Solid ionic conductors, and ionic liquids: ceramics, glasses, polymers, and gels and their composites

C. Austen Angell,
Arizona State University

Based on work over the decades by Stuart Smedley (**Li borate glasses**) Steve Martin (**Li B, Si & P glasses**), Emanuel Cooper (**PLICFICS**), Changle Liu (**polymer-in salt**) Marcelo Videa (**inorganic ionic liquids**), Kang Xu (**new salts and solvents sulfones**) Wu Xu (**LiBOB and poly-LiMOB and ionic liquids)** J-P. Belieres (**protic ionic liquids**) Zuofeng Zhao (**new PILs**) and Kazu Ueno (**ionic liquid gels**)

Energy storage strategies

Chemical storage vs physical storage.
Why not pump water uphill?

Examples of energy density:

CO_2 air guns vs chemical propellants:

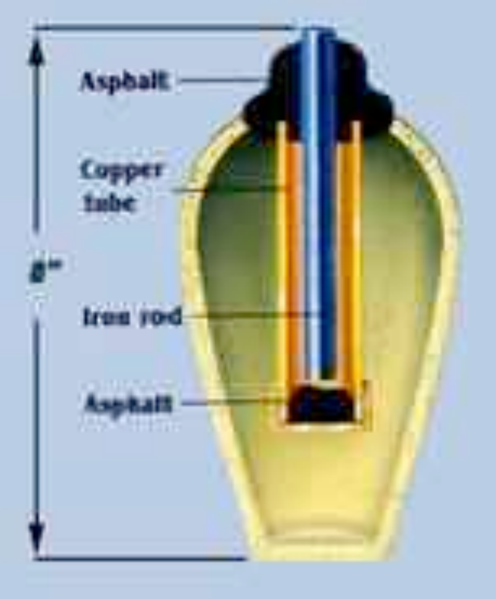
Compressed nitrogen vs ammonium azide

Concentration cells (mV) vs redox cells (V)

Ancient electrochemistry

$Fe + Cu^{2+} \rightarrow Cu + Fe^{2+}$

248 B.C.- 226 A.D.



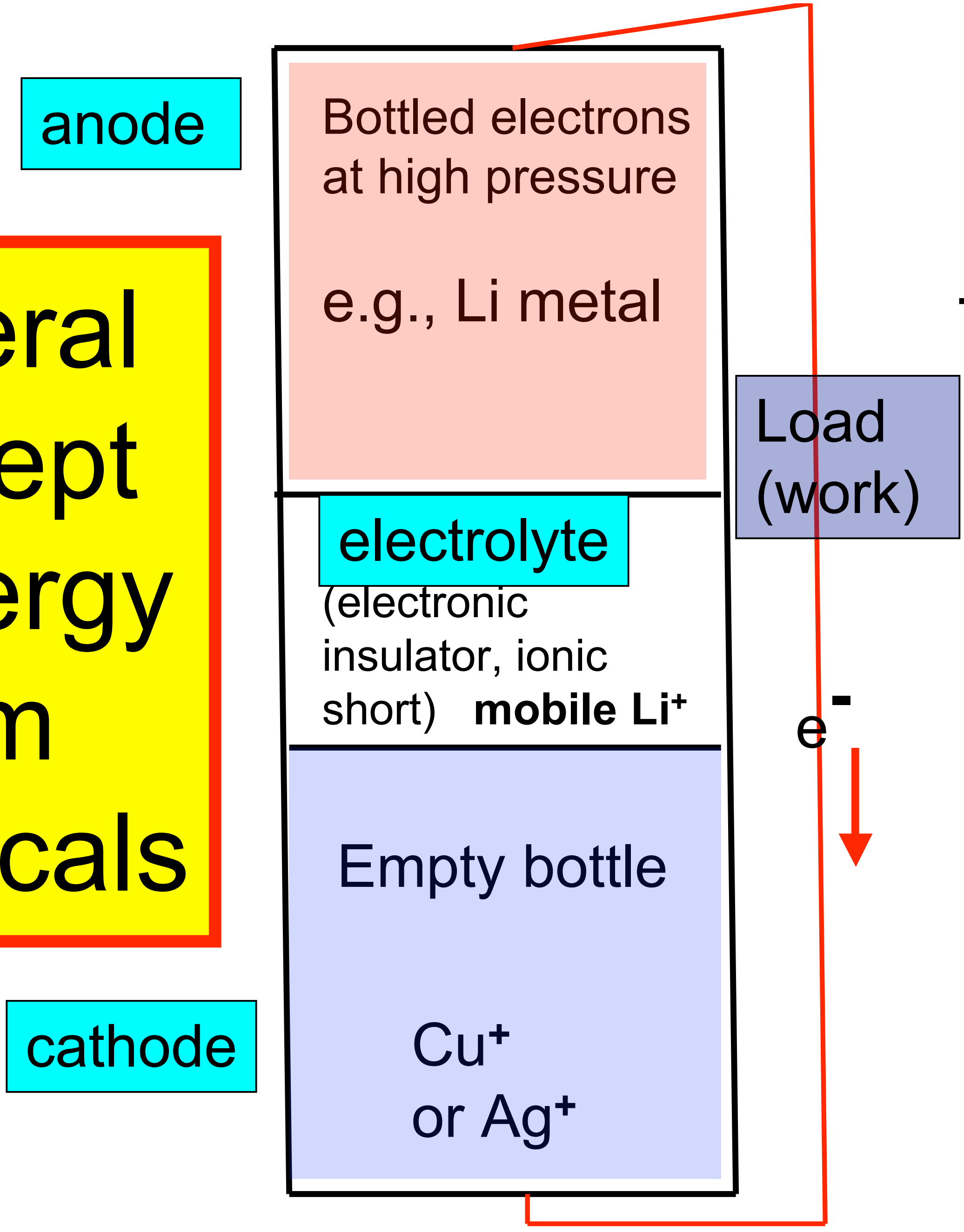
The ancient battery in the Baghdad Museum

The ancient battery in the Baghdad Museum, as well as those others which were unearthed in Iraq, are all dated from the Parthian occupation between 248 BCE and 226 CE. However, Dr. Konig also found copper vases plated with silver in the Baghdad Museum, excavated from Sumerian sites in southern Iraq, dating back to at least 2500 BCE. When the vases were lightly tapped, a blue patina or film separated from the surface, which is characteristic of silver electroplated onto copper base. It would appear then **that the Parthians inherited their batteries from one of the earliest known civilizations**.

http://www.paradigm-sys.com/ae/library.html

Fe?

General concept of energy from chemicals



anode

Bottled electrons at high pressure

e.g., Li metal

electrolyte

(electronic insulator, ionic short) **mobile Li$^+$**

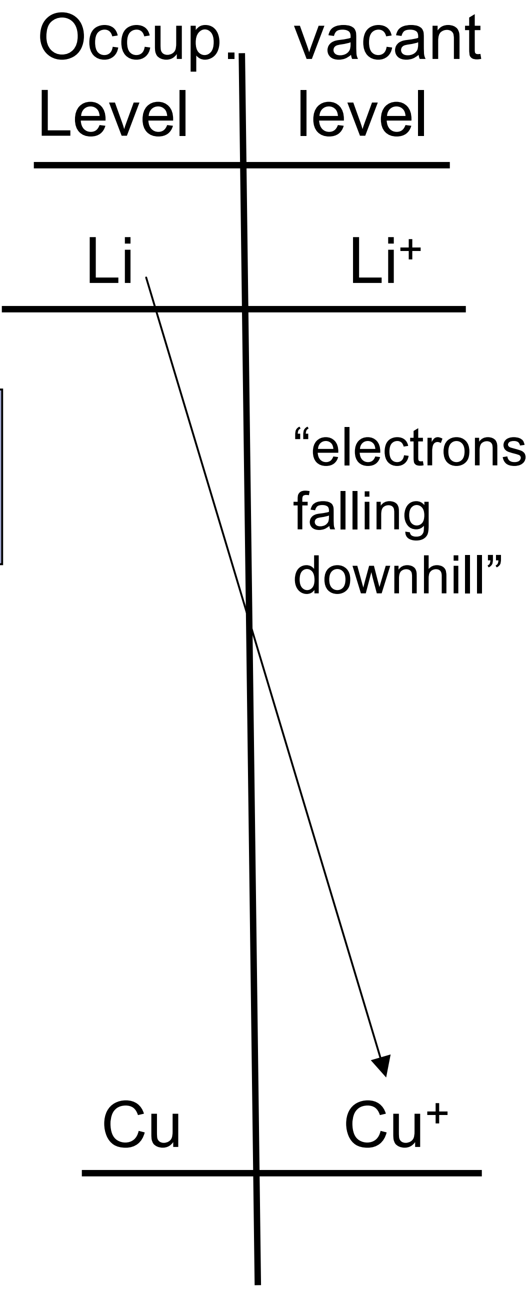
Empty bottle

Cu^+
or Ag^+

cathode

Load (work)

e^-



Occup. Level	vacant level
Li	Li^+
Cu	Cu^+

"electrons falling downhill"

Energy diagram from redox table

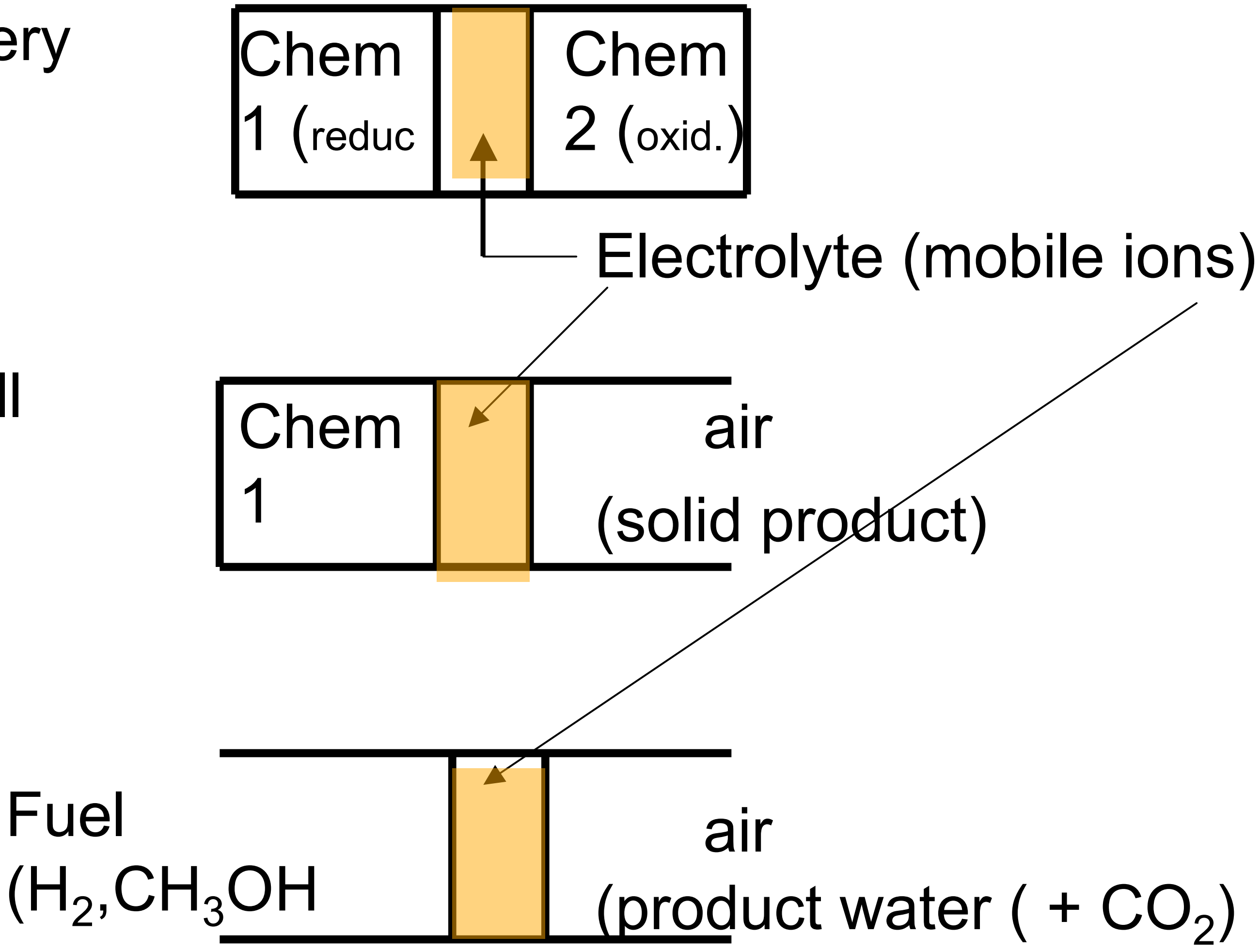
Chemical energy to electrical energy

device strategies

1. The regular battery

2. The metal-air cell

3. The fuel cell



Chem 1 (reduc

Chem 2 (oxid.)

Electrolyte (mobile ions)

Chem 1

air

(solid product)

Fuel $(H_2,CH_3OH$

air

(product water (+ CO_2)

Advantages of 3 are famous but v. difficult to realize

The electrolyte - the ion pathway - is the one common requirement

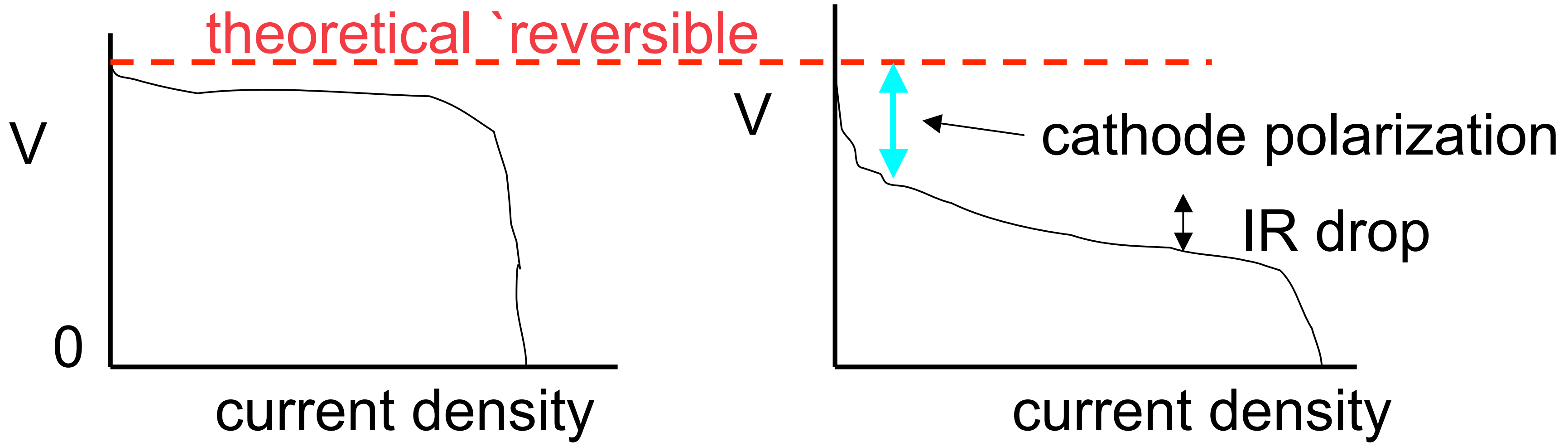
So electrolyte characteristics are a big factor in the success of ANY SYSTEM. We need to store the energy and get it back without losing 50% to ***heat***

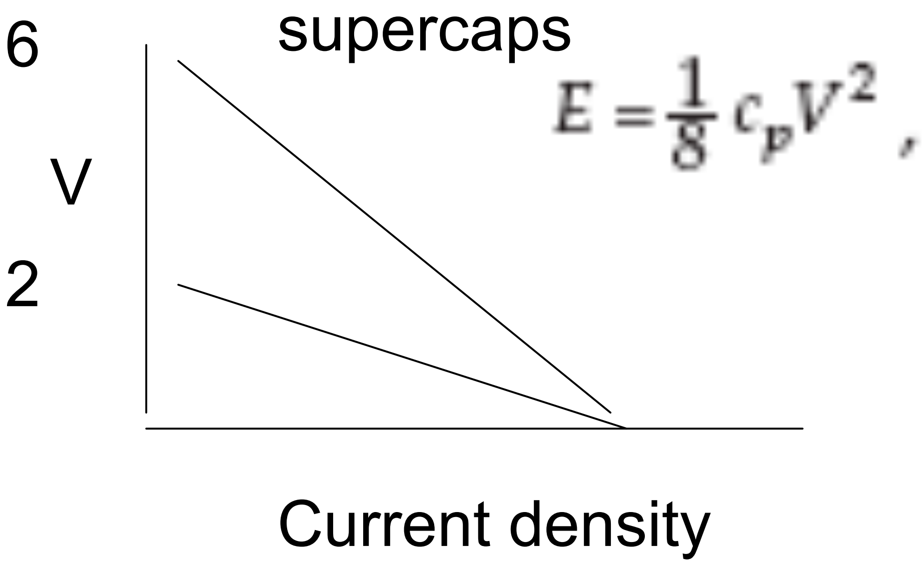
Considerations are:

Kinetics: need to minimize losses in heat (Joule heating)
Stability: no oxidation, reduction, volatilization, chemical degradation
Mechanical properties: self-supporting (solid?) but ***tough***
Toxicity: of course
Cost: of course

(discharge) performance metrics

Li battery (typical) **H_2/O_2 fuel cell**





$$E = \frac{1}{8} c_p V^2 ,$$

The **current** that can be drawn is often setting the performance limit.
With **fuel cells** there is also often a serious output voltage problem, due to cathode kinetic barriers

Aims of the talk

1. Review the types of electrolytes that may be utilized in energy storage and delivery, contrasting Li^+ (Na^+) and protic cases.

2. Review the concepts that are useful in discussing the properties of non crystalline electrolytes.
   (a) relaxation times
   (b) "freezing-in"/glass transitions (in crystals as well)
   (c) decoupling, "superionics", and Walden plots
   (d) "wet" and "dry" protons and Grothus mechanisms
   (e) maximum conductivities
3. Wot to do (a) Decoupliing in liquids (b) tension in solids
4. Electrochemical windows and high voltage systems.
   Solvents, vs ionic liquids, vs glasses

THE OPTIONS ARE:

	$\mathrm{Log}_{(max)}$(S/cm)	
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Ceramics: extraordinary β” alumina …….	-1 to -3	
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Polymer rubbers: operating > Tg	-4.5	
***Plasticized* polymer rubbers**	-2	-1 (Naf)
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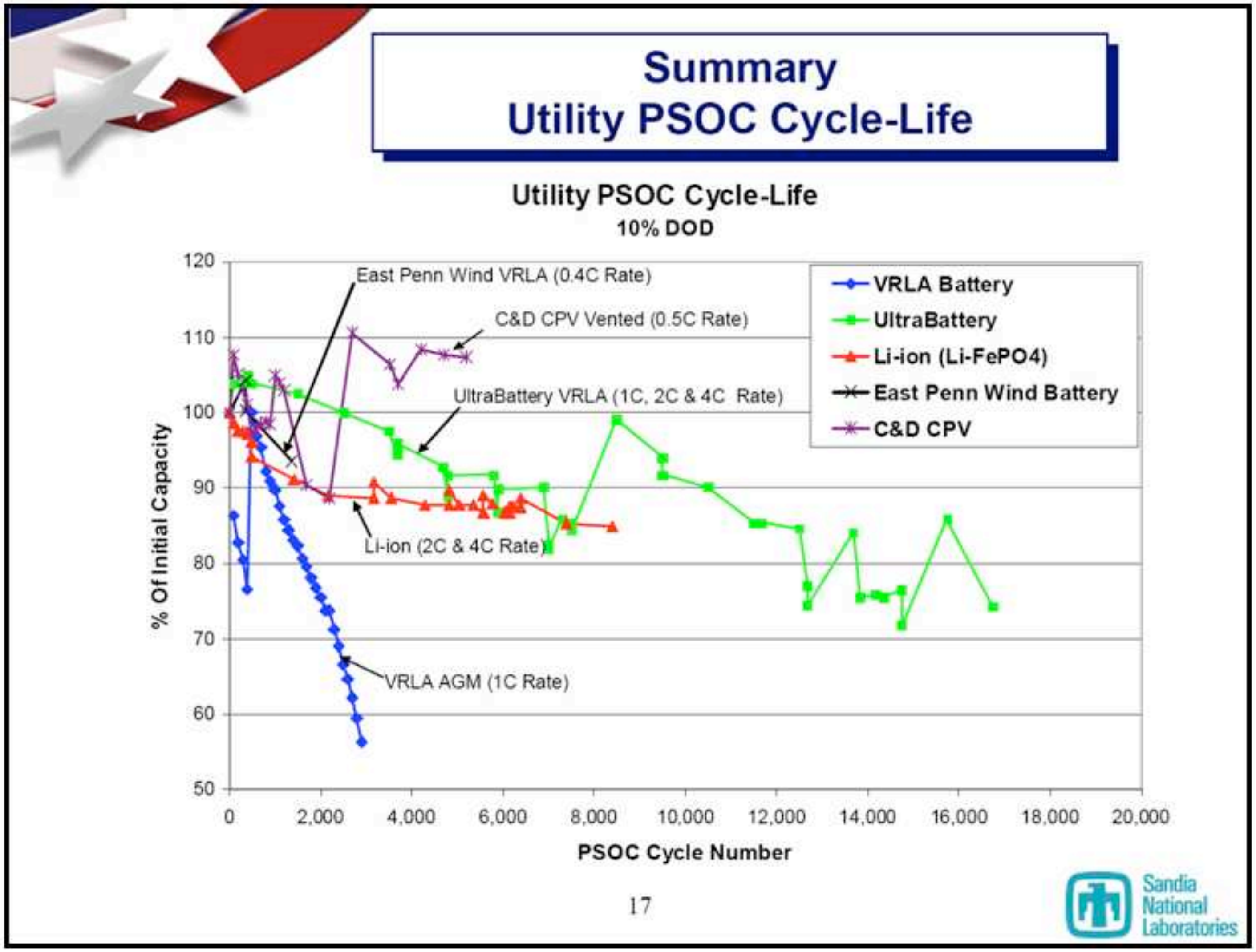
quasi-crystalline molecular support	-2	
Liquids in porous supports:	-1.0	
Liquids: (a) ionic liquids (aprotic or protic)	-2 or -1	
(b) solutions (aqueous or non-aqu)	-1 or -2	
(c.) aqueous protic (acid)	+.5 to 0	

Various combinations/composites of the above

e.g. “Lead-carbon” system continues to exploit H_2SO_4 (aq)

“Lead-carbon batteries are different from other types of batteries because they combine the high energy density of a battery and the high specific power of a supercapacitor in a single low-cost device”



Summary
Utility PSOC Cycle-Life

17

Basics:

Including carbon in the time-honored lead-acid battery.

