Interfacial Behavior of Electrolytes

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Outline

- Purpose of work
- Barriers
- Previous Review Comments
- Approach
- Performance Measures and Accomplishments
- Plans for Next Fiscal Year
- Summary
- Collaborations and Technology Transfer
- Publications/Patents

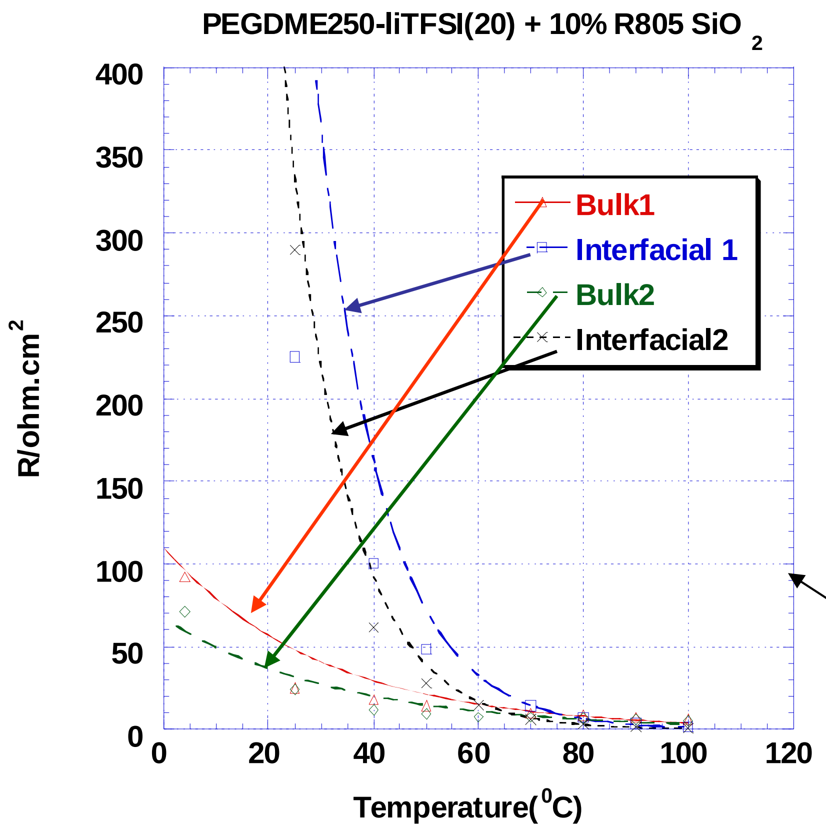
Purpose of the Work

- Investigate the Chemical and Electrochemical reactivity of Li Ion electrolytes.
  - Effect of impurities and additives.
  - How are Calendar and Cycle Life affected?
  - Are 5V electrolytes at all feasible?
- How do the electrolyte components, reaction products and impurities affect the interfacial impedance at the electrodes.

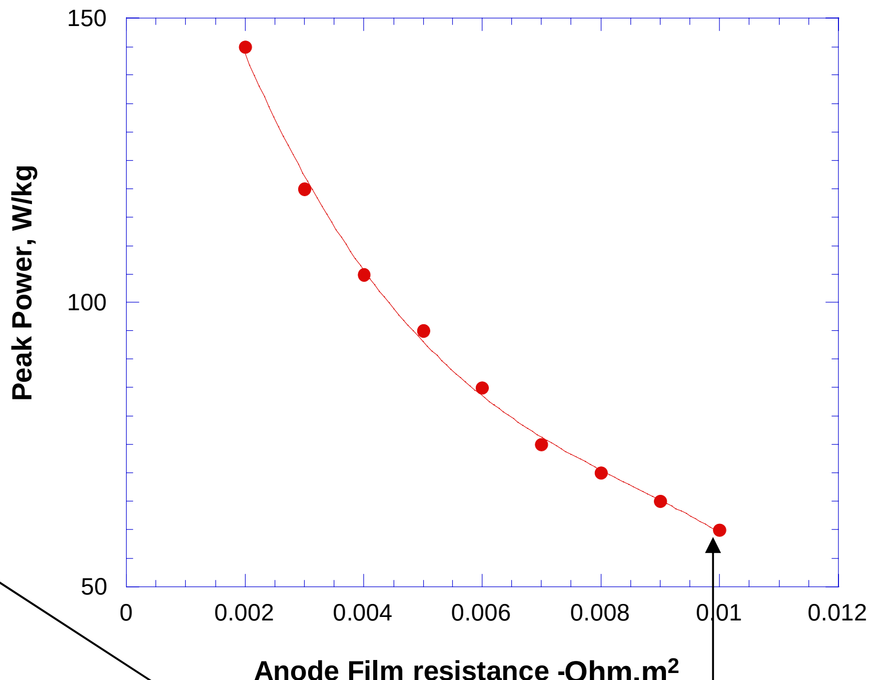
Purpose of the Work.

Impact of Interfacial vs. Bulk Impedance

Experimental Measurements on Li/Li symmetrical cells



Model of effect of Interfacial Impedance on Peak Power. (Karen Thomas-Alyea)



$0.01\ ohm.m^2 = 100\ ohm.cm^2$

Barriers Addressed

- Poor Calendar Life – 2-3 yrs vs. 15 yr goal.
- Poor Cycle Life – 3,000 -5,000 cycle goal.
- Increase Power Density to 750 W/kg
- Increase Energy Density to 100 Wh/kg
- Low temperature (-30^{o}C) performance
- Increased Abuse Tolerance.

Electrolyte chemistry and interfacial behavior impacts these barriers.

Previous Review Comments

Recommendation:

Reevaluate work on SPEs and ionic liquids (IL), as they may not meet low T or power requirements.

DOE Response:

- LBNL/DOE will refocus some of the PIs' who are currently doing support work in these areas (Kerr and Doeff)

Previous Review Comments

- The work on radical polymer electrolytes and ILs is the most interesting project of those listed in future plans.
- IL should be tested further.
- Systematically determine water content vs. degradation (various types) is very useful to industry, very relevant to next generation systems as well as to ameliorate effect of water in present electrolytes.
- Need to dig deeper than just running an experiment to validate or reject a one liner statement.

Reviewer Recommendations for Additional work:

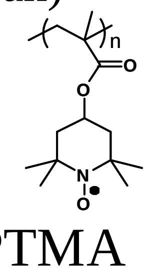
- This work should be continued, need polymer exploration.
- Need to look carefully at the stability of ionic liquids (ILs) at negative potentials.

