Electrolytes and separators for high voltage Li ion cells

(Initially, an investigation of sulfone-based electrolyte solvents)

C. Austen Angell

**Department of Chemistry and Biochemistry,
Arizona State University**

March 12, 2012

Project ID: ES100

Overview

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

Budget:
$709,977
Funding received in FY 2010
for 2010 - 2012
$479,977
Funding for FY 2013
$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

Objectives and Milestones

OBJECTIVES: To devise new electrolyte types (sulfone mixtures and superionic glasses or plastic solid derivatives) that will permit cell operation at high voltages without solvent oxidation and with adequate overcharge protection, and to provide optimized nanoporous supporting membranes for this electrolyte.

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. April, 12)

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

(d) Test and compare glass and glass-stuffed polymer electrolyte types in cells by June, 12.

(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).

(f) Develop covalent-bonded equivalents of the self-assembling nets by July, 12.

Relevance and progress summary: Urgent need for electrolytes for 5V spinel type cathodes; new interest in sodium ion conductors

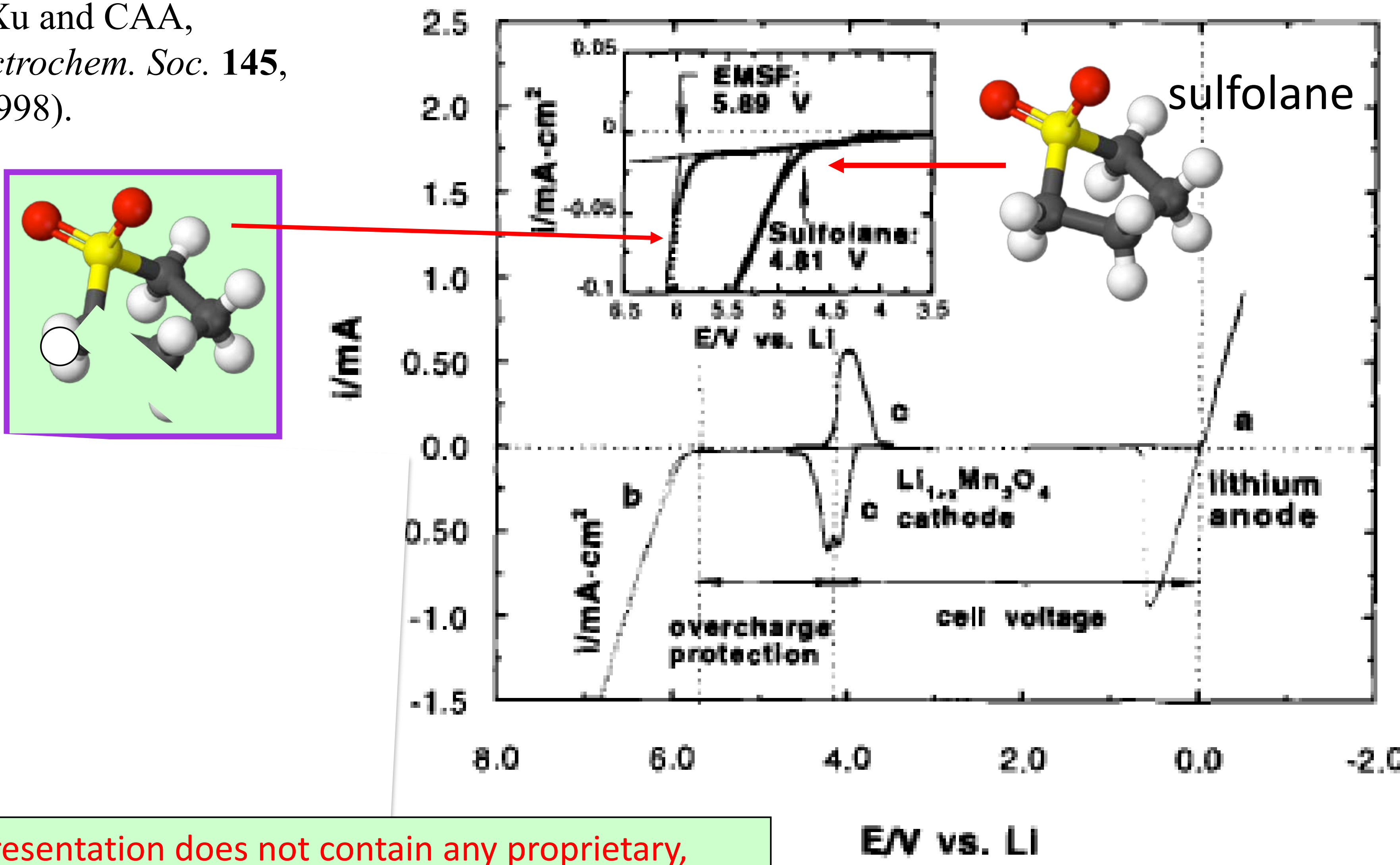
- Sulfone-based electrolytes seen as good prospects for resisting highly oxidizing cathodes.
- Work to lower melting points, increase fluidity supported. Fluorination and some mixed solvent studies reported 2010.
- All-sulfone solutions reported and ionicity analyzed, 2011
- test success in anode half cells but failed in cathode half cells, 2011.
- Arguments for solid electrolytes to avoid side reactions, supported
- Novel class of solid electrolytes developedt, patentted 2012.

- novel nanoporous support materials developed and found to enhance ionicity 2012. Tetrahedral network rubbers promising
- analogs of sodium-conducting ceramics by "chemical stretching" under evaluation..

BACKGROUND SLIDE

STARTING POINT:
A 5.9 volt window with asymmetric acyclic SULFONE !

Kang Xu and CAA,
J. Electrochem. Soc. **145**, L70 (1998).



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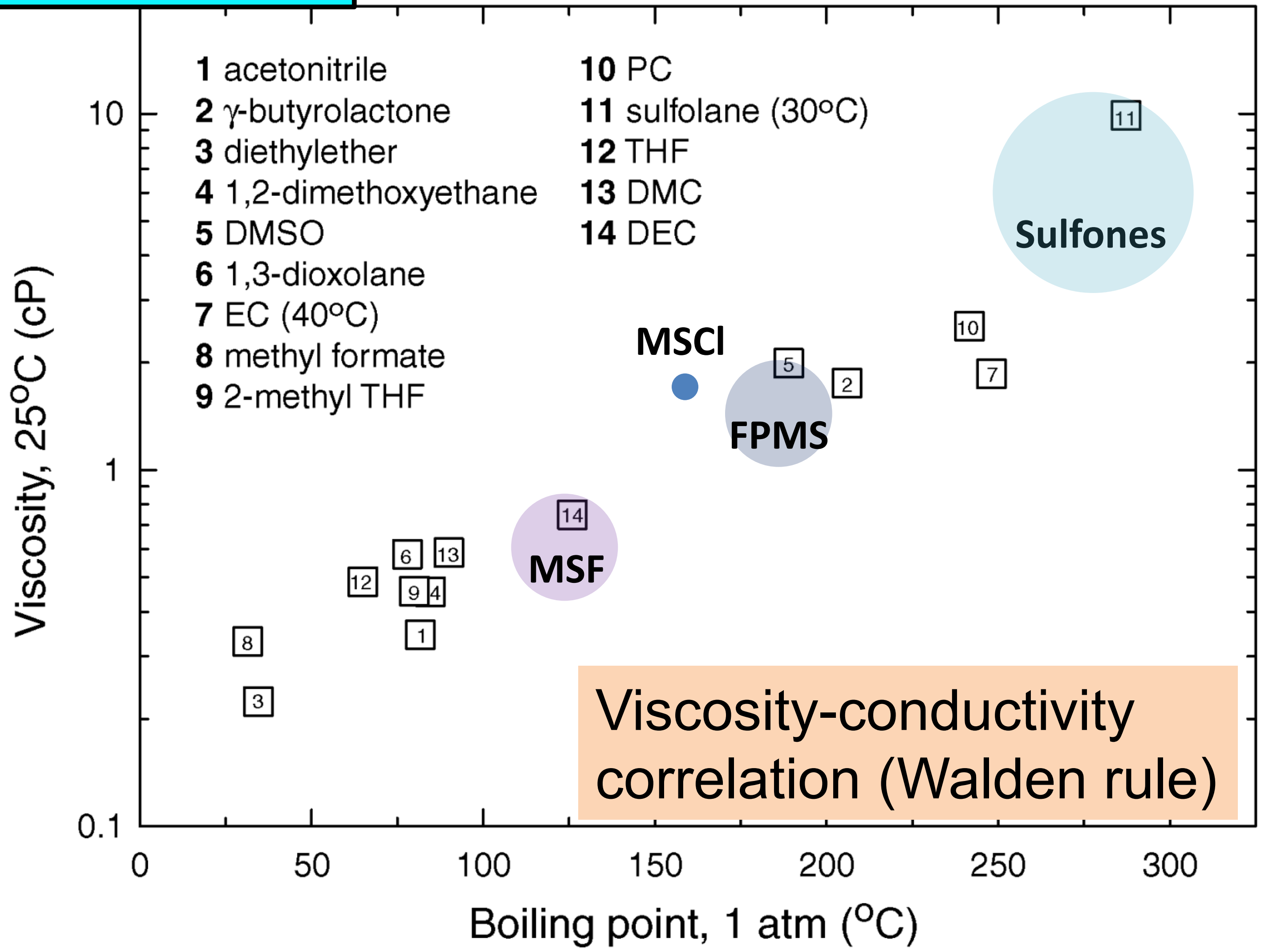
Selection **strategies**: When no viscosity data? boiling point correlation

BACKGROUND S LIDE



Viscosity-conductivity correlation (Walden rule)