“a life cycle four times the average lead-acid battery's 600 to 800 deep discharges. It will last longer, recharge more quickly and has applicability to the plug-in hybrid market."

Read more: http://www.thedailygreen.com/living-green/blogs/cars-transportation/axion-lead-carbon-batteries-460409#ixzz0zi1cm5oD

Ceramics: the extraordinary case of β-alumina

Ionic conductivity in Na+, K+, and Ag+ β''-alumina

Briant, J. L.; Farrington, G. C.

Journal of Solid State Chemistry, Volume 33, Issue 3, p. 385-390.

This paper presents measurements of the ionic conductivity in single crystals of **β''**-alumina (0.84 M_2O . 0.67 MgO . 5.2 Al_2O_3, M = Na, K, Ag). Single crystals of sodium β''-alumina were grown from a melt of Na_2O, MgO, and Al_2O_3 at 1660 to 1730°C. Selected crystals were converted to the other isomorphs by ion exchange. The conductivity of sodium β''-alumina varies from **0.18 to 0.01 S/cm at 25°C** depending upon crystal growth conditions. Potassium β''-alumina has the unusually high room temperature conductivity of 0.13 $(\text{ohm . cm})^{-1}$. Silver β''-alumina has a slightly lower conductivity, 4 × 10-3 $(\text{ohm . cm})^{-1}$ at 25°C. The activation energies of sodium and potassium β''-alumina decrease with increasing temperature, while that of silver β''-alumina is constant from -80 to 450°C.

$K_+ \approx Na_+ > NH_4^+ \approx Ag+ > OH_3^+$

$\mathbf{10^{-1}}$ $\mathbf{10^{-1}}$ $\mathbf{10^{-3}}$ $\mathbf{10^{-3}}$ $\mathbf{10^{-5}}$

Fast Ionic Transport in Solids
Gregory C. Farrington and Jacqueline L. Briant

Science 29 June 1979:
Vol. 204. no. 4400, pp. 1371 – 1379
DOI: 10.1126/science.204.4400.1371

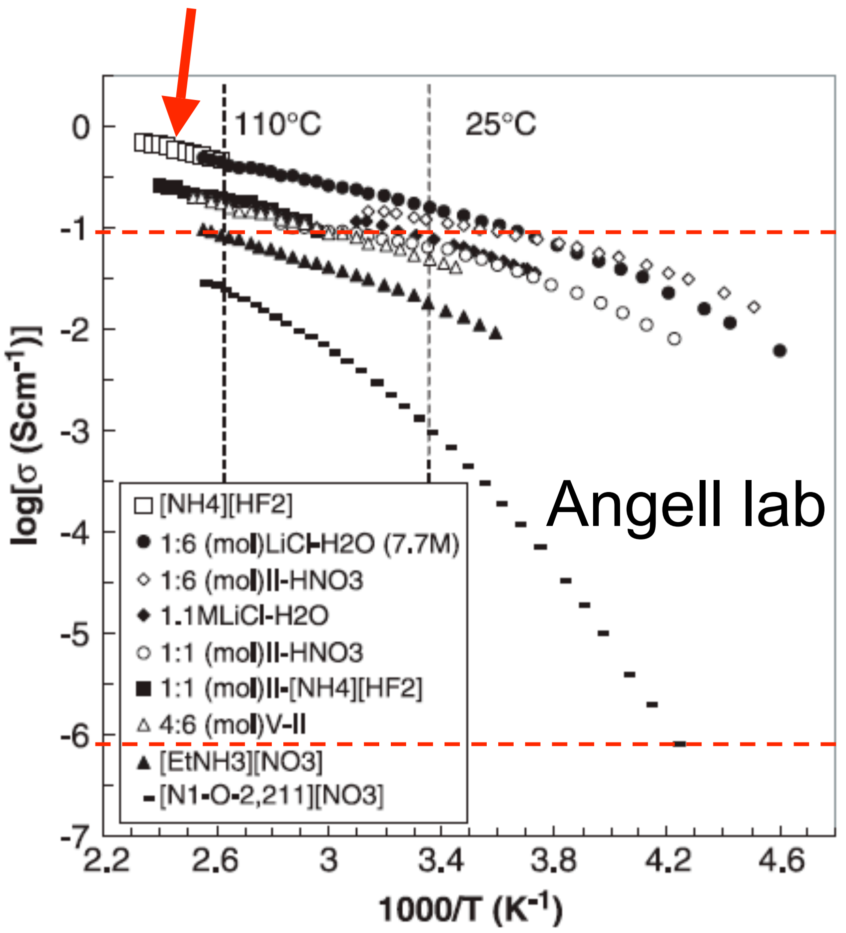
Only 60 cites !

CONDUCTANCE AND SPECTROSCOPY OF PROTONIC BETA AND BETA”-ALUMINAS
G. C. FARRINGTON, J. L. BRIANT and H. S. STORY*
and W. C. BAILEY. J. Electrochem. Soc.

10 cites !!

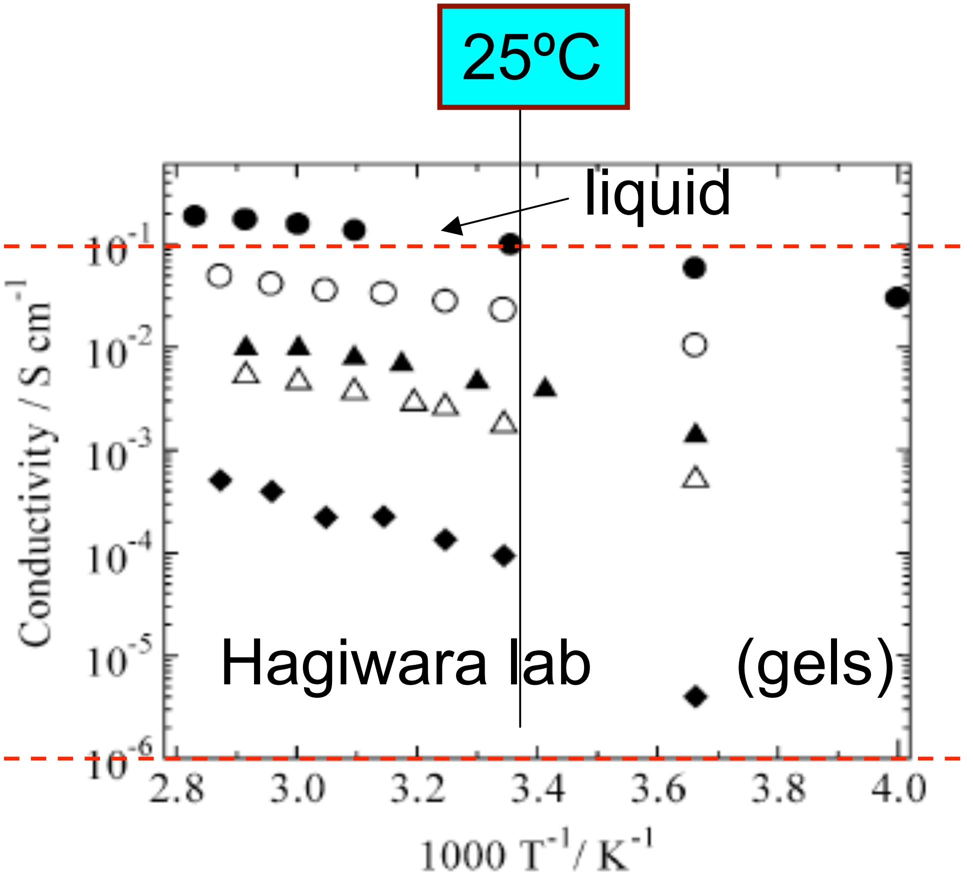
The onset of motional narrowing in hydronium beta”-alumina oecura at - 40$_{\circ}$ C but not until +3O”C in bydrcmium beta-alumina. This is consistent with the higher conductivity reported for hydronium beta”-alumina, 1O$^{-3-1O-'}$ (ohm-cm)-’ at 25”C, in comparison to 10-‘“-IO-” (ohm-cm)-‘for hydronium beta-alumina at 25ºC

β-Al_2O_3 conductivity is comparable to those of aqueous solutions and ILs



Angell lab

Science, 2003
Xu and Angell



liquid

Hagiwara lab

(gels)

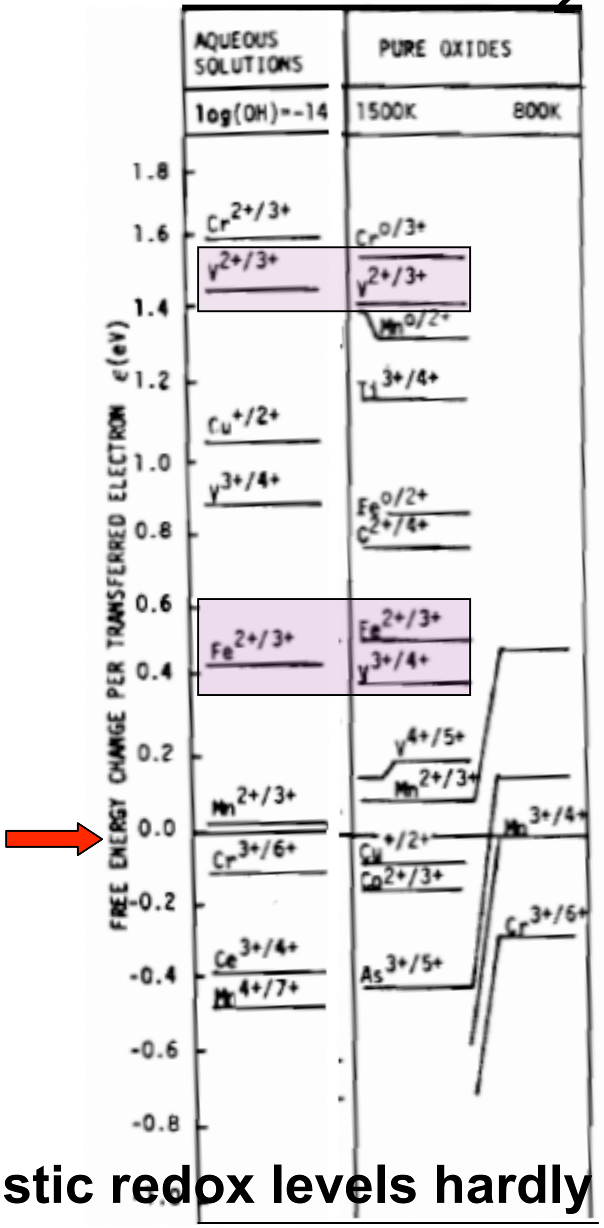
Fig. 1. Conductivity of electrolyte composites of poly-HEMA a
ETMEIM(HF)$_n$F (n=2.3). ●: Neat EtMeIm(HF)$_n$F (N=1.0), co
posite with the molar fraction of EtMeIm(HF)$_n$F, N; ○: 0.60, ▲: 0.
△: 0.40, ◆: 0.20.

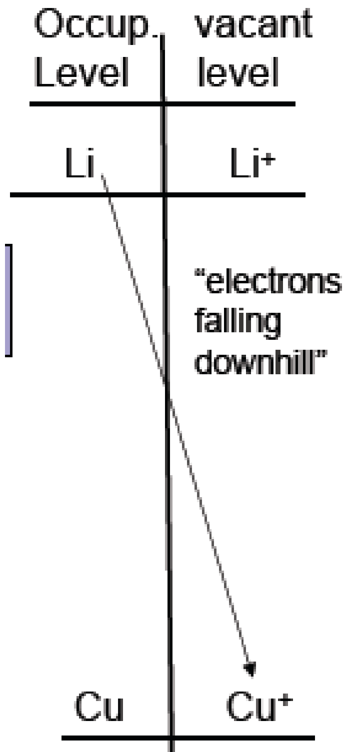
Solid State Ionics, 2002

While ionic liquid (IL) conductivities are “in the air” …. Jun Liu mentioned flow cells and the possibility of using IL substitutes for the aqueous electrolytes, so I briefly make a point

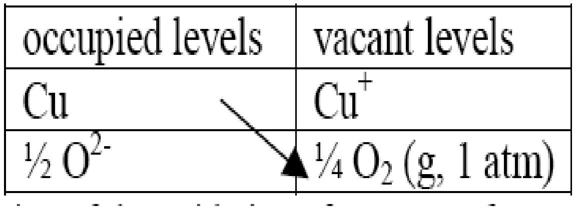
GURNEY diagrams for aqu. solutions referenced to the oxide/oxygen level, and compared to the pure oxides

Rescaled to O^{2-}/O_2 **ref**





Energy diagram from redox table

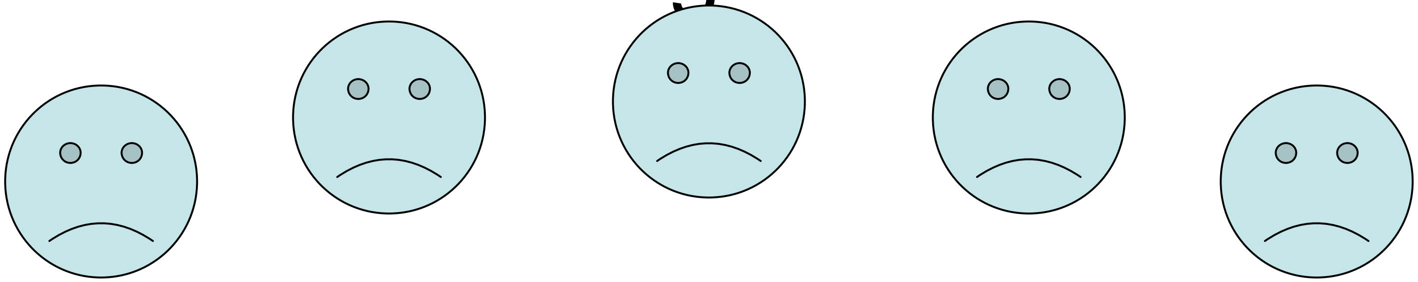


occupied levels	vacant levels
Cu	Cu^+
$\frac{1}{2}O^{2-}$	$\frac{1}{4}O_2$ (g, 1 atm)

Lesson: **the characteristic redox levels hardly change from those assessed from the pure oxide free energies. So, in ionic liquids, the same level scheme will apply but the voltage range of choice will be larger.**

Back to β-Al_2O_3 : an enormous literature:

β-Al_2O_3 and the Zebra battery (Mercedes) and Na-S storage cell histories:

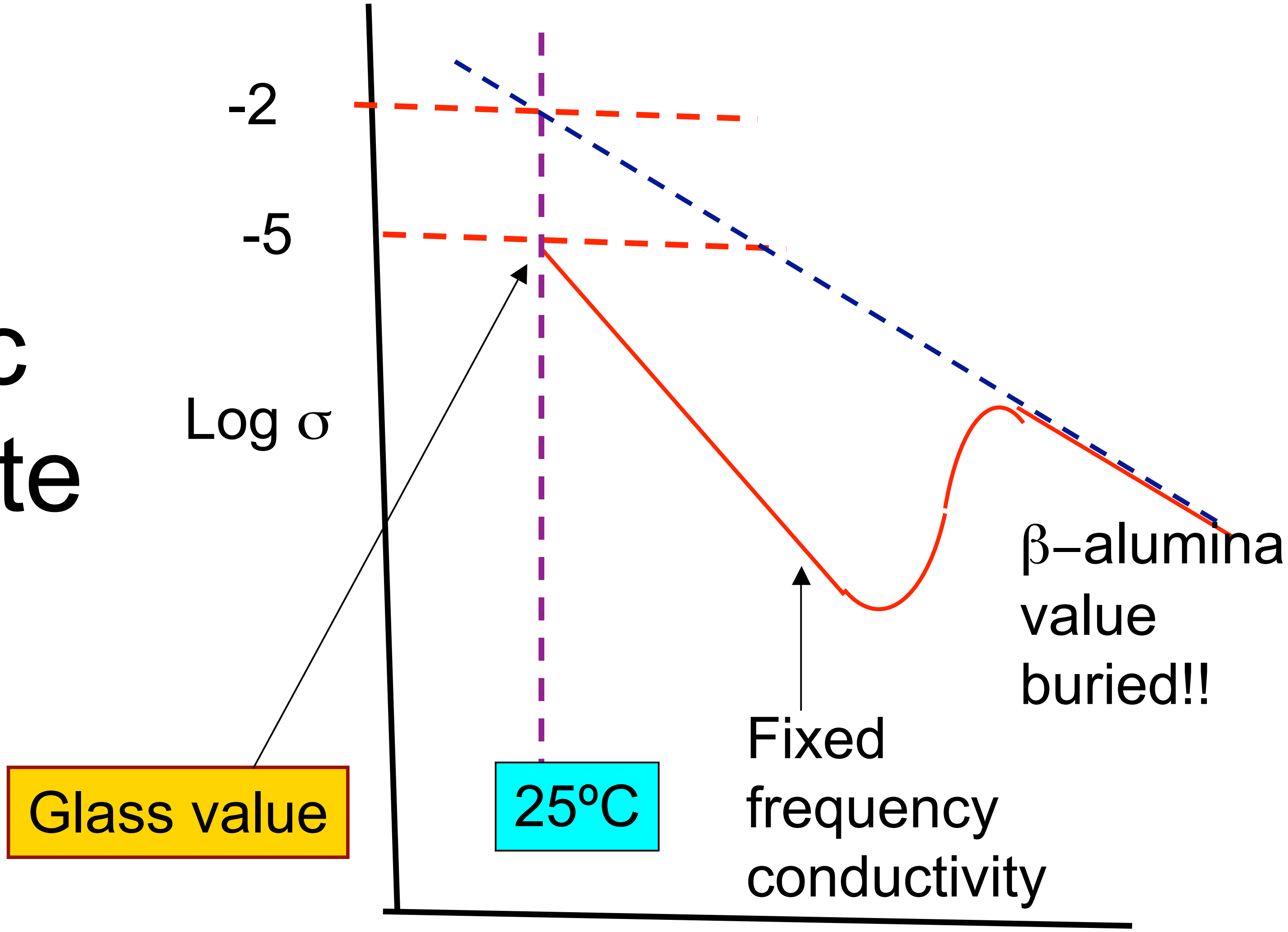


ceramics are fragile and not self-healing

wot to do??

In1973 we thought we knew (We were working with fast ion conducting glasses)

Make glass-ceramic composite



-2

-5

Log σ

β–alumina value buried!!

Fixed frequency conductivity

25ºC

But…..

Glass value

1/T

Series, not parallel, resistance

Turn to plastic crystals -
deform without fracture)

(next on the list)

THE OPTIONS ARE:

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Various combinations/composites of the above

Types of plastic-crystalline electrolytes

Mobile species

lithium electrolytes

1. double salts (PLICFICS)

$LiBF_4 \bullet [R_4N^+]BF_4$ Li^+

Cooper 1982

2. **Solid solutions** of lithium salts in plastic organic cation salts

Li(NTf2) in pyrollidinium X, etc
MacFarlane and co

H^+

protic electrolytes

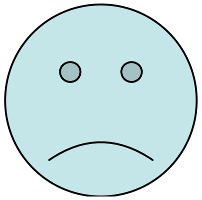
rotator phases

$CsHSO_4$.