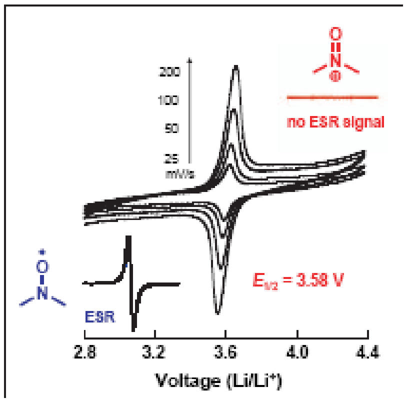
Approach

- Continue Chemical and Electrochemical studies of carbonate-based electrolytes.
  - Better understand the role of water and alcohols
  - Understand the roles of acid and base components, impurities and side products.
  - Improve correlation of chemical measurements with electrochemical observations
- Bring Ionic Liquid Work to some conclusions.
- Exploratory work on Polymer-electrode/IL systems

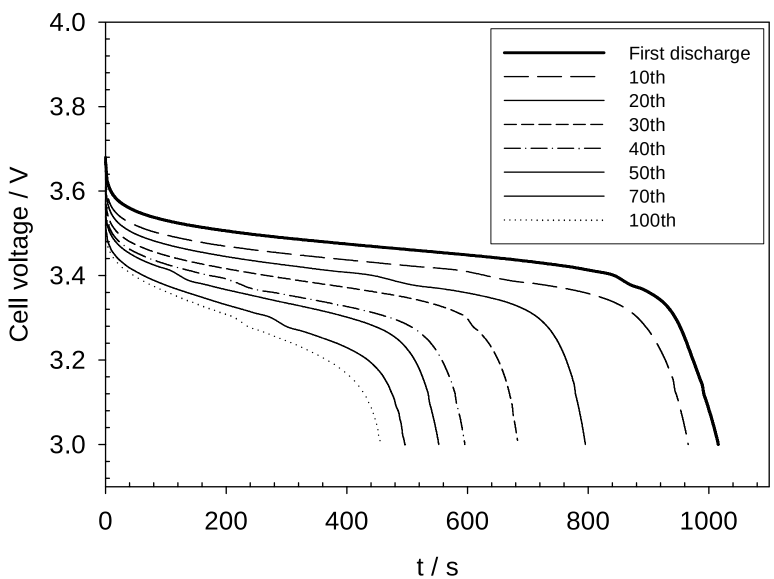
Radical Polymer Electrodes and Ionic Liquids

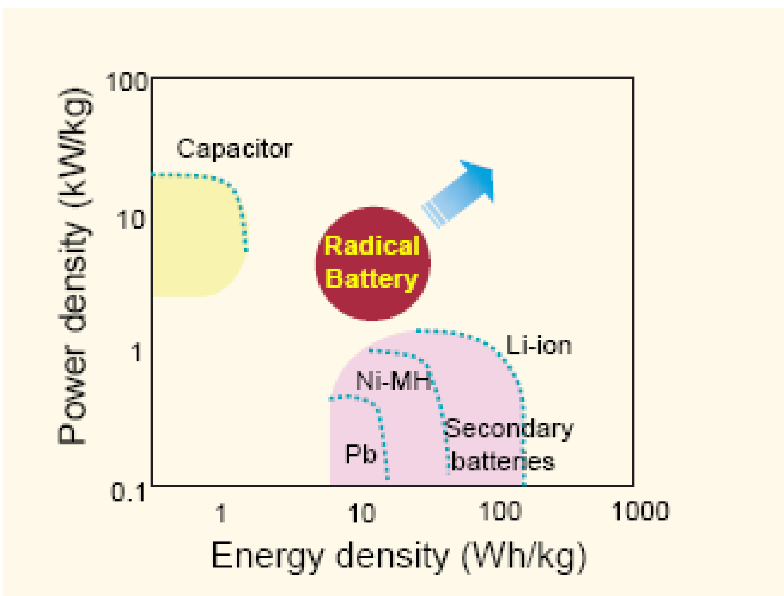
Justin Salminen, Kentaro Nakahara (NEC, Japan)





H. Nishide
Waseda Univ.
Science, 2008, 319(Feb 8), 737;
Interface, 2005, 14, 32.

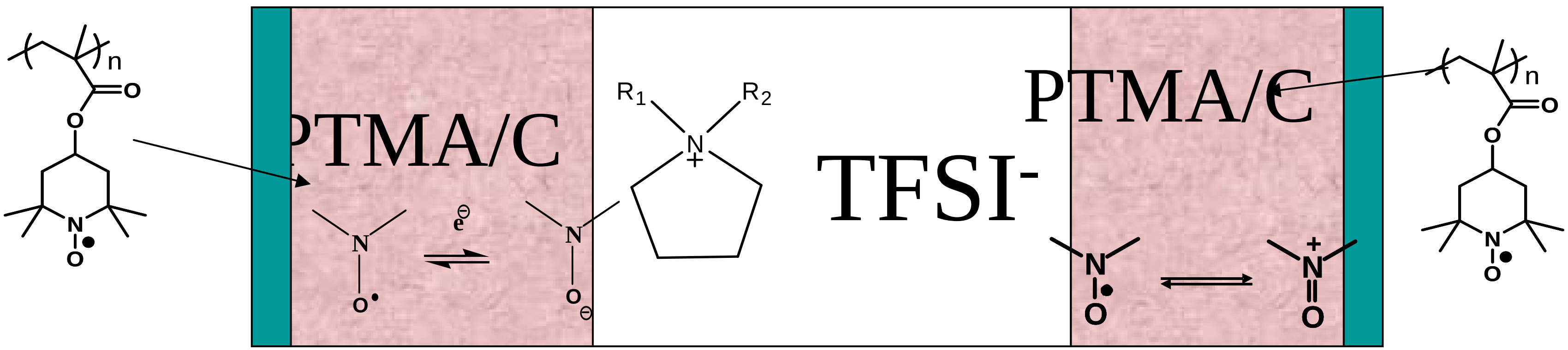




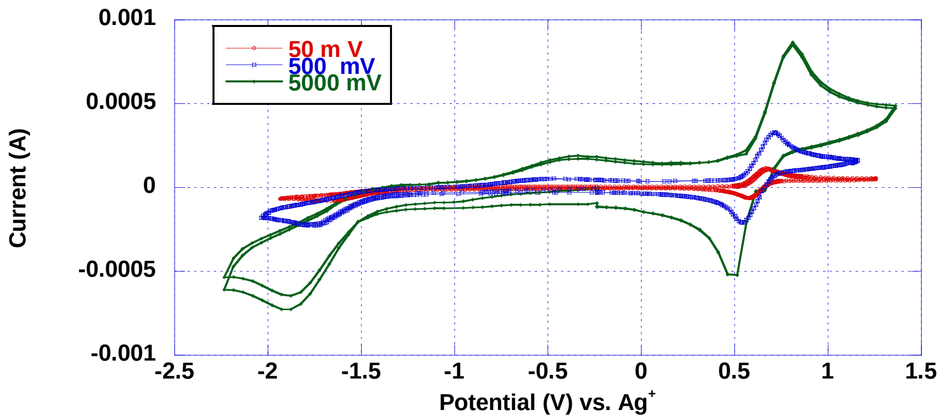
Remove the Li^+

Both Electrodes are Redox Polymers.