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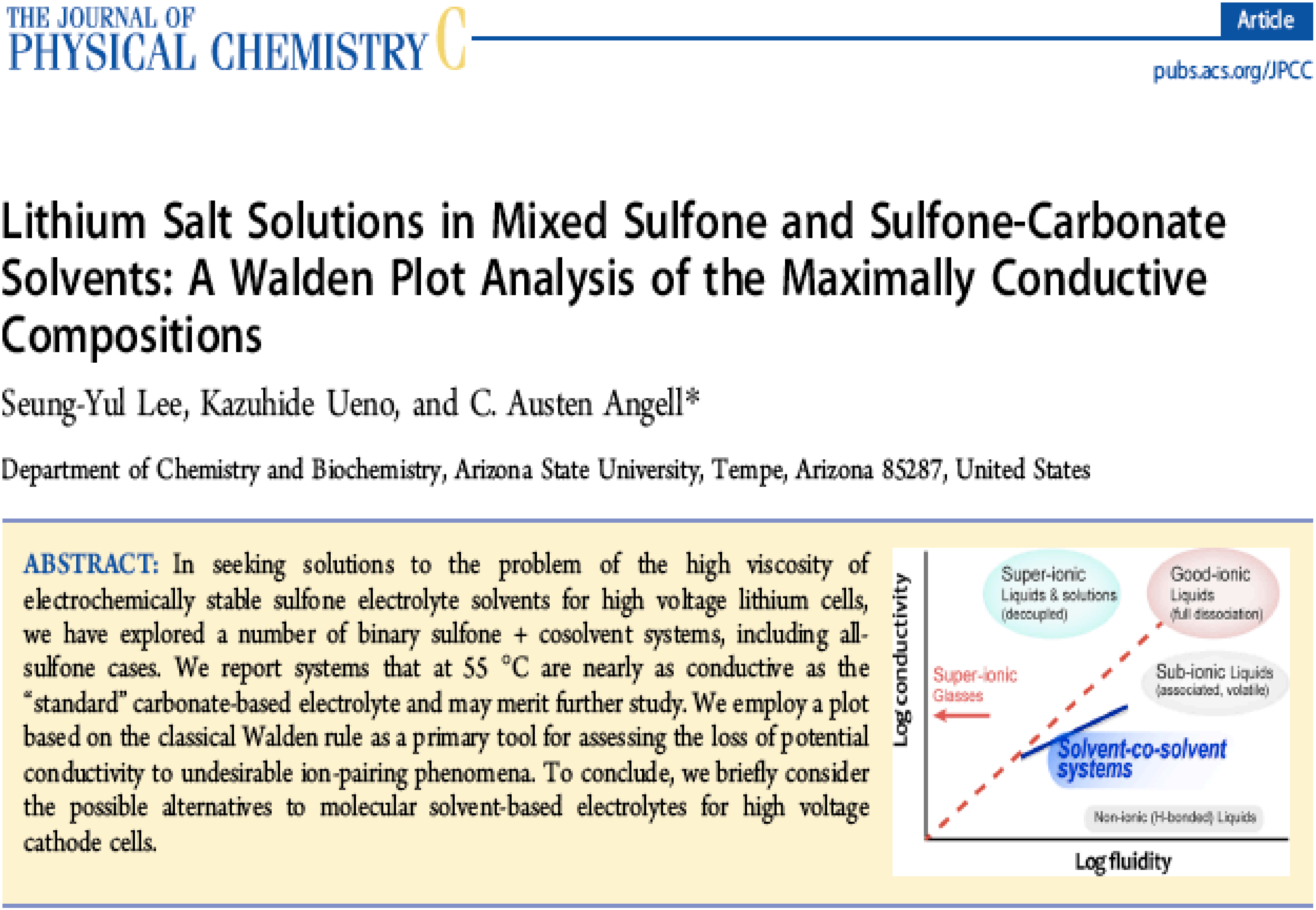

THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

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Lithium Salt Solutions in Mixed Sulfone and Sulfone-Carbonate Solvents: A Walden Plot Analysis of the Maximally Conductive Compositions

Seung-Yul Lee, Kazuhide Ueno, and C. Austen Angell*

Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287, United States

ABSTRACT: In seeking solutions to the problem of the high viscosity of electrochemically stable sulfone electrolyte solvents for high voltage lithium cells, we have explored a number of binary sulfone + cosolvent systems, including all-sulfone cases. We report systems that at 55 °C are nearly as conductive as the "standard" carbonate-based electrolyte and may merit further study. We employ a plot based on the classical Walden rule as a primary tool for assessing the loss of potential conductivity to undesirable ion-pairing phenomena. To conclude, we briefly consider the possible alternatives to molecular solvent-based electrolytes for high voltage cathode cells.

Walden plot evaluations of electrolytes

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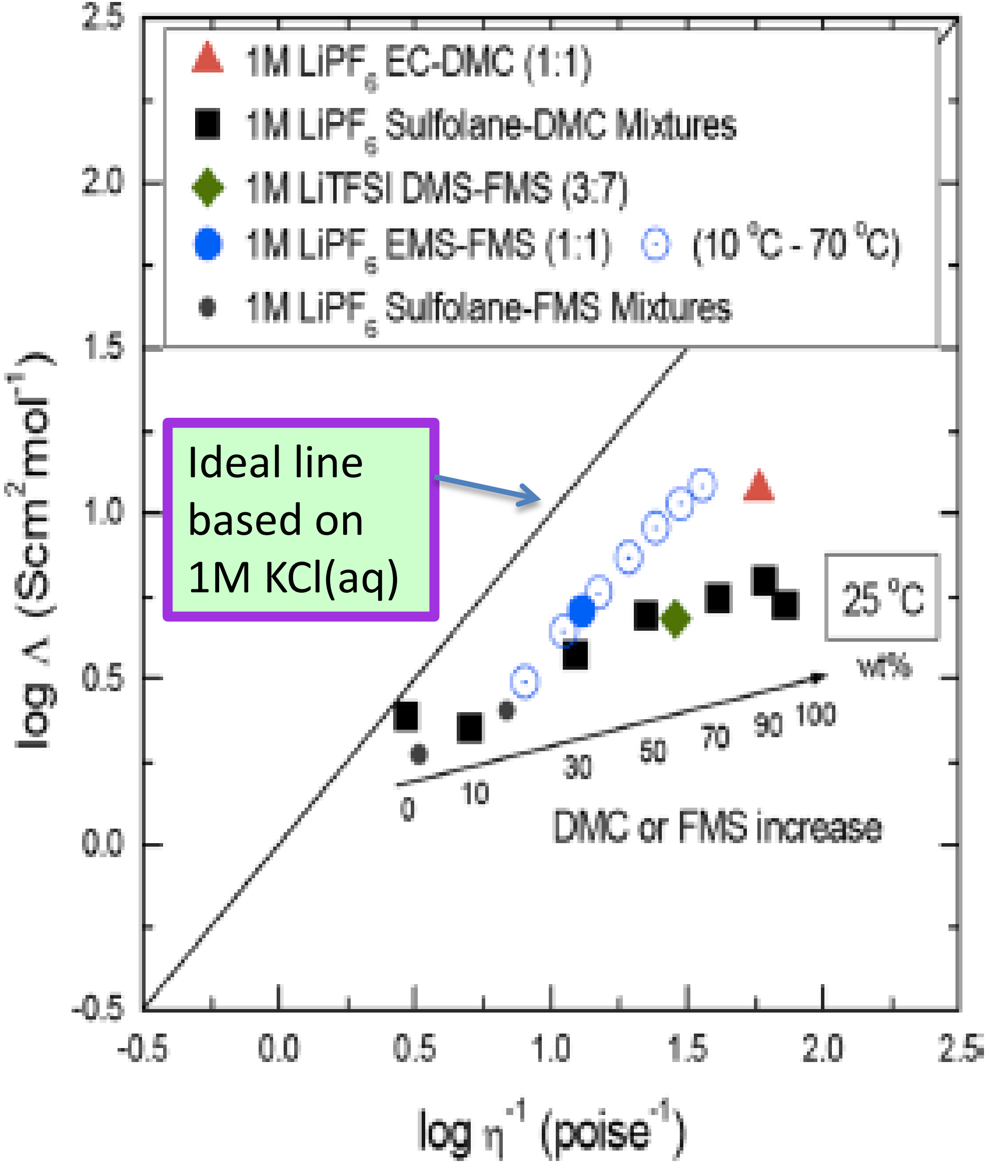
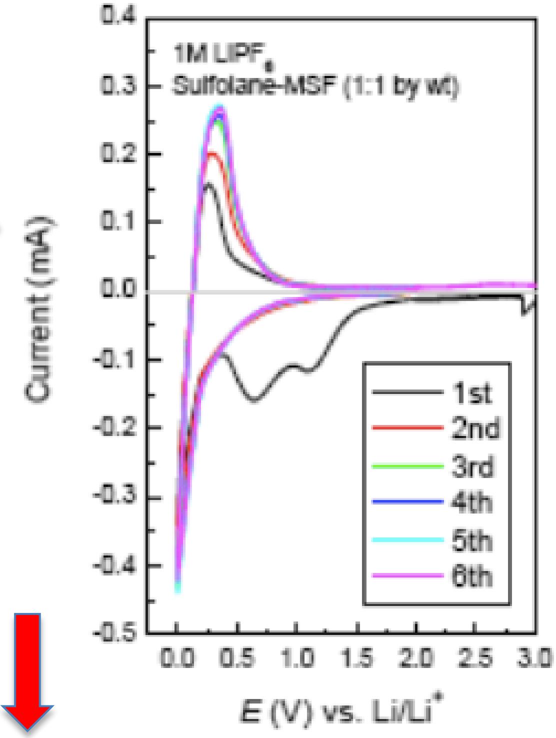


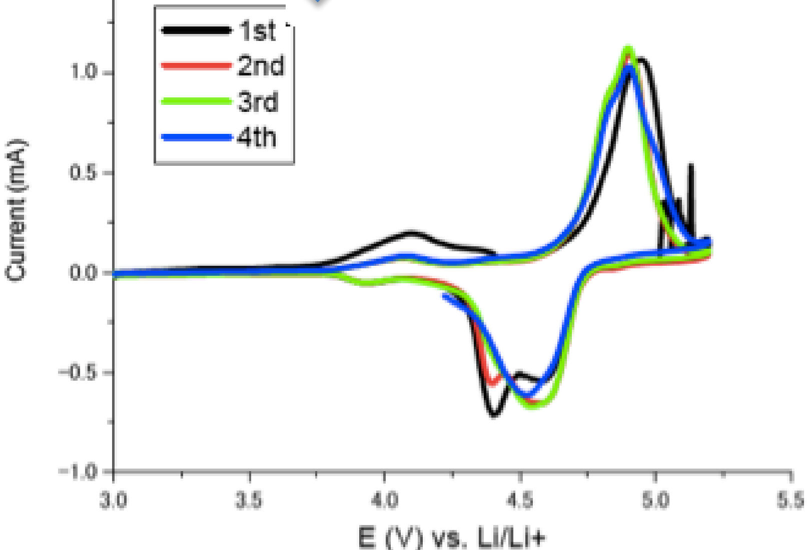
Ideal line based on 1M KCl(aq)