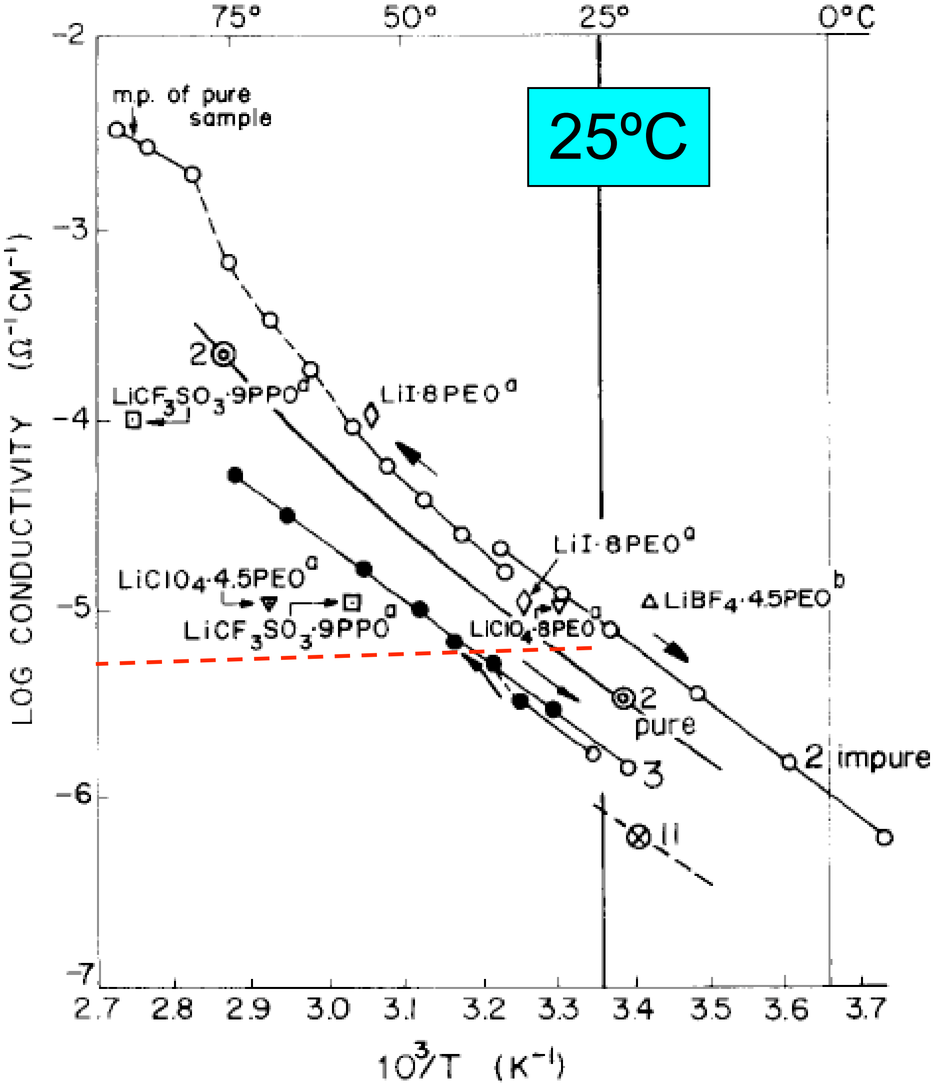
Haile and coworkers 2001

“solid solutions” from
$CsHSO_4 + DBAHSO_4$
Mizuno et al (Angell 2006)

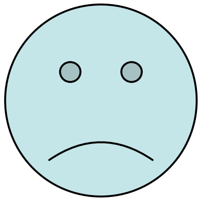
$\sigma_{25^oC} = 10^{-2}$ S/cm



PLICFICS compared with PEO salt-in-polymer electrolytes



No advantage



Cooper and CAA, 1984

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Various combinations/composites of the above

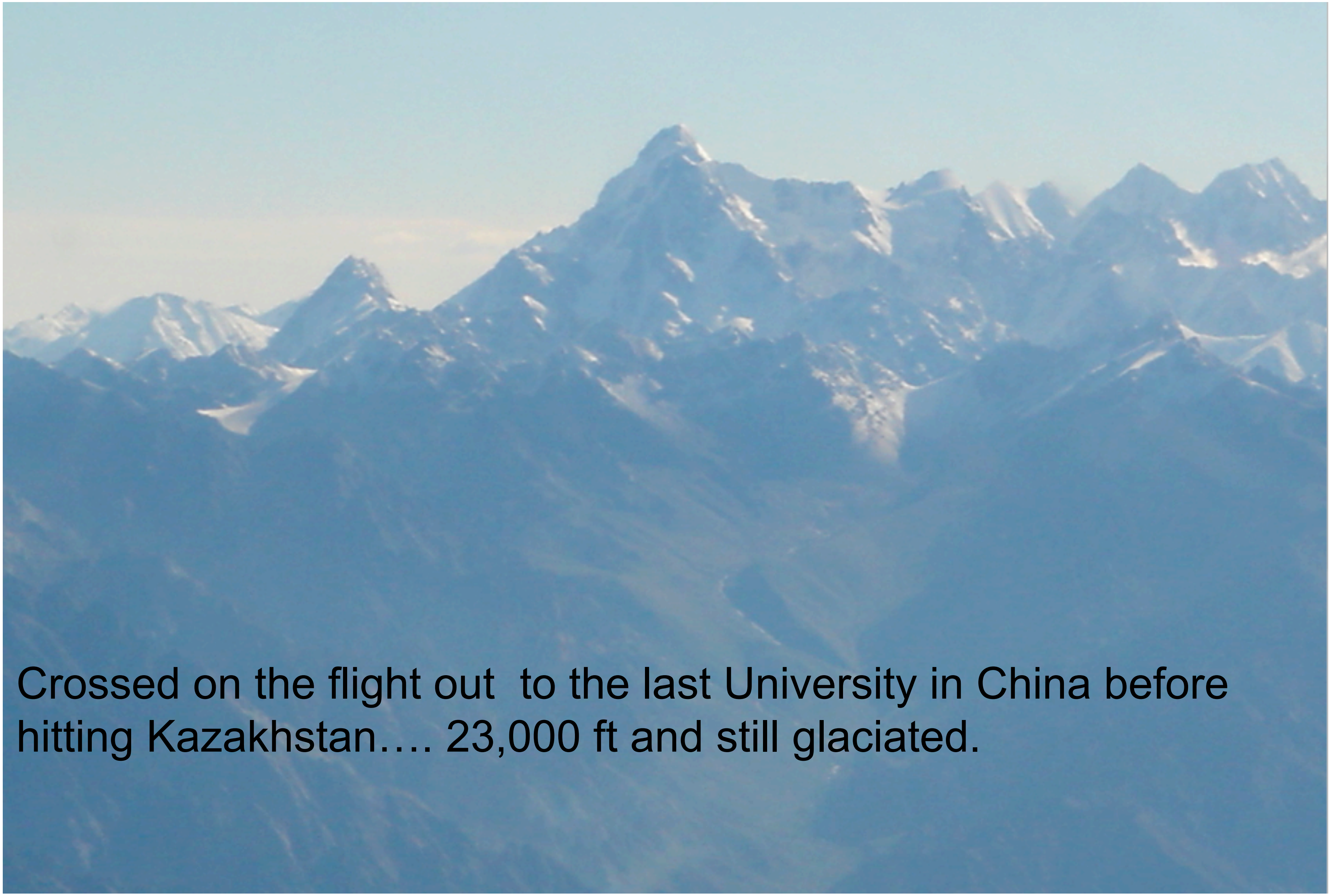
Need some conductivity concepts to help in the discussion

- Mobile ion decoupling
- Ergodicity-breaking (glass temperatures)
- Walden plot
- "dry" proton conductivity
- Limiting high ionic conductivities

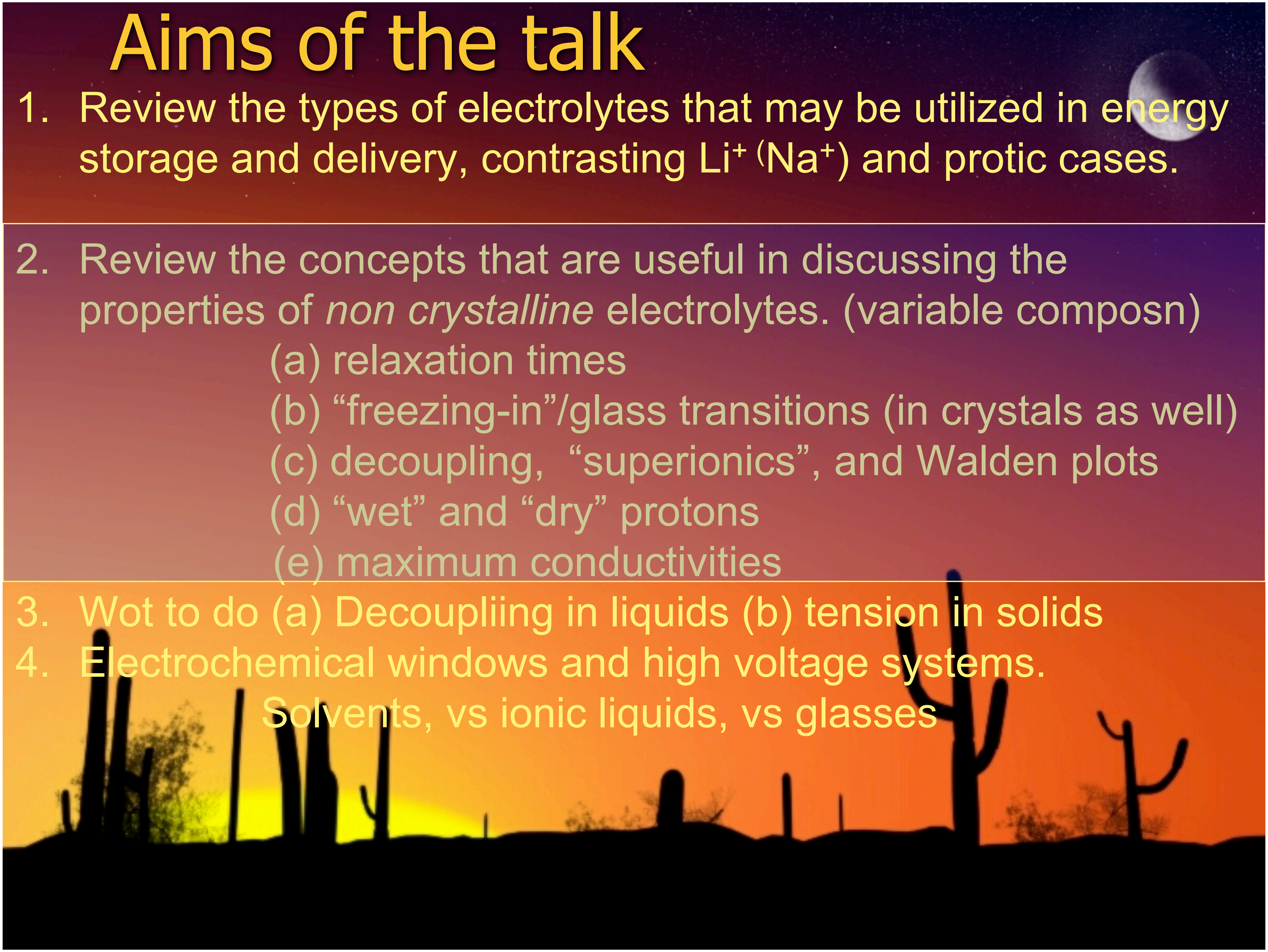
* Conductivity maxima due to oppositely directed factors affecting the mobility of ions

(**for later**)
*ionicity
*proton activity and acidity
proton energy level diagrams

Tsien Shan Mtns, Western China



Crossed on the flight out to the last University in China before hitting Kazakhstan…. 23,000 ft and still glaciated.



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   (d) "wet" and "dry" protons
   (e) maximum conductivities
3. Wot to do (a) Decoupliing in liquids (b) tension in solids
4. Electrochemical windows and high voltage systems.
   Solvents, vs ionic liquids, vs glasses

Conductivities are limited by:

1. Friction against neighbors - repulsive forces
   Minimize by (a) increasing empty space (“free volume”),
   (b) making neighbors polarizable

2. Friction from other ions of opposite charge- attractive forces
   Minimize by (a) eliminating multivalent ions,
   and (b) increasing charge separation (lower conc.)

3. Insufficient charges crossing reference area (electrode surface)
   Counter by increasing charge concentration, (in conflict with 2)
   (SO expect maximum)
4. Insuffficient thermal energy.
   counter by (a) raising the temperature !
   (b) lowering the cohesive energy (T_g)

Concepts: relaxation times

Maxwell relaxation time for shear

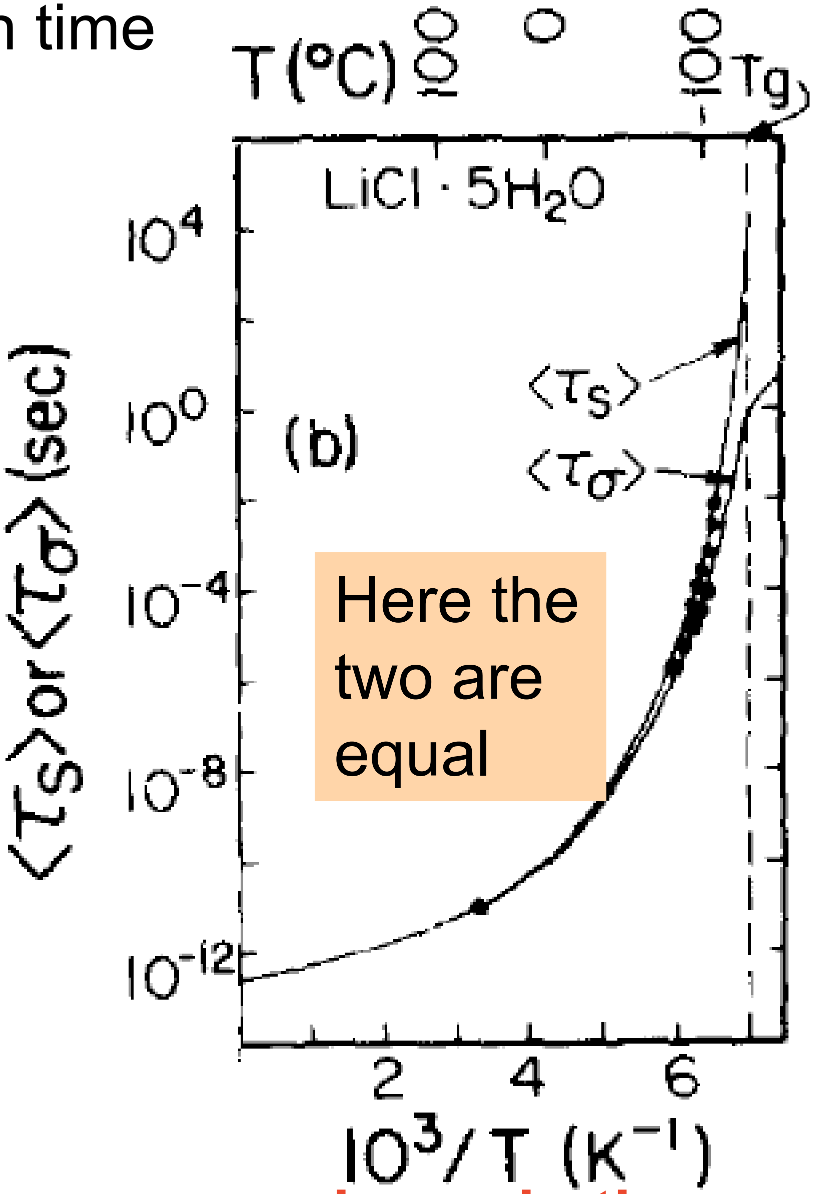
viscosity η (Pa.s)

relaxation time

$\tau_\eta = \eta/G_\infty$

Solid-like property

Liquid- like property



Here the two are equal

Analog for electrical stresses

conductivity σ S/cm

conductivity relaxation time:

$\tau_\sigma = \rho/M_\infty$

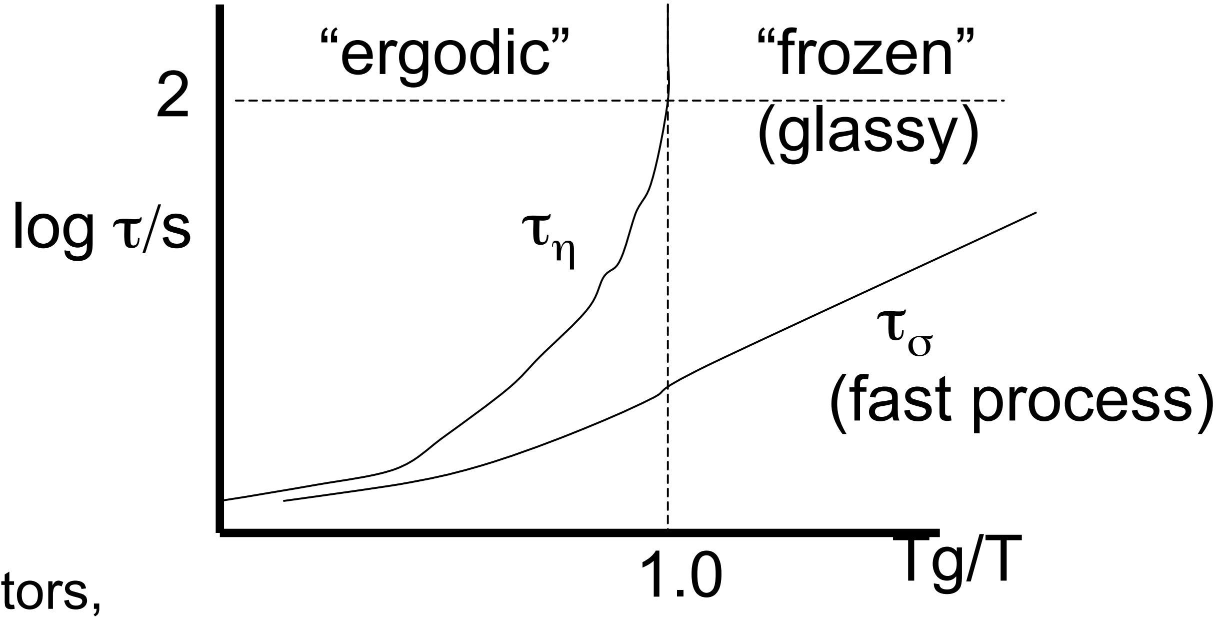
$= e_o\varepsilon_\infty / \sigma_{dc}$

Advantage: allows comparisons in the same units

Concepts: *decoupling* of relaxation processes, And “freezing” of structure

- **decoupling:**

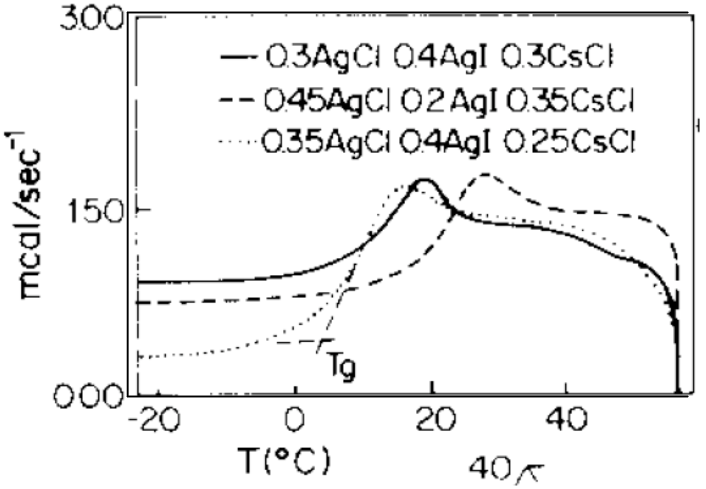
decoupled vs coupled systems (to get faster ions)



