Electrolytes and separators for high voltage Li ion cells

(an investigation of sulfone-based electrolyte solvents)

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Overview

Timeline:
Start: May 2010
Finish: Dec./2013

Budget:
$709,977
Funding received in FY 2010 for 2010 and 2011
$249,977
Funding for FY 2012
$230,000

Barriers:

- High viscosities, and melting points, of existing examples.
- Lack of information on additives and mixtures that can lower viscosities while avoiding side reactions
- Safety issues: flammability ionic shorts from liquid electrolytes
- Separator issues: containment impedance and toughness

Partners:

- Oleg Borodin, U. Utah
- Goying Chen, LBL
- Brett Lucht, U. Rhode Island
Jason Zhang, PNNL

Relevance: Urgent need for electrolytes compatible with 5V spinel type cathodes

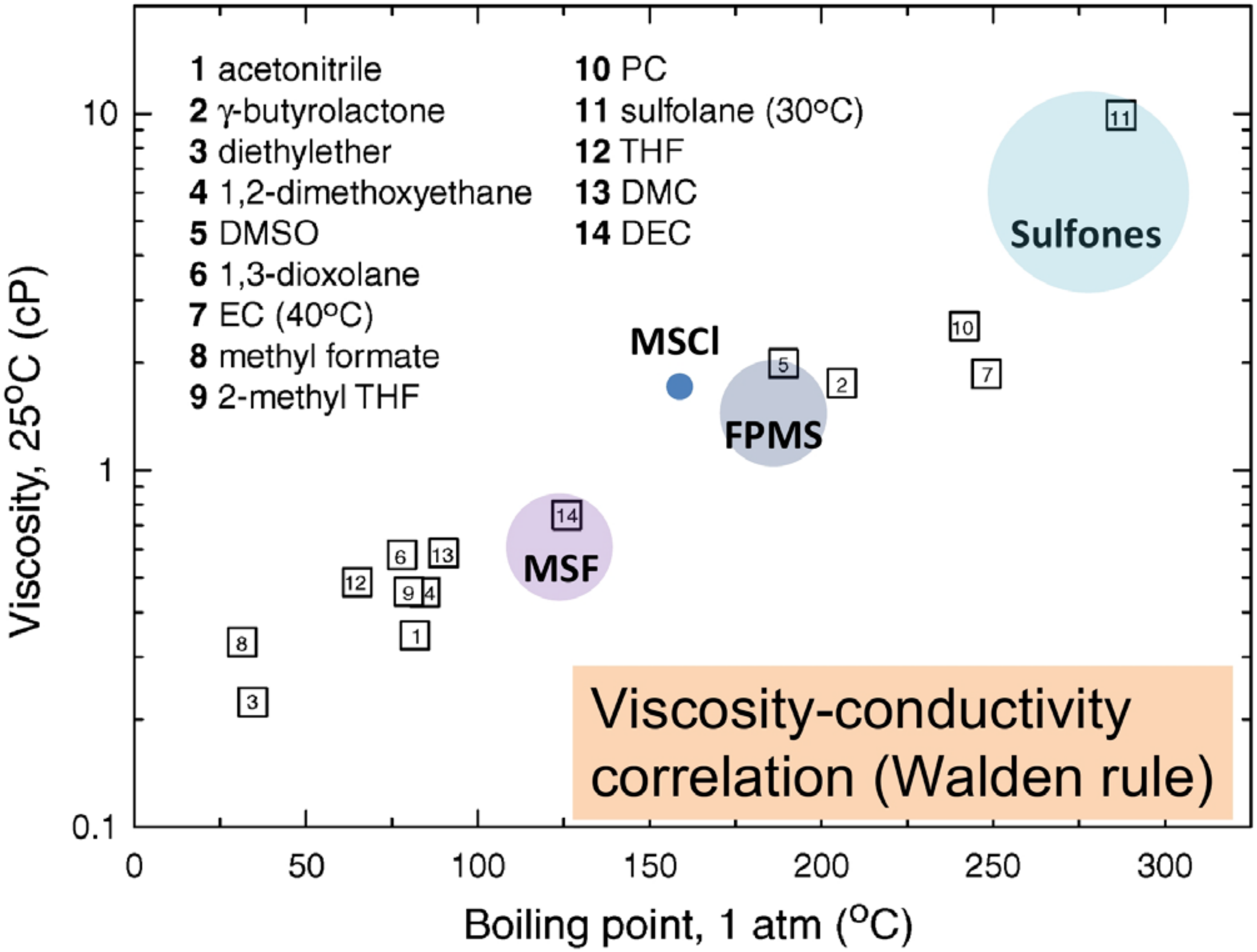
Sulfone-based electrolytes have been seen, by most, as the best prospect for resisting highly oxidizing cathodes. Our original work on structurally modifying sulfones to lower their high melting points without increasing their viscosities was seen as meriting further development. Fluorination studies and some mixed solvent studies were reported last year.