Anode half cell tests good

but

Cathode tests not good,



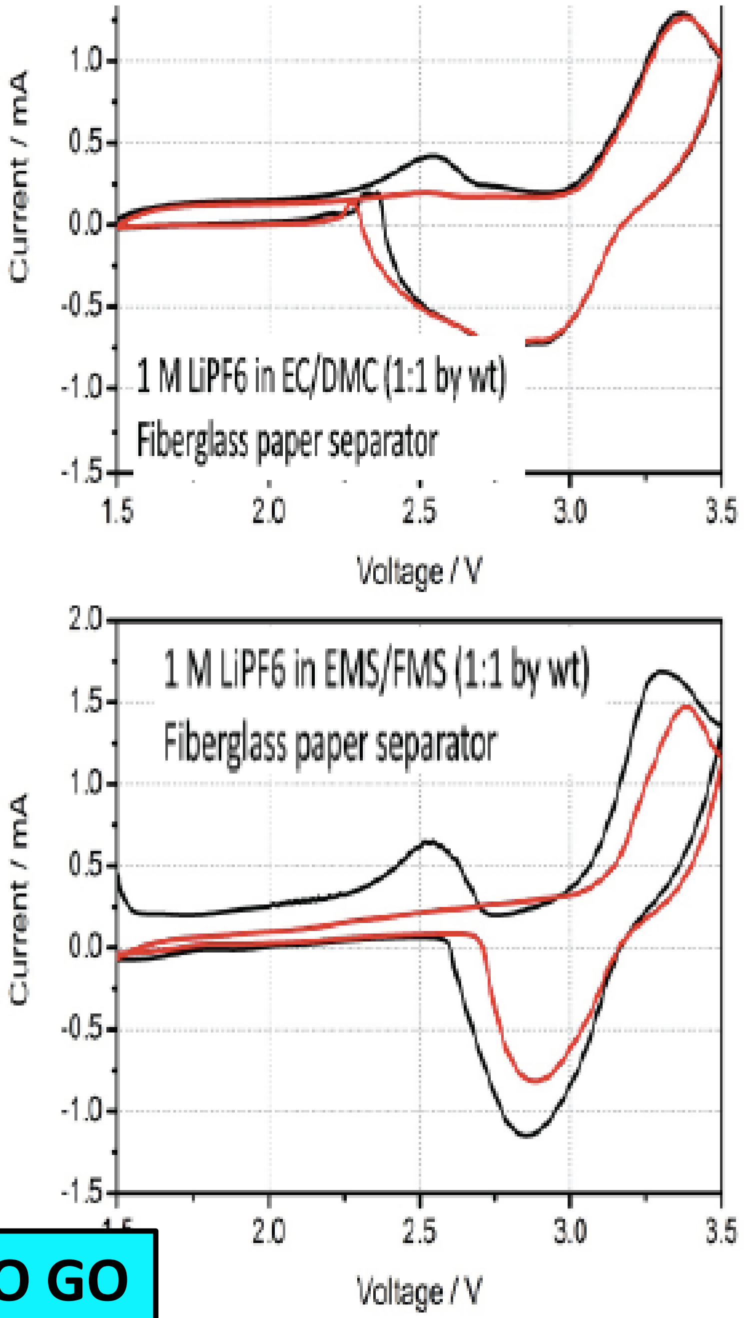


ACCOMPLISHMENT SLIDE

New testing using the LBL cathodes: whole cell LTO-LMNO with all-carbonate vs all-sulfone electrolytes

There is rapid capacity fade with the sulfones. Only course left is via additives for SEI formation, an Eddisonian challenge (not for us). New approach needed.

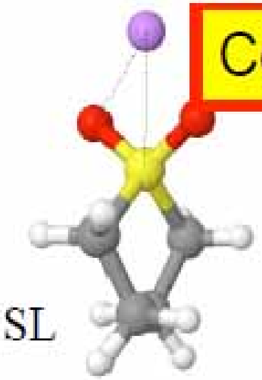
$Li_4Ti_5O_{12}$ ‖ electrolyte, separator ‖ $LiNi_{0.5}Mn_{1.5}O_4$

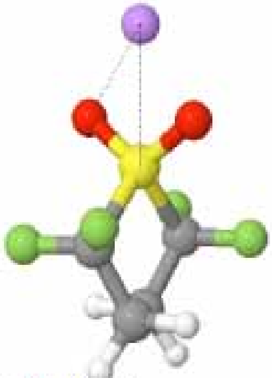


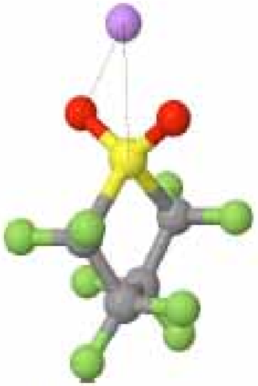
Go/No Go……….NO GO

Contribution from Collaborating laboratory- **Oleg Borodin**

Fluorinated Solvents


SL


$SL(F_4)$


$SL(F_8)$

★ **Influence of sulfolane fluorination on the solvent oxidative stability, transport properties and its ability to coordinate Li^+ has been investigated complementing experimental studies that are currently performed by Austen Angell group (ASU)**

The Li^+/solvent binding energy (in kcal/mol) from QC					
	Li^+/SL	$Li^+/SL(F_4)$	$Li^+/SL(F_8)$	Li^+/EC	Li^+/DMC
MP2/cc-pvTz or ***MP2/aug-cc-pvTz***	-52.7	-40.8	-29.5	***-47.5***	***-40.9***
Solvent self-diffusion coefficient					
T (K)	303	303	303	313	298
D (10^{-10} m^2/s)	1.1	2.5	4.7	8	25.4

★ **Completely fluorinated $SL(F_8)$ is not expected to be good solvent for typical Li salts such as $LiPF_6$ or LiTFSI.**

★ **Semifluorinated sulfolane $SL(F_4)$ is expected to have lithium salt dissociation similar to DMC, while $SL(F_4)$ dynamics is predicted to be a factor of 2.5 faster than SL but a factor of five slower than DMC.**

OTHER COLLABORATIONS: The order-disorder transition in $LiNi_xMn_{2-x}O_4$ (with **Guoying Chen**, LBL)

BACKGROUND SLIDE

Side reactions of the high voltage cathode

Title: LiNi0.4Mn1.6O4/Electrolyte and Carbon Black/Electrolyte High Voltage Interfaces: To Evidence the Chemical and Electronic Contributions of the Solvent on the Cathode-Electrolyte Interface Formation

Author(s): Demeaux, Julien; Caillon-Caravanier, Magaly; Galiano, Herve; et al.

Source: JOURNAL OF THE ELECTROCHEMICAL SOCIETY Volume: 159 Issue: 11 Pages: A1880-A1890 DOI: 10.1149/2.052211jes Published: 2012

Times Cited: 0 (from Web of Science)

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[Hide the abstractHide abstract]

Solvent and lithium salt decomposition products on LiNixMnyO4-type electrodes are known to be ROM, ROCO2M (M = Li, Ni, Mn), LiF, LixPFyOz, polycarbonates and polyethers. These compounds are chemically formed due to the high nucleophilic character of spinel oxide and LiPF6 decomposition. The high potentials (> 4.7 V vs. Li/Li+) may cause EC and PC polymerization, while DMC forms oligomers. The use of carbon black-based electrodes highlights electronic and, surprisingly, chemical contributions to the cathode-electrolyte interface. A comparison between EC/DMC (1:1 in weight) 1 M LiPF6 and PC/DMC (1:1 in weight) 1 M LiPF6 electrolytes for Li/carbon black-PVdF cells demonstrated a superior ability of the EC/DMC solution to form a well-covering passivation film via faradaic reactions thanks to a higher stability toward oxidation. Electrochemical cycling in Li/LiNi0.4Mn1.6O4 cells confirms this EC/DMC superiority when it comes to forming passivation films, in turn leading to reduced capacity losses and a higher Columbic efficiency. (C) 2012 The Electrochemical Society. [DOI:

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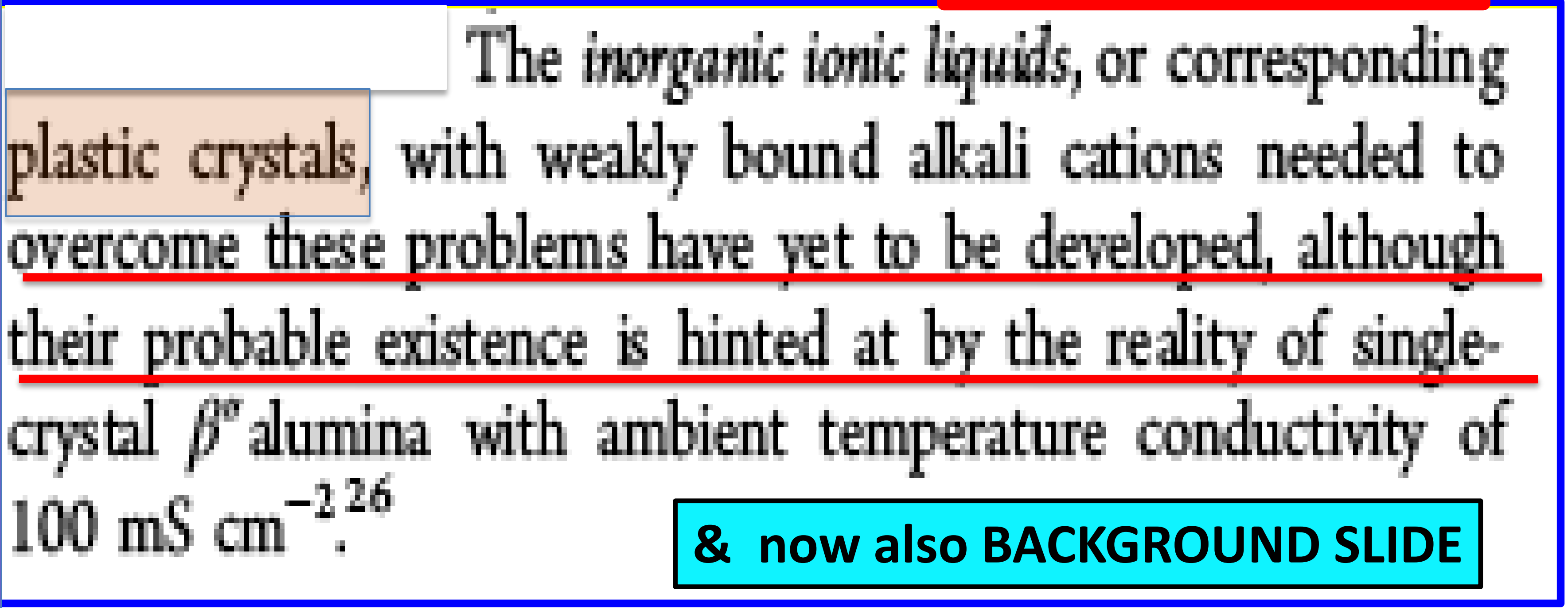
ACCOMPLISHMENT SLIDE

Lithium Salt Solutions in Mixed Sulfone and Sulfone-Carbonate Solvents: A Walden Plot Analysis of the Maximally Conductive Compositions

Seung-Yul Lee, Kazuhide Ueno, and C. Austen Angell*

Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizo

Concluding discussion



The *inorganic ionic liquids*, or corresponding plastic crystals, with weakly bound alkali cations needed to overcome these problems have yet to be developed, although their probable existence is hinted at by the reality of single-crystal β'' alumina with ambient temperature conductivity of 100 mS cm^{-2}.[26]