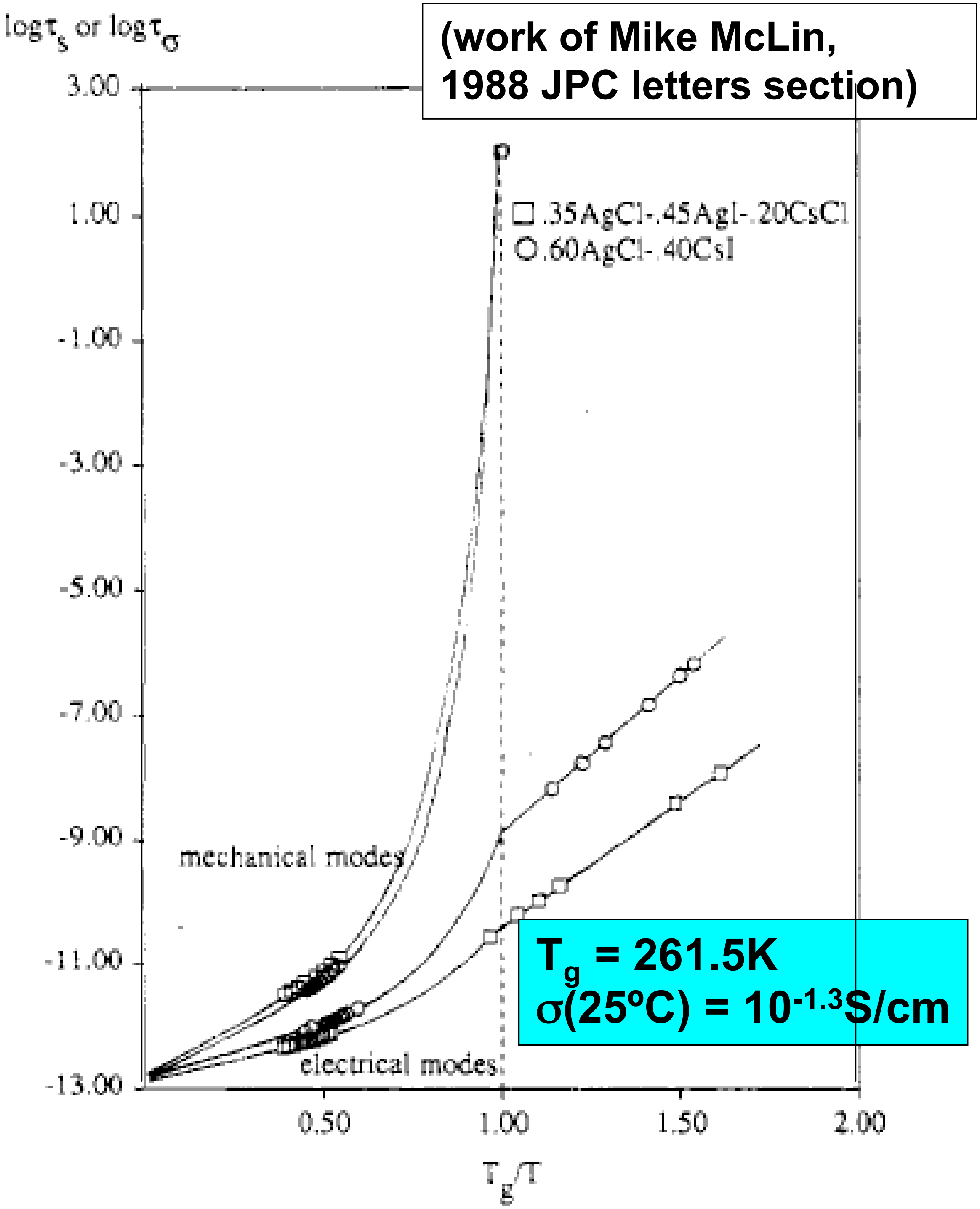
(typical of glassy conductors,
But not most polymer conductors)

- **Glass transitions** and the freezing-in of processes.

Example: a silver ion halide superionic



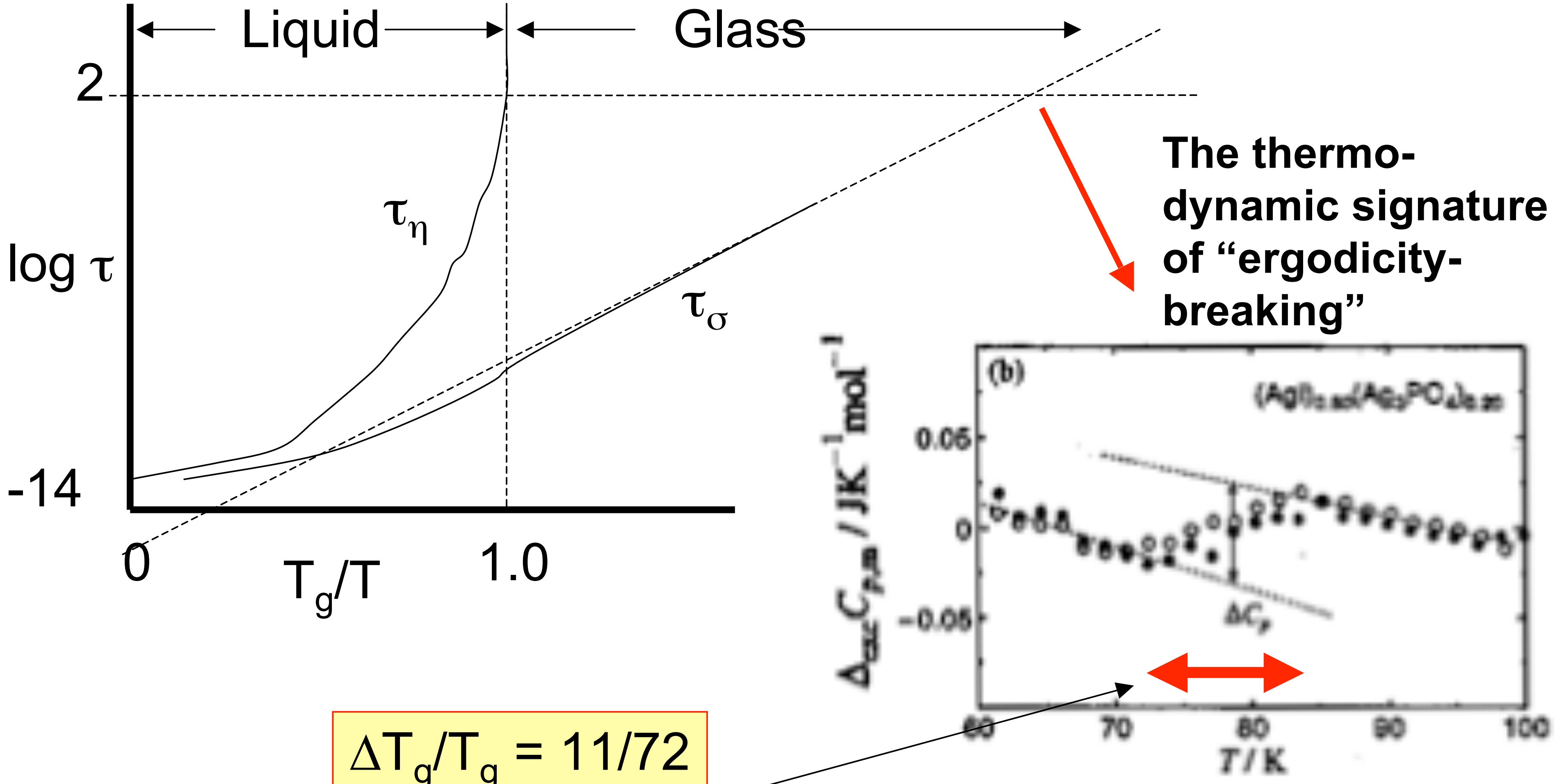
Glass transition by DSC (work of Changle Liu)
Glassy conductivity at 25ºC is closest approach to β”-Al_2O_3



(work of Mike McLin, 1988 JPC letters section)

T_g = 261.5K
σ(25ºC) = $10^{-1.3}$S/cm

T_g, and the "mobile ion T_g"



The thermo-dynamic signature of "ergodicity-breaking"

$\Delta T_g/T_g = 11/72$
$= 0.15$
(Arrhenius)

Figure 6. Heat capacity behavior in the superionic glass system AgI-Ag$_3$PO$_4$ at

Mizuno et al JNCS,

(Hayashi and Oguni)

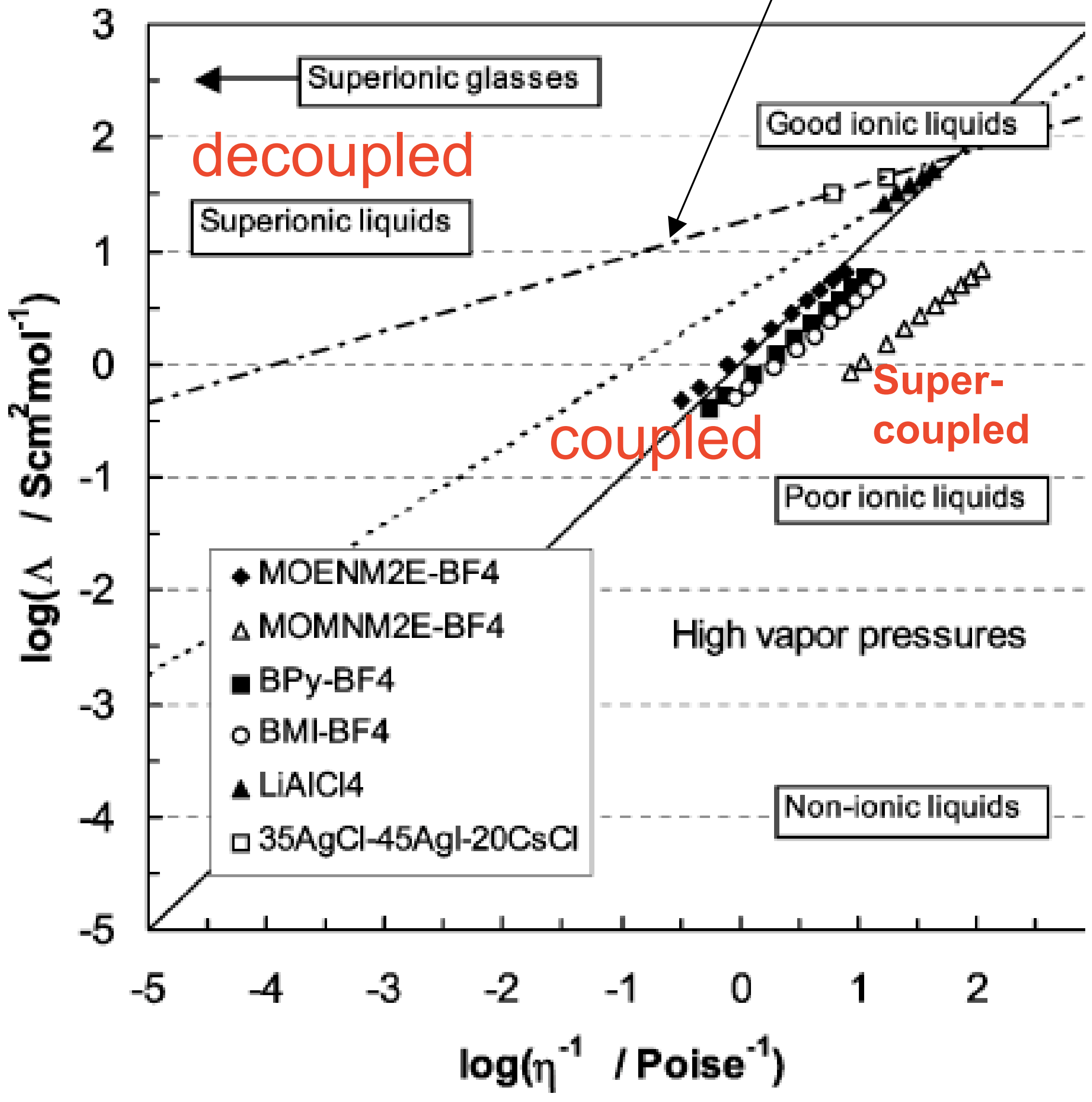
An alternative way of comparing processes: the Walden plot (and a classification tool)

The “fractional Walden rule

$\Lambda\eta^{\alpha} = \text{constant}$

Xu, Cooper and CAA

6176 *J. Phys. Chem. B, Vol. 107, No. 25, 2003*



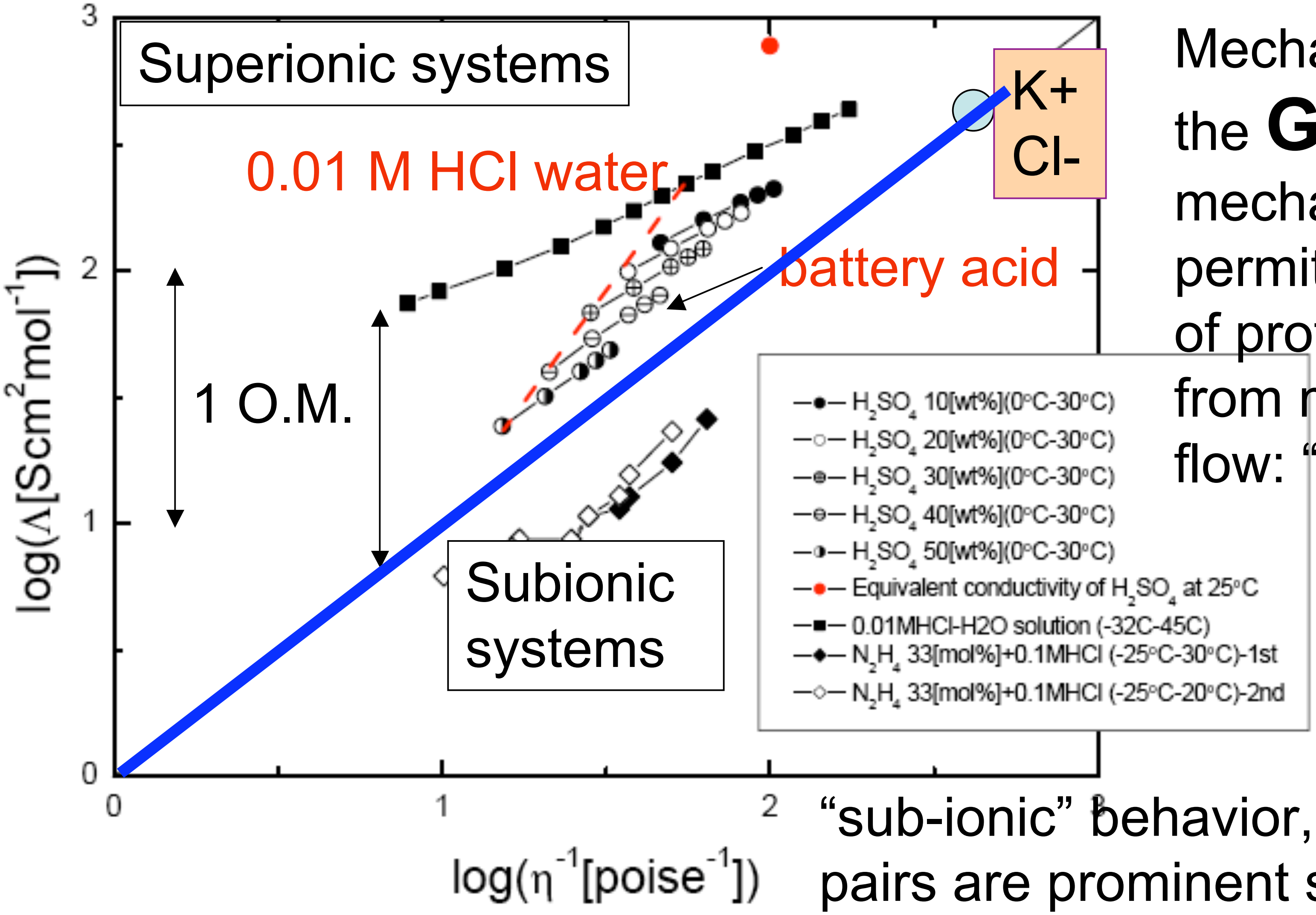
Walden (1905), based on aqueous solution studies

$\Lambda\eta = \text{constant}$

(signature of a coupled system)

Aqueous acid systems are decoupled

The Walden plot: when the ion flow is determined by the solvent viscosity alone, points fall on the line.



Mechanisms like the **Grotthus** mechanism permit decoupling of proton flow from molecular flow: "superionic".

"sub-ionic" behavior, when ion pairs are prominent species

DRY PROTON CONDUCTIVITY

What is it ?

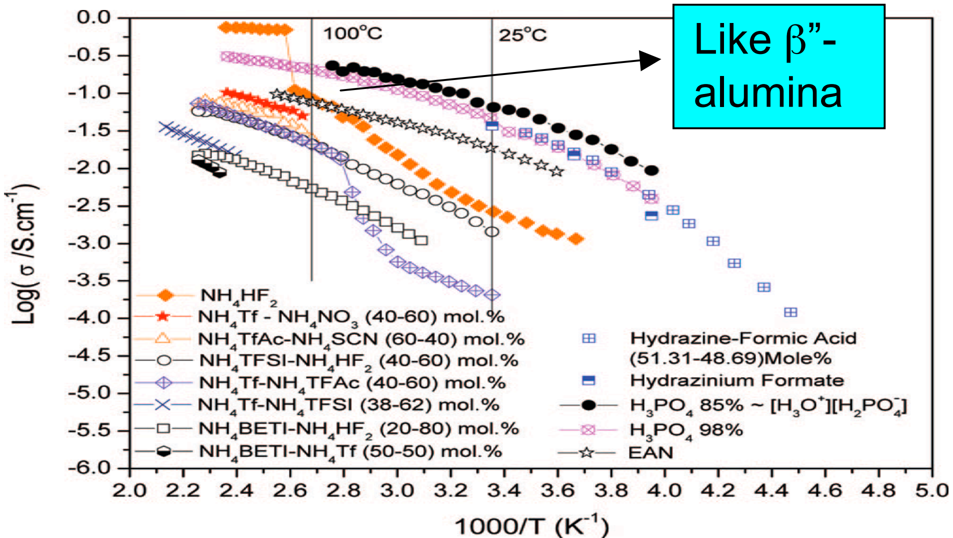
When the current flow is overwhelmingly (>99%) due to the flow of protons, unattached to any other species.

Easy to get, …….BUT… conductivity must also be useful.

Ambition: to find conditions where this is true, and conductivity is

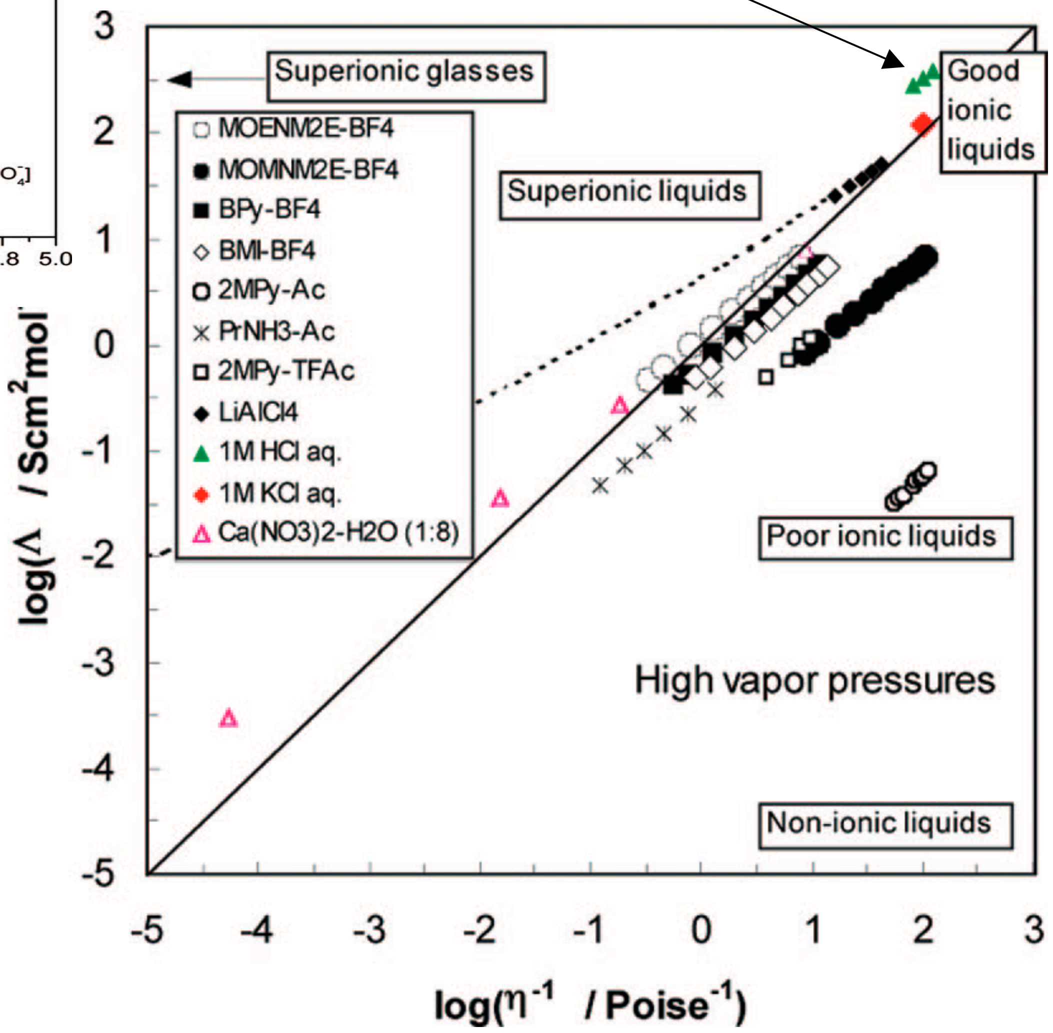
>100 mS/cm at ambient and >1 S/cm at 100ºC.