As will be seen, persistent problems and perceived limitations in this line of work, viewed against striking developments in solid electrolyte alternatives, have led to some diversion of effort to the exploration of novel solid electrolyte formulations – with tentatively very promising findings.

Novel methods of containing non-aqueous electrolytes that promise to enhance, rather than depress their conductivities, are also coupled to the electrolyte objective, and progress will be described.

Selection **strategies**: When no viscosity data? boiling point correlation

BACKGROUND SLIDE



The need for mixtures (see Xu review)

BACKGROUND SLIDE

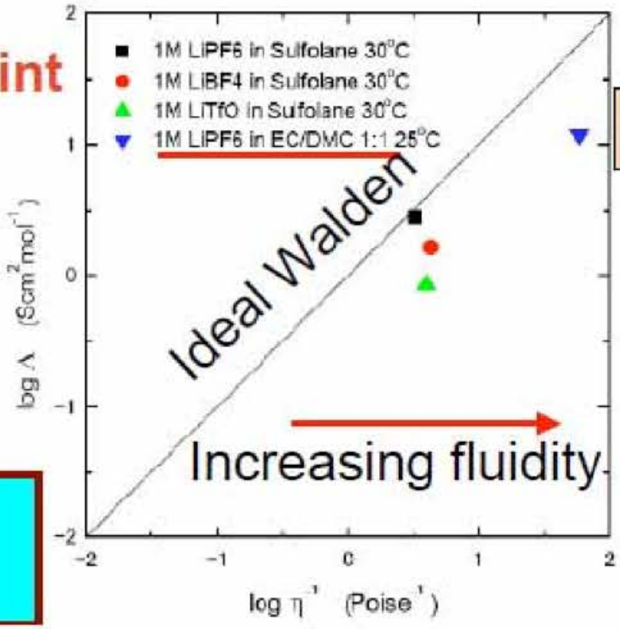
No single solvent can satisfy simultaneously all solvent needs

e.g Large dipole moment needed for overcoming crystal lattice energy (dissolving) causes high melting point and high viscosity, so low conductivity.

Resolution: mix with co-solvent of low dielectric constant and low boiling point. Thus EC-DMC

Mixing also reduces freezing point

Ionicity. How free are the ions from one another? Are we optimizing the decrease of viscosity, or losing some of the ions to associated pairs?



?

The first Walden plot for Li battery electrolytes

Objectives and Milestones

MILESTONES:

(a) Complete full evaluation of sulfone solvent-based high voltage cells.(Dec.10 [OK, concluded])

(b) Complete evaluation of ionic liquid-based, and hybrid, solvent electrolytes. (by April, 12)- on track

