USE OF IONIC LIQUIDS IN ROD-COIL BLOCK CO-POLYIMIDES FOR IMPROVED LITHIUM ION CONDUCTION

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Introduction

Solvent-free, solid polymer electrolytes (SPE) have the potential to improve safety, increase design flexibility and enhance performance of rechargeable lithium batteries.[1] Solution based electrolytes are flammable and typically incompatible with lithium metal anodes, limiting energy density. We have previously demonstrated use of polyimide rod coil block copolymers doped with lithium salts as electrolytes for lithium polymer batteries.[2] The polyimide rod blocks provide dimensional stability while the polyethylene oxide (PEO) coil portions conduct ions. Phase separation of the rods and coils in these highly branched polymers[3] provide channels with an order of magnitude improvement in lithium conduction over polyethylene oxide itself at room temperature. In addition, the polymers have been demonstrated in coin cells to be compatible with lithium metal. For practical use at room temperature and below, however, at least an order of magnitude improvement in ion conduction is still required. The addition of nonvolatile, room temperature ionic liquids has been shown to improve the ionic conductivity of high molecular weight PEO.[4] Herein we describe use of these molten salts to improve ionic conductivity in the rod-coil block copolymers.

Use of ionic liquids in rod-coil block copolyimides for improved lithium ion conduction

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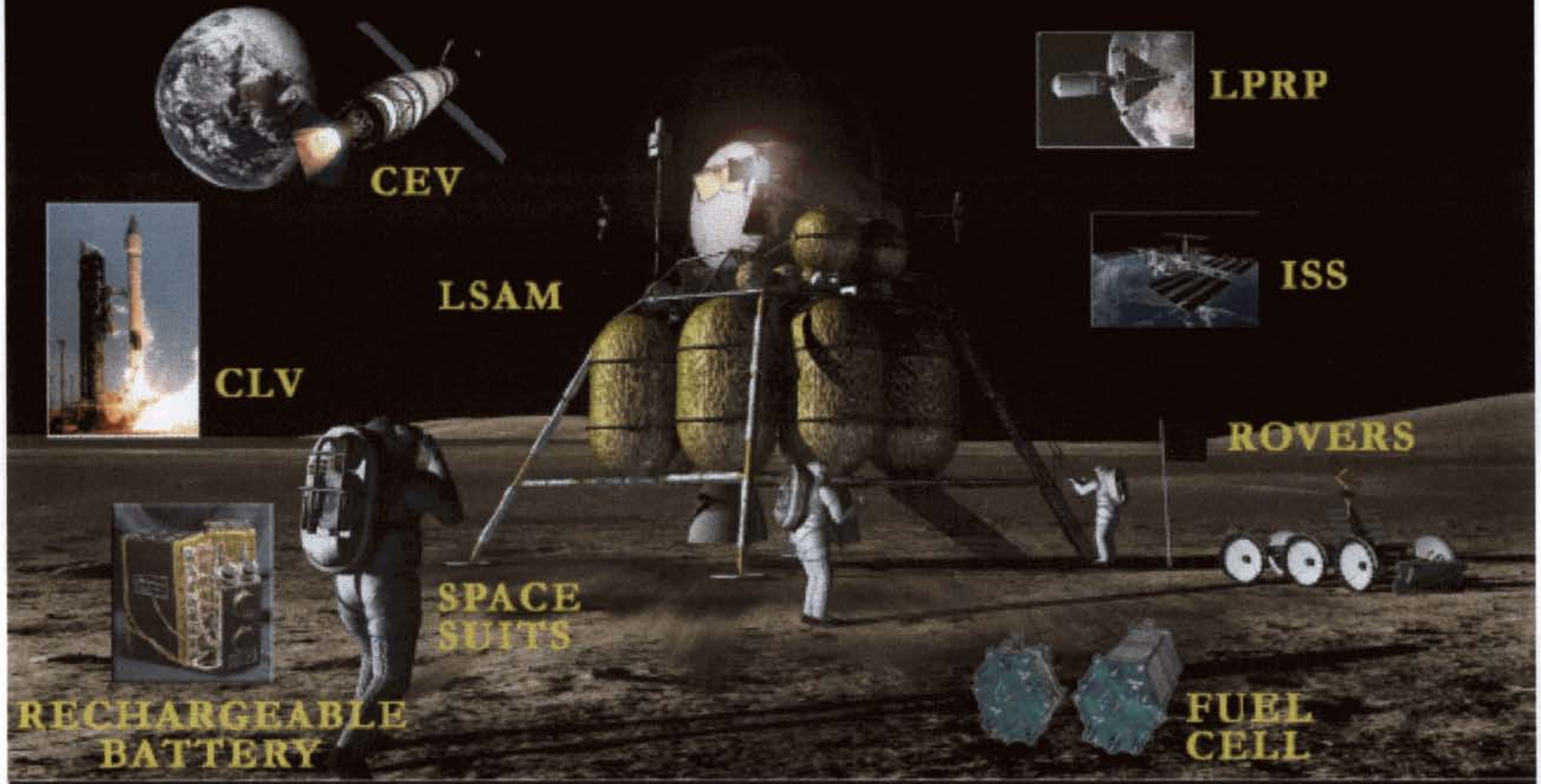
Energy Storage Technology for Exploration Missions



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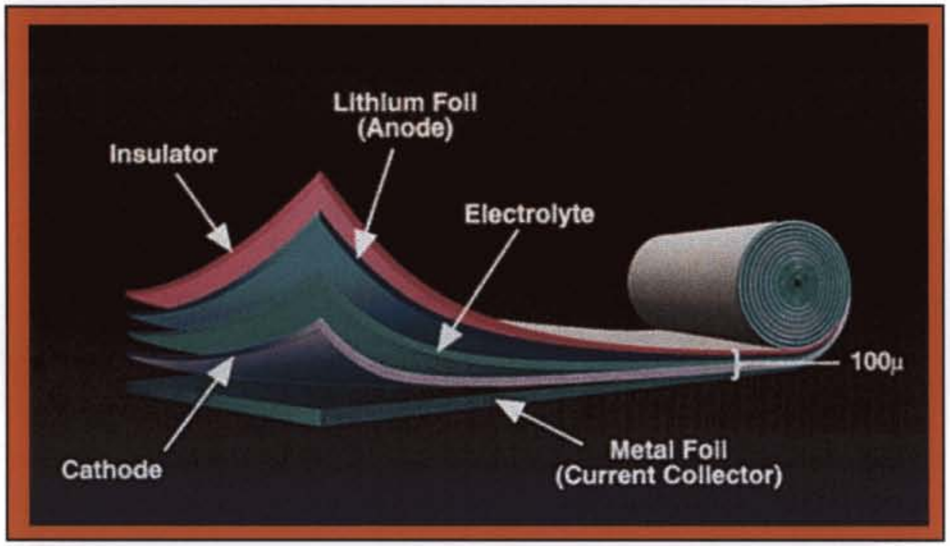
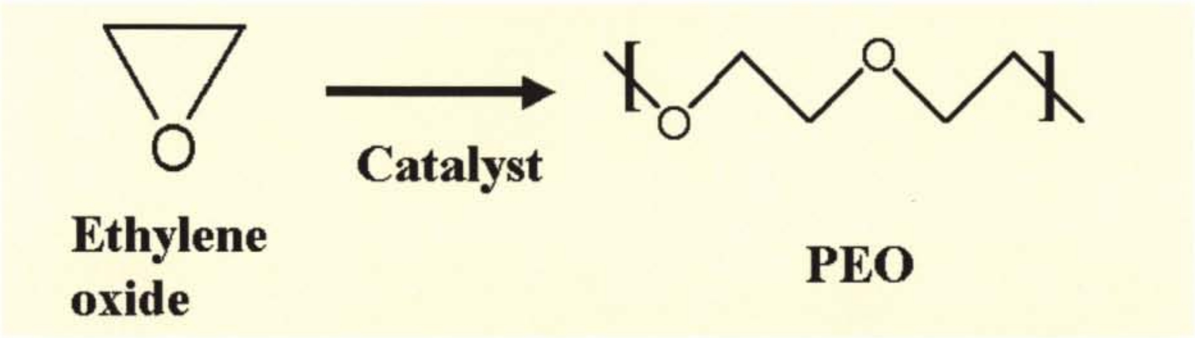
Strategic Importance

- Lithium batteries for space applications need electrolytes with ionic conductivities 10^{-4} to 10^{-3} S/cm at temperatures as low as -40°C.



- Higher conductivity is achieved at room temperature and lower by adding solvent (gel systems).
- However, this compromises dimensional and thermal stability of the electrolyte, compatibility with electrodes, mission safety