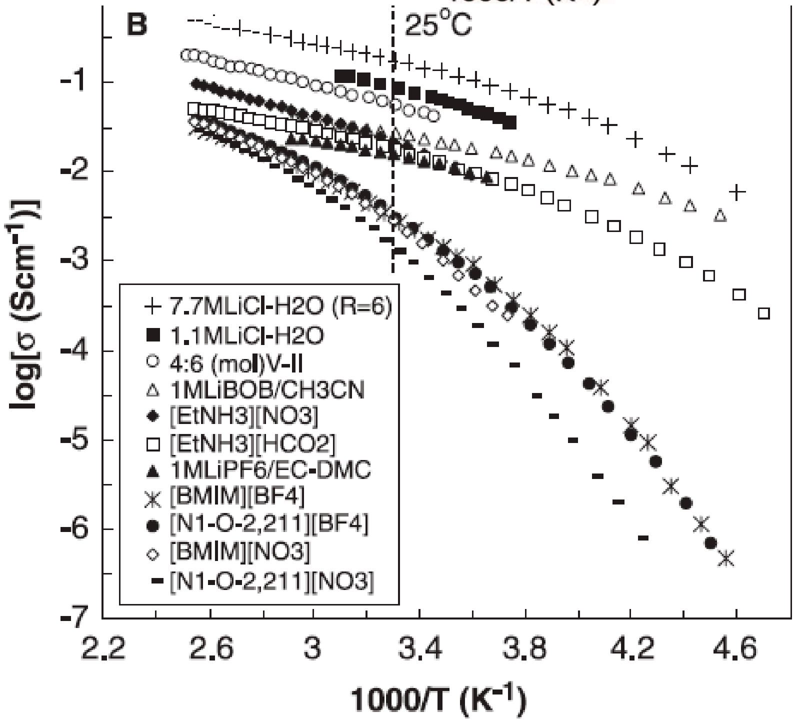
The highest conductivities, at 25ºC



Like β”-alumina

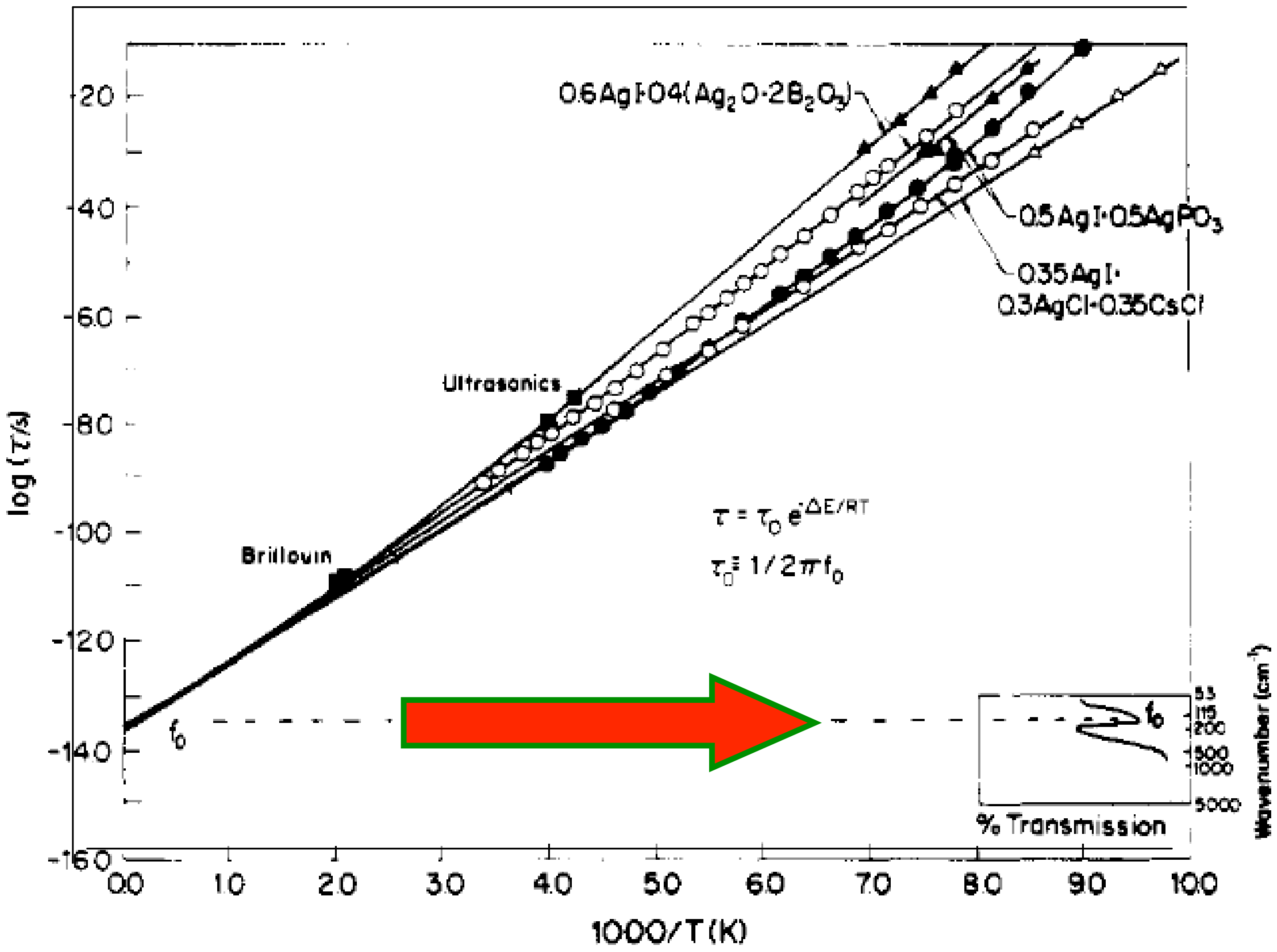
Are obtained with aqueous acid systems





Concept: ***limiting high conductivity***
Arrhenius plots for superionic glass τ_i

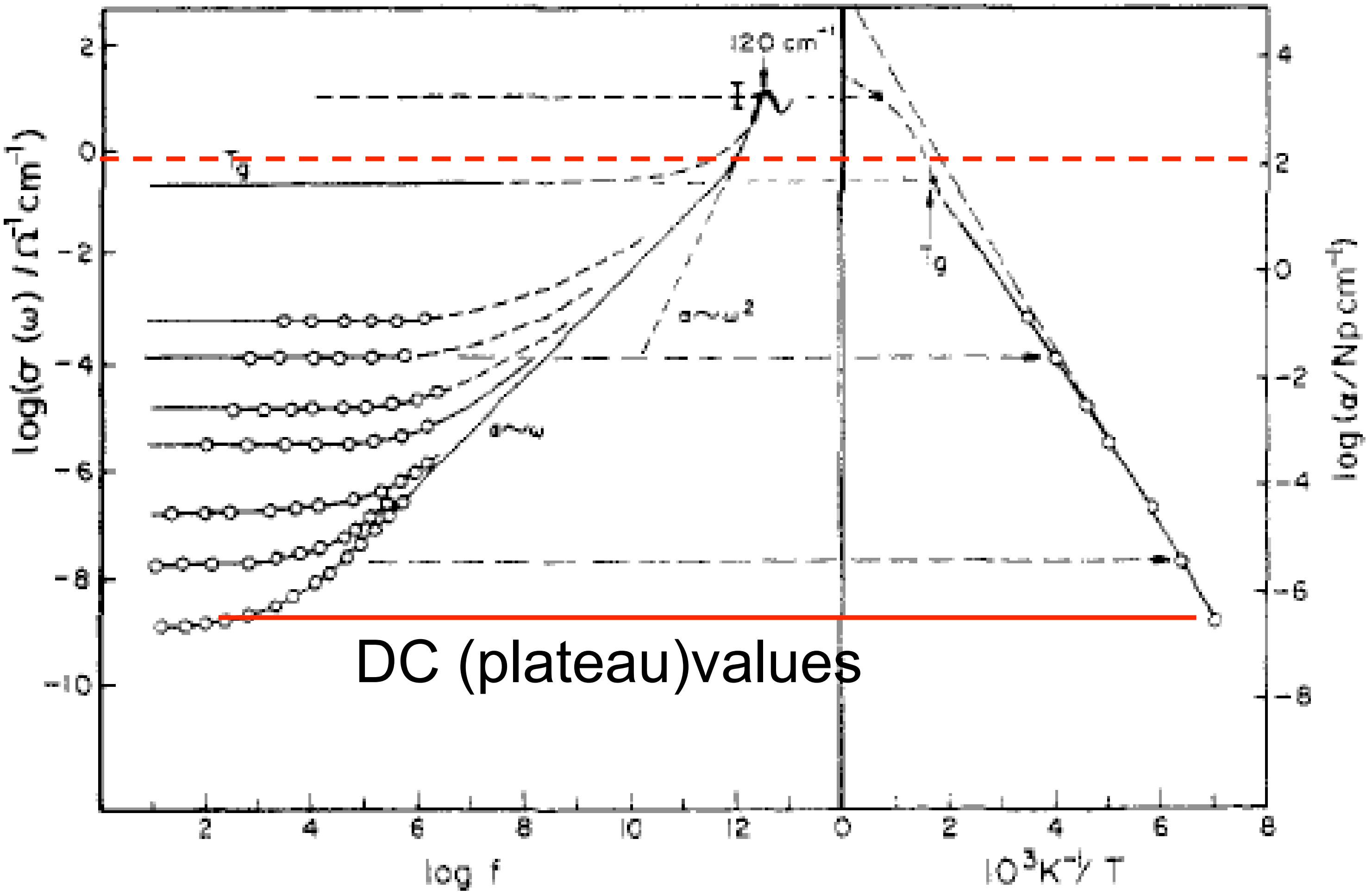
Chemical Reviews, 1990, Vol. 90, No. 3 **537**



Relation between conductivity limit from FIR and from Arrhenius plot

538 Chemical Reviews, 1990, Vol. 90, No. 3

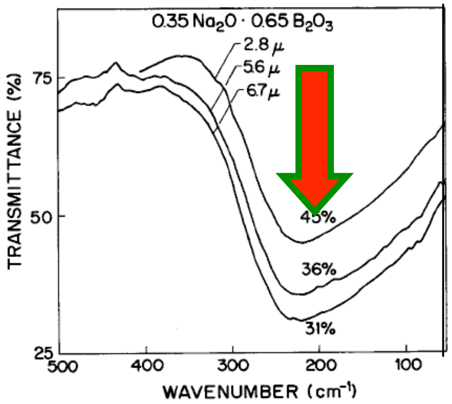
How close can we get?



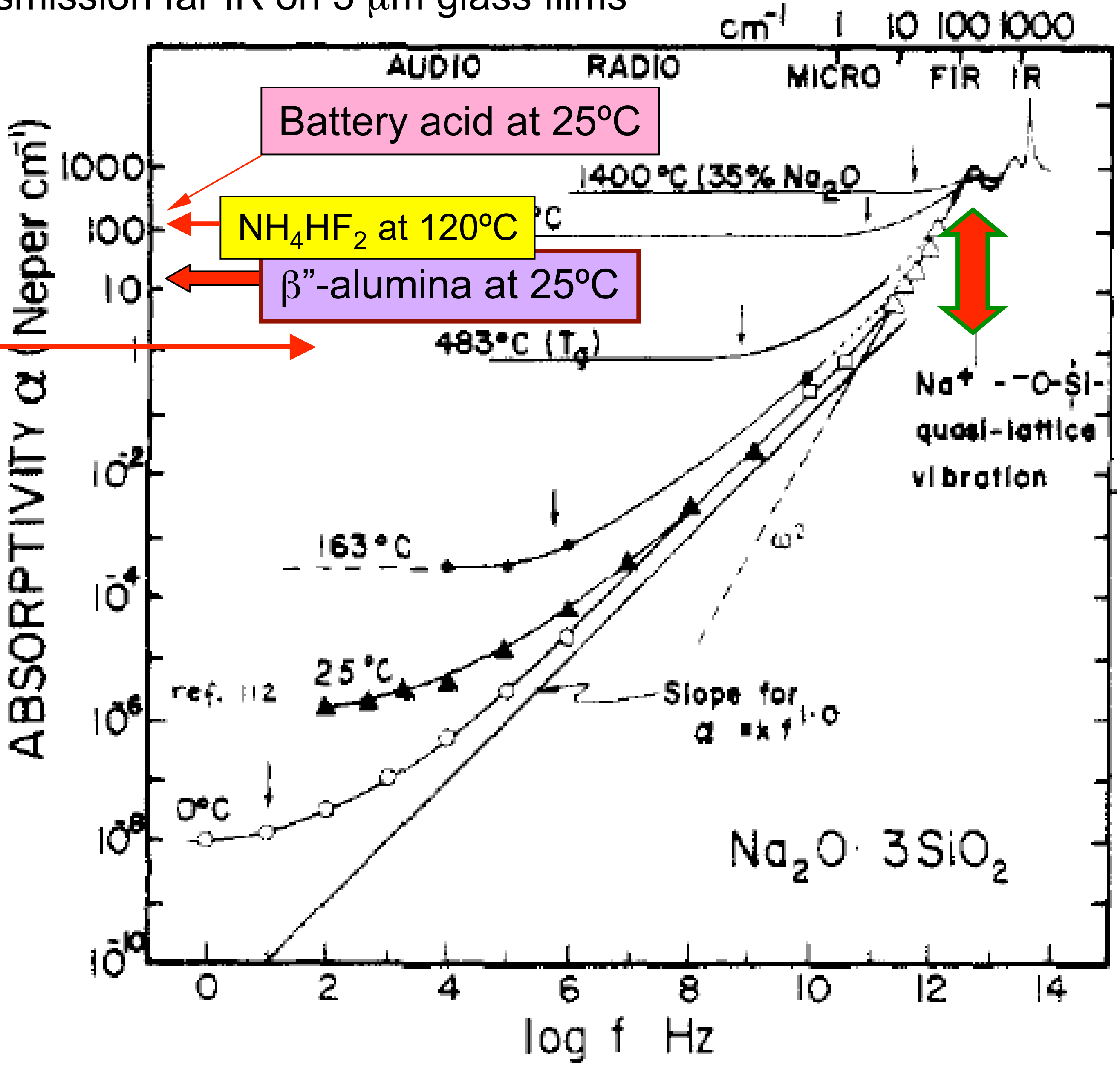
DC (plateau)values

The big picture (of absorptivity and conductivity in ionic liquids)