Ionic Liquid Electrolyte increases Safety



CV: 5mM TEMPO, 0.1M $TEAClO_4$ in acetonitrile on glassy carbon



TEMPO

Electrolyte water content 1000ppm
Cathode reaction not sensitive to water.
Anode reaction sensitive **and Kinetically very slow.**
Replace anode polymer with polynitrostyrene
(Miller, JACS 1980, 102, 3833)

Electrolyte System Studied

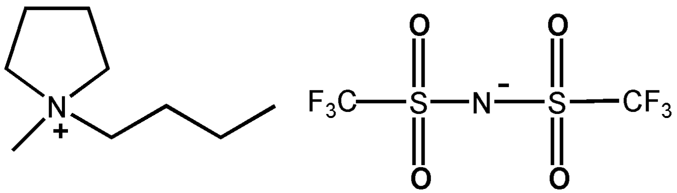
Ternary mixture electrolytes

$PYR_{14}TFSI$ + x LiTFSI + y PEGDME 250 (or 500)

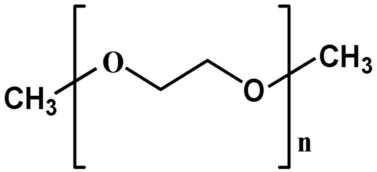
x = LiTFSI mol/PYR_{14}TFSI-kg, x = 0.5

y = PEGDME-kg/PYR_{14}TFSI-kg, y = 1.0, 1.5 and 2.0

EO/Li ratio: 18 (y = 2.0), 13 (y = 1.5), 9 (y = 2.0)



N-methyl-N-butylpyrrolidinium bis(trifluoromethane sulfonyl)imide (PYR_{14}TFSI)

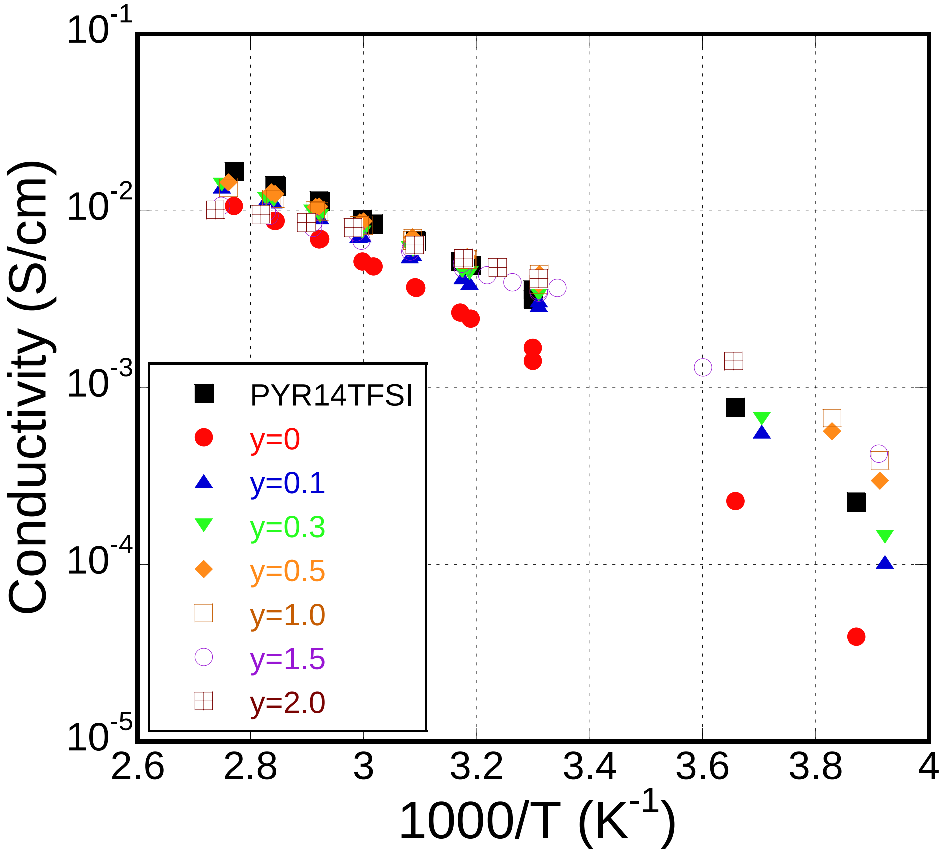


Poly (ethylene glycol) dimethyl ether (PEGDME); n ~5 or 10

Ionic Liquid with Co-solvents Conductivity and Viscosity

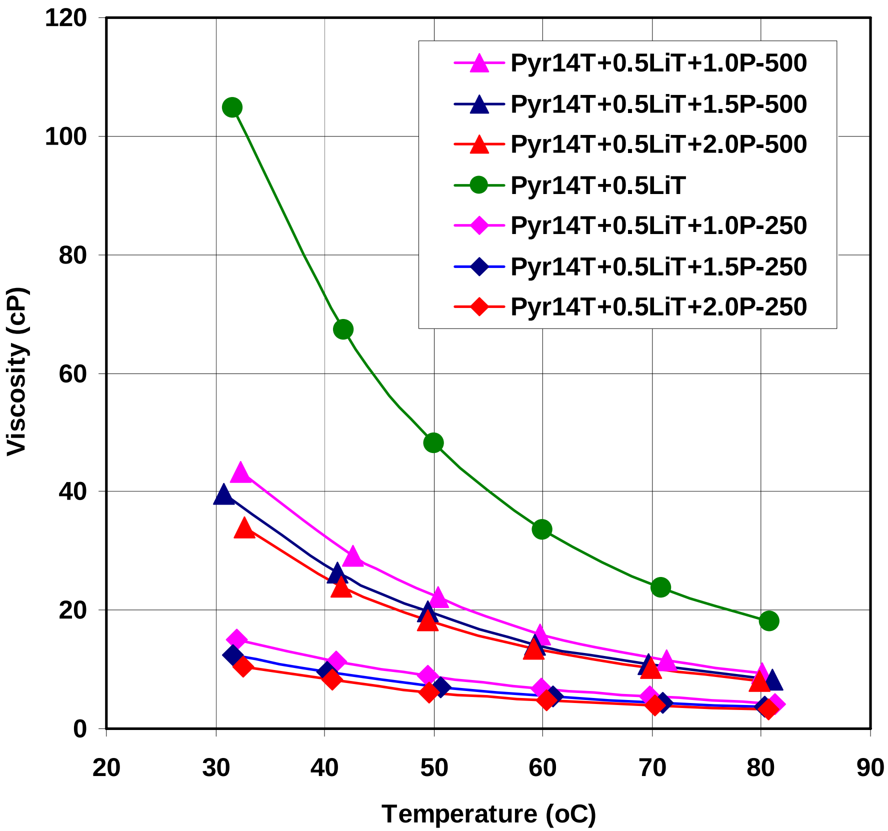
Ionic conductivity

$PYR_{14}TFSI$ + 0.5M LiTFSI
+ (y) PEGDME 250 mixtures.



Viscosity

$PYR_{14}TFSI$ + 0.5M LiTFSI
+ PEGDME 250 and 500 mixtures.

