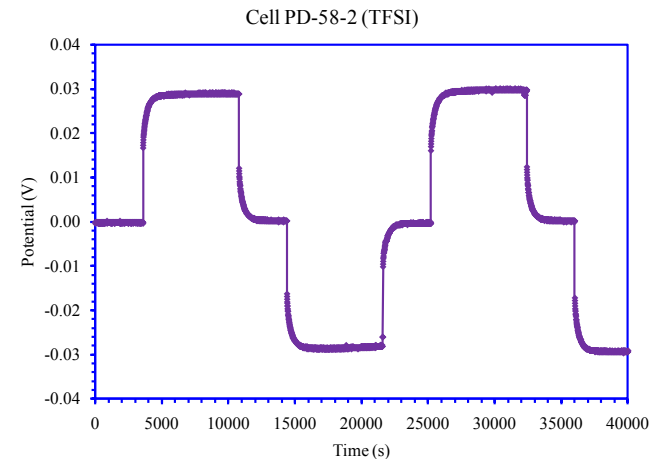
Conductivity of LiMDFB and LiTFSI in PEO as a function of temperature.

Conductivities in liquids and polymers are acceptable.

LiMDFB/PEO Impedance and Li Cycling



First cycles of Li/Li PEO MDFB cell #1.



First cycles of Li/Li PEO TFSI cell.

Arrhenius plot of $1/\text{interfacial impedance}$ shows much higher impedance for LiMDFB than LiTFSI. E_{act} is higher for LiMDFB than TFSI. Cycling with Li metal shows immediate roughening (dendrites) and rapid cell shorting. LiTFSI/PEO under the same conditions is shown for comparison. High impedance of LiBAMB network polymer may be due to same problem. This implies solution to high Impedance on Li metal lies in TFSI polyelectrolytes.

LiMDFB in Li Ion Systems

Quallion Graphite anodes and LiCoNiO_x cathodes

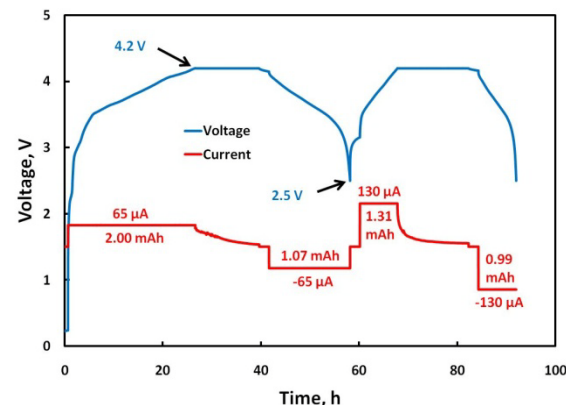
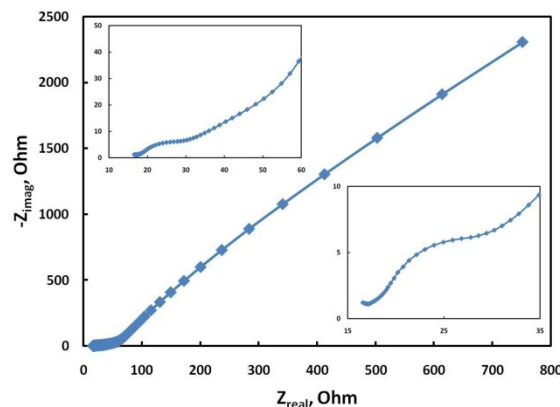
1.43 cm²