Transmission far IR on 5 μm glass films



Value from conductivity of EAN at 25ºC, using n(ω) of EAN



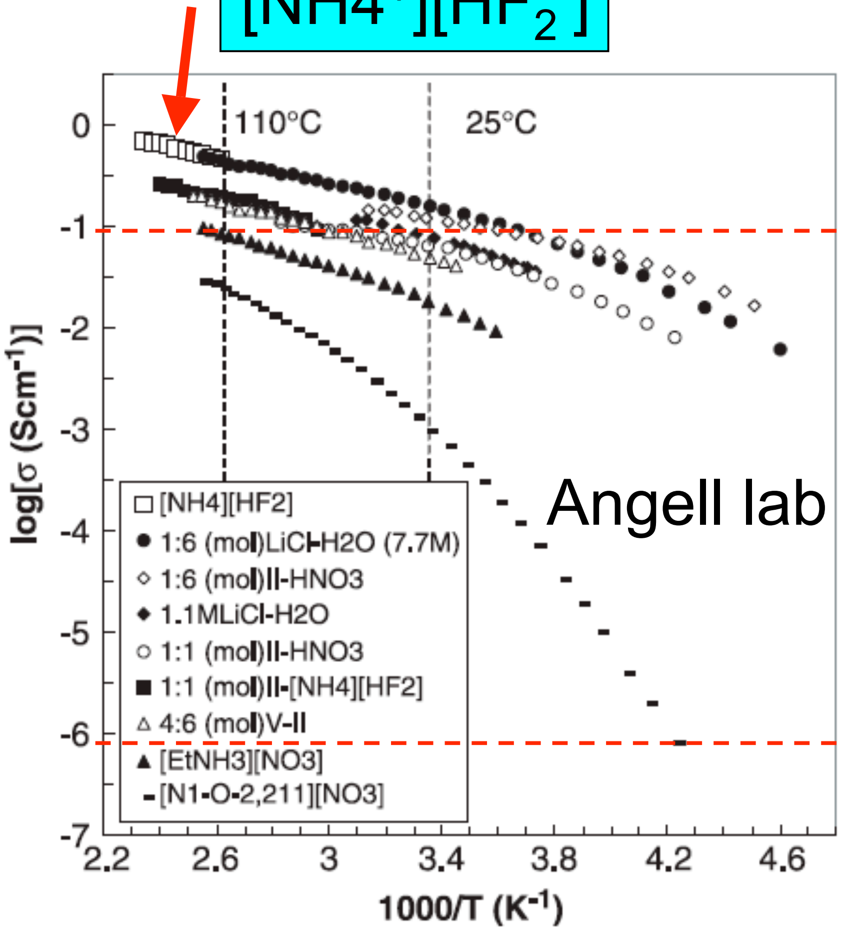
Battery acid at 25ºC

NH_4HF_2 at 120ºC

β”-alumina at 25ºC

β-Al_2O_3 conductivity is comparable to those of aqueous solutions and ILs

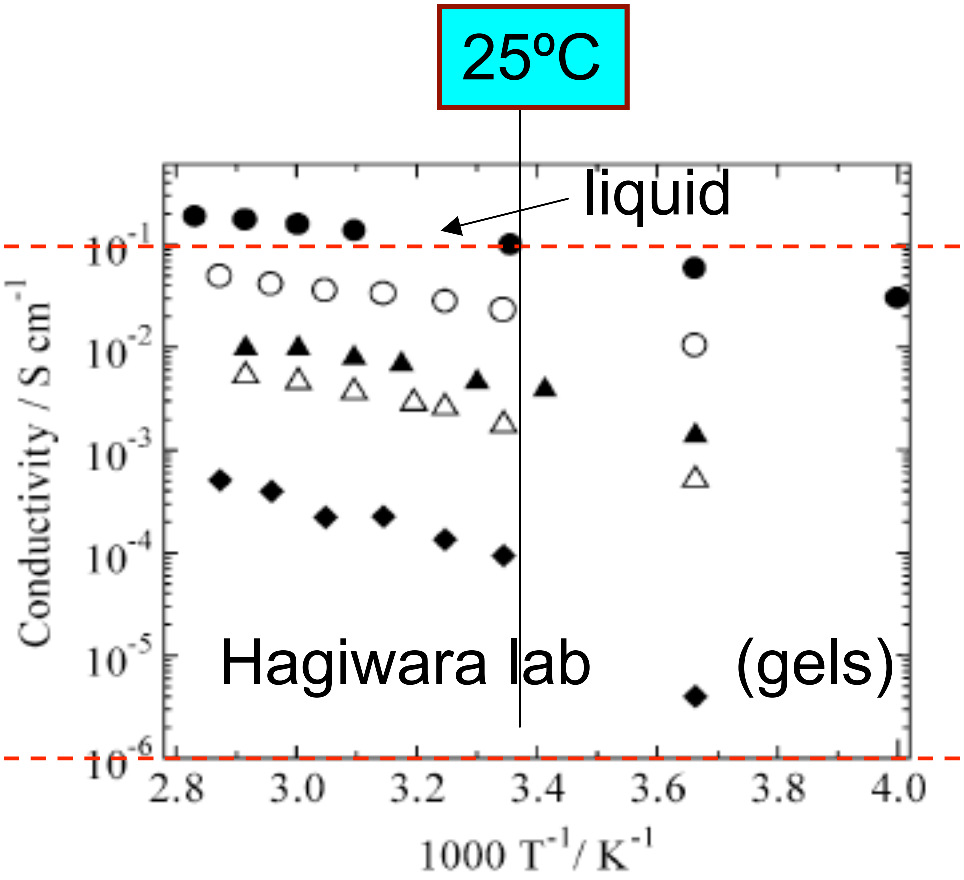
$[NH4^+][HF_2^-]$



Angell lab

Science, 2003
Xu and Angell

25ºC



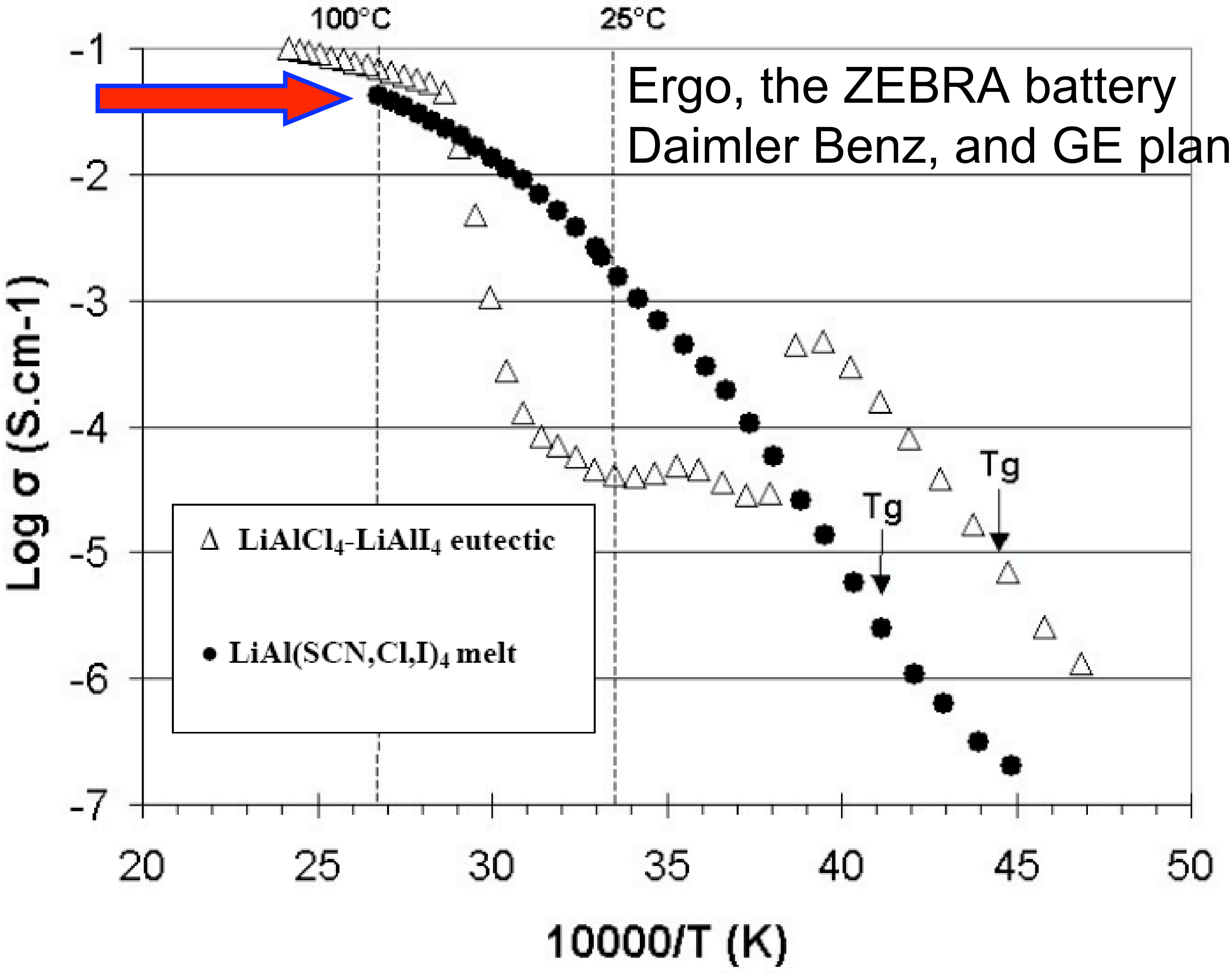
Hagiwara lab

(gels)

Fig. 1. Conductivity of electrolyte composites of poly-HEMA a ETMEIM(HF)$_n$F (n=2.3). ●: Neat EtMeIm(HF)$_n$F (N=1.0), co posite with the molar fraction of EtMeIm(HF)$_n$F, N; ○: 0.60, ▲: 0.5 △: 0.40, ◆: 0.20.

Solid State Ionics, 2002

LiAl halide and pseudohalide liquids



Ergo, the ZEBRA battery
Daimler Benz, and GE plans

Conductivity decreases, are due to:

1. Friction against neighbors - repulsive forces
   Minimize by (a) increasing empty space ("free volume"),
   (b) making neighbors polarizable

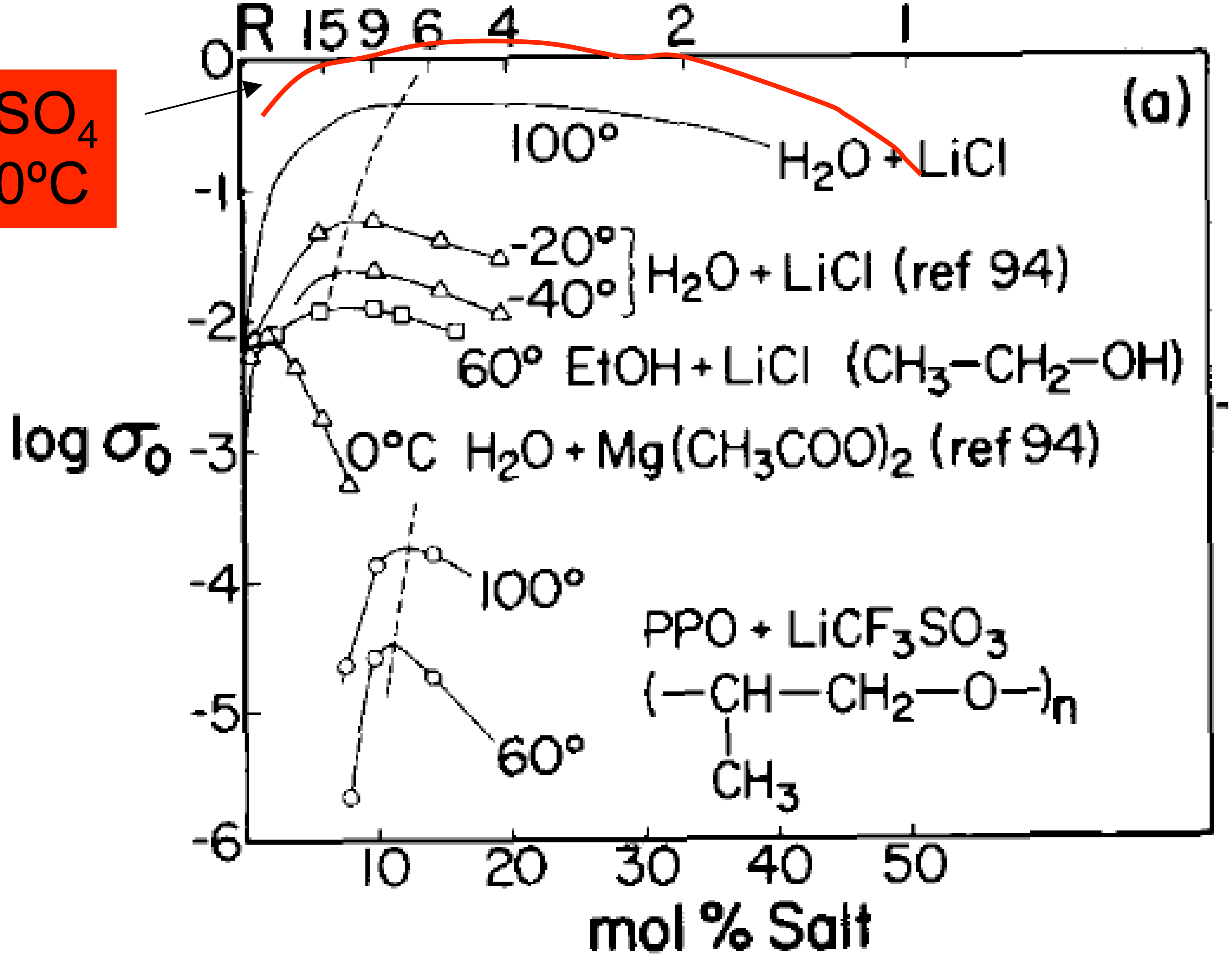
2. Friction from other ions of opposite charge- attractive forces
   Minimize by (a) eliminating multivalent ions,
   and (b) increasing charge separation (lower conc.)

3. Insufficient charges crossing reference area (electrode surface)
   Counter by increasing charge concentration, (in conflict with 2)
   (so, expect maximum)

4. Insuffficient thermal energy.
   counter by (a) raising the temperature
   (b) lowering the cohesive energy (T_g)

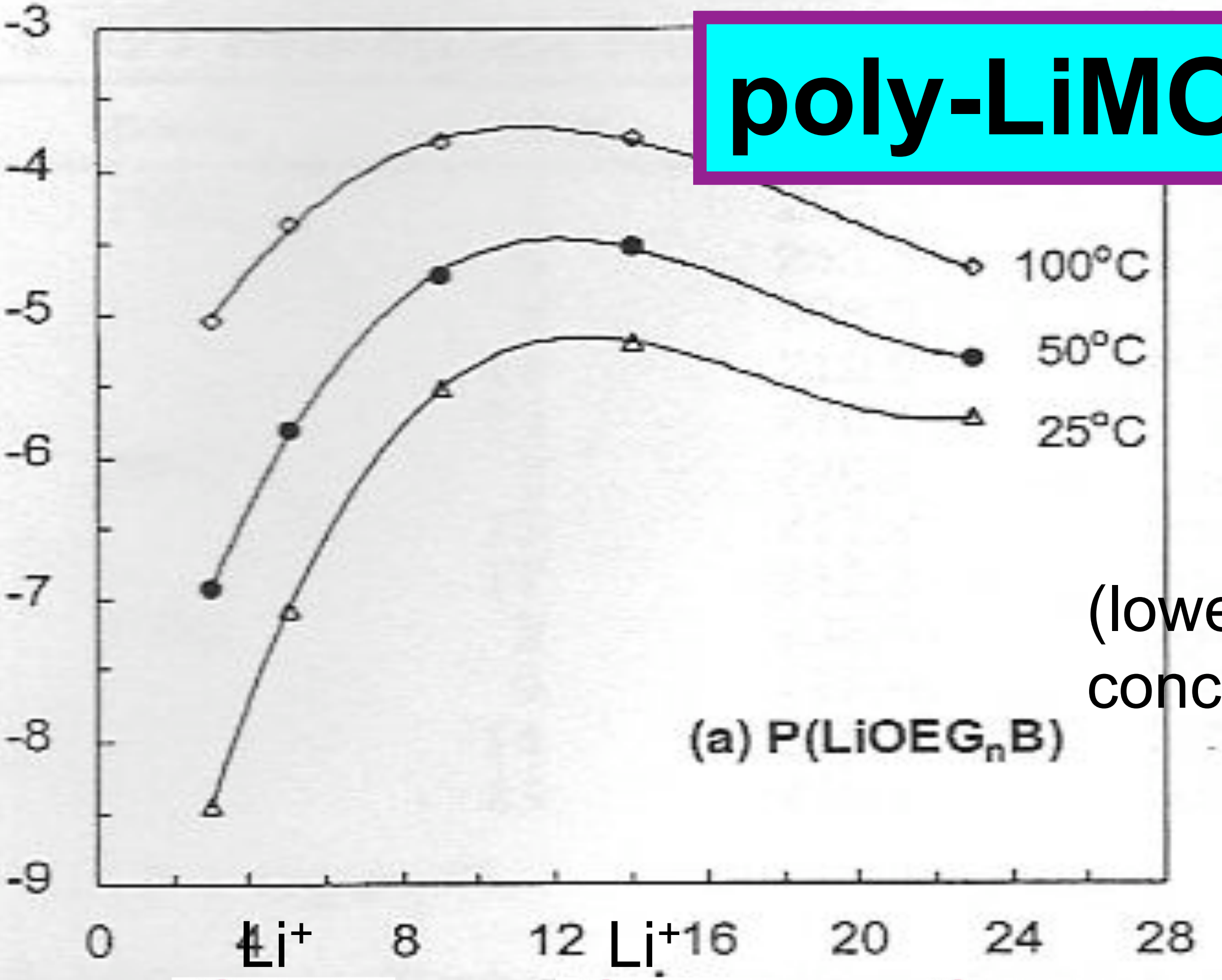
Concept: mobility-concentration competition, and σ(max): Contrast between electrolyte types

H_2SO_4
100ºC



Novel Polyanionic Solid Electrolytes

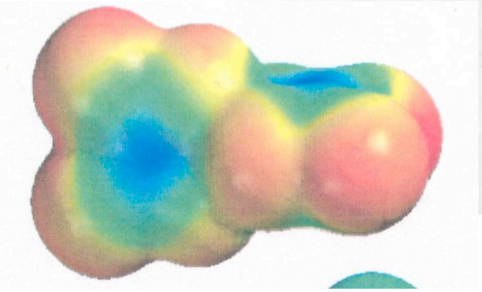
Xu, Williams and Angell, Chem. Mater. **14**(2) 401-409 (2002).



poly-LiMOB

(lowest [Li+] concentratio

The BOB$^-$ anion



Li$^+$ Li$^+$

Polymeric form linked by polyether, n=3

Wot to do?

Attempts were made to synthesize Li salts which would be low melting and lithium ion decoupled and then rubberize by polymer additions. (The “polymer-in-salt” electrolyte concept). The attempts were only partly successful.

Attempts to make glassy analogs of the β”alumina have been made without success. The possibility of putting GF liquids under tension and trapping them as glasses in the stretched state has not yet been tried.

The current situation:

Li ion batteries run with non-aqeous solvent salt solutions. The salts dissolve because of ion dipole interactions so the ions are all trapped in their solvation shells.. No chance of decoupled motion.. They are slaved to the solvent motions. NO Walden plots are available to demonstrate this situation. The fluidities are limited by involatility requirements. The end of the line is close at hand

Silent watch over Easter Island

Dormant giant, still in
the crater wall, waiting.

Aims of the talk

1. Review the types of electrolytes that may be utilized in energy storage and delivery, contrasting Li^+ (Na^+) and protic cases.

2. Review the concepts that are useful in discussing the properties of non crystalline electrolytes.
    - (a) relaxation times
    - (b) “freezing-in”/glass transitions (in crystals as well)
    - (c) decoupling, “superionics”, and Walden plots
    - (d) “wet” and “dry” protons
    - (e) maximum conductivities
3. Wot to do (a) Decoupliing in liquids (b) tension in solids
4. Electrochemical windows and high voltage systems.
    - Solvents, vs ionic liquids, vs glasses

WOT TO DO WHEN CONDUCTIVITY HAS MAXED AND POWER IS STILL NEEDED?

Must increase the **cell voltage**… a new set of problems

1. We need the cathode chemistry
2. We need electrolytes that will “take the heat” i.e. be stable under the more oxidizing conditions

The ABC battery for Chevy Volt

Problem for the US is that most of the IP for batteries is owned not by battery companies or car companies but by **OIL** companies !!

Think about that a bit…..

Chevy Volt is an electric car that goes 40 miles on an electric charge. ... how Volt performs, aggressive driving will result in fewer miles per charge. ..

for the Volt's battery pack was "many hundreds of dollars per kilowatt hour ...

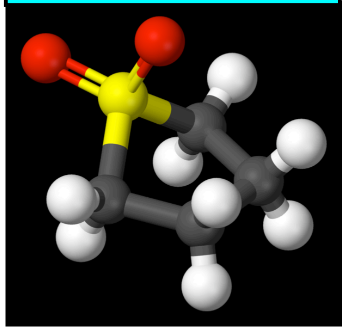
But can charge very quickly, as we’ll see

OTHER CONTRIBUTORS

THE ARGONNE NAT. LAB. LI ION BATTERY GROUP:

A recent contribution to sulfone electrolyte technology

electrolyte



+ $LiPF_6$

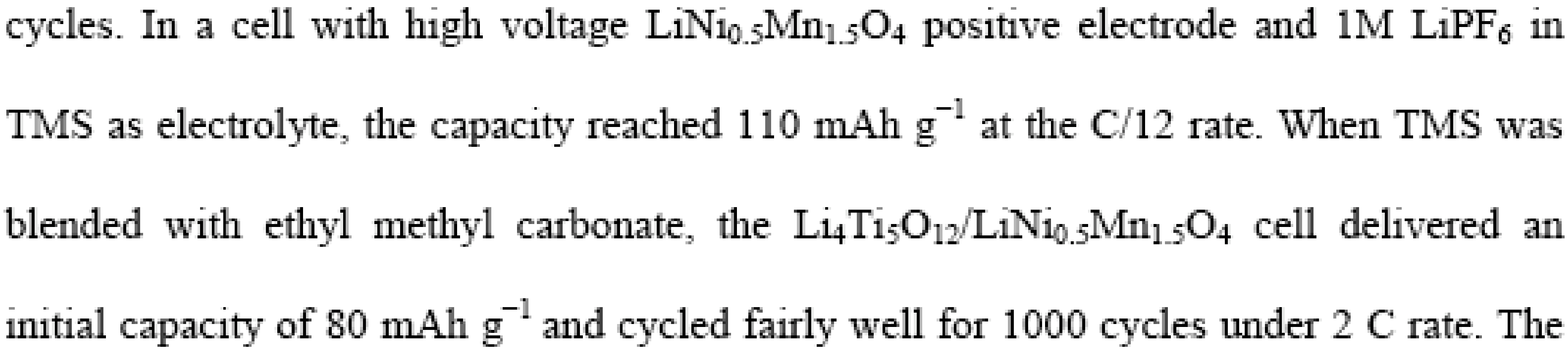
Tetramethylene sulfone

anode

Lithium titanate (1.5 V above Li)

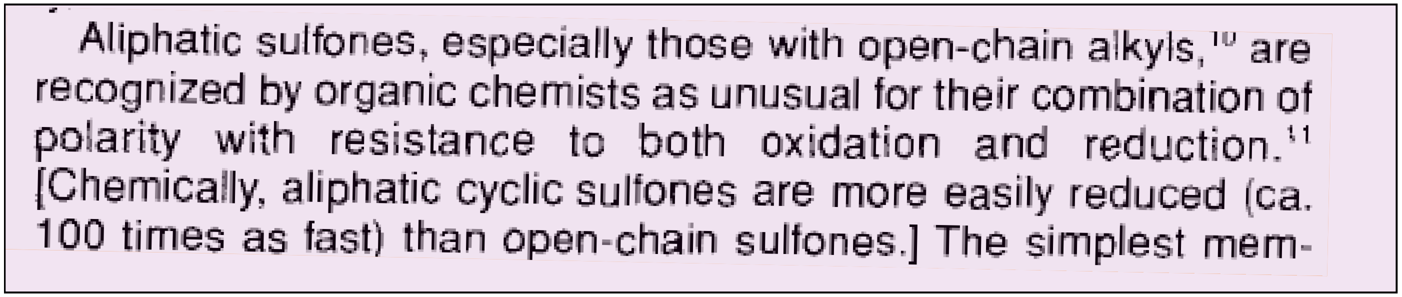
cathode

Lithium nickel manganate: a very high voltage cathode (5V above Li)

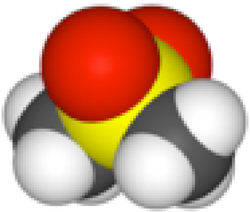


cycles. In a cell with high voltage $LiNi_{0.5}Mn_{1.5}O_4$ positive electrode and 1M $LiPF_6$ in TMS as electrolyte, the capacity reached 110 mAh g^{-1} at the C/12 rate. When TMS was blended with ethyl methyl carbonate, the $Li_4Ti_5O_{12}/LiNi_{0.5}Mn_{1.5}O_4$ cell delivered an initial capacity of 80 mAh g^{-1} and cycled fairly well for 1000 cycles under 2 C rate. The

Sulfones known very stable against reduction or oxidation



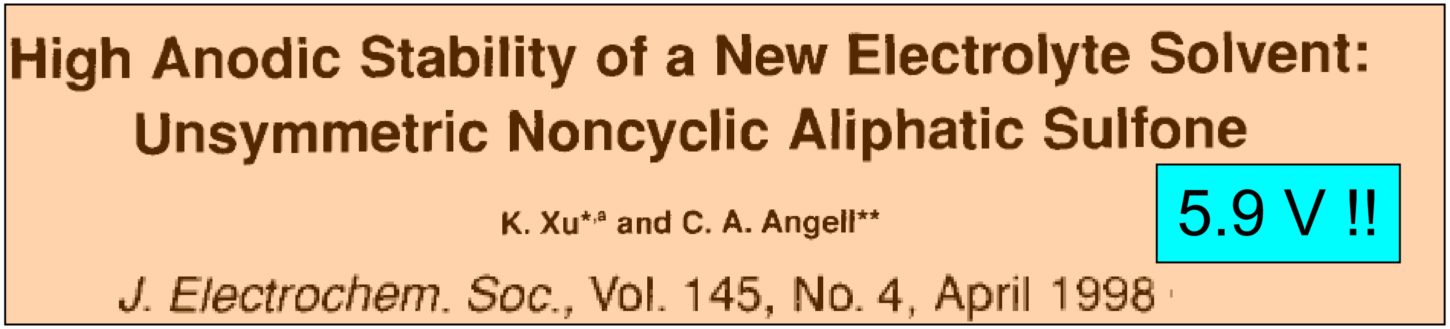
Aliphatic sulfones, especially those with open-chain alkyls,[10] are recognized by organic chemists as unusual for their combination of polarity with resistance to both oxidation and reduction.[11] [Chemically, aliphatic cyclic sulfones are more easily reduced (ca. 100 times as fast) than open-chain sulfones.] The simplest mem-



but		T_m
Dimethyl sulfone	$(CH_3)_2SO_2$	109ºC
Diethyl sulfone	$(Et)_2SO_2$	70ºC
Dipropyl sulfone	etc	

Try destabilization of crystal lattice by making the molecule asymmetrical.