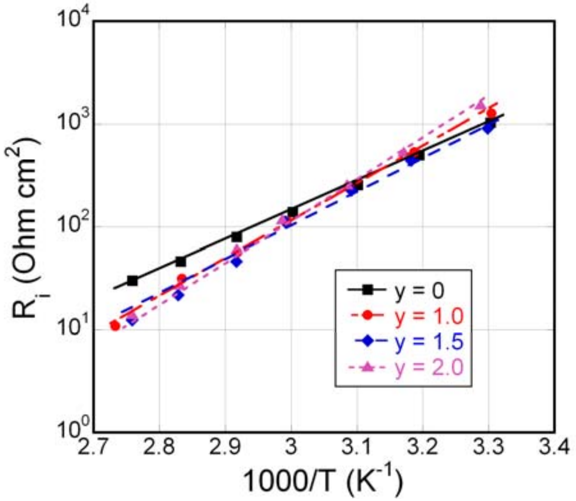


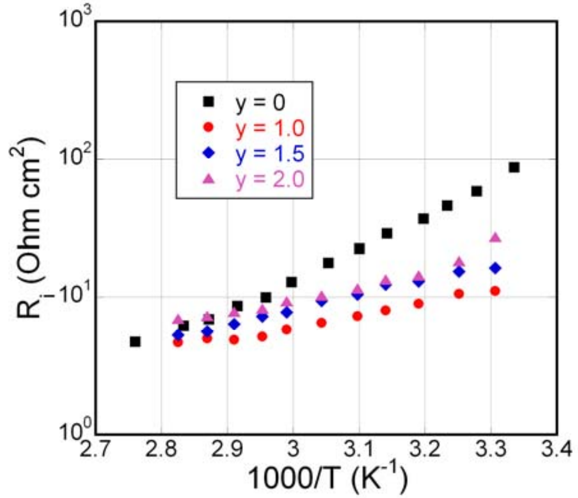
Interfacial Impedance of Ionic Liquids with co-solvents

Li/Li

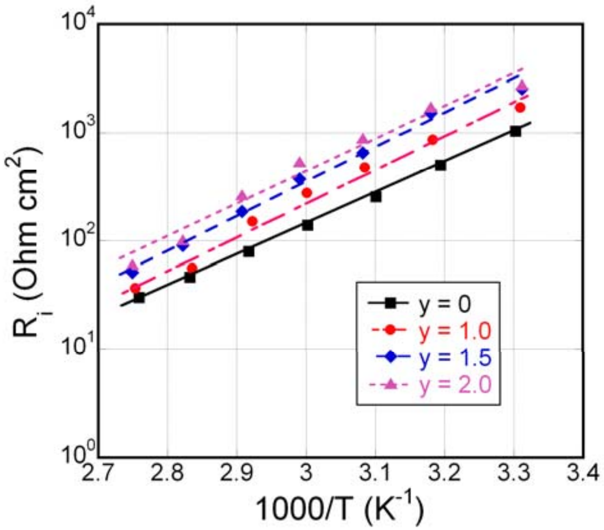
Graphite vs. Li reference

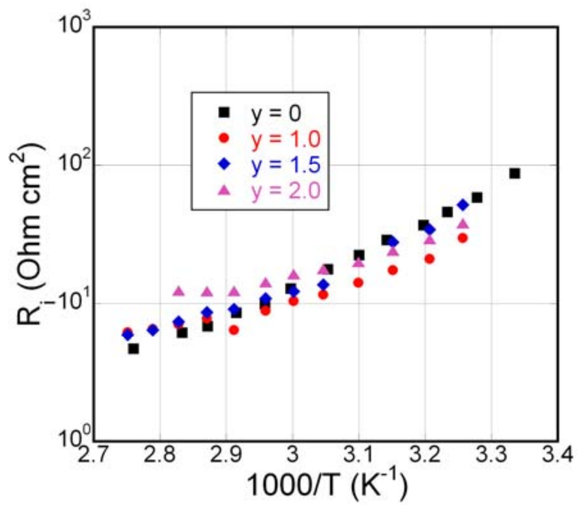
PEGDME 250





PEGDME 500



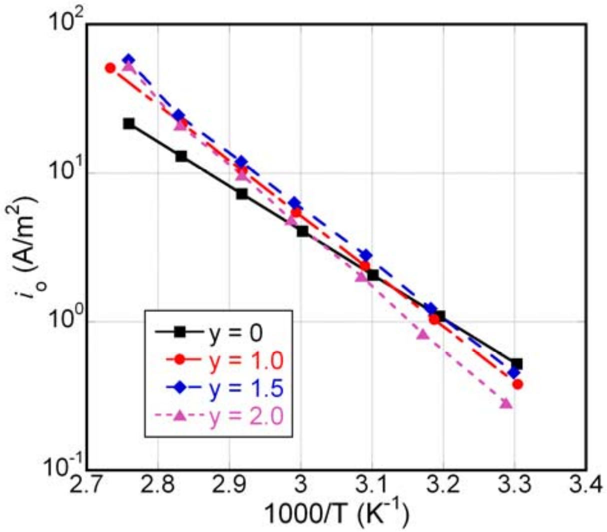


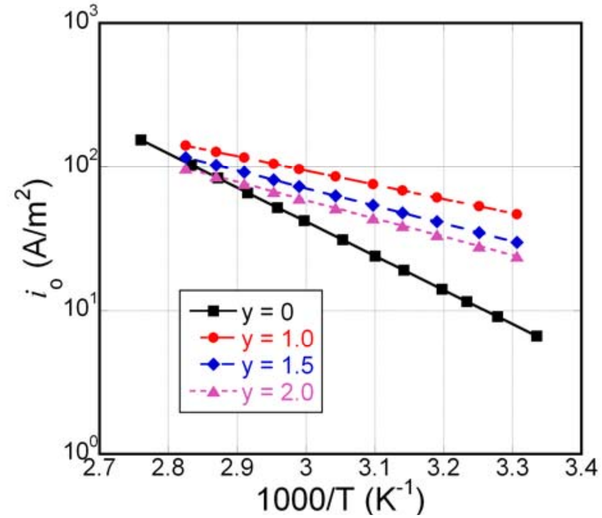
Exchange Current Density of Ionic Liquid Co-solvent Mixtures at Lithium and Graphite