Quallion Anode

LiMDFB in EC/EMC=3/7

Quallion Cathode

1.10 cm²



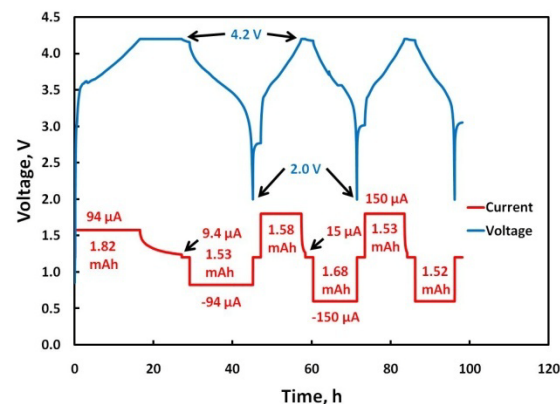
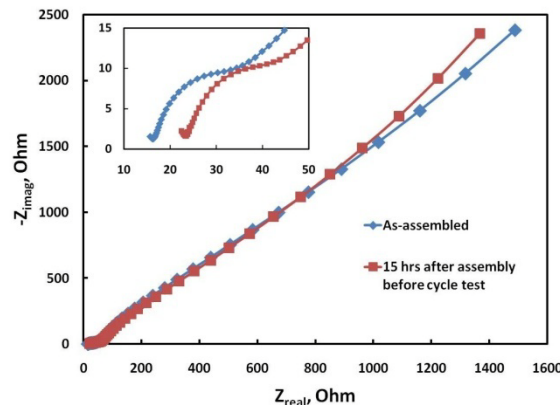
1.43 cm²

Quallion Anode

1.0 M LiPF₆ in EC/DMC=1/2

Quallion Cathode

1.10 cm²



LiMDFB performs reasonably well in EC/EMC solvents and Li ion electrodes. Impedance is acceptable. In Li metal half cells large impedances are observed.

The AMDFB anion should be attached to polysulfone polymers and only used with Li ion systems – no Li metal.

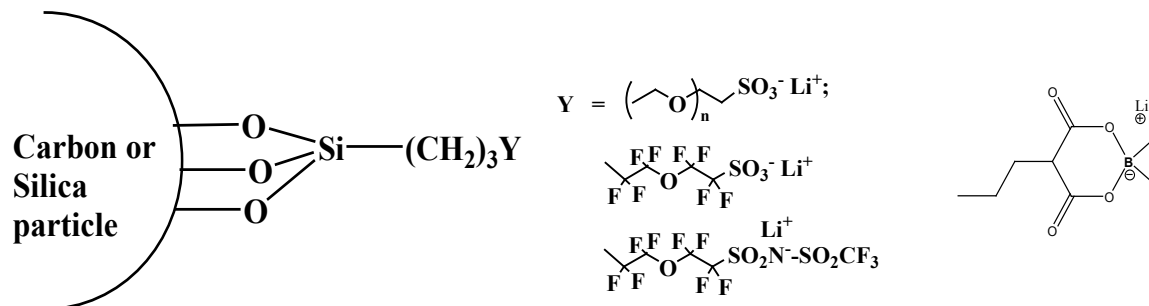
Other sources of impedance.

Optimum concentration of salt in PEO-type polyelectrolytes is EO:Li⁺ 40:1.(~ 0.5M)

$$R_{\text{int}} \propto 1/i_{\text{exchange}} \text{ and } i_{\text{exchange}} \propto C_o \times i_o$$

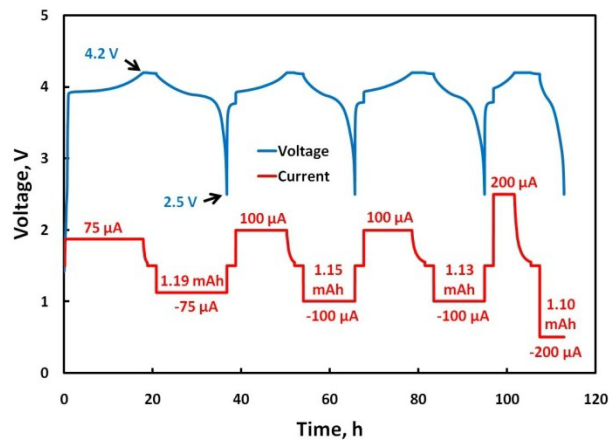
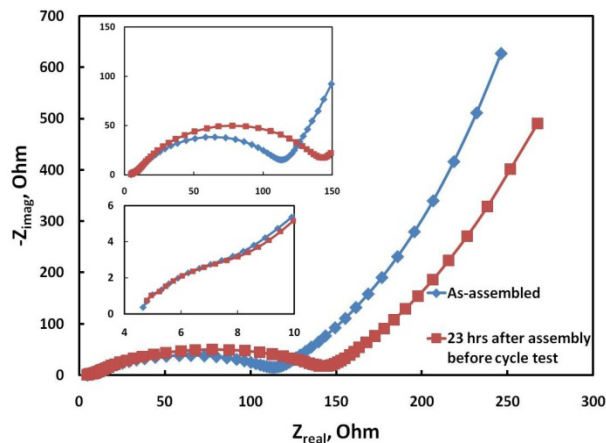
It seems reasonable to increase the ionic concentration at the surface of the electrode. Two methods are being pursued:

- 1) Prepare polyelectrolytes with different equivalent weights and measure interfacial impedance at Li metal. Spin coat thin (~1μm) layers of polyelectrolyte on to lithium metal and combine with optimum polyelectrolyte for bulk transport.
- 2) Prepare composite electrodes (both anodes and cathodes) with polyelectrolyte binders with different ion content and measure impedances.
- 3) Since preparation of many different polyelectrolyte concentrations is a long synthesis project, functionalization of electrode components with ions is a method of increasing local concentration of ions in the electrodes. Surface functionalization of carbon or silica particles added to the composite electrodes is envisioned.

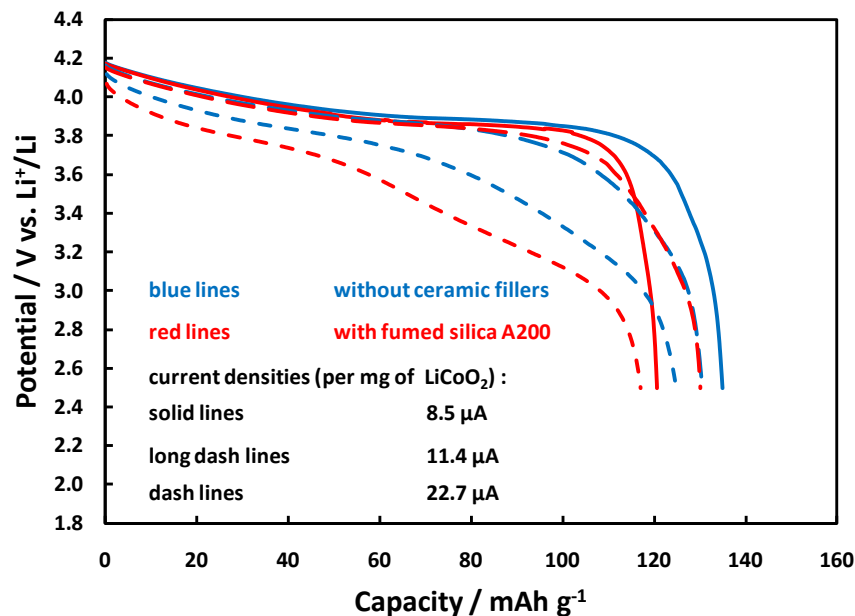


Electrode Preparation and Cell Building

Need reproducibility before can proceed.modifications



Li Metal – Co O_x half cell



Li Metal – Co O_x half cell.

Cathode prepared normally with 10% Carbon Black and with 5% Carbon and 5% Fumed silica

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 Newman group.
- Electrolyte reactivity and surface reactions requires surface analysis collaborations (Kostecki)
- Need sources of reproducible electrode materials (Zhagib, ANL, 3M, other industrial collaborators).
- Need 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

- Synthesis of polyelectrolyte materials
 - TFSI and fluoroalkylsulfonate anions attached to both polyether and polysulfone backbones with a range of equivalent weights.
 - LiAMDFB attached to polysulfone backbone only with a range of equivalent weights.
 - If appropriate, investigate block copolymer backbones.
- 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.
 - Cathodes. Focus on Low voltage materials (LiFePO_4 if available) for polyether materials, LiCoO_x 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.

Future Work

- Composite electrode component functionalization.
 - Complete baseline performance characterization.
 - Continue detailed study of electrolyte instability issues and the effect of trace water.
 - Develop chemical modification of carbon and silica particles for incorporation in composite electrodes
 - Characterize composite electrodes electrochemically, thermally, mechanically and spectroscopically (collaborate with surface analysis groups).

Summary

- Single ion conductor polyelectrolytes can potentially 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 that alters the surface concentration of ions should impact the interfacial impedance and this is being pursued.
- Lewis acid salts such as LiPF_6 , LiBF_4 , LiBOB are reactive with ethers as well as water and lead to products that may contribute to the interfacial impedance. Carbonate solvents hydrolyze with water. However, these reactive mixtures perform adequately with lithium ion battery electrodes. An ongoing careful (and tedious) study is called for.
- Meaningful studies of interfacial behavior requires careful control of conditions to obtain reproducibility. This requires considerable collaboration.