T_m = 35ºC: eutectic with DMS is 25ºC



High Anodic Stability of a New Electrolyte Solvent: Unsymmetric Noncyclic Aliphatic Sulfone

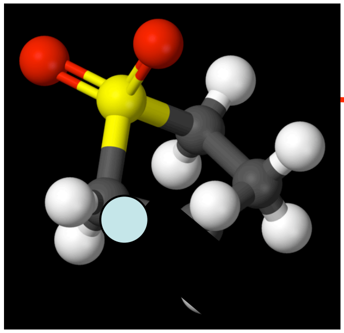
K. Xu*,a and C. A. Angell**

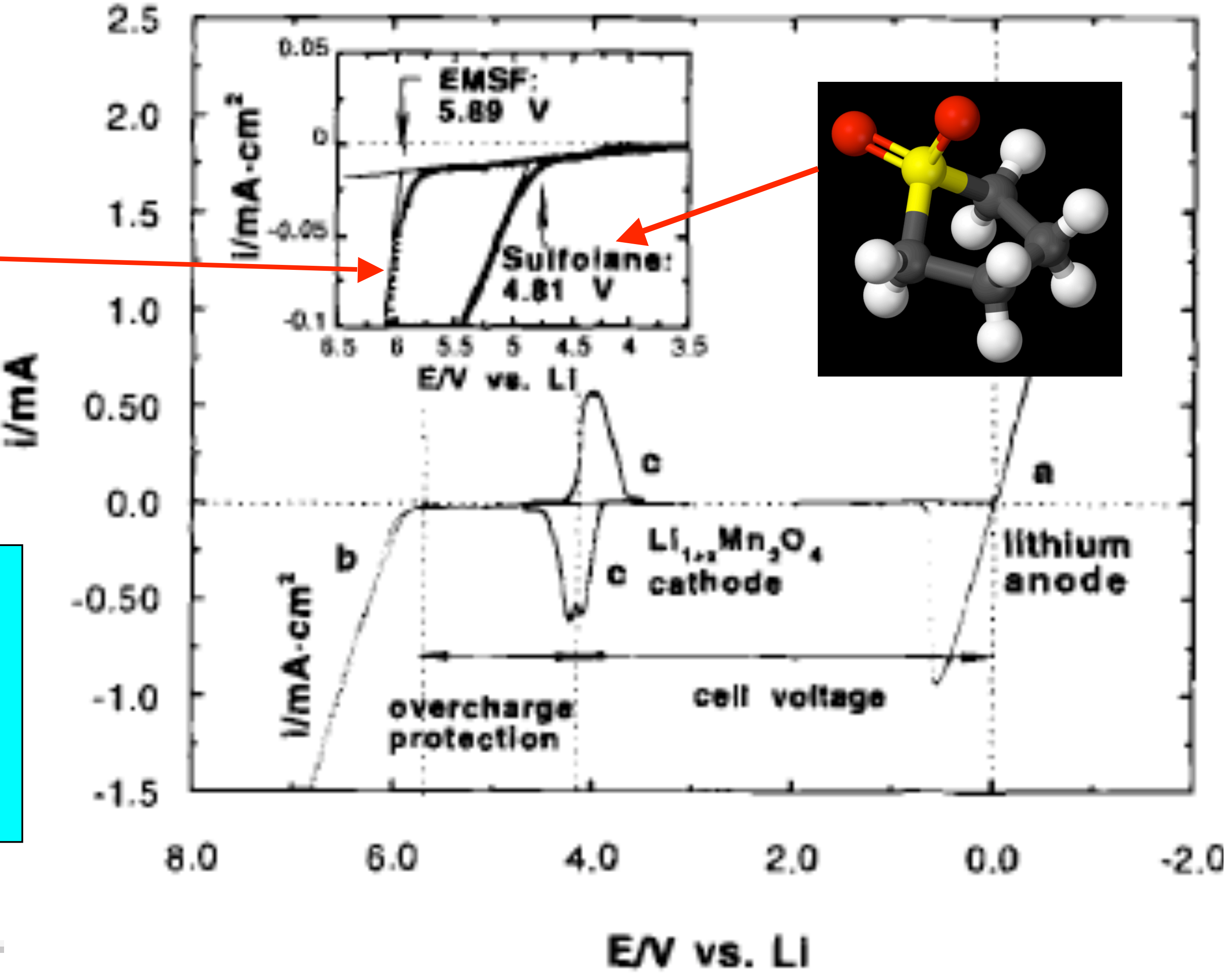
J. Electrochem. Soc., Vol. 145, No. 4, April 1998

5.9 V !!

A 5.9 volt window !

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





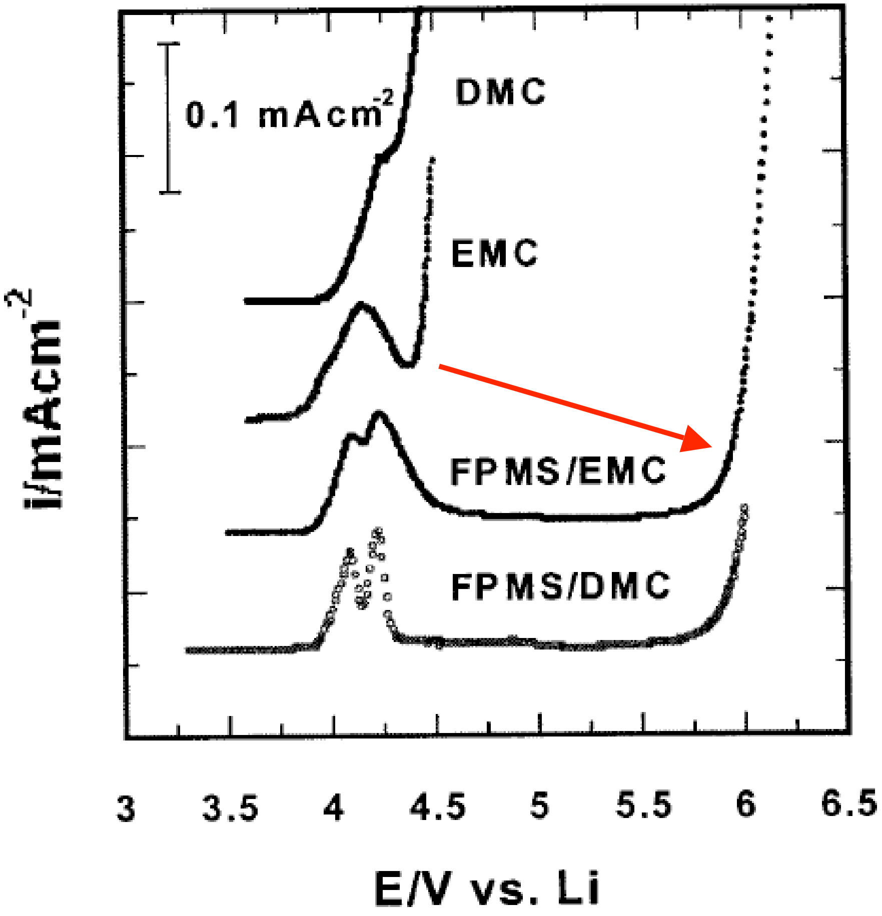
For capacitative storage, note that the energy of a capacitor is given by:

$$E = \frac{1}{8} c_p V^2 ,$$

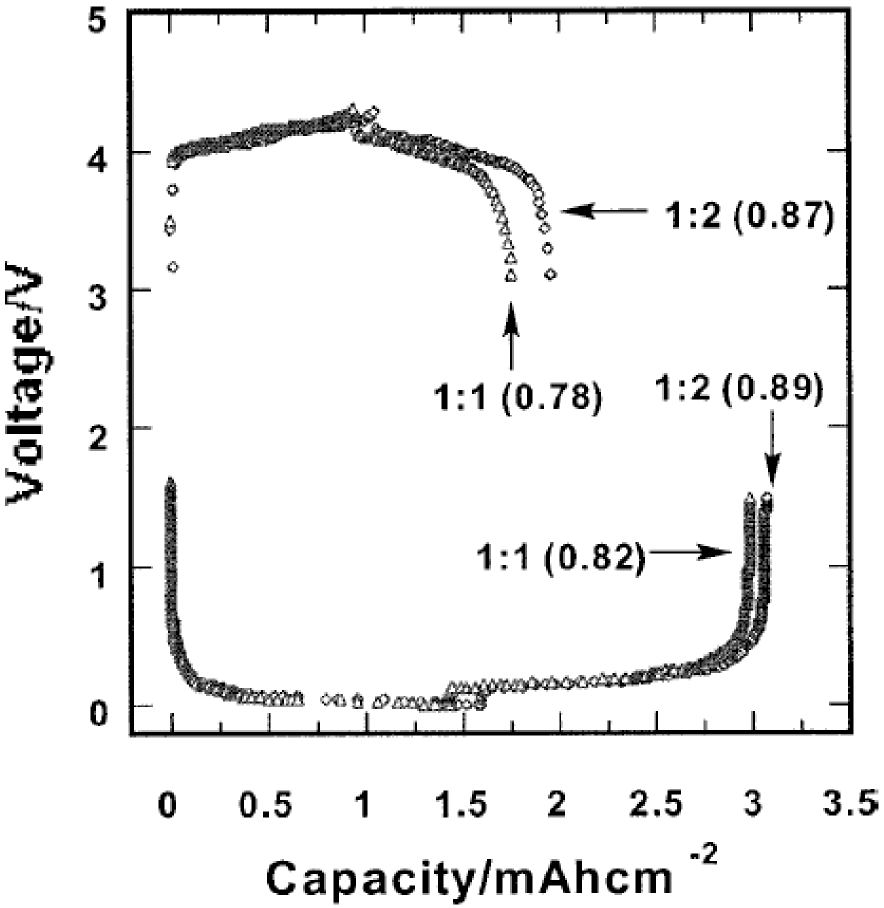
And sulfones seem to protect lower EC "window"(but higher fluidity) co-solvents

Work of Kang Xu (JECS,2002)

FPMS is **CF_3**CH_2CH_2[**SO_2**]CH_3

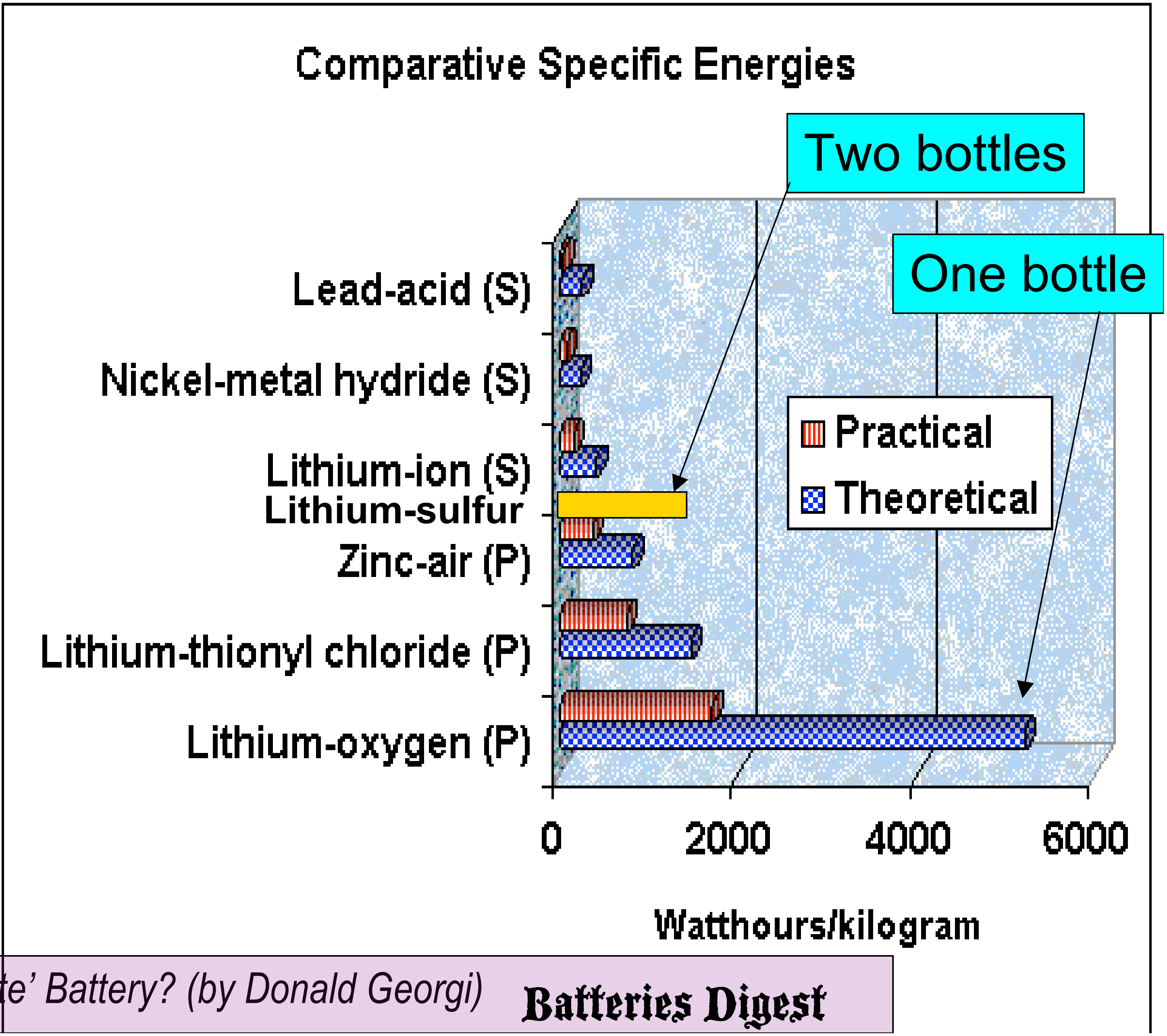


Forms good SEI



Specific energies of battery systems

How much energy can we store per unit mass of the storage system (cell) ?



*

Lithium-Air...the 'Ultimate' Battery? (by Donald Georgi) **Batteries Digest**

SUMMARY

1. Electrochemical devices seem to have been around a very long time.

2. There are a number of important system variables to be played with (capacity, output voltage, cyclability, discharge rate, safety) developments in any one of which can make one system superior to the others, but the electrolyte is always a central actor.

3. A wide range of electrolyte types are possible, some surprising ceramics being among the best of all. Assessment of electrolyte properties involves a number of conceptual problems.

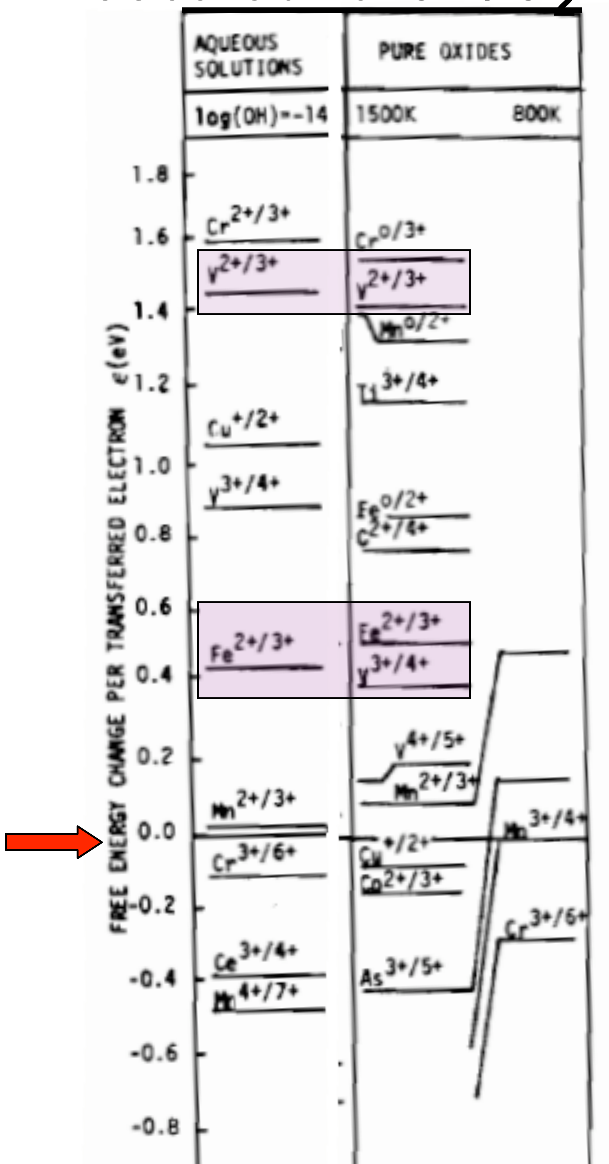
4. Electrolytes with wide electrochemical windows are needed to optimise energytransfer and storage possibilities

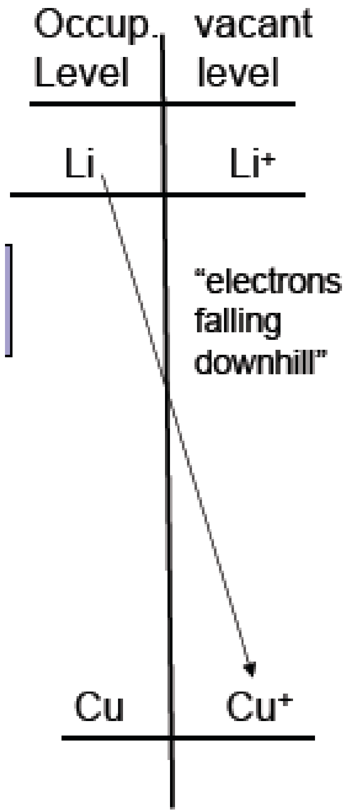
Addendum:

electron energy levels for redox systems, and proton energy levels for protic systems.