& now also BACKGROUND SLIDE

Well, we are hoping we may have done it

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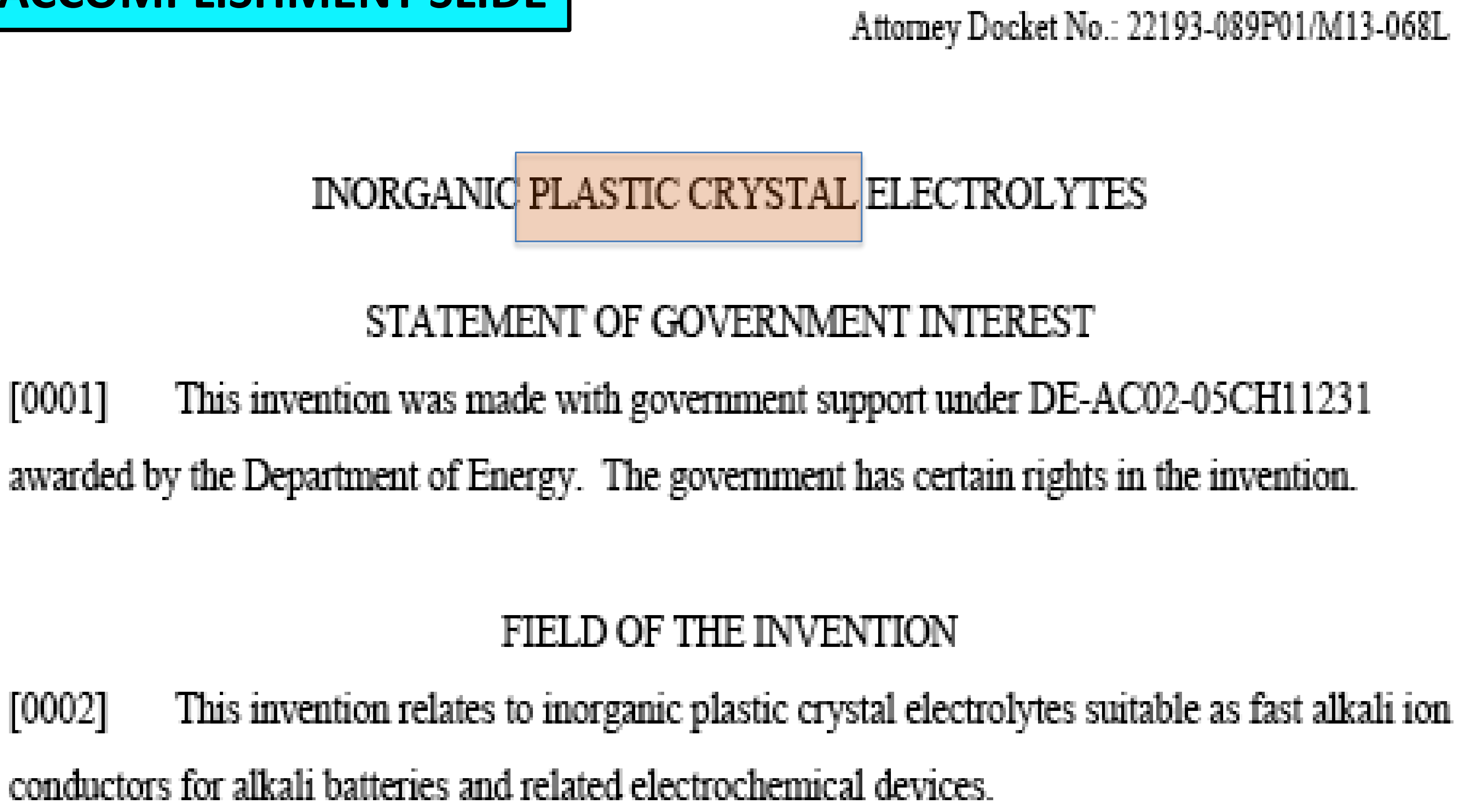


Attorney Docket No.: 22193-089P01/M13-068L

INORGANIC PLASTIC CRYSTAL ELECTROLYTES

STATEMENT OF GOVERNMENT INTEREST

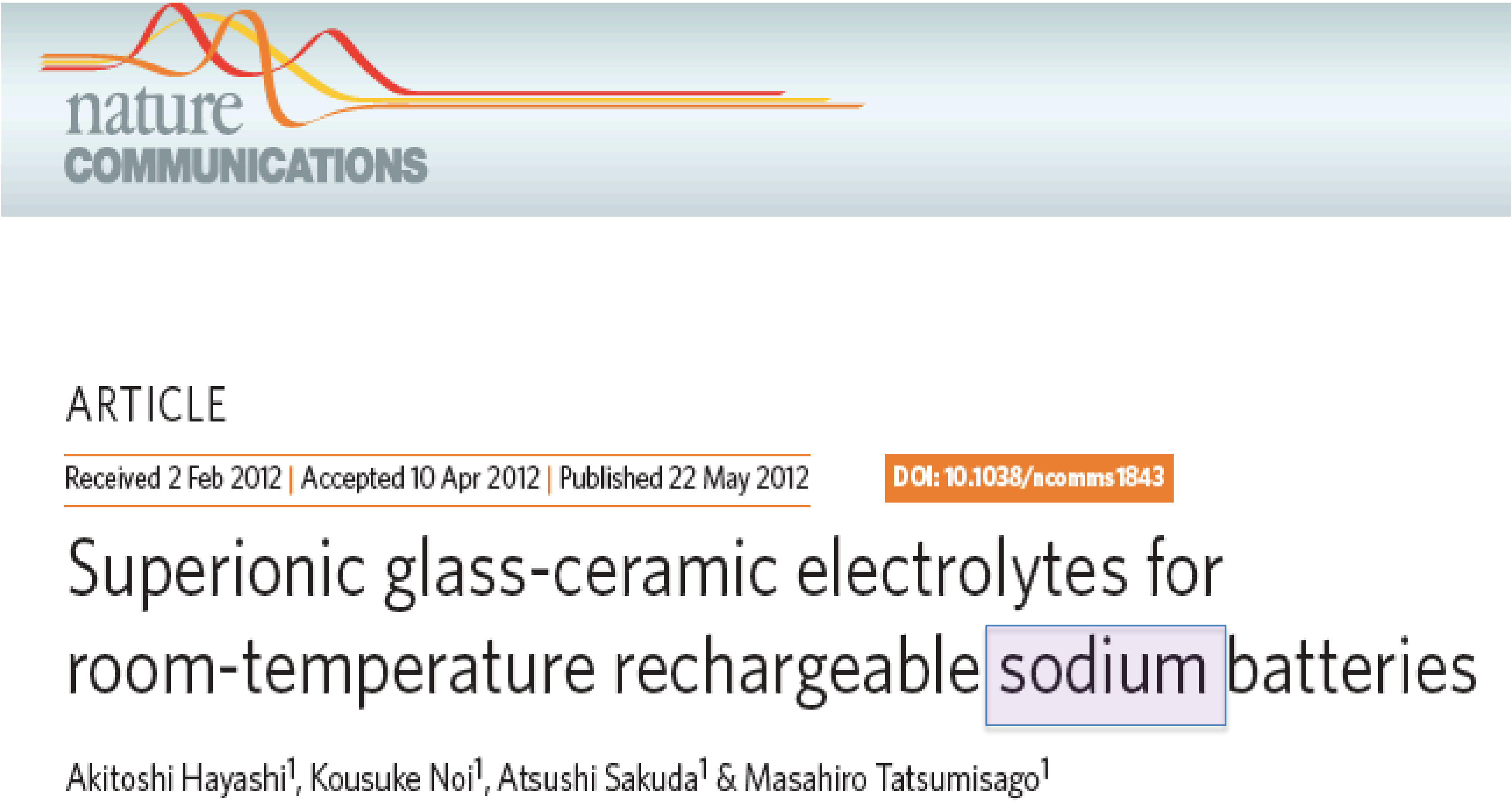
[0001] This invention was made with government support under DE-AC02-05CH11231 awarded by the Department of Energy. The government has certain rights in the invention.

FIELD OF THE INVENTION

[0002] This invention relates to inorganic plastic crystal electrolytes suitable as fast alkali ion conductors for alkali batteries and related electrochemical devices.

BACKGROUND SLIDE

What do we already know about solid state conductors for batteries?



nature COMMUNICATIONS

ARTICLE

Received 2 Feb 2012 | Accepted 10 Apr 2012 | Published 22 May 2012

DOI: 10.1038/ncomms1843

Superionic glass-ceramic electrolytes for room-temperature rechargeable sodium batteries

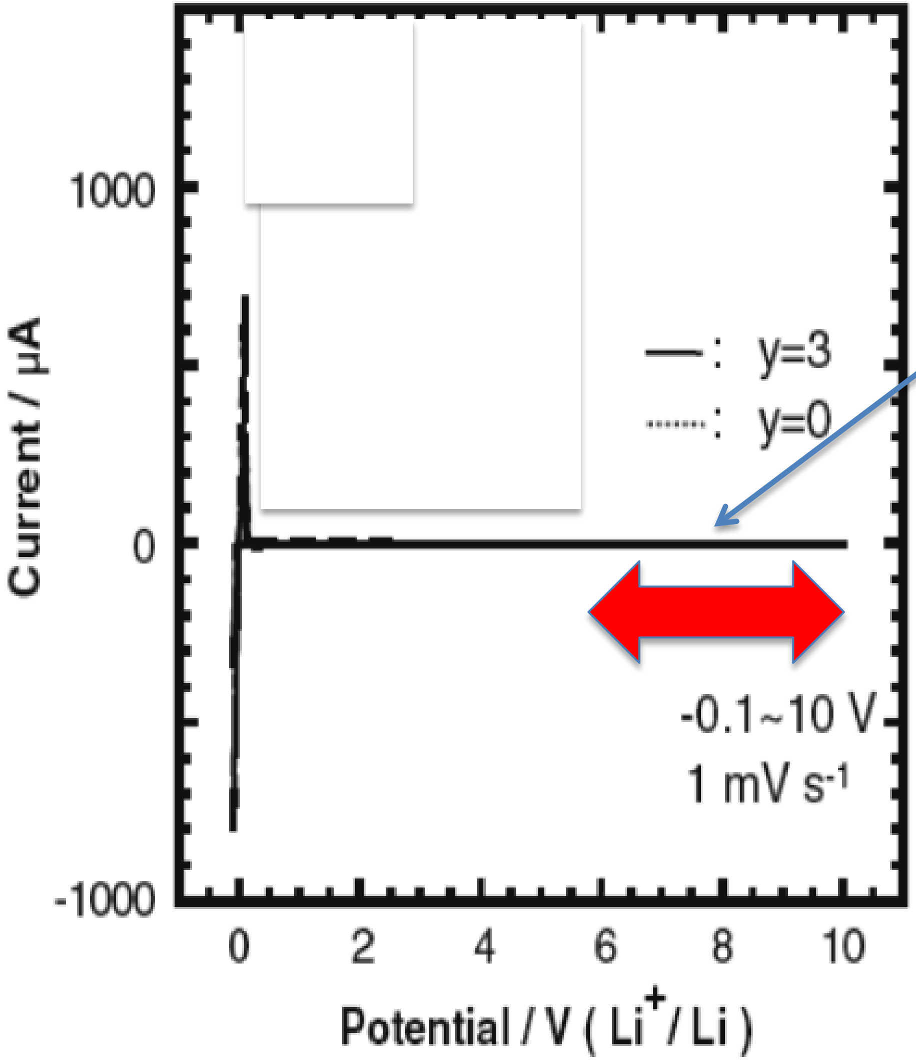
Akitoshi Hayashi[1], Kousuke Noi[1], Atsushi Sakuda[1] & Masahiro Tatsumisago[1]