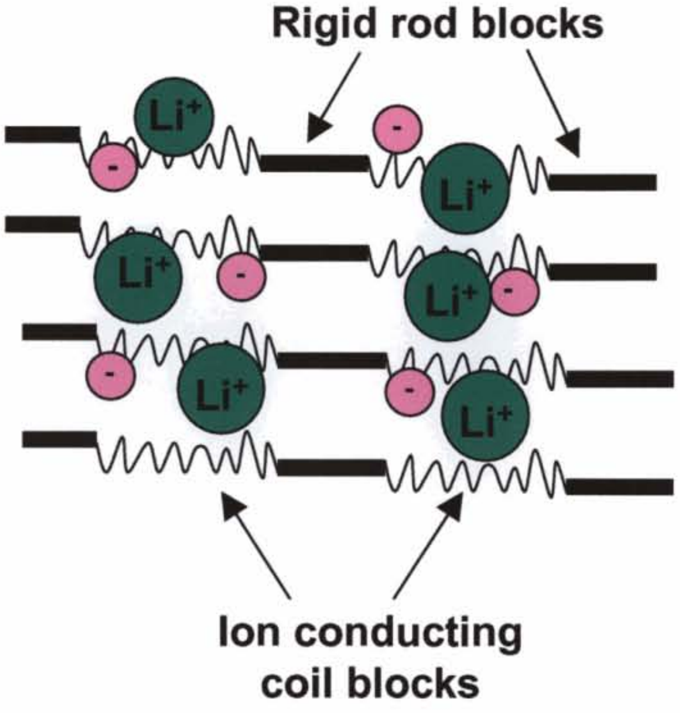
State of the Art Polymer Electrolytes



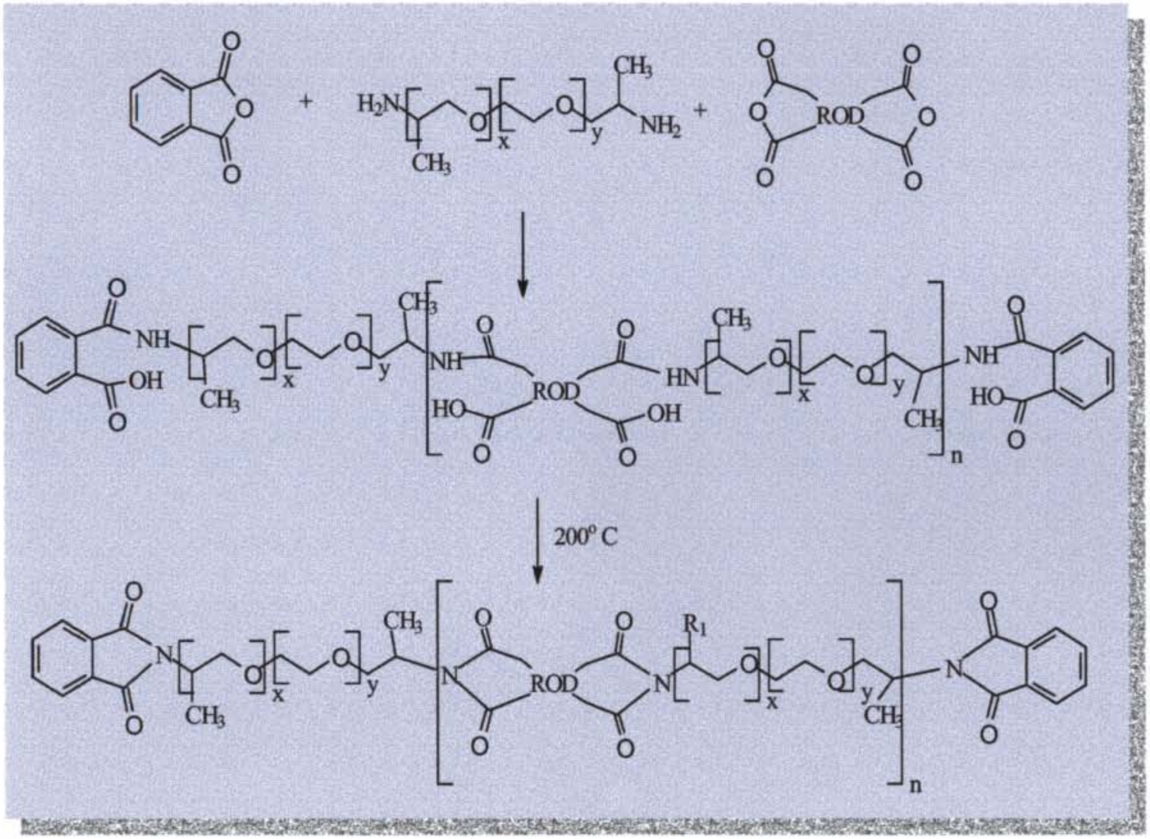
- Ionic conductivity is highest for amorphous polymers with low Tg
- Strong coulombic forces/low free volume trap ions in the crystalline regions
- Trade-off between
  - Dimensional stability (high molecular wt solid)
  - Molecular motion (short oligomers, liquid)
- Desired: Conductivity of liquid in a solid material

Rod-Coil Polymers

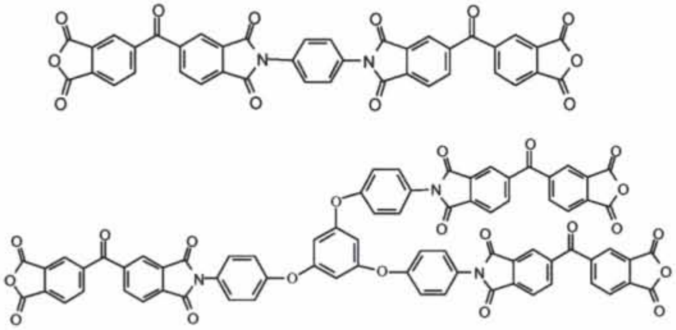
- Utilizes alternating rigid rods and liquid like coils as highly incompatible blocks
- Rod phases form mechanical support
- Liquid-like phases conduct ions
- Combination forms strong, rubbery films that are easy to fabricate



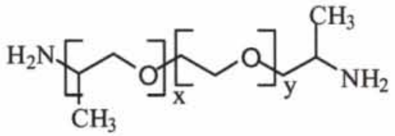
Rod-Coil Polyimides



Rods



Coils



	MW	EO/PO
XTJ-500	2000	38.7/6
XTJ-502	600	9/3.6
XTJ-506	1000	0/16.6

Salt

Lithium bis(trifluoromethanesulfonyl)imide)

LiTFSI: $LiN(SO_2CF_3)_2$

Processing films

- Polyimides formulated from amine-capped polyether, aromatic dianhydride, aromatic diamine or triamine
- All operations carried out in dry box

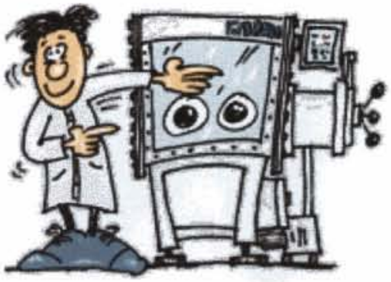
Dianhydride, polyether and end cap combined in dry solvent in dry box in glass jar with stirring until in solution

Diamine or triamine added, stirred until dissolved

Resulting polyamic acid in 30-40 wt % solution cast into films

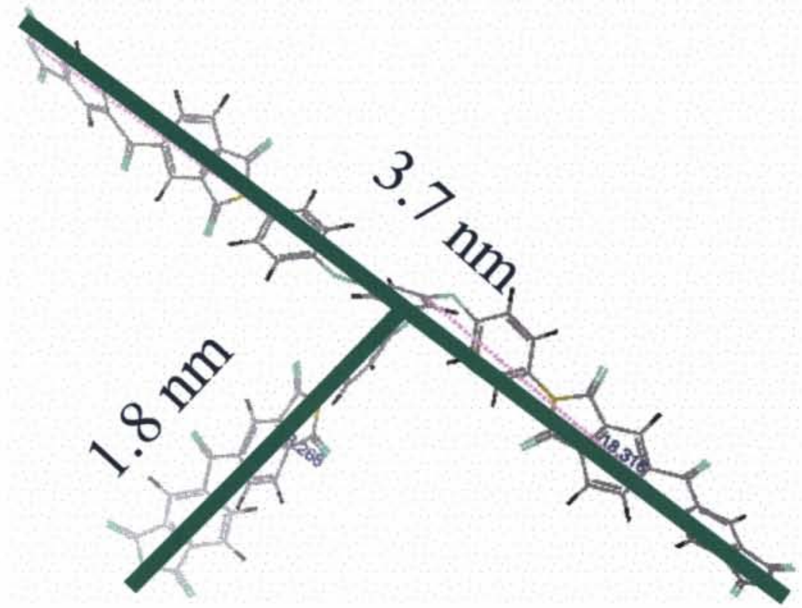
-or-

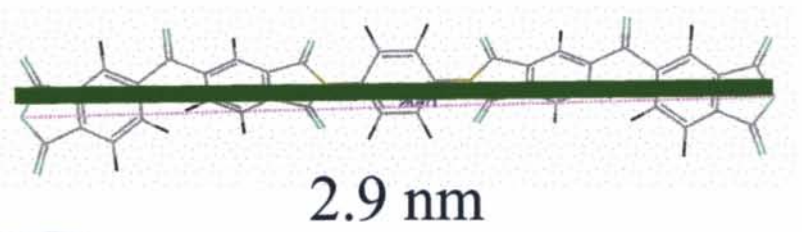
Salt added and then cast

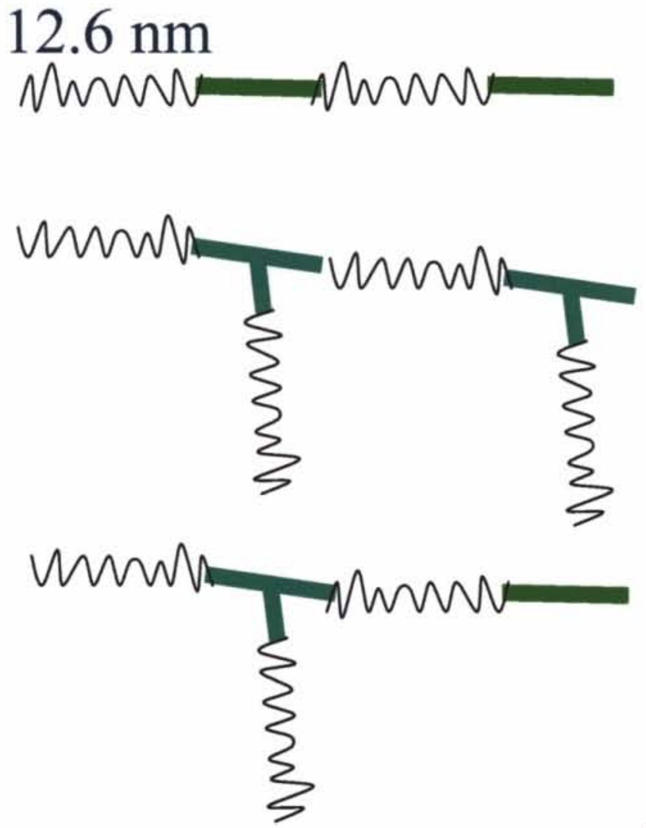


Transferred to vacuum oven attached to dry box for imidization (200C)