Li/Li

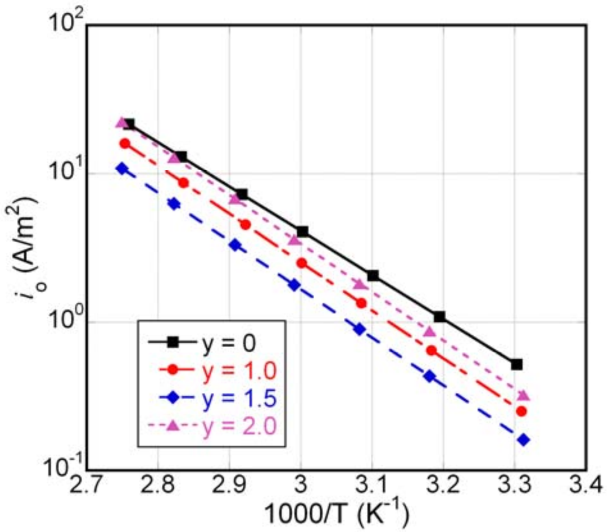
Graphite vs. Li Reference

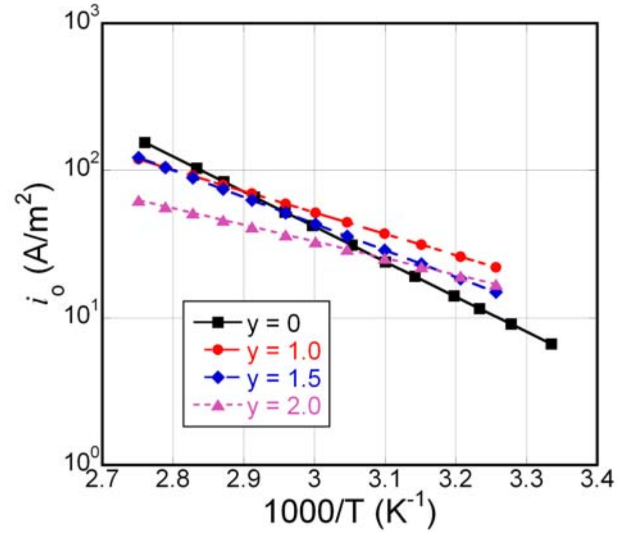
PEGDME 250



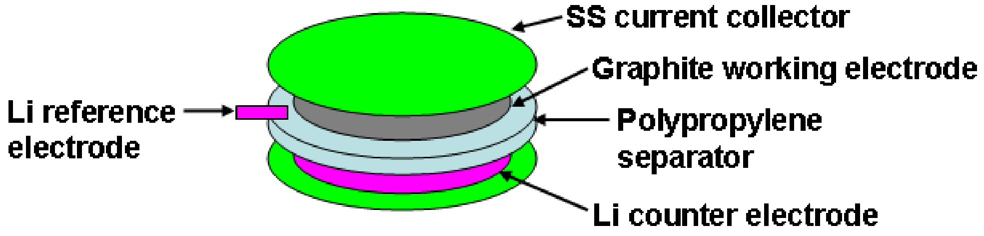


PEGDME 500

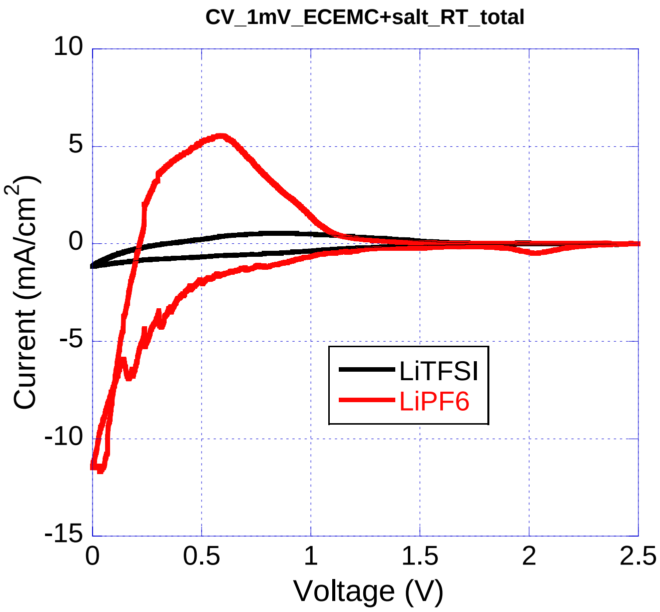




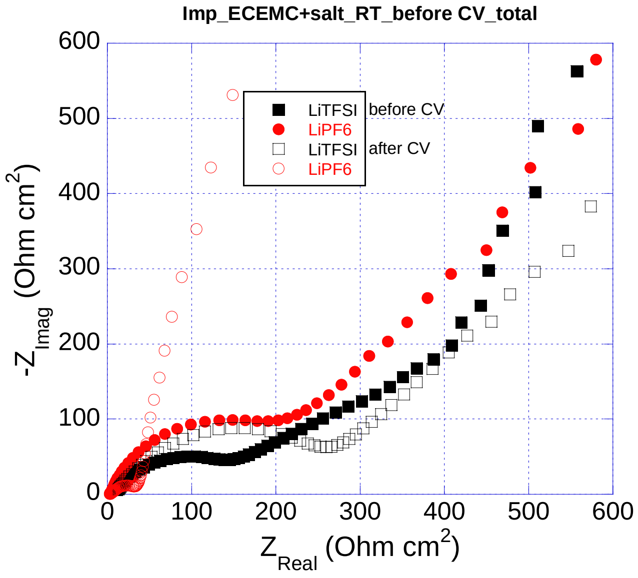
Carbonate Based Electrolytes - Anode Formation Experiments on Gen 2 Anode (ATD-ANL)



Schematic of three electrode cell



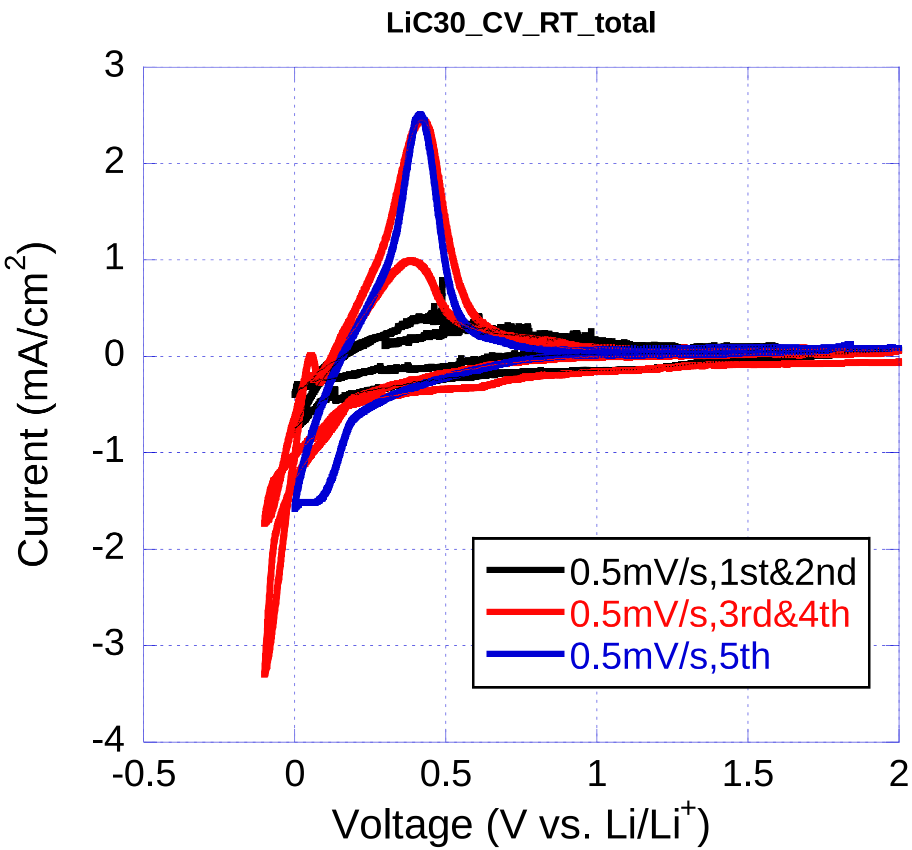
$LiPF_6$ soln.
Water = 0 ppm
but pH low;
LiTFSI soln.
H_2O = 30 ppm