BACKGROUND SLIDE

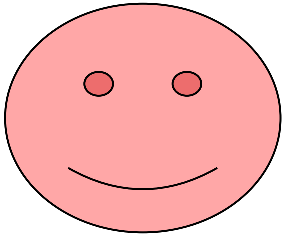
Hayashi et al Nature Communications(2011)

Sodium ion conducting **glass** CV to 10V

$70Li_2S\cdot(30-y)P_2S_5\cdot yP_2O_5$ (y=0 - 3)



No high voltage oxidation current: only sodium ions move: ergo no side reactions



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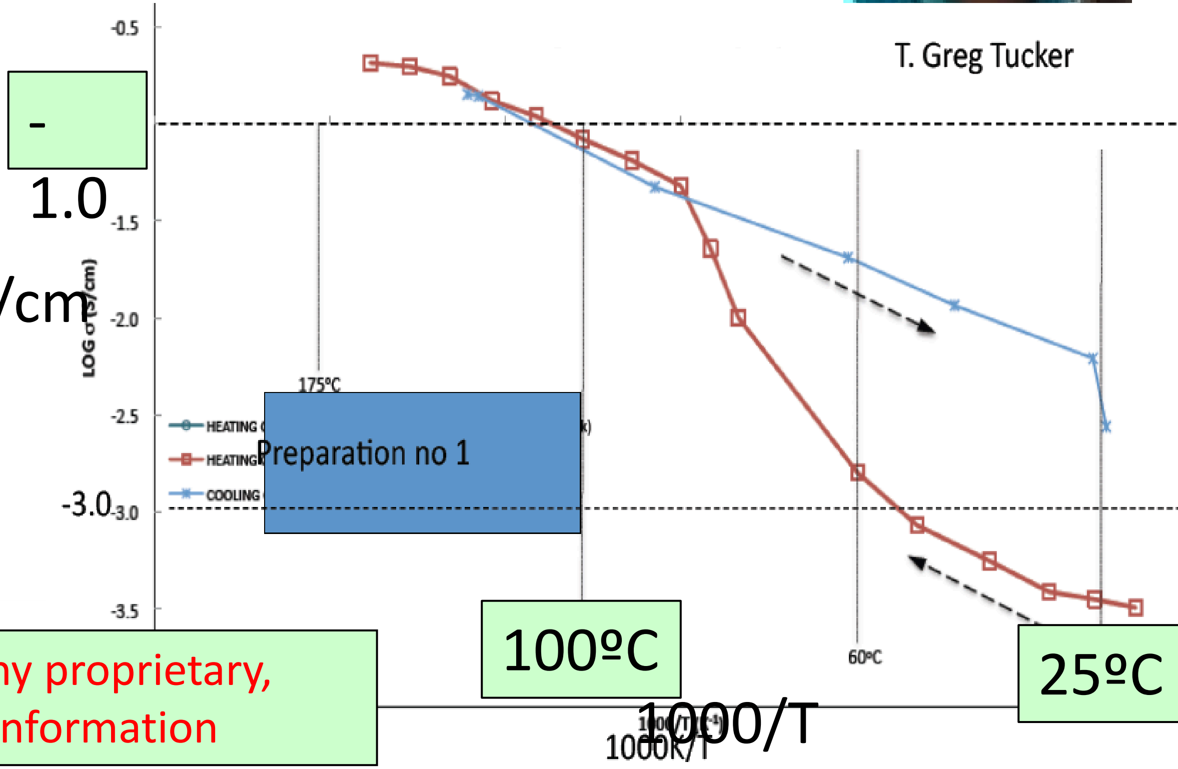
New Class of alkali-conducting Electrolytes

BACKGROUND SLIDE

Student Iolanda Klein

Credit also to Tel G. Tucker, who first saw suggestions of these phases in the case of sodium ion conductors, and is listed as a co-inventor on the submitted provisional patent.

T. Greg Tucker



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What is claimed is

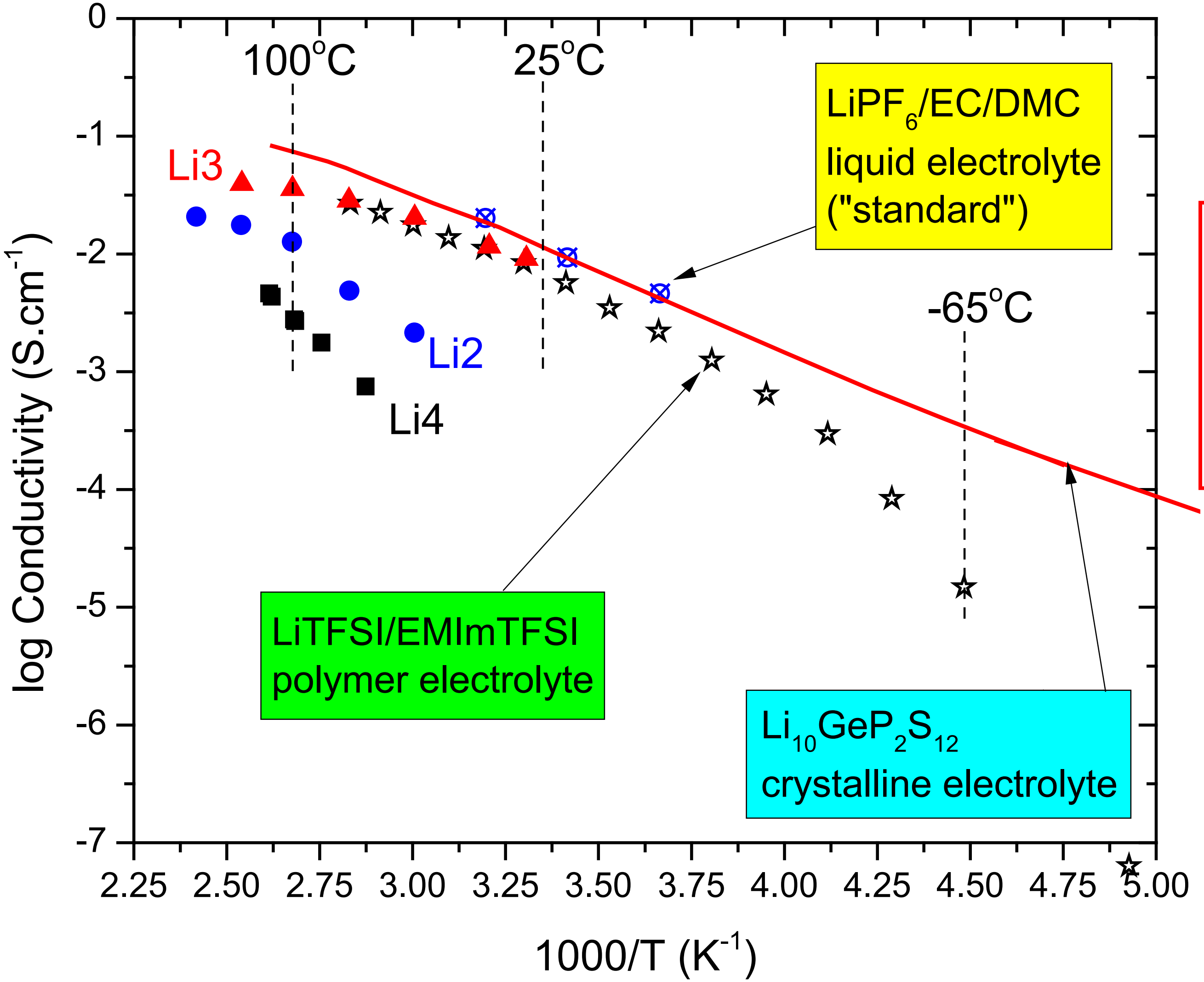
1. A composition comprising $[AB_{x\text{-}y}C_y]^{y-}[M]_y^{+}$, wherein:
   A is a tetravalent to hexavalent atom,
   B is a monovalent ligand,
   C is an oxyanion,
   M is an alkali metal,
   x is an integer from 4 to 6 inclusive,
   y is an integer from 1 to 5 inclusive, and
   $[AB_{x\text{-}y}C_y]^{y-}[M]_y^{+}$ is rotationally disordered and electrically conductive.

2. The composition of claim 1, wherein A is selected from groups 14 to 16 in the periodic table.

3. The composition of claim 2, wherein A is carbon, silicon, or phosphorus.

ACCOMPLISHMENT SLIDE

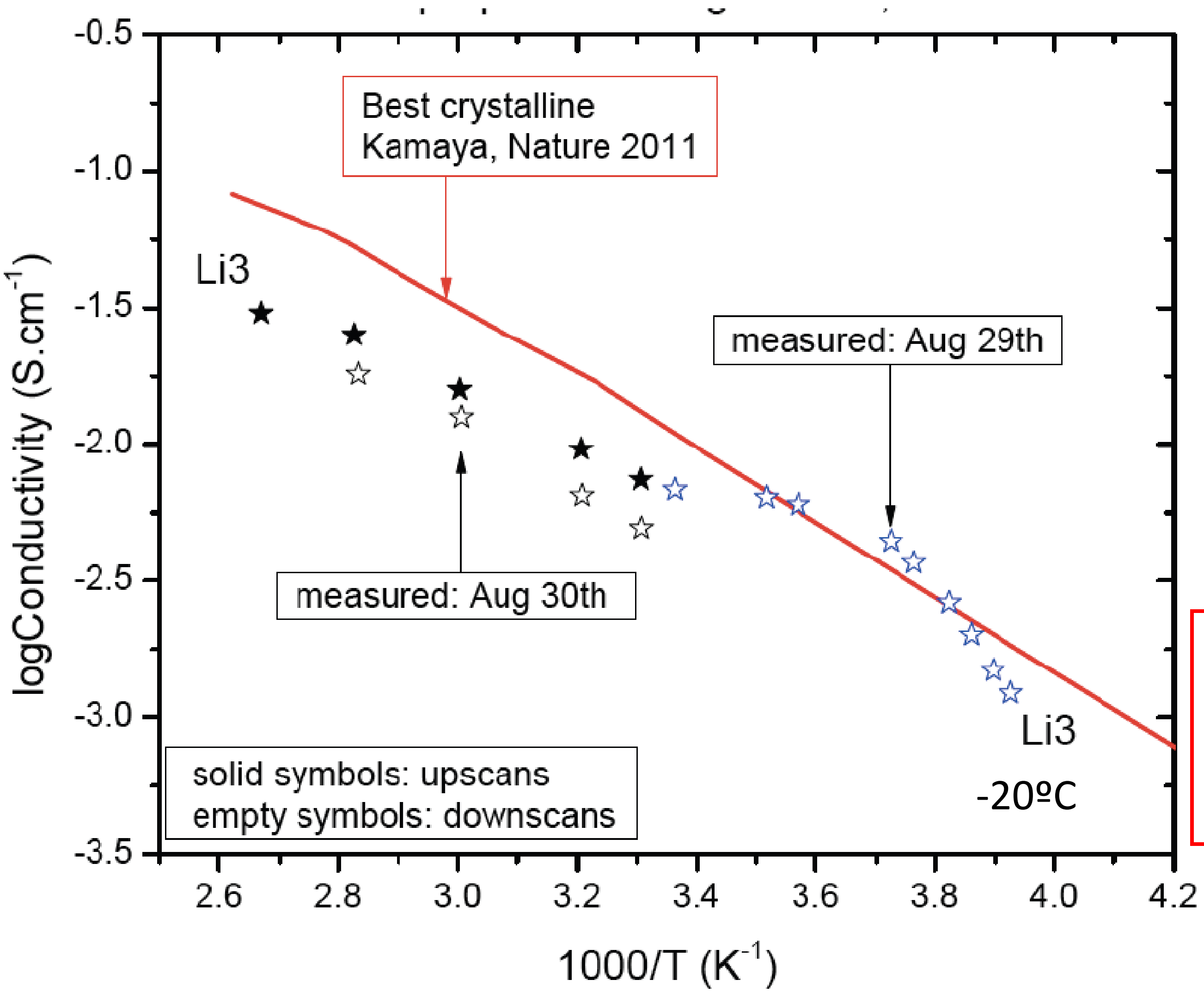
Conductivity of Li2, Li3 and Li4 preps relative to literature electrolytes



Li3, solid state, is as good as a liquid electrolyte! And is single alkali metal ion conductor

AcCCOMPLISHMENT SLIDE

At low temperature, and vs. the best crystalline material to this date



Best crystalline
Kamaya, Nature 2011

measured: Aug 29th

measured: Aug 30th

solid symbols: upscans
empty symbols: downscans

Low temp studies need repetition with a different cell to maintain electrode contact

Looking good, but what about stability over time, and with temperature cycling…

To retain the electrolyte in the high conducting state..?