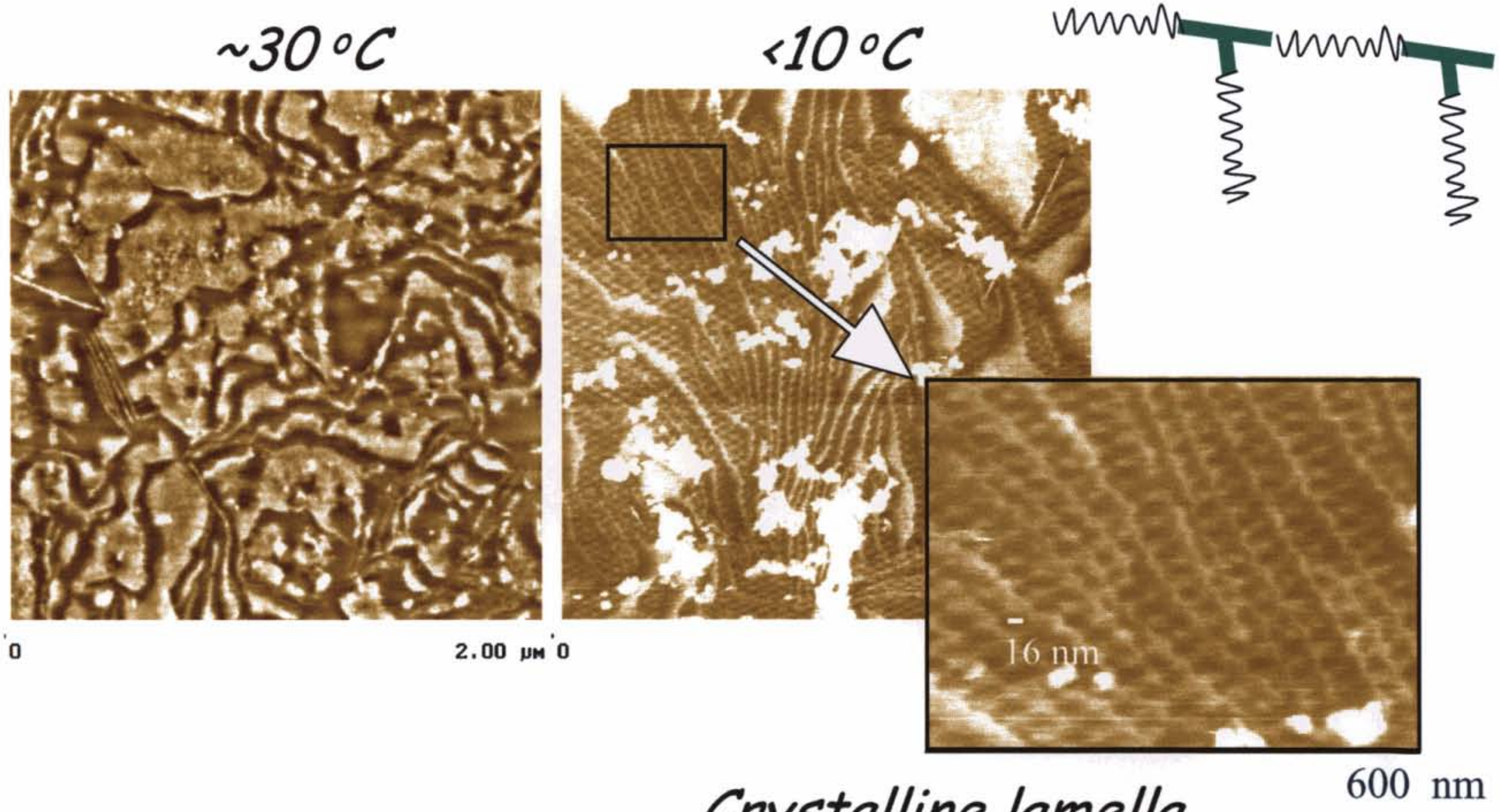
Rods either T-shaped or linear





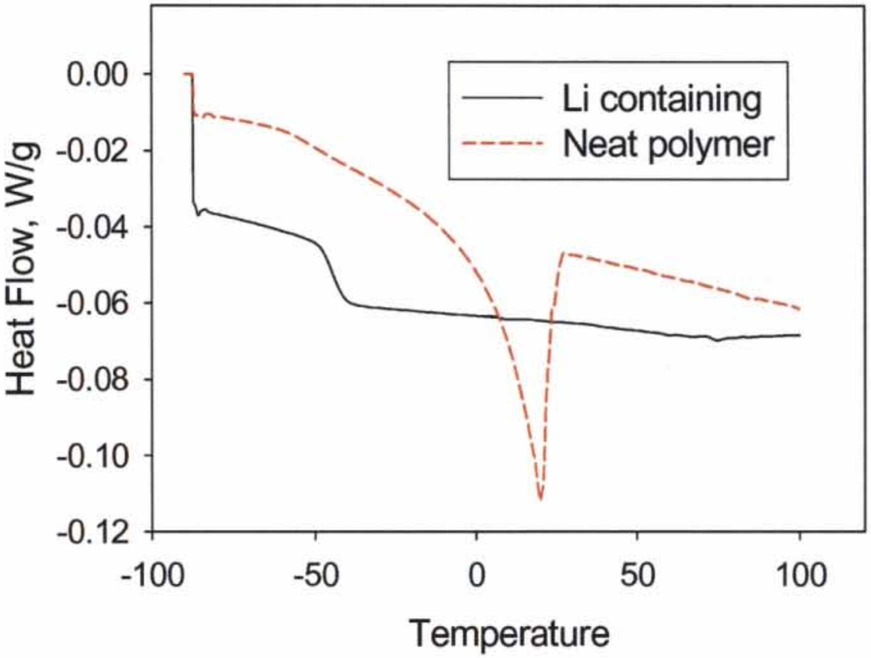


AFM of neat rod-coil polyimide above and below crystalline transition

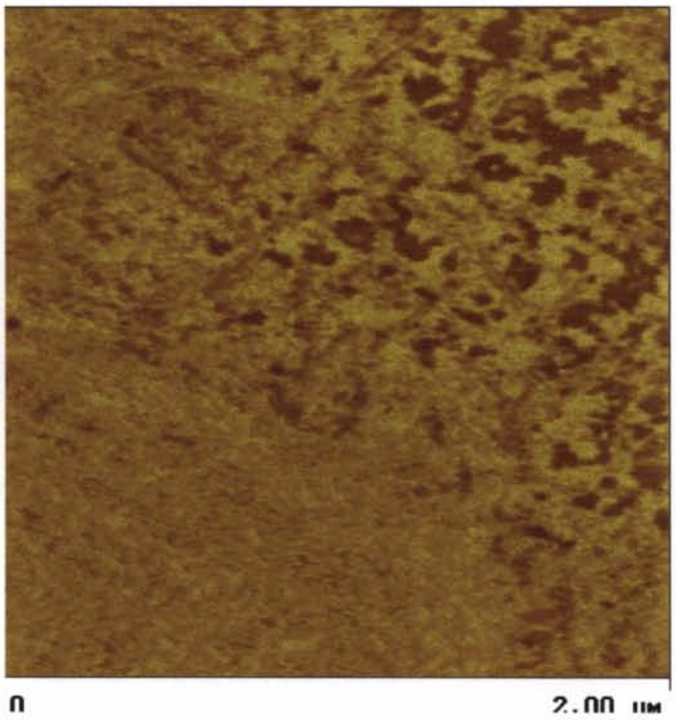


Crystalline lamella

Crystalline transition is suppressed in presence of salt

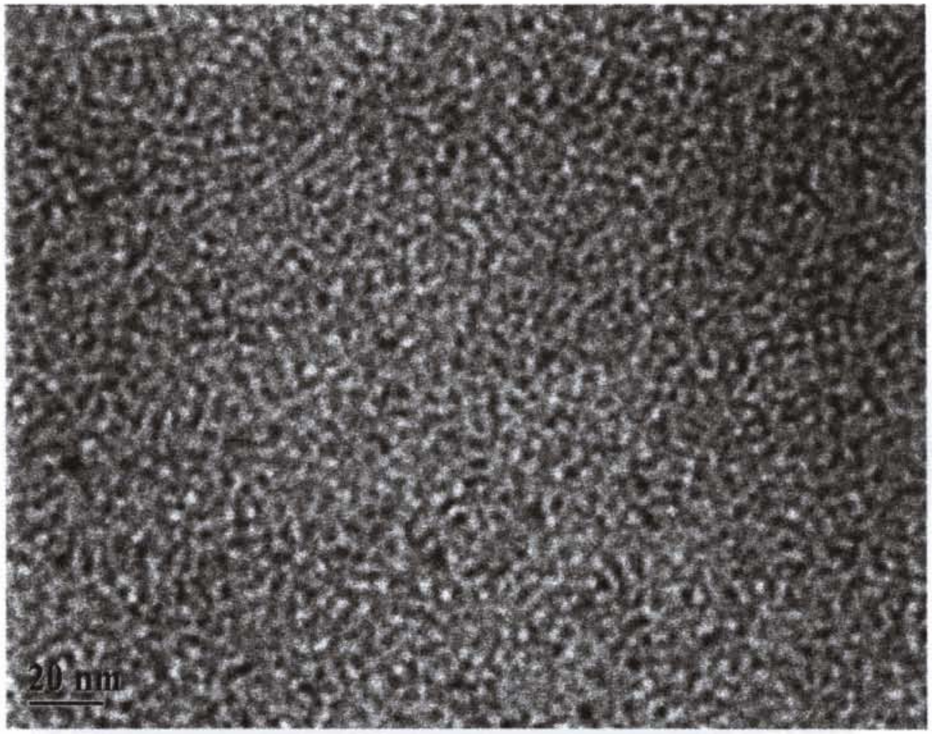


Reversible DSC

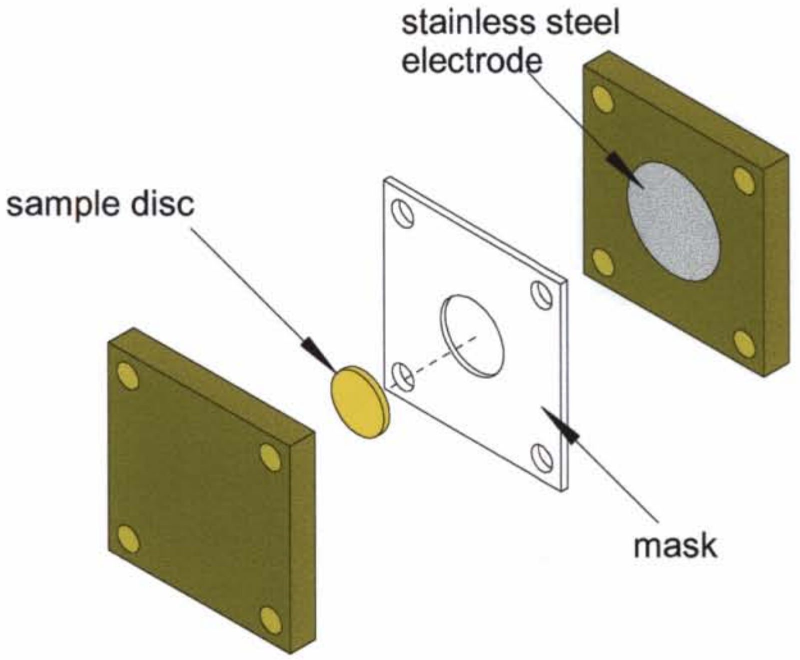


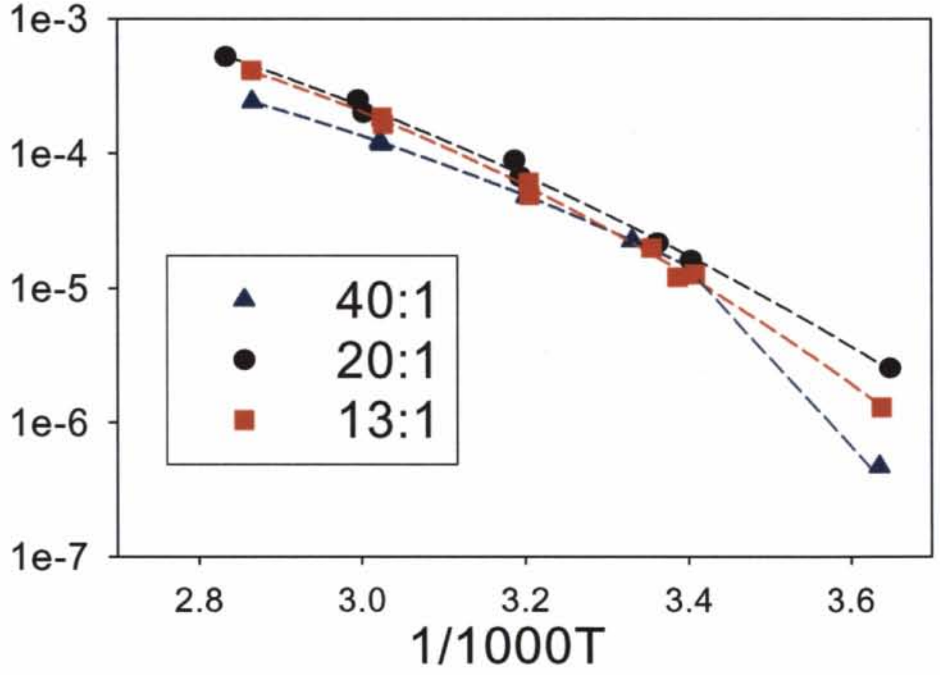
TEM of rod-coil film at room temperature

- Coil portions stained dark
- Rod portions (lighter areas)



Conductivity Measurements of Typical Rod-Coil Polymers



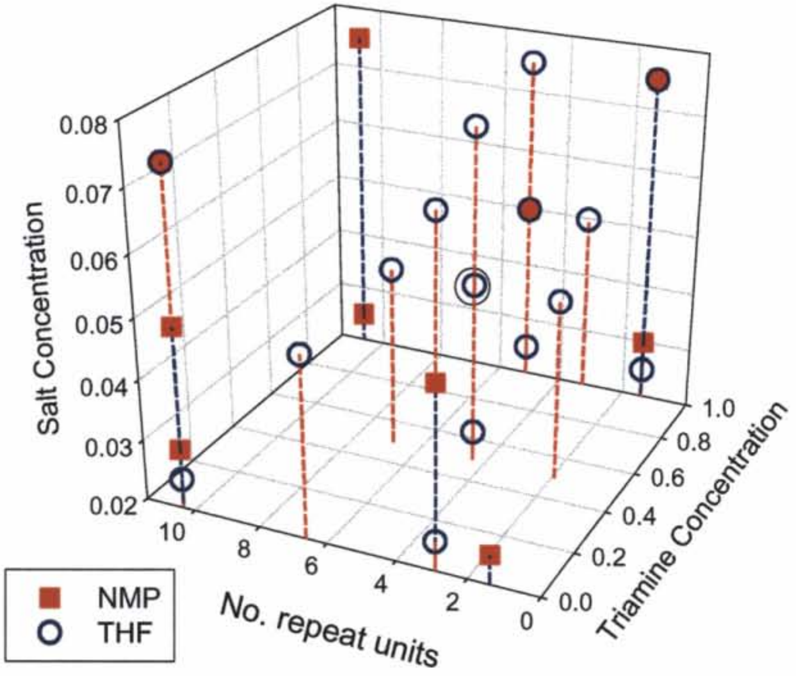


Ionic Conductivity

Experimental Design Study

Four variable study

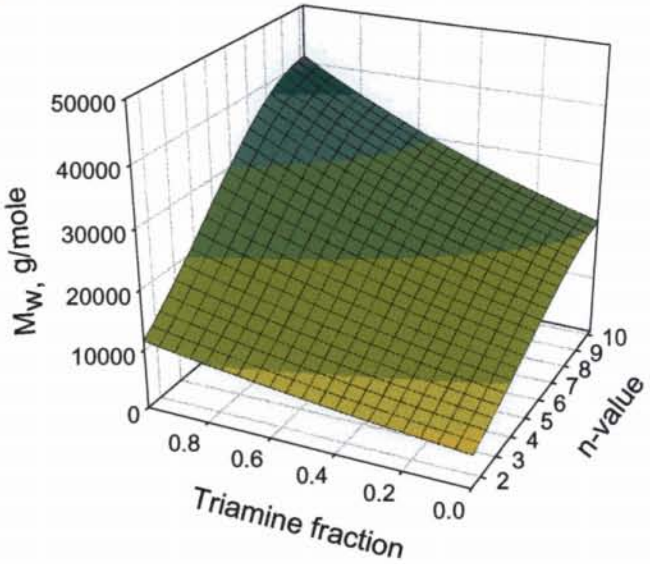