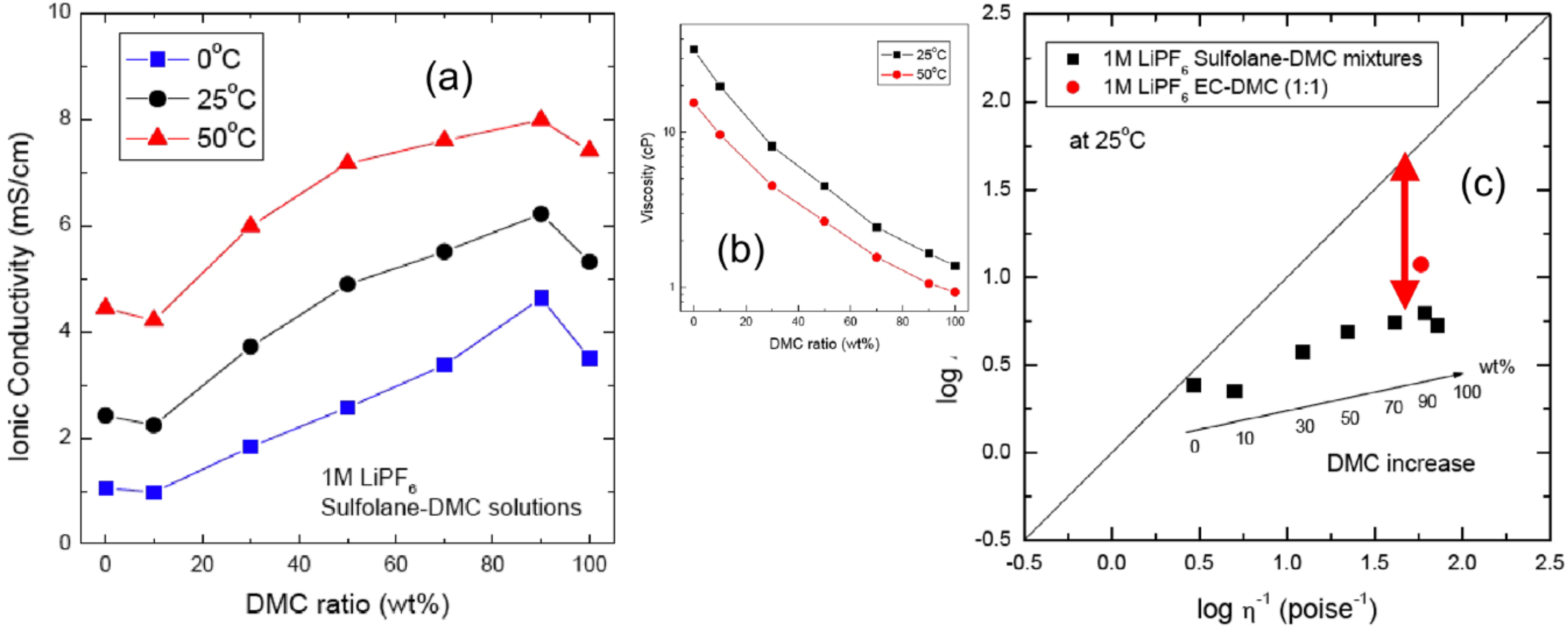
(c) Test and compare Li(Ni,Mn) spinel cells using ionic liquid-based electrolyte by May, 12 (on track)

(d) Test and compare glass and glass-stuffed polymer membrane types in cells by June, 12 (diverted to inorganic IL and plastic crystal).

(e) complete development of water-soluble self-assembling models of "Maxwell slat" porous solids for creation of self-supporting nanoporous membranes, by Dec. 11 (OK, concluded, by cessation in favor of (f)).

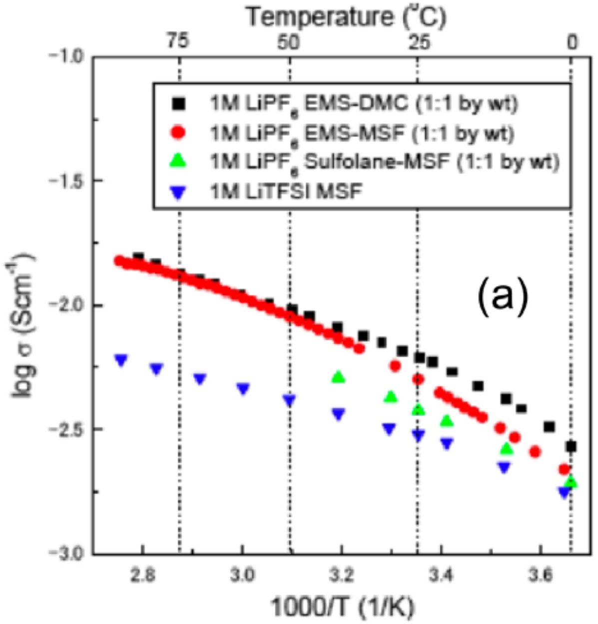
(f) Develop covalent-bonded version of the nanoporous glass, finding means of making continuous film. (accomplished, March 2012, now under testing, and extension)