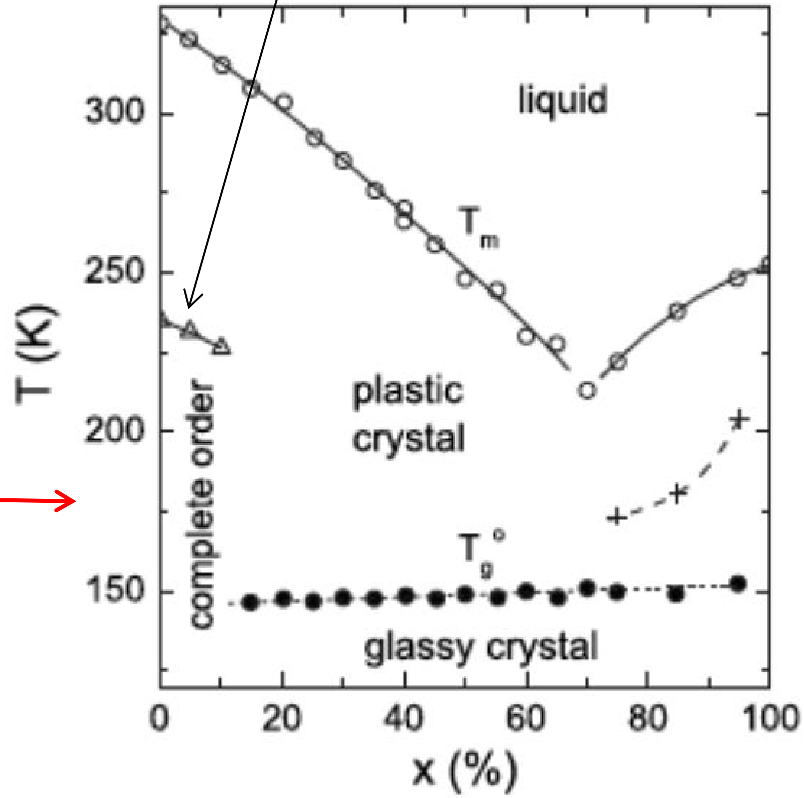
Mix it with a second component .

Prior knowledge available

Idea: the introduction of a second component lowers the transition temperature, trapping the mixture in the disordered state

Obvious candidate, …

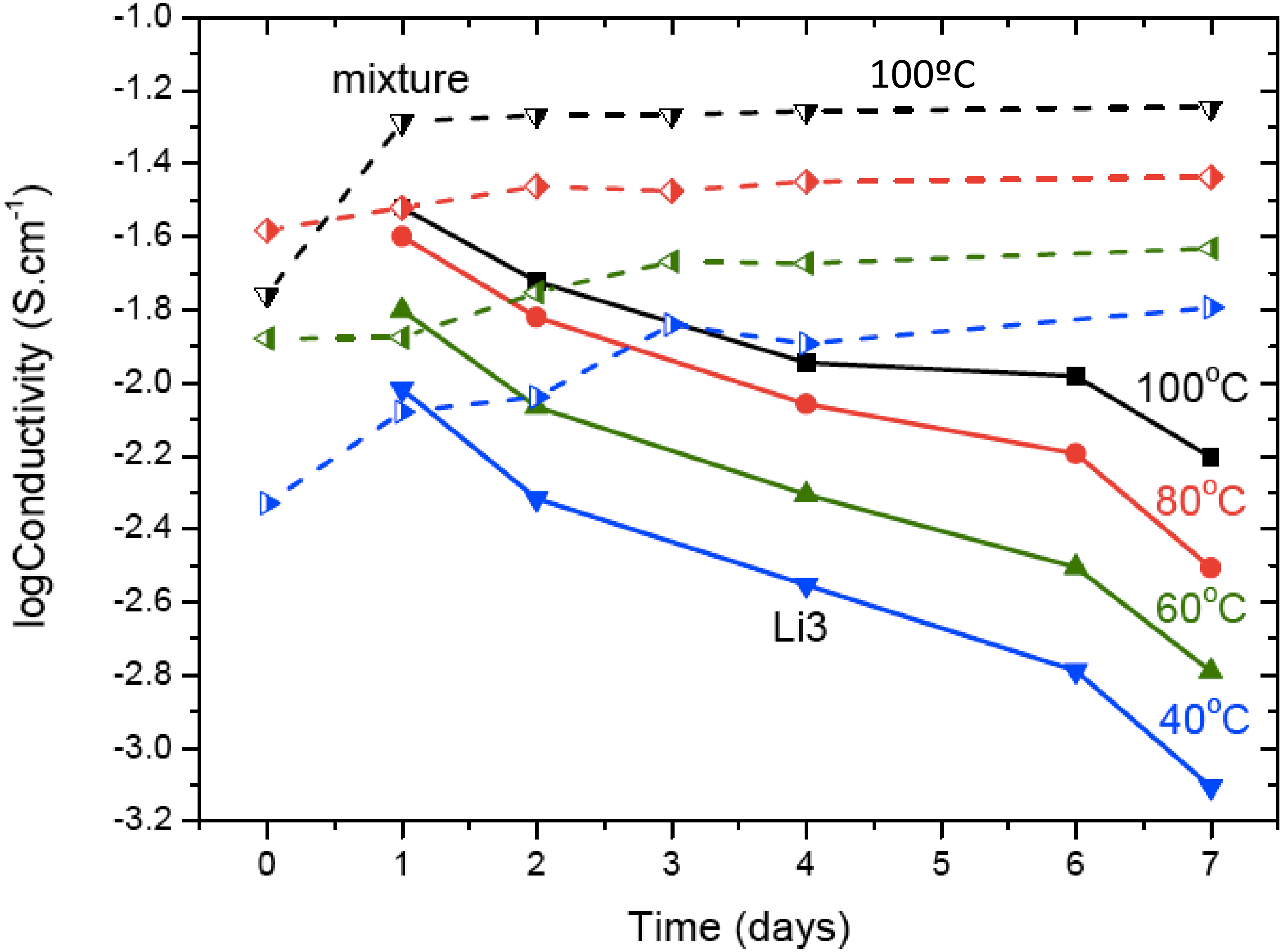
…Li2, a very good solid state electrolyte (but not as impressive as Li3)



Succinonitrile ordering transition

ACCOMPLISHMENT SLIDE

New data on mixtures. Stabilized in high conducting state !



So, Now we have

(1) Conductivity as good as for most LIQUID ELEClytes

(2) Conductivity by a single species, as in the glass (no organics… no possibility for side reactions)

(3) Conductivity in the solid state
    (a) all inorganic
    (b) inoxidizable, non-flammable
    (c) cheap

(4) An electrolyte that can't dissolve, or can't transport
    Mn^{2+} or Ni^{2+}

From Objectives:

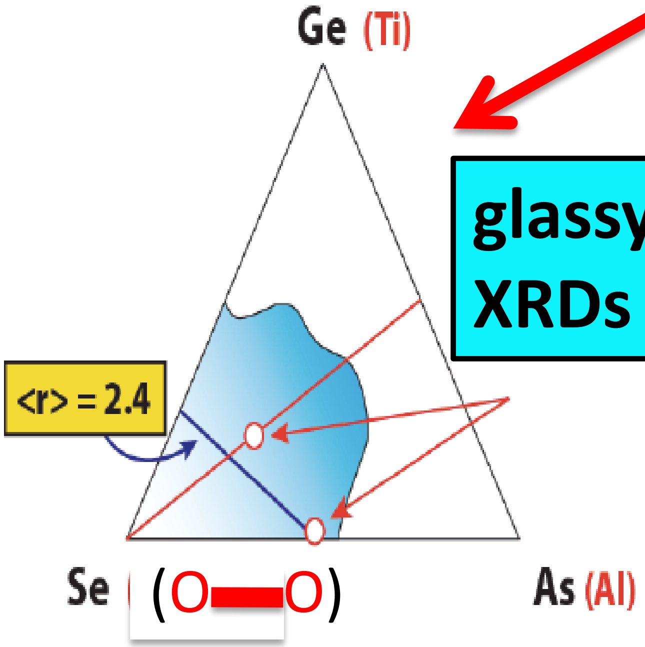
”and to provide optimized nanoporous supporting membranes for this electrolyte”.

BACKGROUND SLIDE AND ACCOMPLISHMENT SLIDE

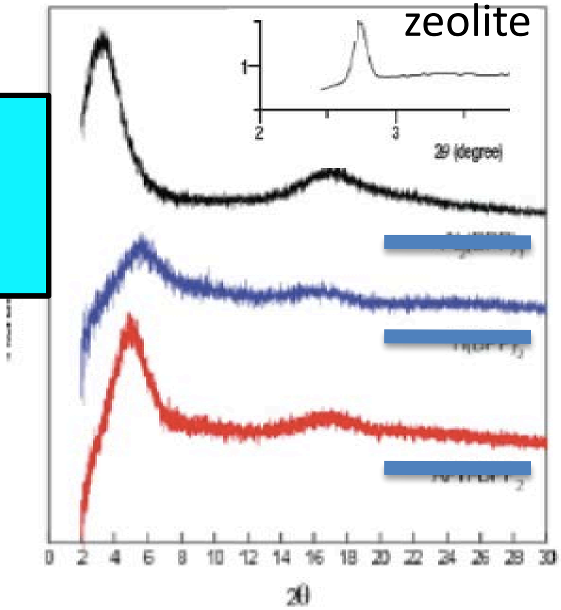
Strategy to make nanoporous supports (g-MOFs)

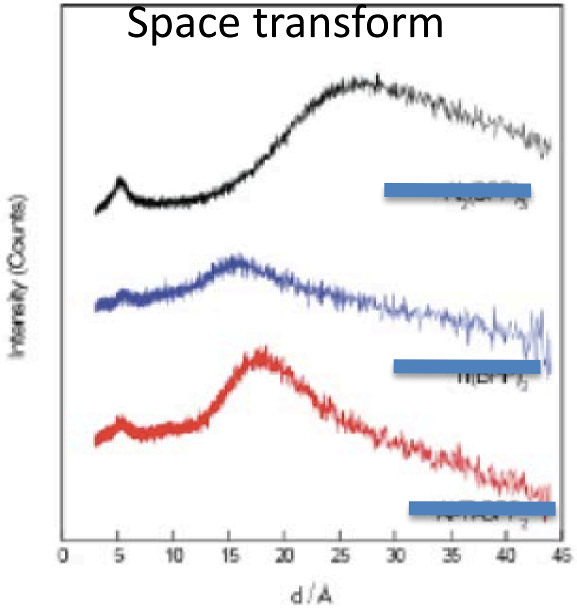
We apply the same constraint theory principles (Phillips) used to find stable chalcogenide glasses (Ge-As-Se) but increase the length of the divalent linker (-Se-) by putting the two bonds separately at the end of a chemical slat.