- Solvent (THF, NMP)
- No. of repeat units (1.2 to 10.72)
- Percent triamine vs. diamine (0 to 100%)
- Li:O ratio (0.025 to 0.075)
- D-Optimal design (25 runs and 6 repeats)
- Response surface models derived to predict optimal formulations for highest conductivity

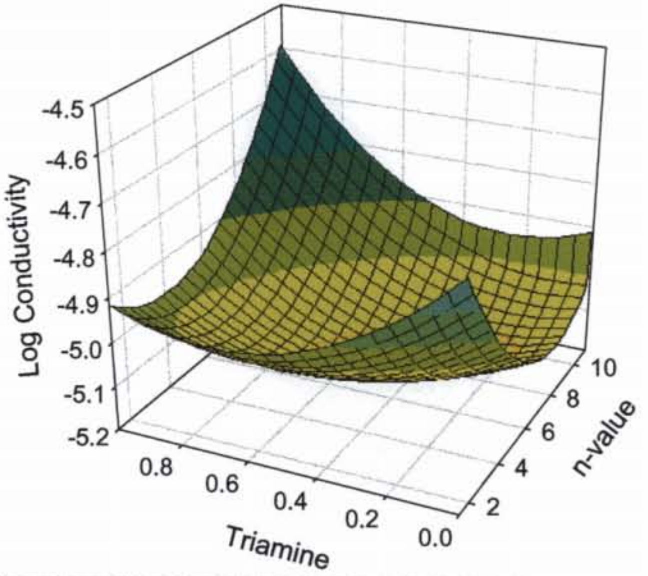


GRC

Response Surface Models—GPC and ionic conductivity

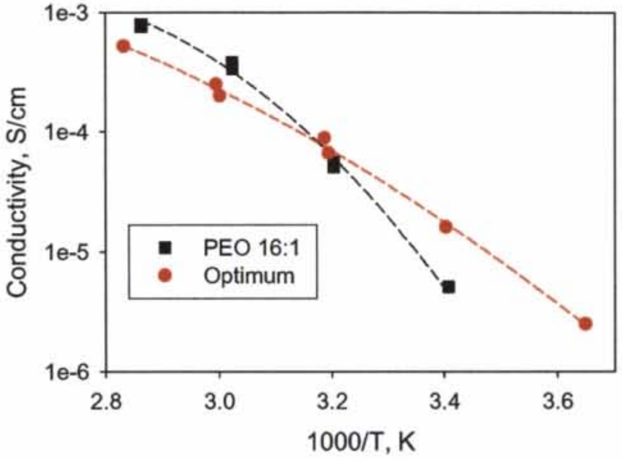
- Significant effects of branching and n-value on MW
- FMW agrees with measured MW for all but the most highly branched
- Significant effects of salt concentration, branching and n-value on conductivity
- Graph shows data at 20:1 O to lithium ratio (optimum)
- Highest conductivity (2.5×10^{-5} S/cm) achieved with highest MW and most branching