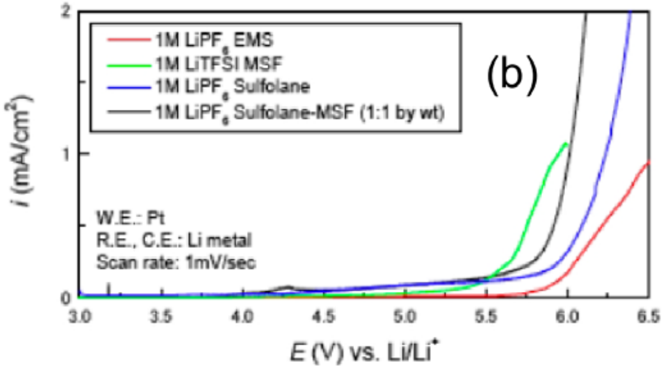
Accomplishment slide: evaluation of mixture compromises



Since sulfolane was known, from a background slide, to be completely dissociated, hence efficient from the point of view of usage of the electrolyte ions, sulfolane was a logical case for evaluating the loss of ion efficiency on dilution with low dielectric constant, but low viscosity co-solvent. This required conductance (a) and viscosity (b) and density (not shown) measurements, from which the Walden plot (c) could be constructed. The Walden plot shows that, if ionic dissociation were not repressed by co-solvent, the conductivity could increase by a factor of ~10 (see ↕). It is shown below, considering separator technology, how this might be accomplished.

Accomplishment slide: evaluation of sulfone + co-solvent mixtures for anode and cathode compatibility





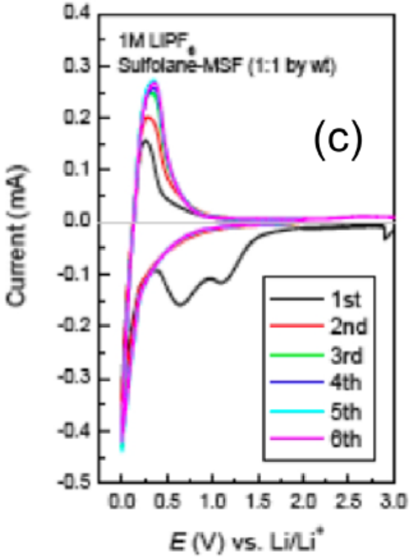
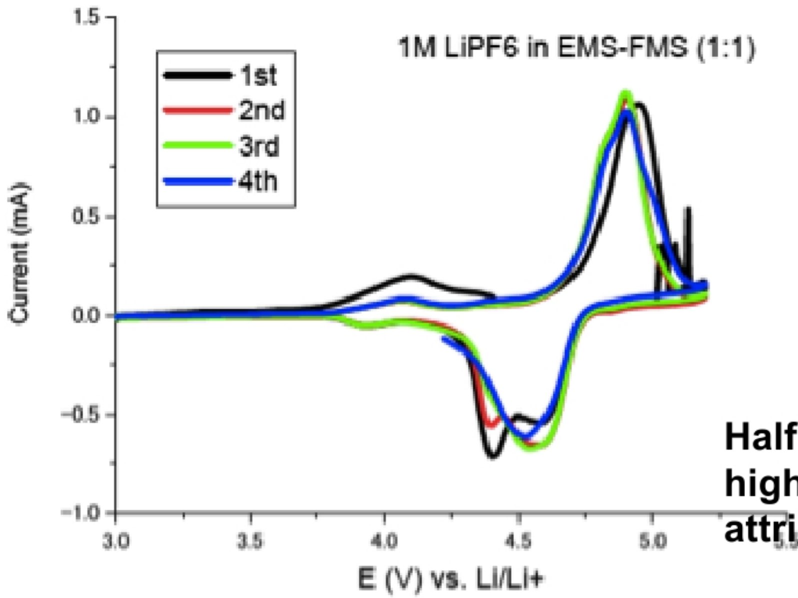


Figure a4. conductivities as per legend
Figure b5. oxidative stabilities
Figure c6. Lithium deposition and stripping at graphite electrode vs cycle

Here, some new sulfone + co-solvent mixtures, including MSF (fluoromethylsulfone) are evaluated for conductivity (part (a)), and oxidation stability (part (b) and finally for performance at the graphite anode (part (c)) - where the stability (after SEI formation in first cycle), is excellent. It remains to find the behavior at the highly oxidizing spinel cathode.