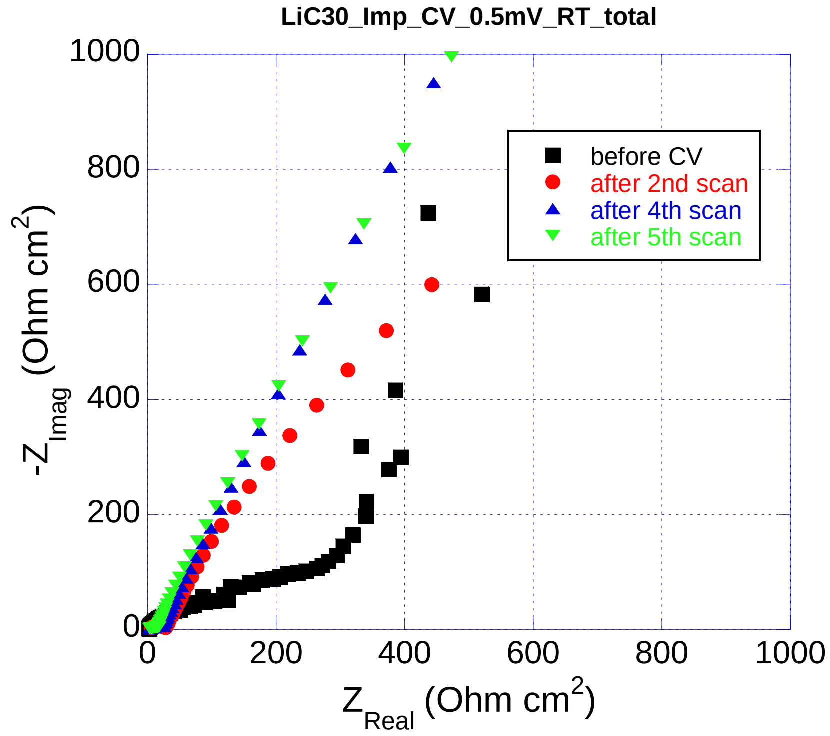


Cyclic voltammetry of Li/EC/EMC (3/7 v/v) + 1.2M LiX/Graphite cell; 1mV/s, 25°C

Nyquist plot of ac impedance of Li/EC/EMC (3/7 v/v) + 1.2M LiX/Graphite cell at 25°C. 3-electrode measurement

Effect of Formation Potential on Gen 2 Anode with LiTFSI



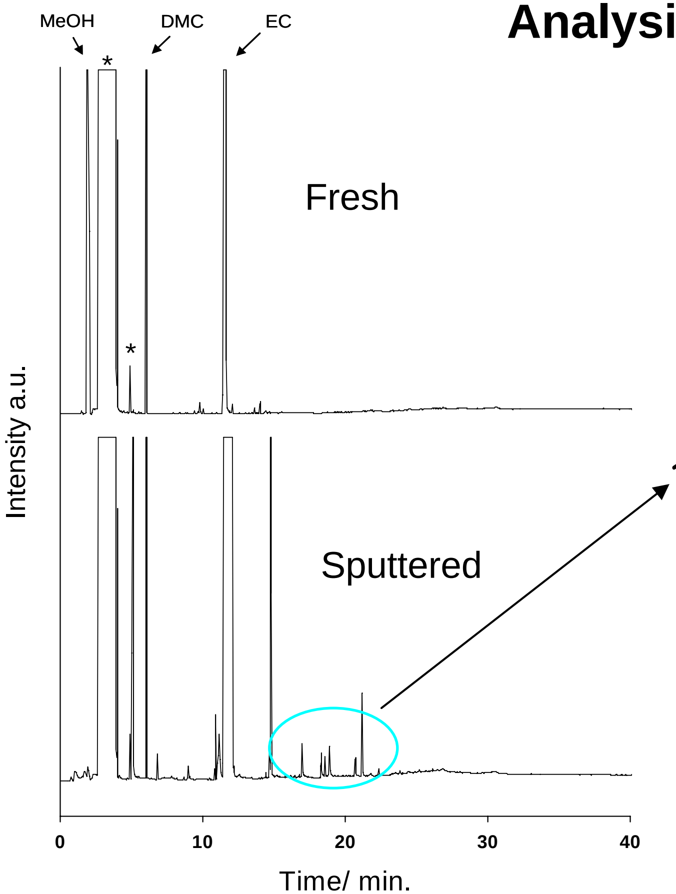


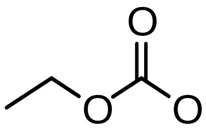
Cyclic voltammograms(left) and Nyquist plots (right) of Li/EC/EMC(3/7v/v),1.2M LiTFSI/graphite, scan rate 0.5mV/s, 25°C

Nature of Surface

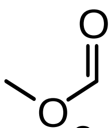
Analysis of Products after formation cycling at Sputtered Mag-10 Anodes

Gas Chromatography Analysis





1



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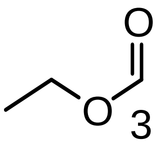

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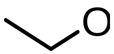

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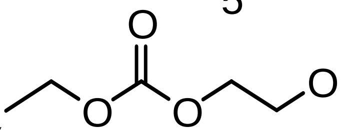
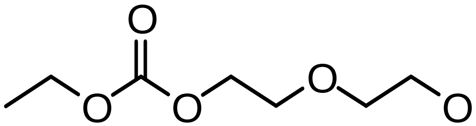
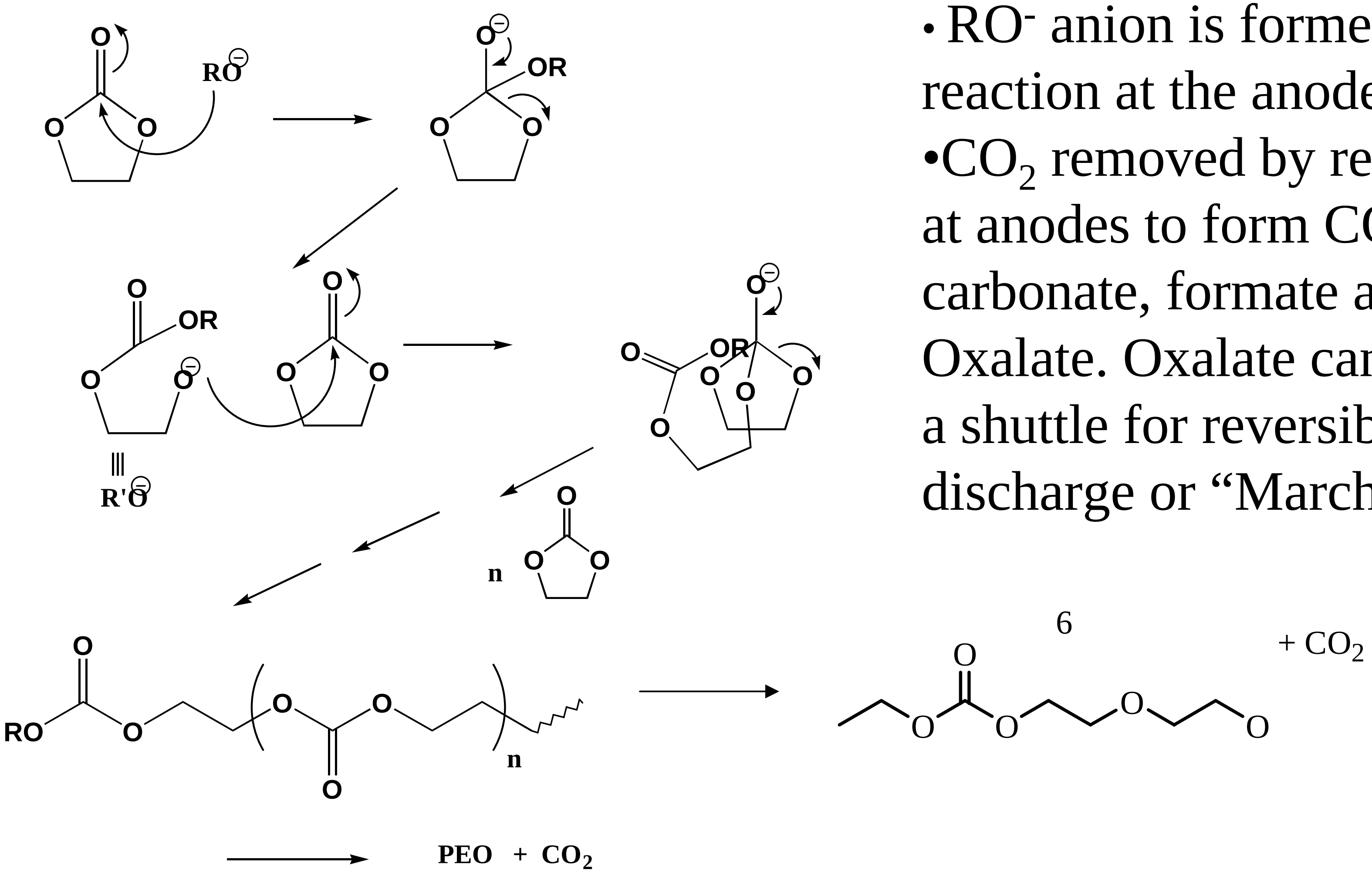