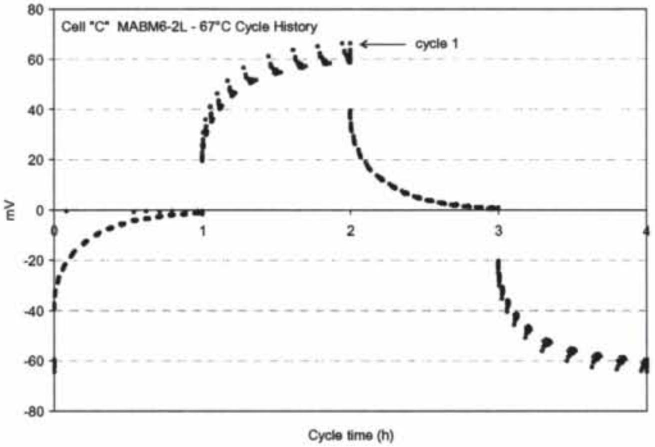


Rod coil polyimides summary

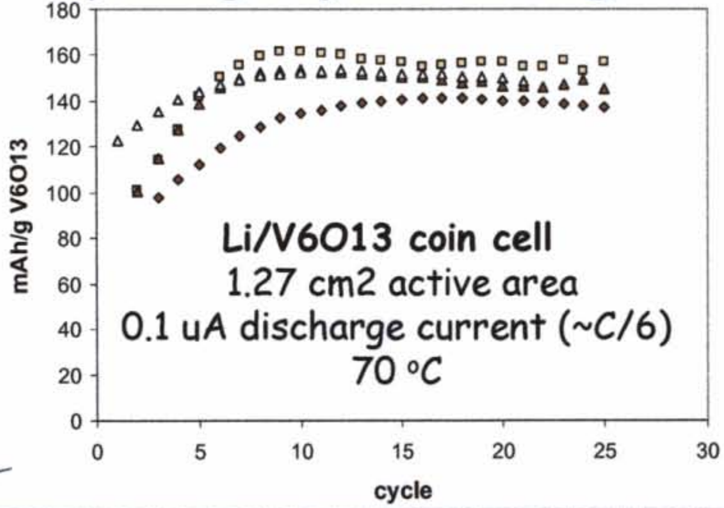
Improved Ionic Conductivity



Lithium compatible

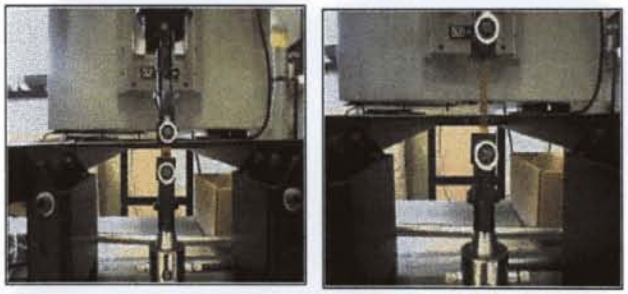


Cycling in functioning cell



Li/V6O13 coin cell
1.27 cm2 active area
0.1 uA discharge current (~C/6)
70 °C

Improved Mechanicals

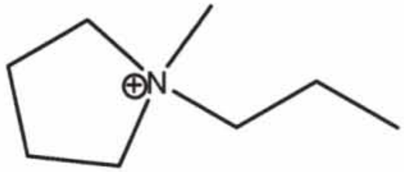


Before Stretching After Stretching

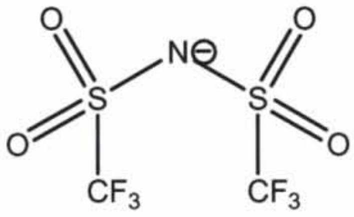
Lithium conductivity in optimum rod-coil formulation not good enough

- Cycles in cells at 70 °C and above
  - Advantage over PEO—it is still a true solid at those temps
- Still 1-2 orders of magnitude too low for working battery at lower temp
  - Can increase conduction by addition of organic solvents, but volatile and flammable
- Ionic liquids are attracting attention as way to increase ion conduction
  - Typically consists of an asymmetric organic cation and a bulky anion with highly delocalized charge
  - Both nonvolatile and nonflammable
  - Maintains the safety advantage of polymer electrolytes while adding a liquid component

Room temperature ionic liquids stable



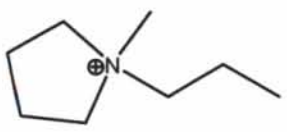
P_{13}



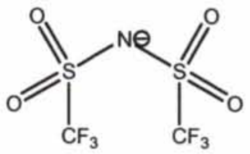
TFSI

- Shin, Henderson, Passerini (*Electrochem. Comm.* **2003**, *5*, 1016) reported addition of N-propyl-N-methylpyrrolidinium trifluoromethanesulfonimide (P13) to PEO
  - 30% P13 to PEO:LiTFSI increases conductivity from 7×10^{-6} S/cm to 6×10^{-5} S/cm.
  - Addition of 150% P13 increases conductivity to 4.5×10^{-4} S/cm.
  - Li transference number only decreases from ~0.3 to ~0.15
  - Ionic conduction still tends to drop off with decreasing temperature since PEO still crystallizes even with large amounts of P13

Rod coil polymers with ionic liquid

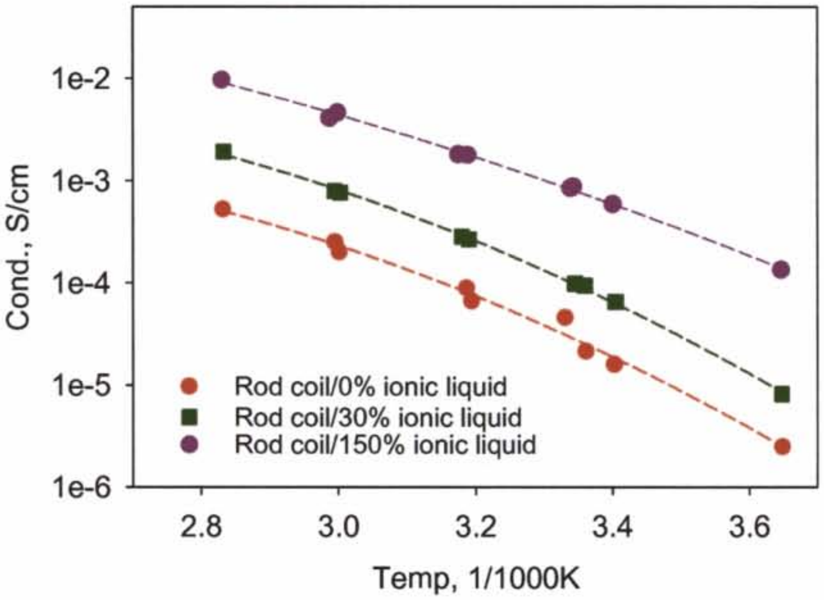


P_{13}



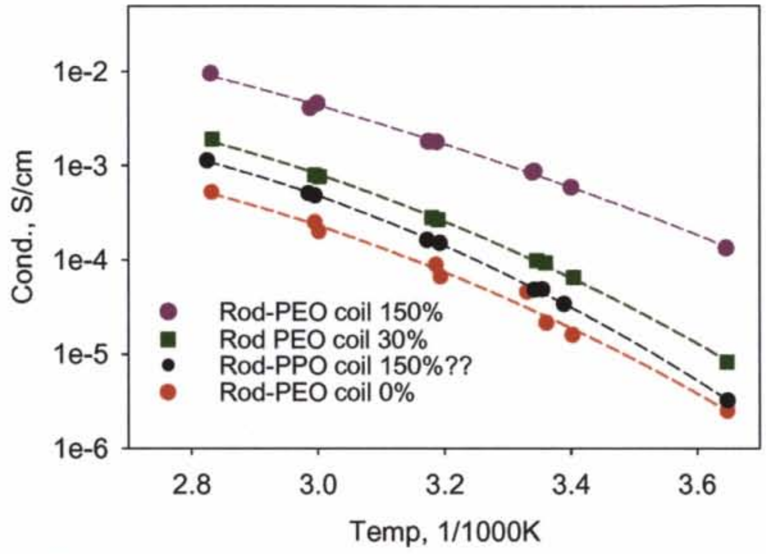
TFSI

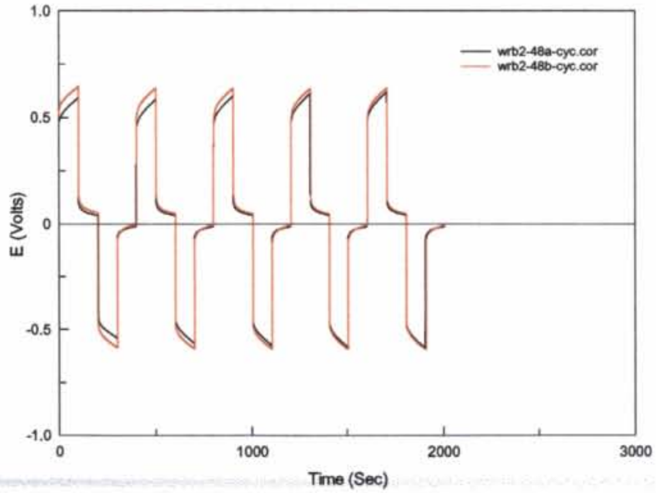
- Made in the same way—P13 is added to the solution before imidization along with salt
- Two orders of magnitude improvement in ionic conductivity at 0 °C
- But cycling data similar to dry polymer
- Probably due to lower Li transference number
  - ~0.2 for dry polymer
  - ~0.03 for 150% ionic liquid
- Li ions more attracted to polymer phase?



Rod Coil made with PPO coil and ionic liquid

- PPO coil has lower ionic conductivity but improved Li transference
  - 0.08 for 150%
- Preliminary cycling at room temp somewhat better then dry polymer

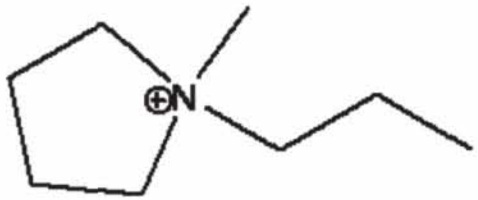




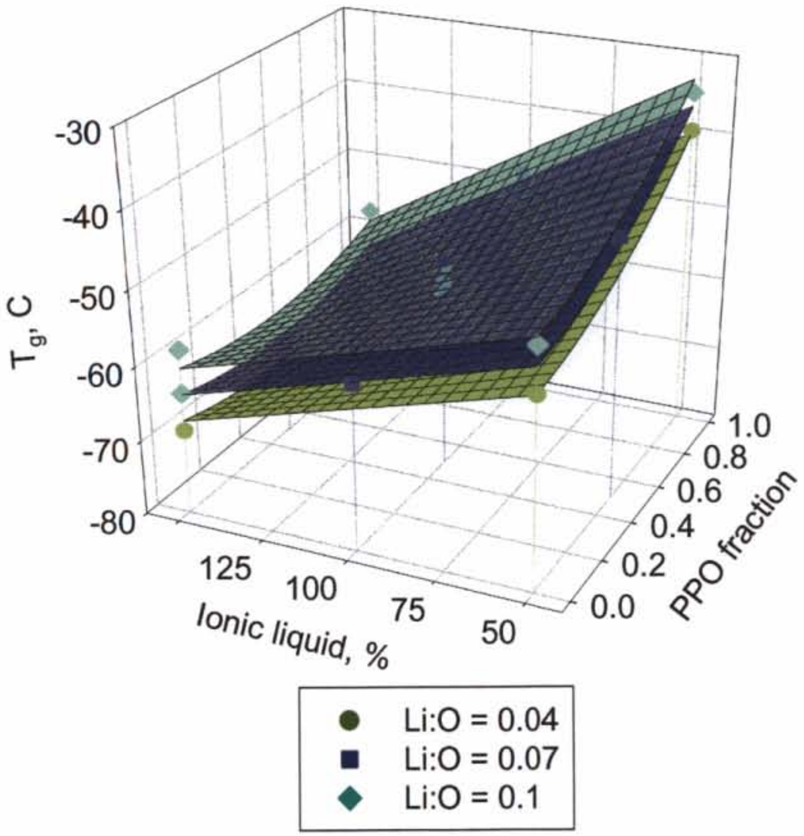
Experimental design study

Variables:

- Coil type
  - Poly(ethylene oxide): XTJ-502 (2000 molecular weight)
  - Poly(propylene oxide): XTJ-506 (1000 molecular weight
- Salt type
  - Lithium bis(trifluoromethanesulfonyl)imide):LiTFSI: $LiN(SO_2CF_3)_2$
  - Lithium bis(perfluoroethylsulfonyl)imide): LiBETI: $LiN(SO_2CF_2CF_3)_2$
- Salt concentration
  - Lithium:oxygen ratio from 0.04 to 0.1
- Ionic Liquid concentration
  - 50-150% P13:
  - Anion same as salt

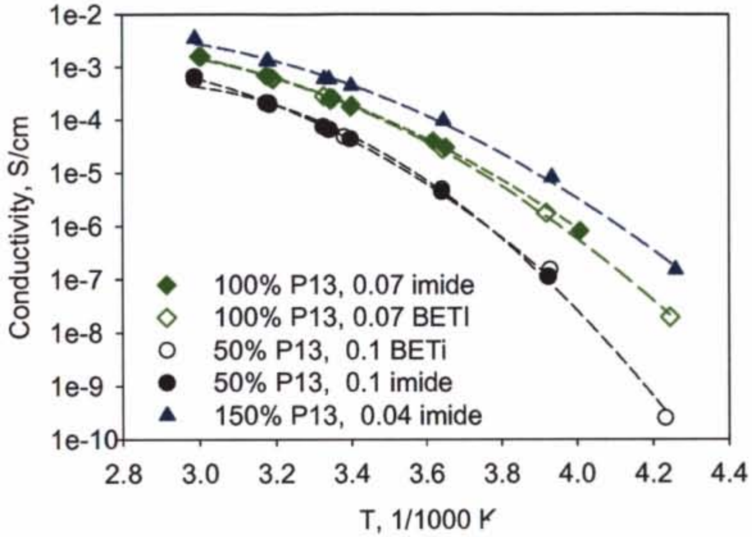


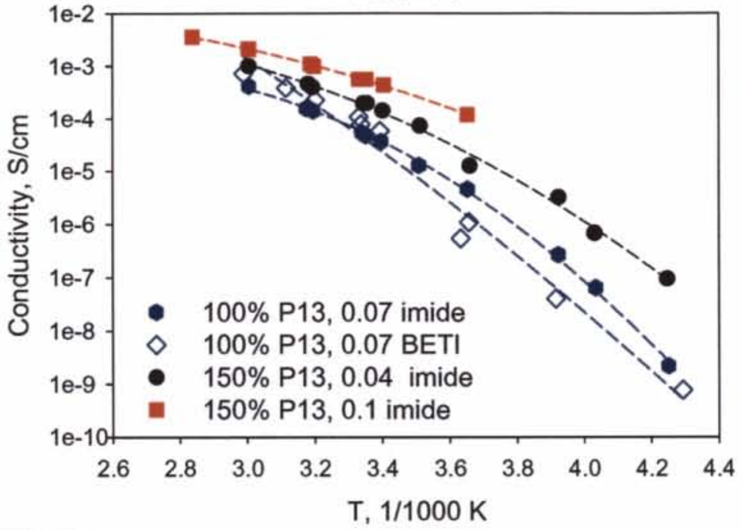
Experimental Design Study Glass Transition Temperature: T_g

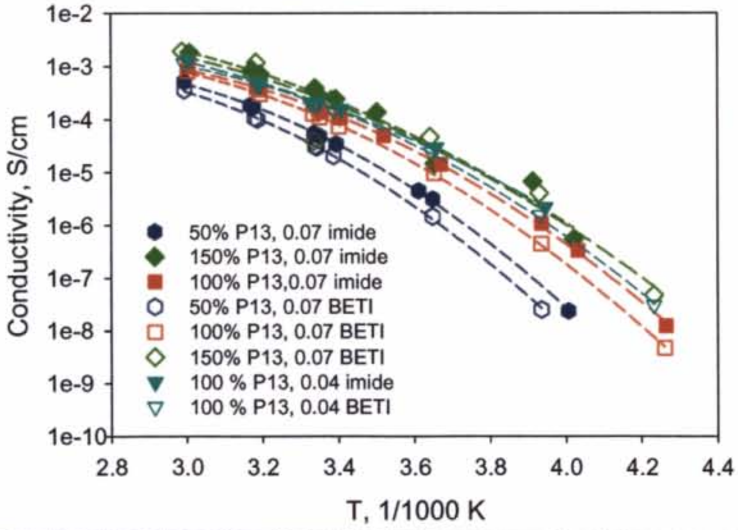


- Lower T_g corresponds to higher conductivity
- Variables
  - PPO in PEO
  - Percent Ionic Liquid to Polymer
  - Li:O ratio (0.04 to 0.1)
- Lower T_g by:
  - Decreased PPO fraction
  - Increase % ionic liquid
  - Decreased salt conc.

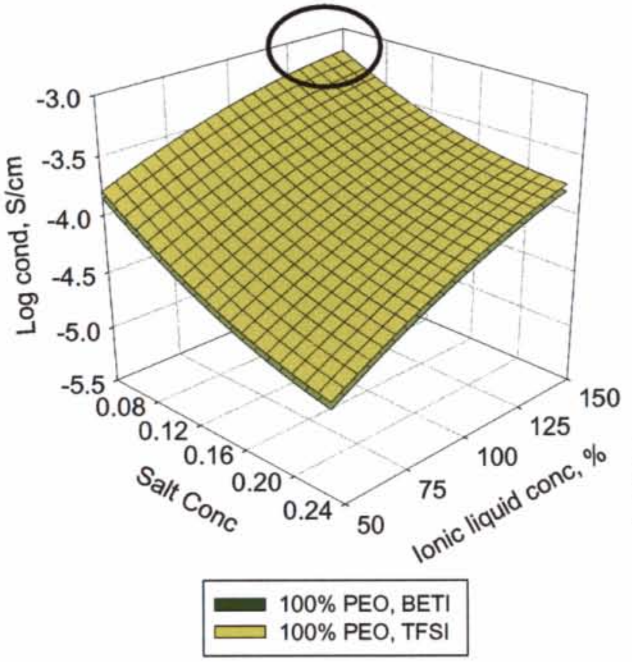
Sample ionic conductivity measurements from study

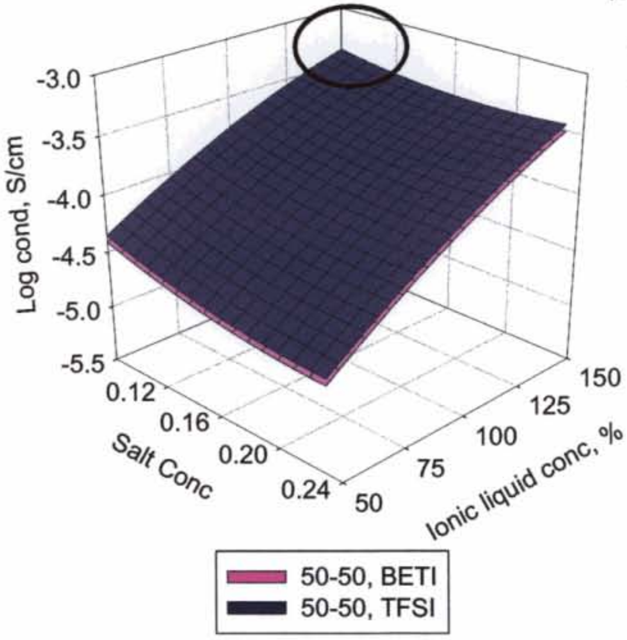

100% PEO

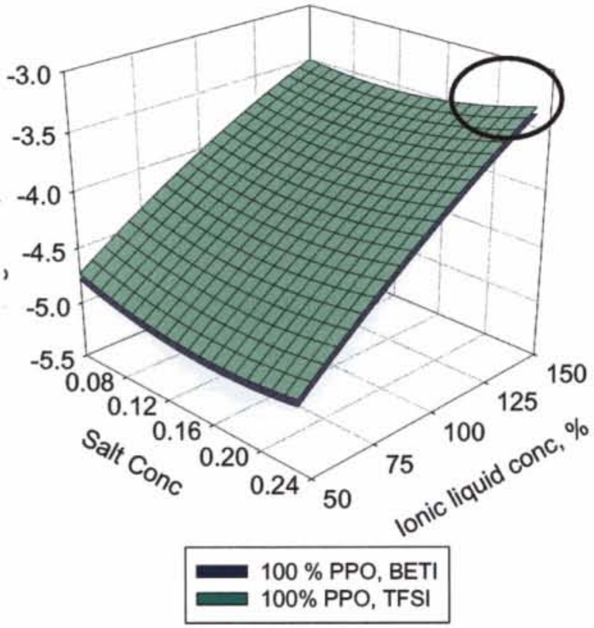

100% PPO


50% PEO, 50% PPO

Response surface models for log conductivity with about half experiments completed





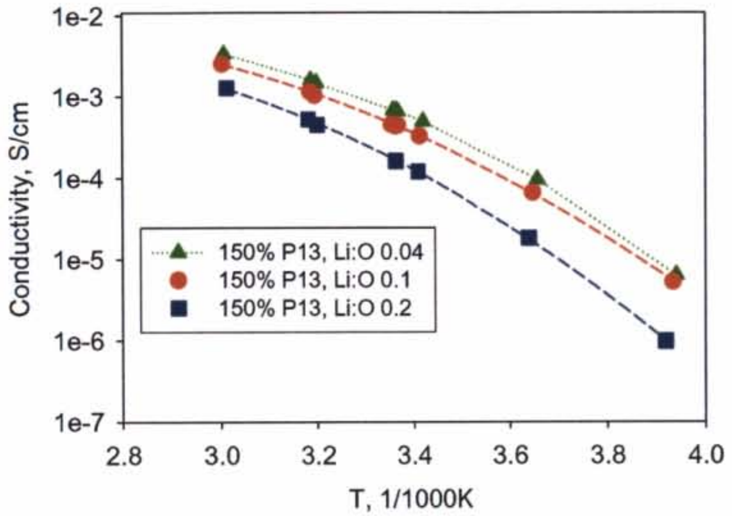


◯ Optimal conductivity identified

Samples down-selected for further electrochemical characterization

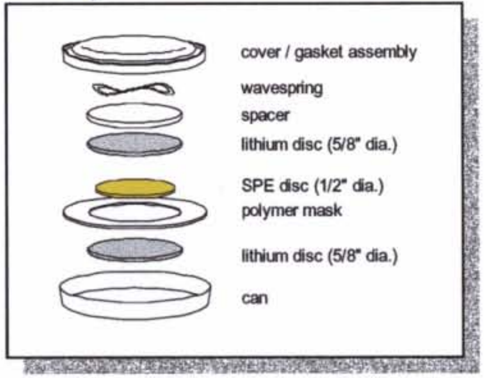
- Small but significant difference in conductivity between BETI and TFSI anions—BETI salt dropped
- Samples with 100% PPO tend to lose ionic liquid during testing especially at 150% P13—drop from study for now
- For further study:
  - Samples made with 100% PEO
    - 1 to 1 ionic liquid to polymer at low salt concentration
    - 1.5 to 1 ionic liquid to polymer at low salt concentration
    - 1.5 to 1 ionic liquid to polymer at higher salt concentration
  - Samples made with 50% PPO—50% PEO
    - 1 to 1 ionic liquid to polymer at low salt concentration
    - 1.5 to 1 ionic liquid to polymer at low salt concentration
    - 1.5 to 1 ionic liquid to polymer at higher salt concentration