This forces empty spaces into the net.



glassy XRDs





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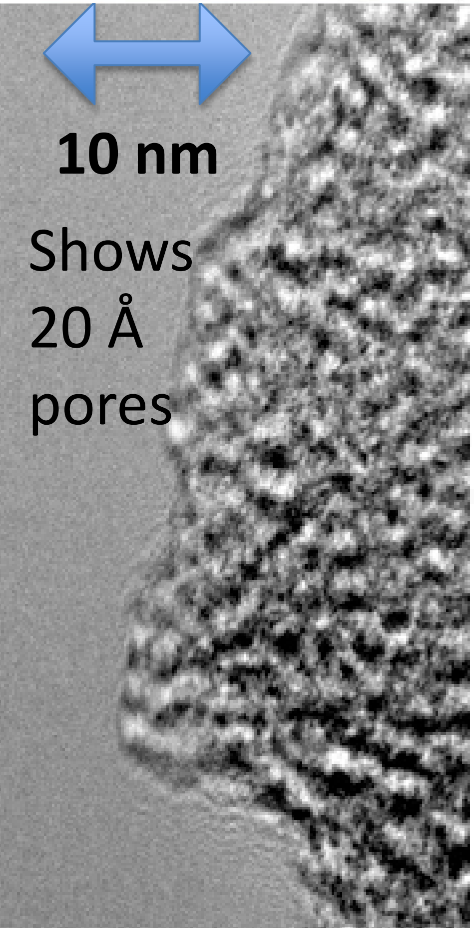
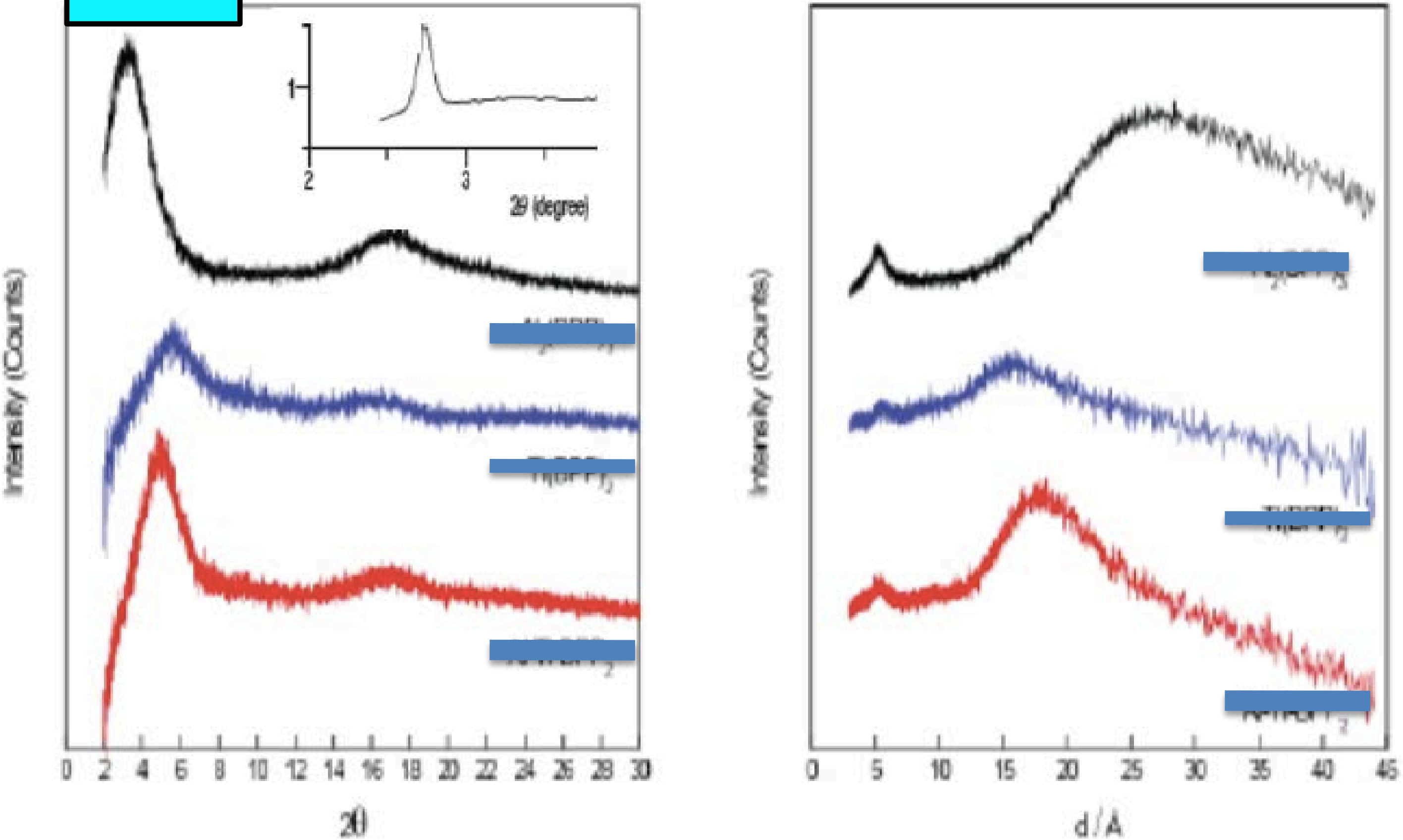
TEM Image, Xray diffraction patterns, and pore size distributions



10 nm

Shows 20 Å pores

XRD



Tests of new nanoporous network solutions (🟦) and rubbery salt-in-polymer electrolyte (●)(to explain)

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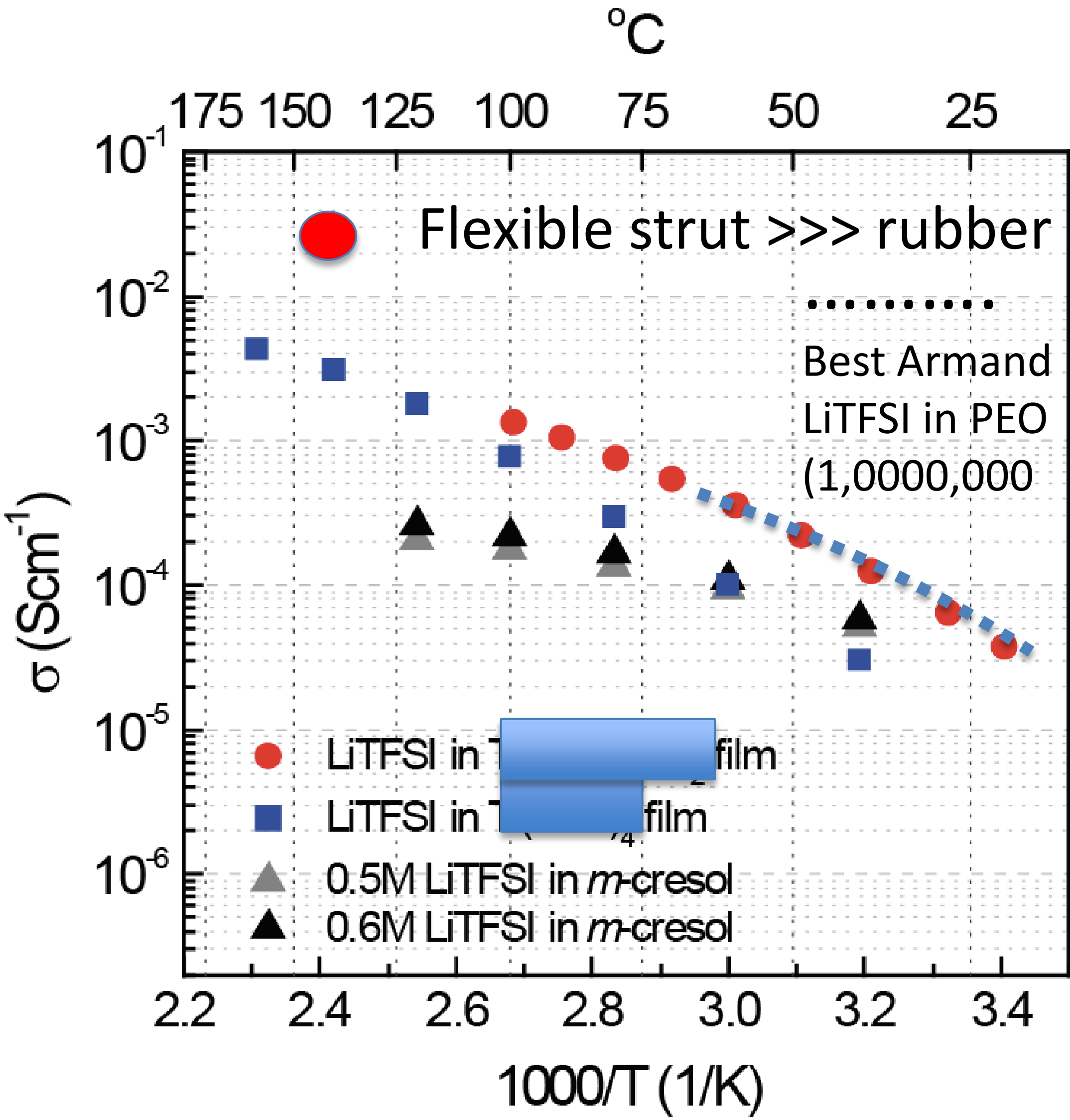
🟦 Solution in net is of higher ionicity than free solution (saturate). i.e. net influences state of ionization