6



Mass Spectral analysis of GC peaks are consistent with structures 1-6 amongst others including higher M.Wt. products (1500) that appear to contain fluorine. Compound 6 is consistent with base catalyzed ring opening of EC CE analysis also detects phosphates.

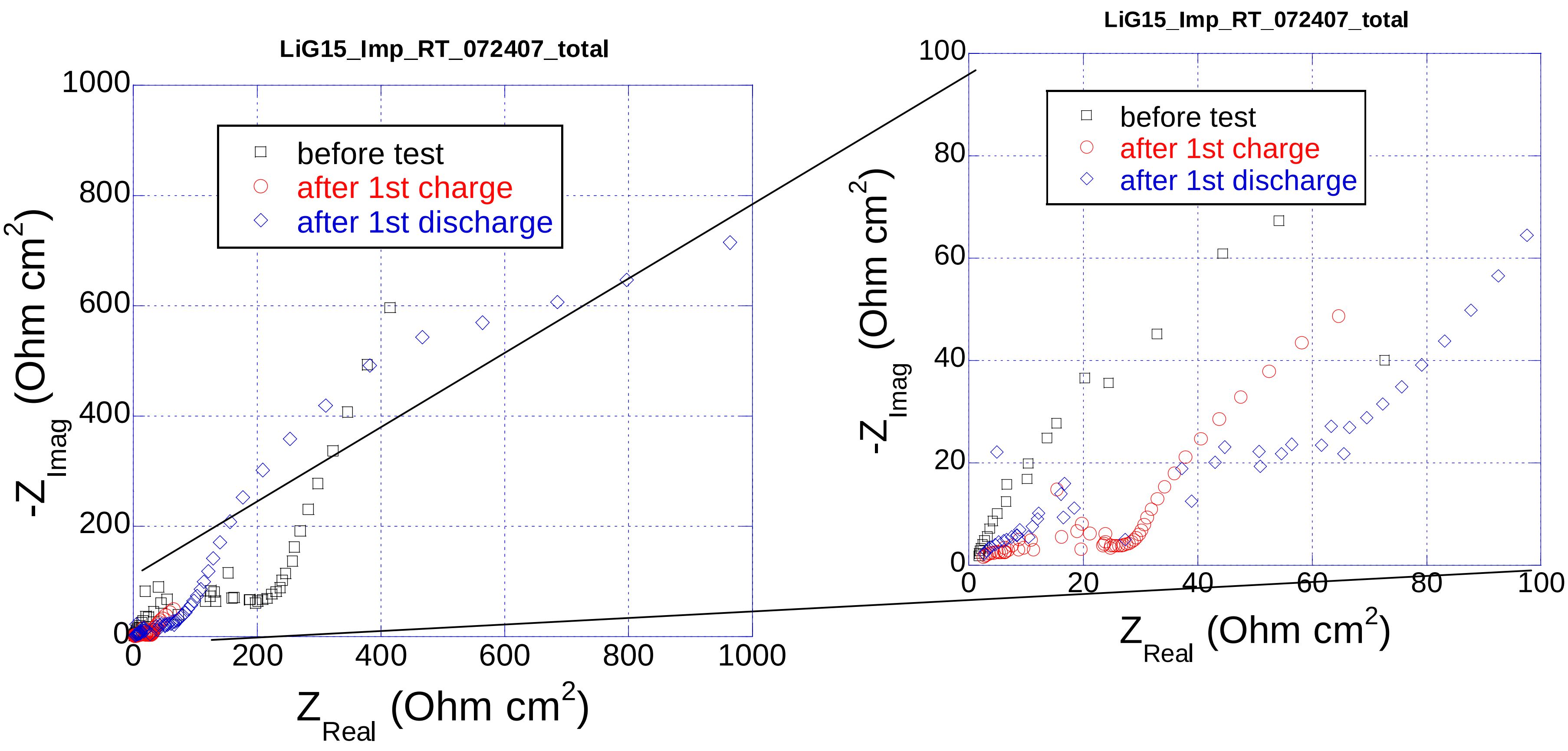
Ring-opening of EC initiated by Electrogenerated base.



• RO^- anion is formed by reaction at the anode.
•CO_2 removed by reduction at anodes to form CO, carbonate, formate and Oxalate. Oxalate can act as a shuttle for reversible self-discharge or “Marching”

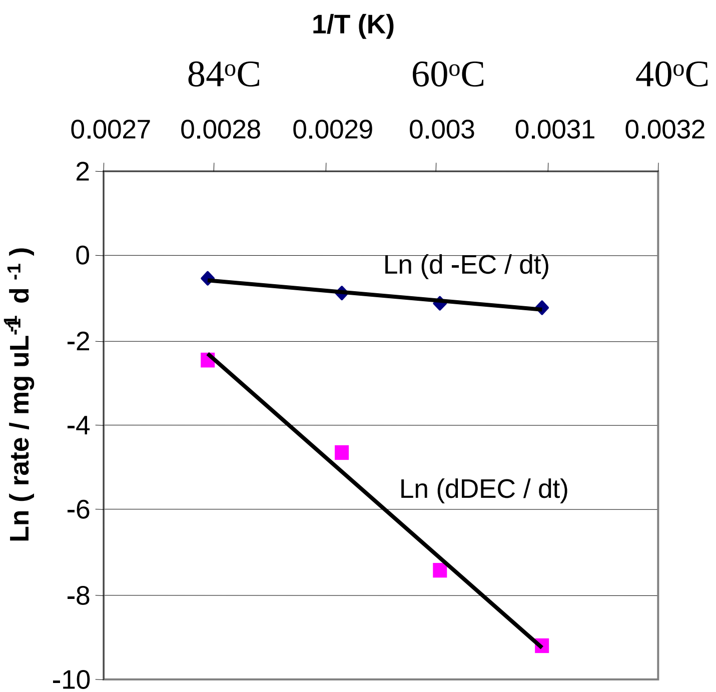
Cathode Interfacial Impedance

Postulated that side reaction products alter wetting characteristics.