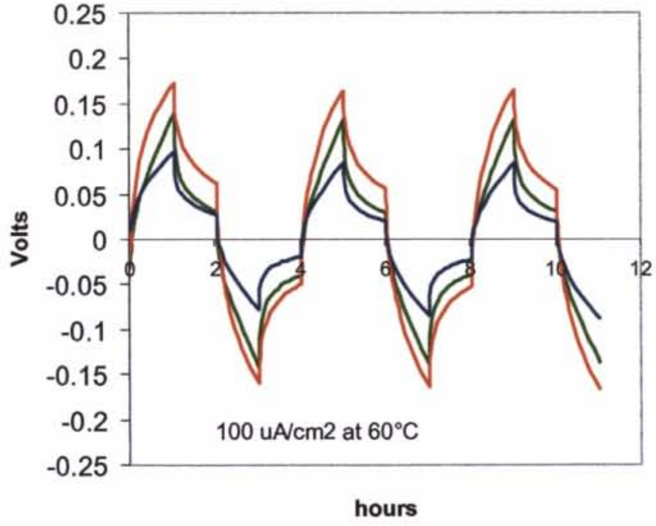
Films from 100% PEO rod-coil polyimide, 150% P13 and different salt concentrations



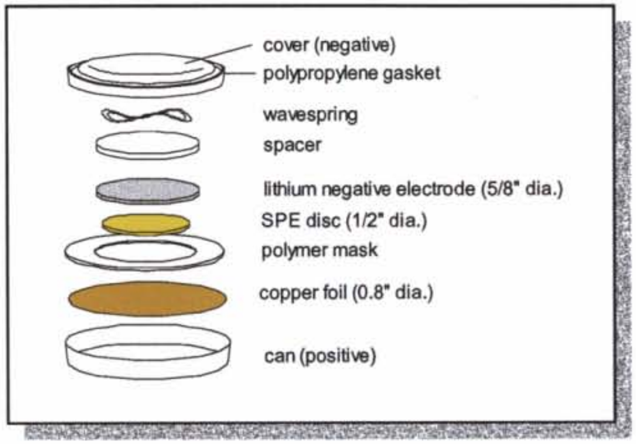
- Transference numbers measured by d.c. polarization
  - Li:O 0.04, $t_{Li} = 0.010$
  - Li:O 0.1, $t_{Li} = 0.009$
  - Li:O 0.2, $t_{Li} = 0.038$

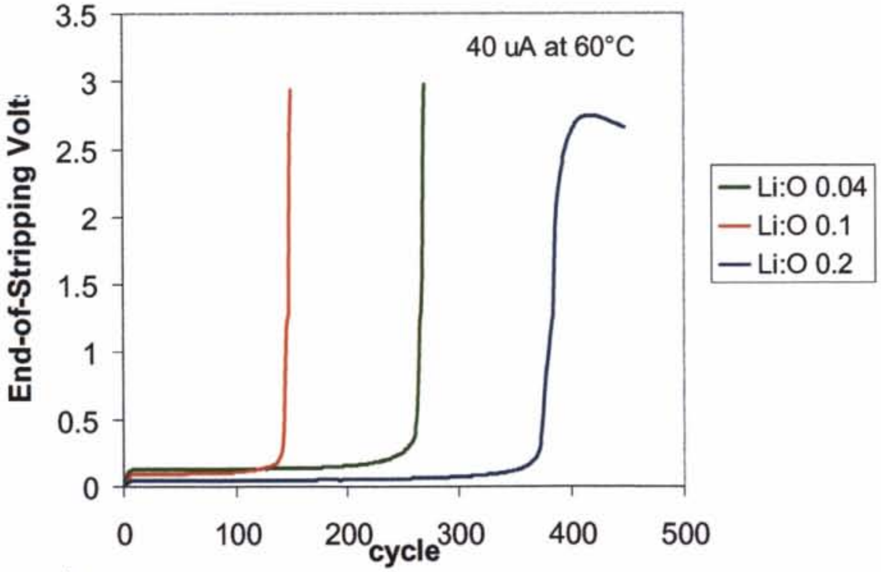
Symmetric cell





Li plating and stripping efficiencies of films with 150% P13

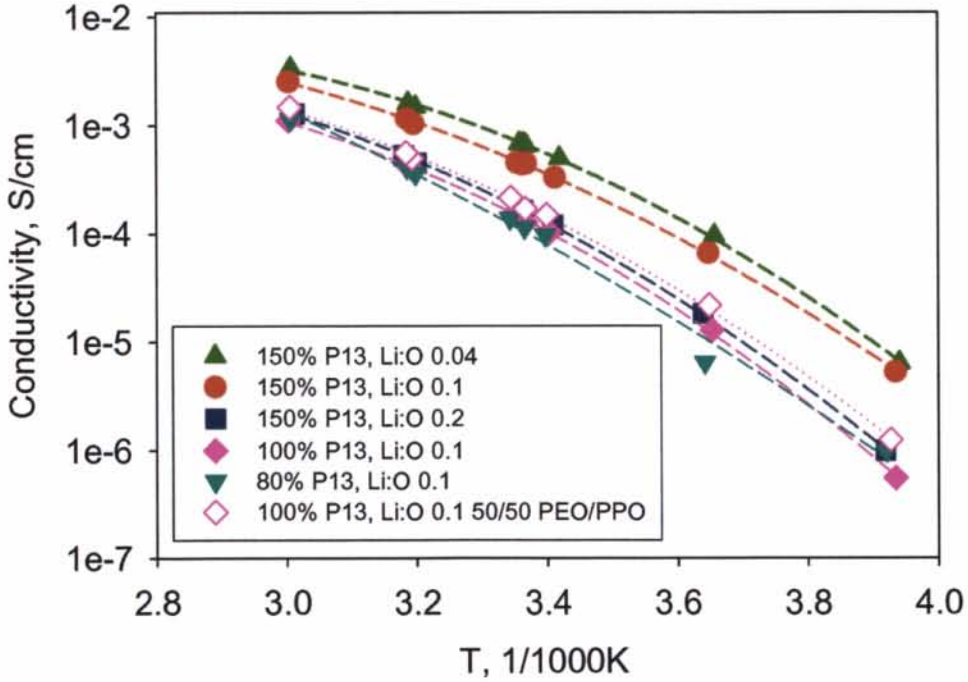




- Plating efficiency on copper at 60°C
- Deposit quantity of lithium onto copper (14-hour plating).
- Measures ability to cycle 1/10 of the deposited amount in repeated stripping/plating
- 3-Volt cutoff potential to terminate cycles
- Improvement over PEO films which do not have acceptable long term stability toward stripping and plating with > 90% P13

Other films of interest

- Fabricated films with less ionic liquid, 50/50 PEO/PPO
- Ionic conductivity measured
- Plating/stripping efficiencies, cycling in progress



Conclusions

- Optimum rod-coil films have better room temperature ionic conductivity then PEO, but not high enough for batteries at lower temperatures
- Use of ionic liquids in rod-coil polymers improves ionic conductivity, cycling in cells
- Highest loading of ionic liquids tested (1.5 times weight of polymer) resulted in highest conductivities
- Lowest salt concentrations resulted in highest conductivities but not necessarily the best Li plating and stripping efficiencies
- Electrochemical characterization and stability measurements are underway

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Solvent-free, solid polymer electrolytes (SPE) have the potential to improve safety, increase design flexibility and enhance performance of rechargeable lithium batteries.[1] Solution based electrolytes are flammable and typically incompatible with lithium metal anodes, limiting energy density. We have previously demonstrated use of polyimide rod coil block copolymers doped with lithium salts as electrolytes for lithium polymer batteries.[2] The polyimide rod blocks provide dimensional stability while the polyethylene oxide (PEO) coil portions conduct ions. Phase separation of the rods and coils in these highly branched polymers[3] provide channels with an order of magnitude improvement in lithium conduction over polyethylene oxide itself at room temperature. In addition, the polymers have been demonstrated in coin cells to be compatible with lithium metal. For practical use at room temperature and below, however, at least an order of magnitude improvement in ion conduction is still required. The addition of nonvolatile, room temperature ionic liquids has been shown to improve the ionic conductivity of high molecular weight PEO.[4] Herein we describe use of these molten salts to improve ionic conductivity in the rod-coil block copolymers.