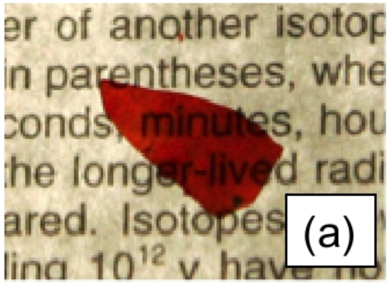
Accomplishment slide: evaluation of sulfone + small MSF sulfone co-solvent mixture for cathode compatibility

Although prior success of sulfolane at the Ni-Mn spinel cathode was expected, on the basis of studies of Amine and co-workers using sulfolane + DMC mixtures, results have been disappointing. Stability during charging above 5V is lacking . At first cathode preparation was suspected but further evaluation by post-doctoral coworker, K. Ueno, on return to Watanabe lab where better equipment is available, found side reactions to be just as serious as in the ASU laboratory. It is not clear whether this is due to the small sulfone co-solvent, or to deficient cathode fabrication skills. An elaborate hunt in “cosolvent space” can be successful we know (NDA), but is beyond our scope. Knowing of unsolved difficulties with side reactions in other labs, while at the same time hearing of success with solid electrolytes in still other labs, agreement has been sought to test out some novel single ion solid state electrolyte concepts. Highly favorable results have been obtained which are described within proprietary boundaries, below.



Half cell cyclic voltammogram at the Ni,Mn spinel high voltage cathode, showing irreversible behavior attributed to solvent side reactions.

Accomplishment slide: Success with nanoporous net separator technology and a serendipitous electrolyte discovery



After months of effort to prepare model reversibly self-assembling porous nets using hydrogen bonding strategies, this approach was abandoned, and immediate success obtained using a quite different covalent bond formation approach. A powder obtained by reacting bis-phenol A (epoxy-resin precursor) with a corner-linker has been manipulated to form the transparent film seen in adjacent **Figure (a).**

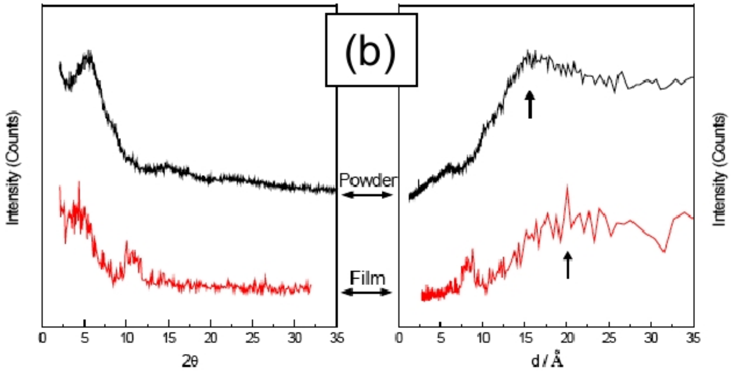


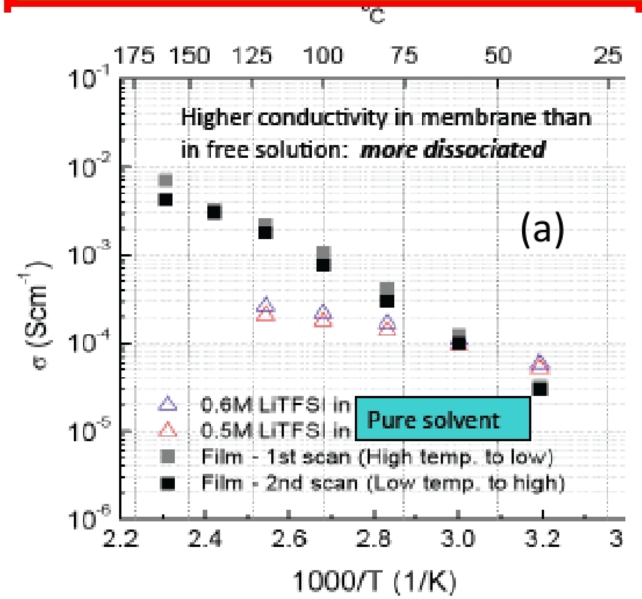
Figure (b). XRD patterns and their conversion to real space distributions. These establish that an open network, with ~15-20Å pores, has been obtained.