Impedance of Gen 2 Cathode before and after cycling

Kinetic Measurements of Electrolyte Reactions



EC/EMC- $LiPF_6$ heated in glass vials

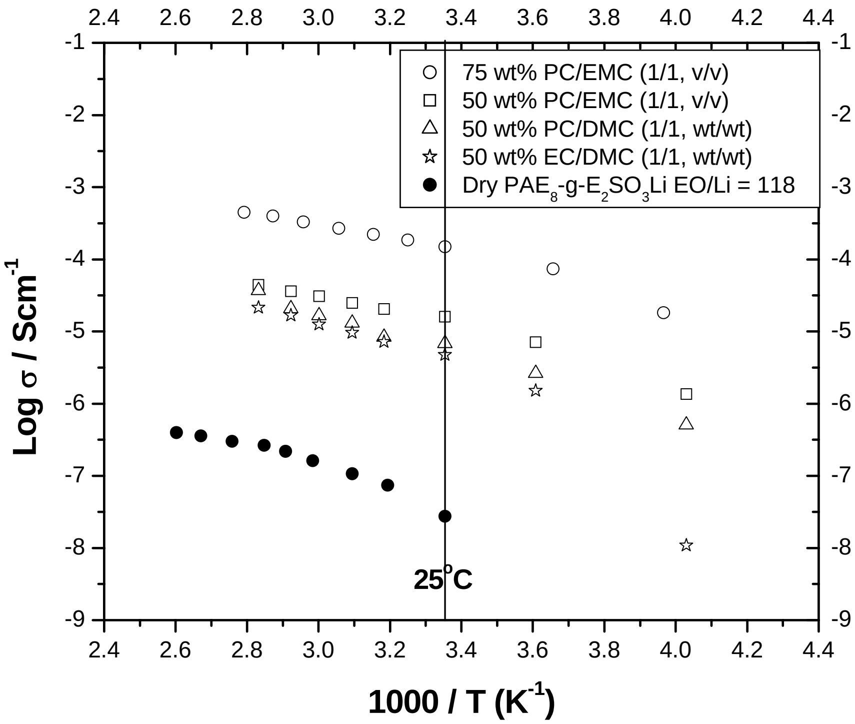
- Previous measurements of Electrolyte reactivity carried out under poorly controlled conditions
– e.g. variable moisture content.
- Prepare solutions under better control and add known amounts of moisture, acids, bases and additives (LiF).
- EC/EMC-$LiPF_6$+ 0.2mM H_2O gelled at 43°C!
  -followed by thinning and coloring.
- EC/EMC-LiTFSI – no reaction at 85°C for 2 years!
  - addition of 5mM HTFSI at 43°C results in no visible reaction.

Polymer Exploration

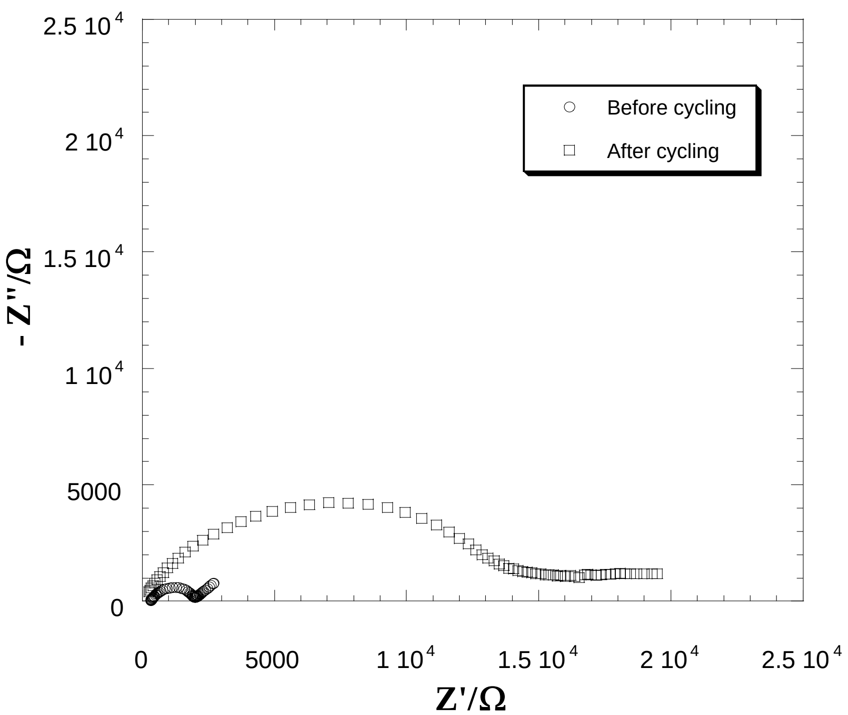
Single-ion Conductors (NASA funded)

Possess adequate bulk transport but enormous interfacial impedance. What is the source of this?

Ionic Conductivity



Interfacial Impedance at Lithium



Plans for Next Fiscal Year

- Complete electrolyte degradation analysis under rigorously controlled conditions
  - All operations in Glove-box or Schlenk-line.
- Continue to explore how electrolyte degradation affects impedance growth at both electrodes.
- Expand interfacial studies to cathodes.
  - Detailed analysis of cathode side reaction products and effects on interfacial behavior
  - Study the effects of impurities (water, acids, additives) on interfacial behavior.
- Use Single Ion Conductor polymers from DOE Hydrogen Program to investigate interfacial impedance.

Summary

- Interfacial behavior of electrolytes is at least as critical as bulk transport properties
  - Electrochemical kinetics.
  - Electrolyte mobility/wettability at surfaces.
  - Chemical/electrochemical degradation.
- Interfacial Impedance of Ionic Liquids precludes their use in high rate conventional cells.
- Ionic Liquids may find use in supercapacitors and hybrid polymer electrode batteries.

Collaborations and Technology Transfer

- ATD Program (Kostecki, Abraham)
- BATT - Doeff, Battaglia, Kostecki, Creager, HydroQuebec, Modeling Groups (Smith/Borodin, Newman/Srinivasan).
- CSIRO (Australia) Tony Hollenkamp. Adam Best
- Synergy with DOE Hydrogen program for Polymer materials.
- NASA

Publications/Patents

Papers:

1. Saint, J., et al., *Compatibility of LixTiyMn1-yO2 (y=0, 0.11) electrode materials with pyrrolidinium-based ionic liquid electrolyte systems.* Journal of the Electrochemical Society, 2008. **155**(2): p. A172-A180.
2. Salminen, J., et al., *Physicochemical properties and toxicities of hydrophobic piperidinium and pyrrolidinium ionic liquids*. Fluid Phase Equilibria, 2007. **261**(1-2): p. 421-426.

Patents:

Shanger Wang, Jun Hou, Steve E. Sloop, Yong Bong Han and John B. Kerr. *Polymeric electrolytes based on hydrosilyation reactions* USP 7,101,643, September 5, 2006.

Presentations:

Joon Ho Shin, John B Kerr, *Thermal Behavior and Interface Property of N-methyl-n-butylpyrrolidinium Bis(trifluoromethanesulfonyl)imide-LiTFSI-PEGDME Mixtures*. Presented at 212th ECS Meeting,Washington, DC, US October 7-12, 2007.