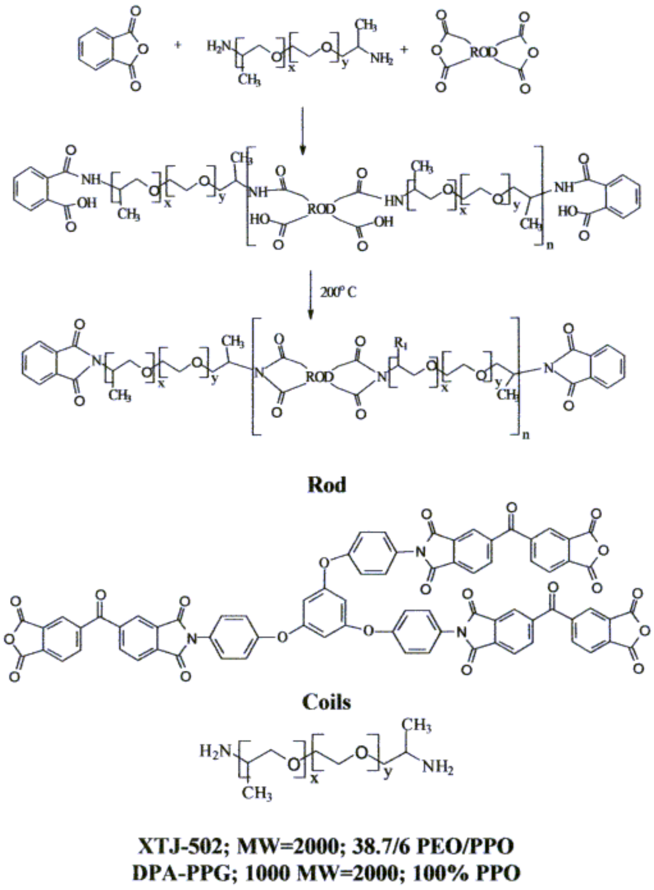
Experimental

Materials. All reagents were used without further purification. Tetrahydrofuran (THF), 3,3',4,4'-benzophenone tetracarboxilic dianhydride (BTDA) and phthalic anhydride (97%) were purchased from the Aldrich Chemical Co. 1,3,5-Tris-aminophenoxybenzene was synthesized by Triton Systems. Lithium bis(trifluoromethanesulfonyl)imide) (LiTFSI) and Lithium bis (perfluoroethylsulfonyl)imide) (LiBETI) were purchased from 3-M Company. Diamine-capped polyethylene oxide oligomer (Jeffamine XTJ-502) was kindly supplied by Huntsman Corporation. Diamine-capped propylene oxide (DPA-PPG 1000) was obtained from Tomah^3 Products, Inc. N-propyl-N-methylpyrrolidinium trifluoromethanesulfonimide (P_{13}) was synthesized and purified according to a literature procedure to give clear liquid.[8-11] PEO ($M_w = 5 \times 10^6$) and PVDF(HFP) ($M_w = 4 \times 10^5$) were purchased from Aldrich and used as received.

Instrumentation. Polymers were characterized by differential scanning calorimetry (DSC) from -90 to 300°C using a Q1000 calorimeter manufactured by TA Instruments. Thermal gravimetric analysis (TGA) was obtained using a TA instruments high resolution TGA2950 analyzer. ATR-FTIR spectra of polymer films were taken with a Nicolet Nexus 470 FTIR spectrometer equipped with a Smart Omni sample ATR accessory.

Ionic conductivity was measured between stainless steel electrodes by electrochemical impedance techniques, using a Solartron/Schlumberger model 1250 FRA and model 1286 Electrochemical Interface.[18,19] Conductivity was measured over the range of 0 to 80°C. Coin cells were made from a film of electrolyte sandwiched between 5/8"diameter lithium discs under internal pressure. Cells were heated to 40°C and cycled at ±50 uA/cm^2 and ±100 uA/cm^2 current density. Cycles used a 3-hour current application followed by a 1-hour rest. A polarization limit of 2-Volt was included to minimize deterioration of the SPE

Synthesis of polymers. Polymers were prepared as previously described in a glove box according to Scheme 1. In general, the amine terminated polyalkylene oxide was combined with the BTDA and PA in enough THF to give a 20-25 w/w% solution of polymer when complete. The mixture was stirred until dissolved at which time TAB was added slowly with more stirring until the mixture was completely dissloved. Lithium salt and ionic liquid was added in the desired amount, and the solution was cast into two inch diameter Teflon petrie dishes. The films were allowed to dry in the glove box. After all the solvent was gone, the films were placed in a vacuum oven attached to the glove box and cured at 200 °C for three hours.



Scheme 1. Structure and preparation of rod-coil polyimides.

Results and Discussion

Ionic conductivity for a 60,000 formulated molecular weight rod-coil polymer using the Jeffamine, XTJ-502 and LiTFSI in a concentration giving a Li to EO ratio of 1 to 20 (or 0.5) is shown in Figure 1 graphed vs. temperature. Addition of ionic liquid P_{13} in amounts up to 150% the weight of the polymer gives over an order of magnitude increase in ionic conductivity across the entire temperature range studied (0 to 80 °C).

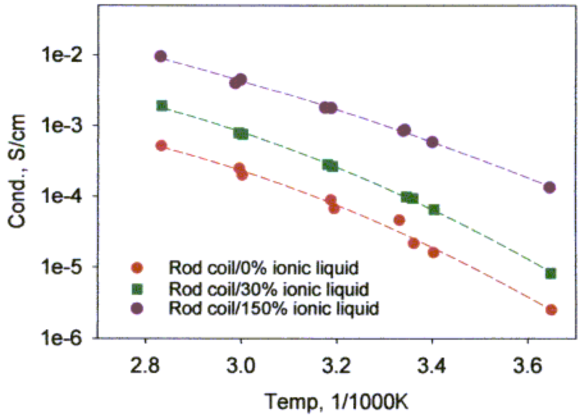


Figure 1. Comparison of ionic conductivity for rod-coil films containing LiTFSi salt at 20:1 O to Li and ionic liquid in quantities of 0, 30 and 150% the weight of the polymer.

Though ionic conductivity is higher in the presence of ionic liquid, an estimate of Li$^+$ transference in the ionic liquid containing films was almost an order of magnitude lower than in the dry polymer films. Hence, that Li mobility is not much different. However, since Li coordinates well with PEO in the polymers, it was thought that perhaps the Li transference number could be improved by substituting some or all of the PEO with PPO coils which does not interact strongly with Li. To this end, a statistical experimental design study was carried out with four variables. The amount of PEO coil was varied from 100% (PPO coil 0% to 0% (PPO coil 100%), the quantity of ionic liquid was varied from 50 to 150 % the weight of the polymer. Also, the type of salt (LiBETI and LiTFSI) and amount of salt was varied. In all, thirty different films were prepared and the ionic conductivity was measured.

Empirical models were calculated from the measured ionic conductivities of the films by linear least squares regression. A full quadratic model containing all main effects, secondary effects of salt, ionic liquid and PEO concentration, as well as all two-way interactive/ synergistic effects was entertained. Terms not deemed statistically significant (<90% confidence) were dropped from the model one at a time using the step-wise modeling technique. Graphs of the models are shown in Figures 2 and 3.

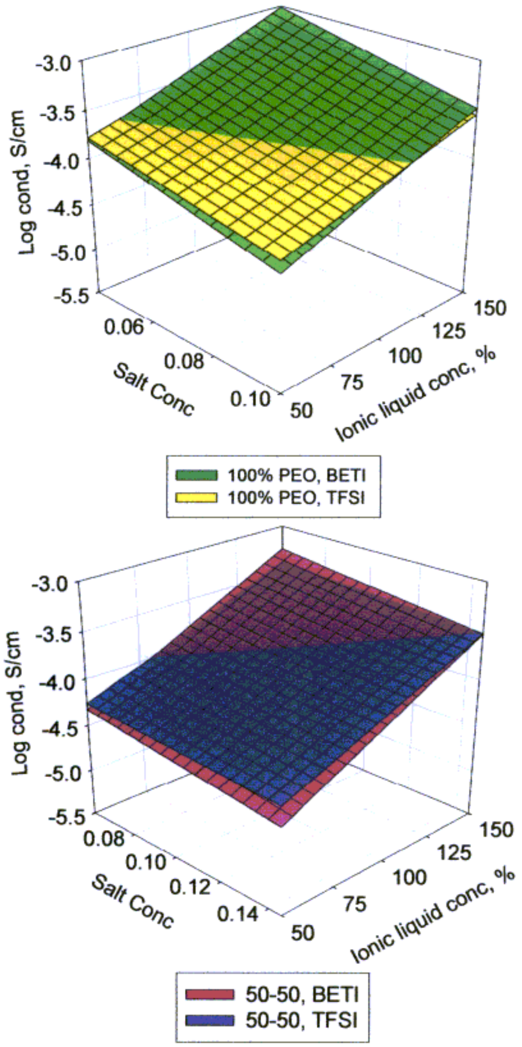


Figure 2. Response surface models of room temperature ionic conductivity vs. salt and ionic liquid concentration for polymers with 100% PEO coil (top), and 50-50 mixture of PEO/PPO (bottom).

Overall, in the study the highest ionic conductivity was obtained for polymers with 100% PEO coil, containing 150% ionic liquid at the lowest salt concentration. Ionic conductivity decreased with increasing salt concentration and decreasing ionic liquid concentration as shown in the top plot in Figure 2. Demonstrating a similar trend, the 50/50 PEO/PPO polymers had nearly the same maximum ionic conductivity (bottom plot in Figure 2.).

In contrast, 100 % PPO containing polymers actually show an increase in ionic conductivity with increasing salt concentration. Though the maximum ionic conductivity at room temperature is slightly lower for this formulation, it is likely that overall lithium ion mobility is higher with a larger number of lithium ions and less interaction with the polymer.

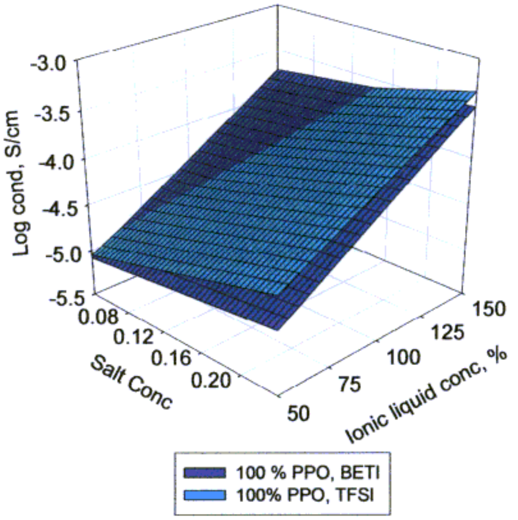


Figure 3. Response surface model of room temperature ionic conductivity vs. salt and ionic liquid concentration for polymers with 100% PPO coil.

Differences in ionic conductivity between the two salts were small and depended on the amount of PPO or PEO contained in the various formulations as well as the salt concentration. At 100% PEO and low salt concentration, for example, LiBETI was slightly higher in ionic conductivity whereas for 100% PPO containing polymers and high salt concentration, LiTFSI had a slightly higher conductivity.

Further electrochemical characterization of the optimum formulations will include study of electrochemical stability, lithium transference measurements, lithium plating and stripping experiments, and cycling stability.

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