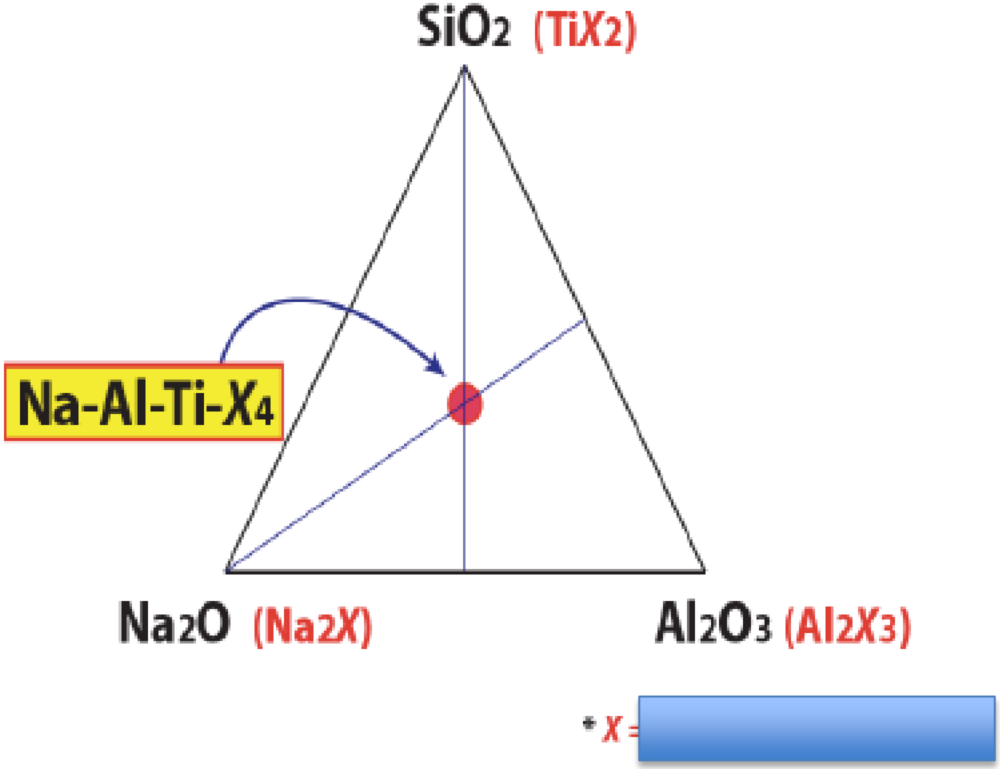


BACKGROUND SLIDE

Exploration of “chemical stretching” idea

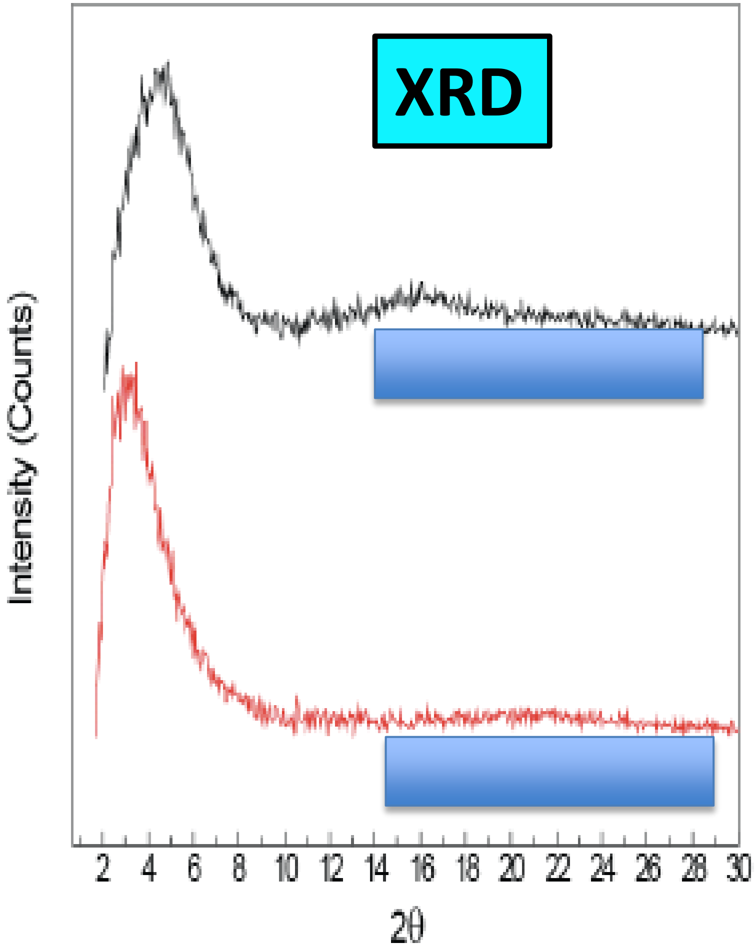
$NaAlSiO_4$ is a well-known ceramic. (sort of zeolite precursor). The charge- compensating sodium is rather mobile.

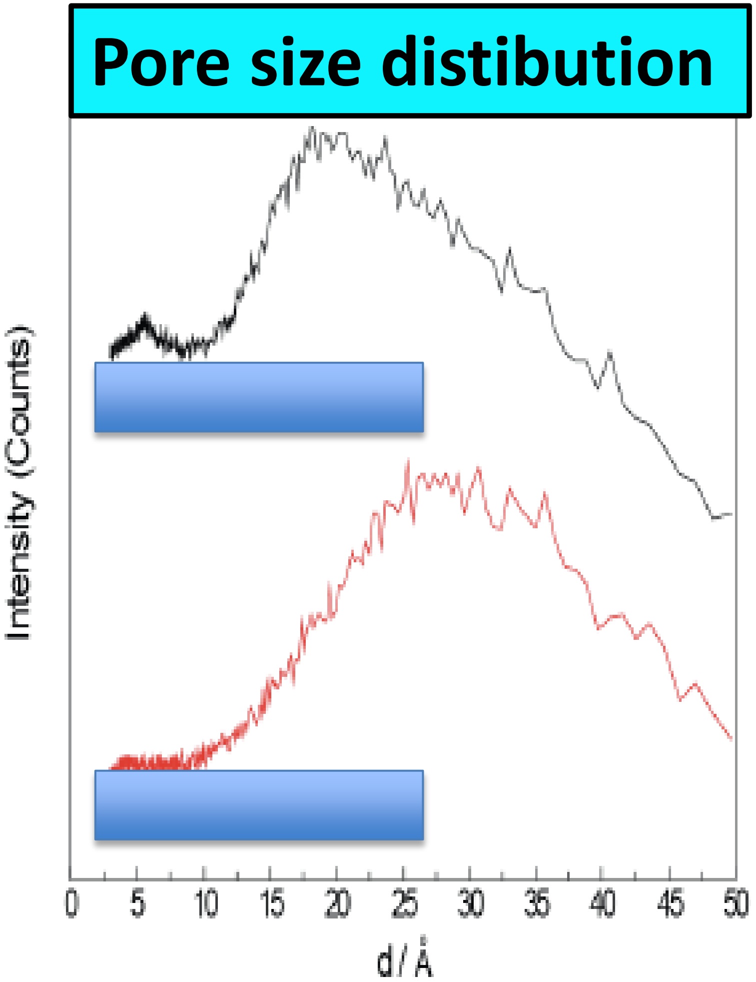
Can we enhancethe mobility by “chemical stretching” (substituting oxide with larger slat)



ACCOMPLISHMENT SLIDE

Nanopore properties


XRD

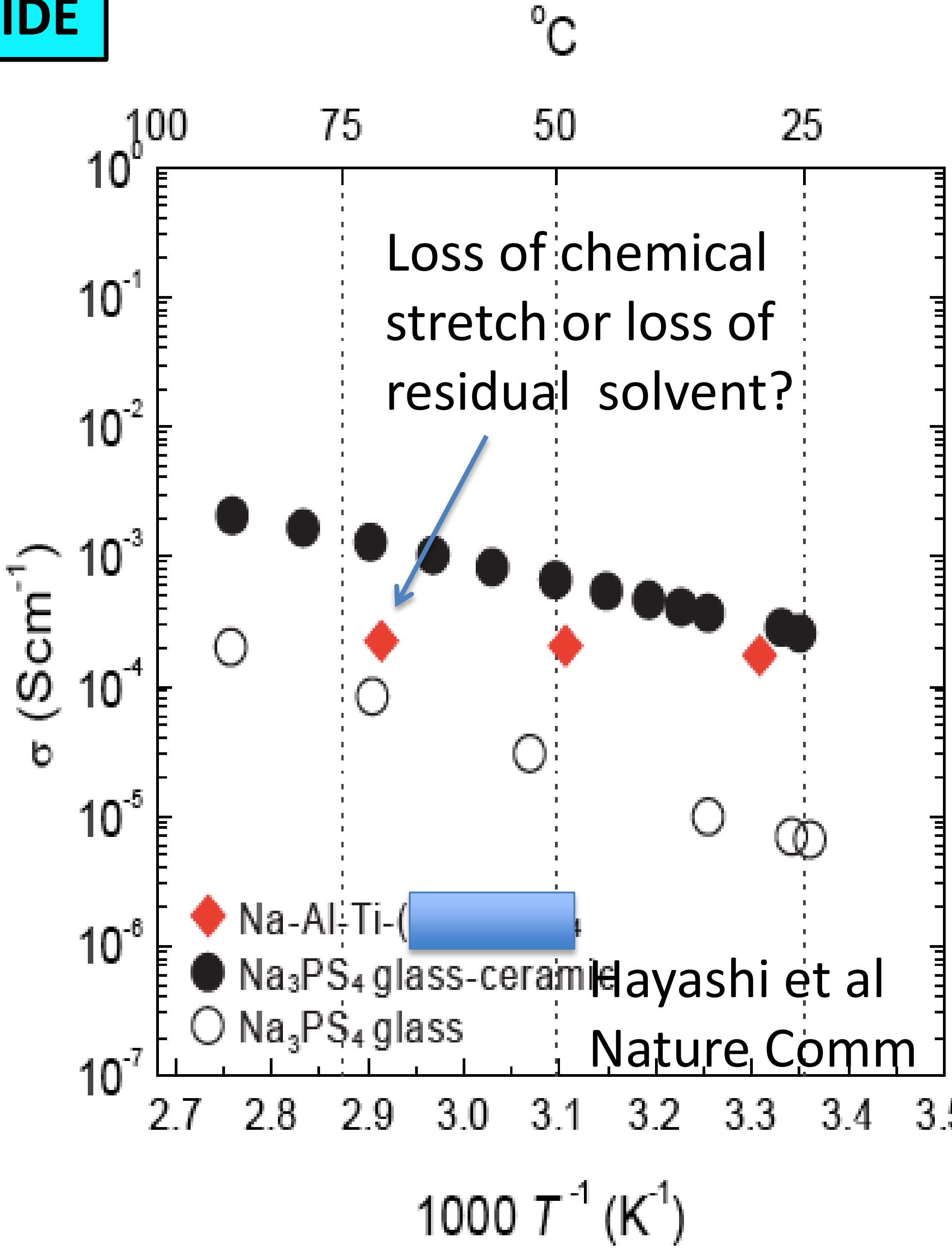

Pore size distibution

Very new ACCOMPLISHMENT SLIDE

Single sodium ion conductors:

New Solid electrolytes from nanoporous glasses (g-MOFs)
(to be "tuned" to hard rubbers)


Cell electrode



Loss of chemical stretch or loss of residual solvent?

Hayashi et al Nature Comm