We have successfully prepared a second version using struts 3 times as long, which are of extremely low density, and should support both solution and ionic liquid electrolytes up to 200ºC.

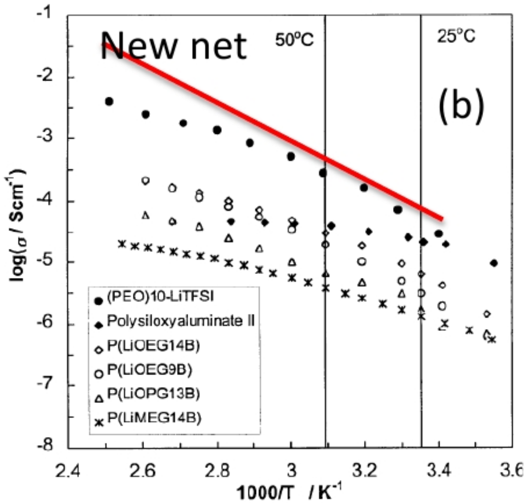
These membranes, in present form, are brittle, and means need to be found to toughen them.

A remarkable characteristic of these membranes, relevant to the dissociation of electrolytes, is seen in the next slide

Accomplishment slide: conductivity of ionic solutions contained in nanoporous net separator

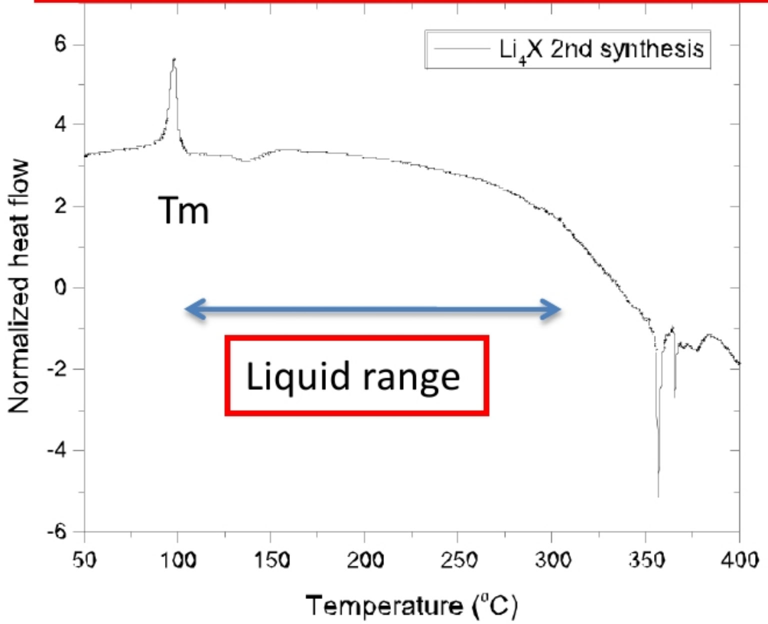


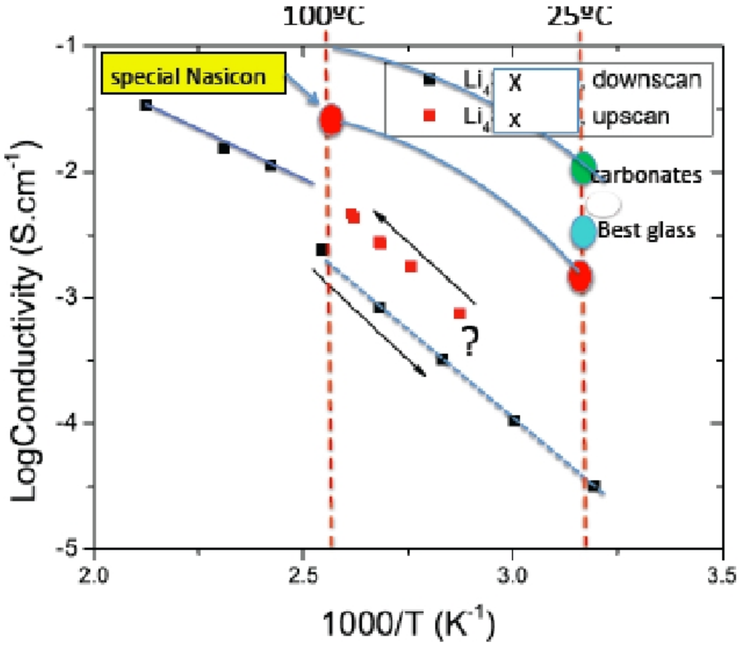
When a lithium salt, $LiNTf_2$, is included in the solvent and a film formed by removing solvent until the film becomes solid, the conductivity can be determined and compared with the value of the free solution. The solvent is poorly dissociating so the conductivity of the free solution is low, see Figure (a). Remarkably, the conductivity of the membrane is higher than the maximum conductivity in the free solution, ***evidently due to enhanced dissociation in nanoconfinement***, an unexpected and encouraging result.



Since the nets are currently too brittle, steps have been taken to make them more pliable. An initial attempt resulted in a rubbery material. When LiTFSI was included, a pliable solid material with conductivity equal to the best yet measured in viscous liquid PEO was obtained, Figure (b). The high T Arrhenius behavior is reminiscent of the solution results of the previous figure (a). A possible artifact due to membrane softening (hence cell constant decrease) at high temperature (unlikely in the first case but possible in the second) has not yet been excluded.

Accomplishment slide: conductivity of new inorganic ionic liquid (Tm < 100ºC) (Na$_n$X), believed to be an almost pure Li$^+$ conductor





This is the DSC heating trace of the first of a family of compounds that could be the forerunners of a field of inorganic ionic liquids, T_m < 100ºC, based on large, low charge density, anions. Results are recent and preliminary. All possible artifacts have not yet been excluded.

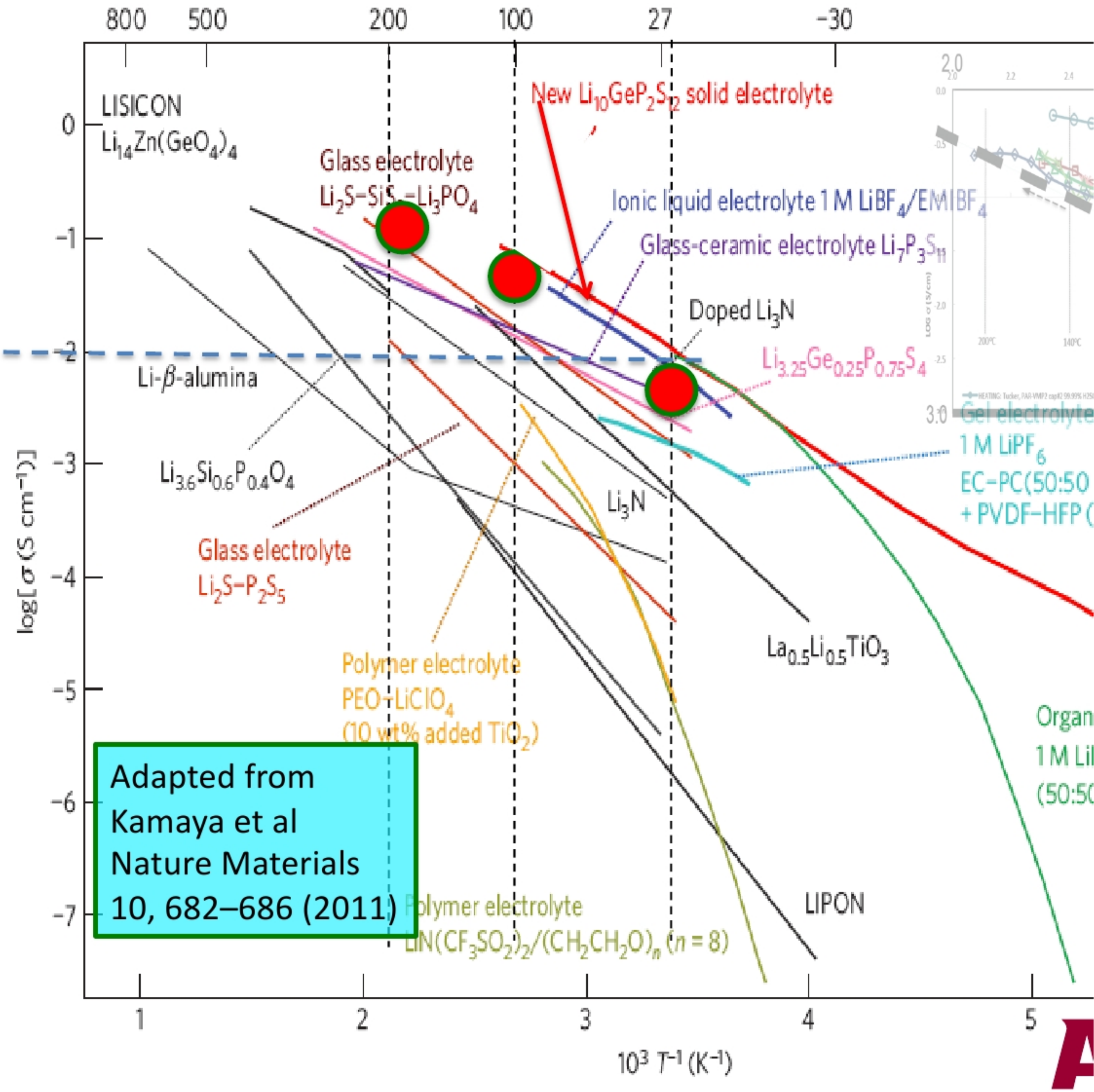
FUTURE WORK SLIDE

Compendium of Li electrolyte types on common scale, highlighting the new Lisicon (ref. Japan Nature Mater.) and (insert) showing how Na+ conductor (from recent work on another project) approaches the same activation energy.

First extensions of current work will be

(a) extend conductivity data to low T to find Lisicon-like low T performance

(b) Show that new Li analog has similar properties



Adapted from Kamaya et al Nature Materials 10, 682–686 (2011)

FUTURE WORK SLIDE

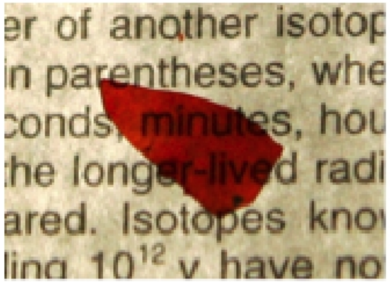
Novel ionic liquids and plastic crystals

The plastic crystal state of an ionically-conducting system offers a route to highly-conducting states of the system that lie at temperatures above the glass temperatures (for the liquid states of the same composition), while retaining a state that does not flow. When the conduction mechanism is by alkali ion motion decoupled from the relaxational states of the plastic crystal, the possibility for really high ionic conduction in solid states exists. Solid conductors that are single alkali ion conductors with dc conductivities above ~10 mS/cm would appear to have advantages over current electrolytes.

Such a state seems to be the one stumbled upon in the system shown in the reviewer-only slide of the sodium salt. We await a proper chemical and physical characterization of this and related systems before knowing whether there is a major exploration waiting to be undertaken in this area.

FUTURE WORK SLIDE

New nanoporous membranes



We will explore the mixing of rigid and flexible struts in our glass-rubbery **MOF** films. The objective will be to find those that are most interactive with the solution components and lead to enhanced solution conductivities, while maintaining adequate mechanical properties. There is a huge parameter field available here with all of strut length, strut flexibility, and strut dipole or basicity character, available for variation. And the field can be extended further by mixing three-fold and four-fold linkers.