GURNEY diagrams for aqu. solutions referenced to the oxide/oxygen level, and compared to the pure oxides

Rescaled to O^{2-}/O_2 **ref**



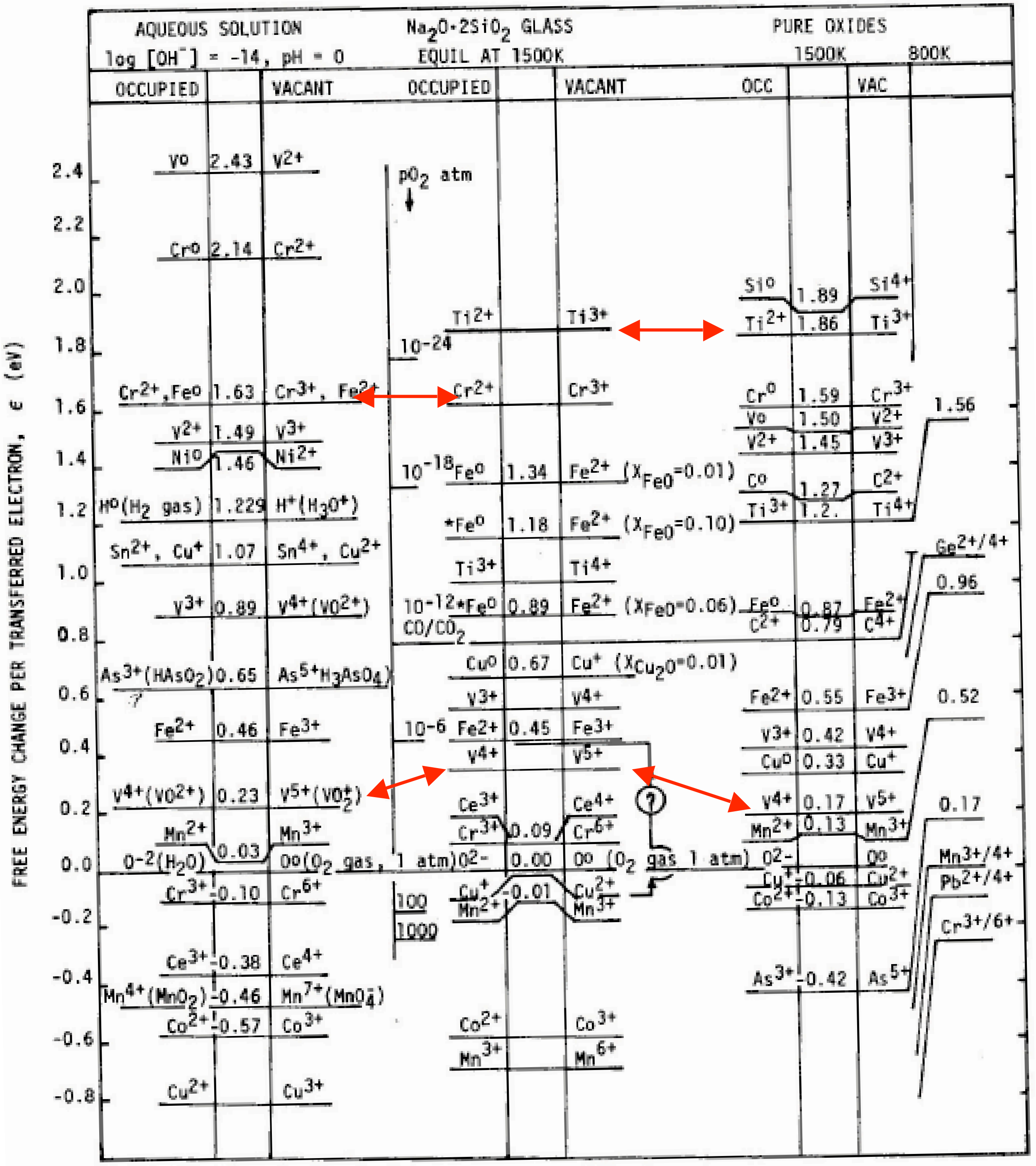


Energy diagram from redox table

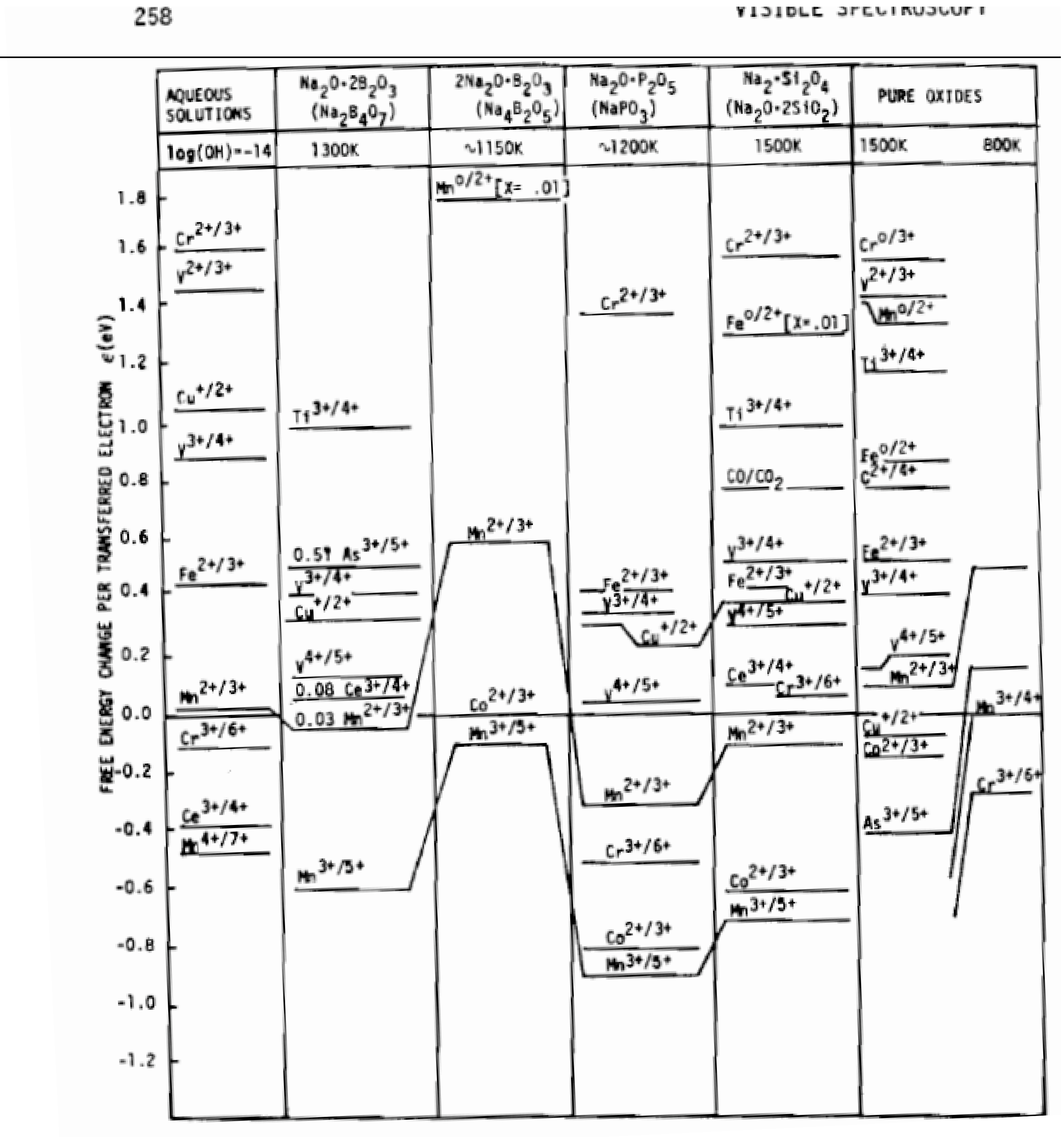
occupied levels	vacant levels
Cu	Cu^+
$\frac{1}{2}O^{2-}$	$\frac{1}{4}O_2$ (g, 1 atm)

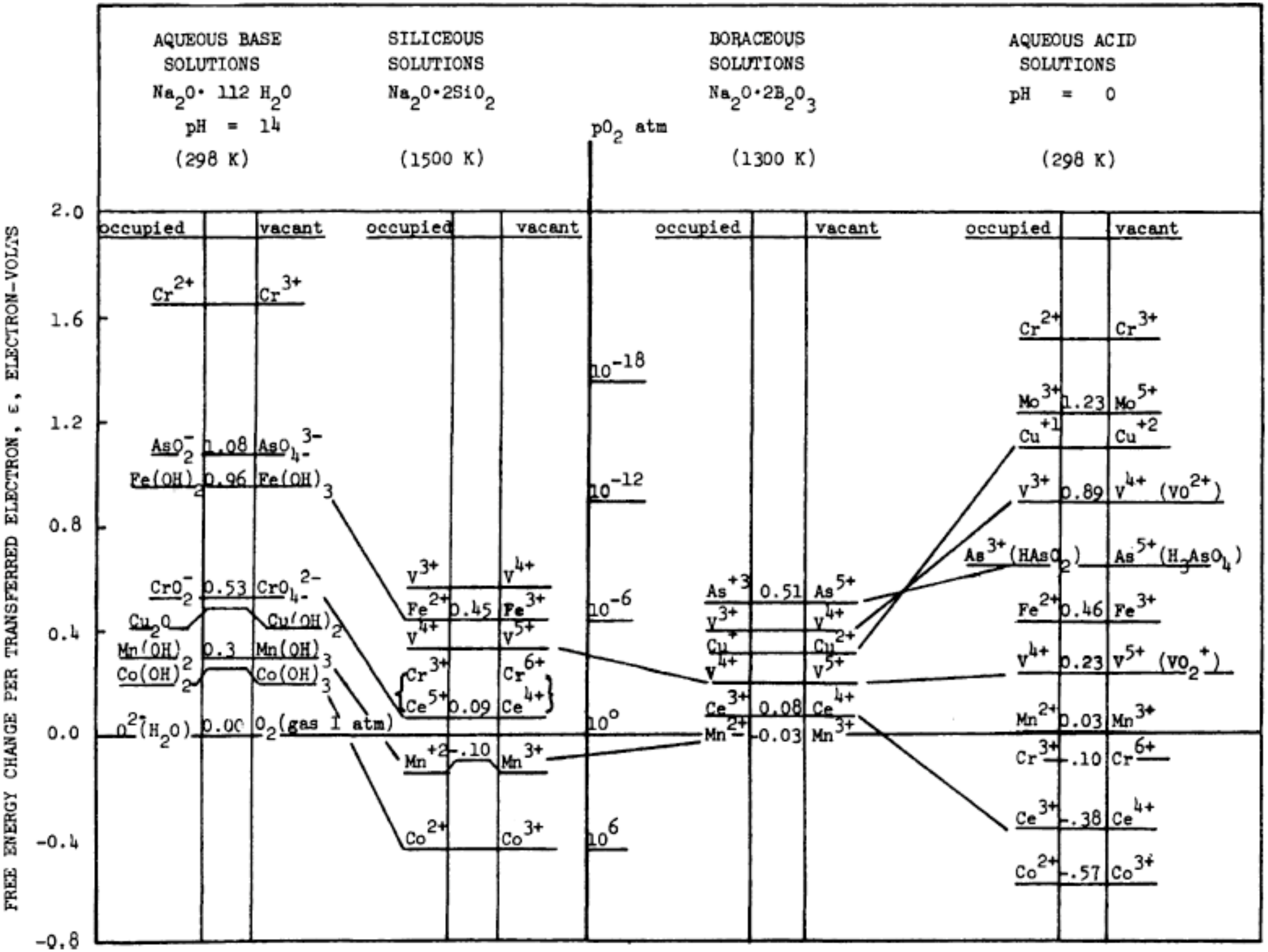
***Lesson*: the characteristic redox levels hardly change from those assessed from the pure oxide free energies. So, in ionic liquids, the same level scheme will apply but the voltage range of choice will be larger.**

EFEL diagrams for aqu., & NaS, solutions vs. pure oxides



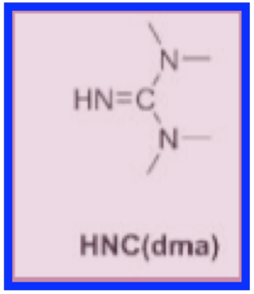
EFEL diagrams for NaB, NaP and NaS solutions



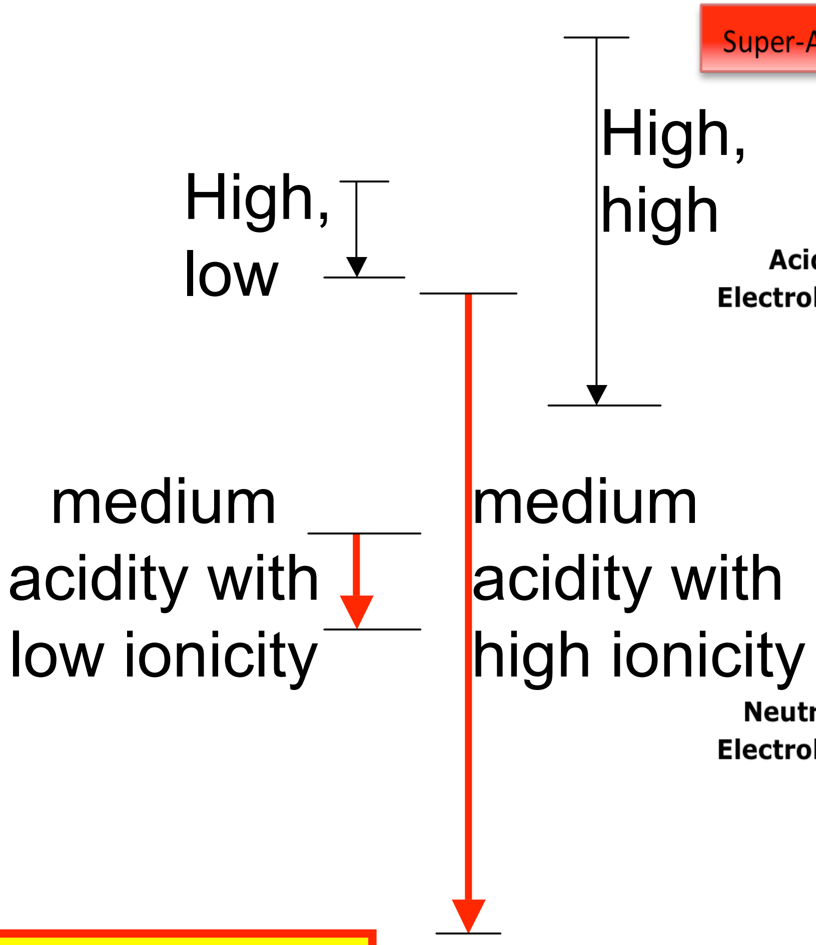

AQUEOUS BASE SOLUTIONS
$Na_2O \cdot 112\ H_2O$
pH = 14
(298 K)
SILICEOUS SOLUTIONS
$Na_2O \cdot 2SiO_2$
(1500 K)
BORACEOUS SOLUTIONS
$Na_2O \cdot 2B_2O_3$
(1300 K)
AQUEOUS ACID SOLUTIONS
pH = 0
(298 K)
pO_2 atm
10^{-18}
10^{-12}
10^{-6}
10^{0}
10^{6}
FREE ENERGY CHANGE PER TRANSFERRED ELECTRON, ε, ELECTRON-VOLTS
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
occupied
vacant
Cr^{2+}
Cr^{3+}
AsO_2^- 1.08 AsO_4^{3-}
$Fe(OH)_2$ 0.96 $Fe(OH)_3$
CrO_2^- 0.53 CrO_4^{2-}
Cu_2O
$Cu(OH)_2$
$Mn(OH)_2$ 0.3 $Mn(OH)_3$
$Co(OH)_2$
$Co(OH)_3$
$O^{2-}(H_2O)$ 0.00 O_2(gas 1 atm)
V^{3+}
V^{4+}
Fe^{2+} 0.45 Fe^{3+}
V^{4+}
V^{5+}
Cr^{3+}
Cr^{6+}
Ce^{5+} 0.09 Ce^{4+}
Mn^{+2} -.10 Mn^{3+}
Co^{2+}
Co^{3+}
As^{+3} 0.51 As^{5+}
V^{3+}
V^{4+}
Cu^{+}
Cu^{2+}
V^{4+}
V^{5+}
Ce^{3+} 0.08 Ce^{4+}
Mn^{2+} -0.03 Mn^{3+}
Cr^{2+}
Cr^{3+}
Mo^{3+} 1.23 Mo^{5+}
Cu^{+1}
Cu^{+2}
V^{3+} 0.89 V^{4+} (VO^{2+})
As^{3+} ($HAsO_2$)
As^{5+} (H_3AsO_4)
Fe^{2+} 0.46 Fe^{3+}
V^{4+} 0.23 V^{5+} (VO_2^+)
Mn^{2+} 0.03 Mn^{3+}
Cr^{3+} -.10 Cr^{6+}
Ce^{3+} -.38 Ce^{4+}
Co^{2+} -.57 Co^{3+}

Full range proton FEL diagram

Finally, today's subject,
PILs that are also superacids

	Occupied	Vacant	pK_a	E(eV)
Super-Acids	$HSbF_6$	SbF_6-		
	HBOB	BOB-		
	HTFSI	TFSI-		
	HSO_3F	SO_3F-	-14	0.83
	pFPyH$^+$	**pFPy**		
	HTf	Tf^-		
Acid Electrolytes	$HClO_4$	ClO_4^-	-10	0.59
	H_2SO_4	HSO_4^-	-9	0.53
	HPO_2F_2	$PO_2F_2^-$		
	HNO_3	NO_3^-	-1.3	0.08
	CH_3SO_3H	$CH_3SO_3^-$ (MS)	-0.6	0.04
	2-Fluoropyridine H$^+$	**2-Fluoropyridine**	**-0.43**	**0.03**
	CF_3COOH	CF_3COO^- (TfAc)	-0.25	0.01
	H_2O^+	H_2O	0	0
	H_3PO_4	$H_3PO_4^-$	2.12	-0.13
	1,2,3-1 H-triazole H$^+$	1,2,4-1 H-triazole	3	-0.18
	HF	F^-	3.2	-0.19
	HCOOH	$HCOO^-$	3.75	-0.22
	CH_3COOH	CH3COOH$^-$	4.75	-0.28
Neutral Electrolytes	**α-MePyH$^+$**	**α-MEPy**	**6.99**	**-0.41**
	hydrazine H$^+$	hydrazine	7.96	-0.47
	NH_4^+	NH_3	9.23	-0.55
	$EtNH_3^-$	$EtNH_3$	10.63	-0.63
	Et_3NH^+	**Et_3N (TEA)**	**11.25**	**-0.67**
	$C(NH_2)_3^+$	**Guanidine**		
	H_2O	OH^-	14	-0.83
Basic Electrolytes	NH_3	NH_2^-		
Super-Bases	**$H_2NC(dma)$**	**HNC(dma)**		
	OH^-	$O^{2-}(Na^+)$	28	-1.660

Ionicity and acidity


High, low

High, high

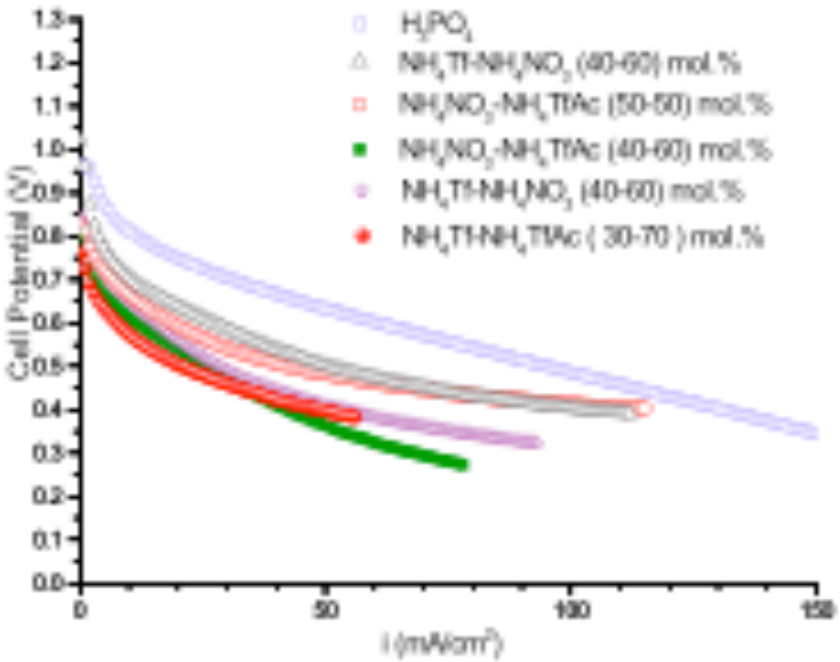
medium acidity with low ionicity

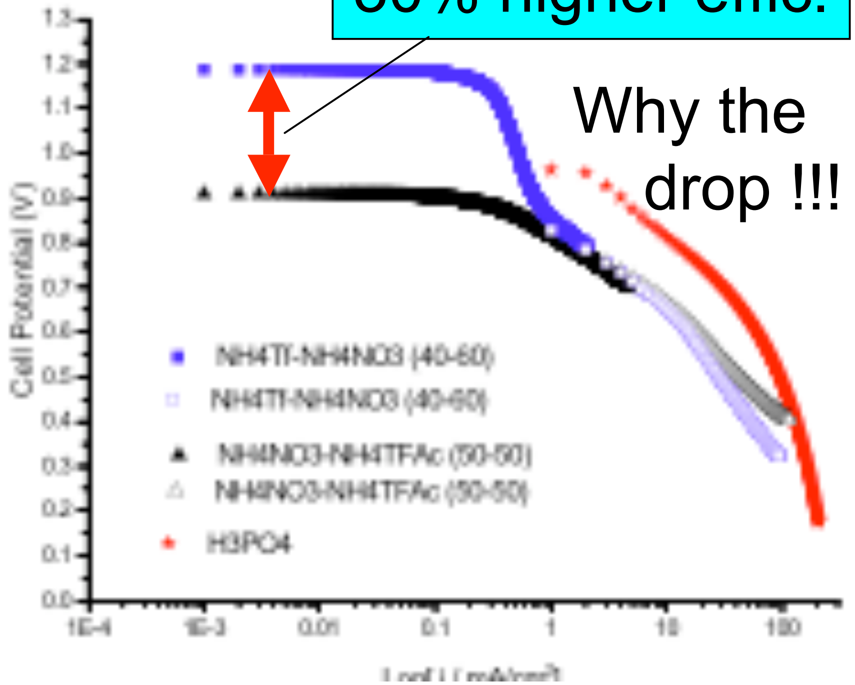
medium acidity with high ionicity

	Occupied	Vacant	pK_a	E(eV)
Super-Acids	$HSbF_6$	SbF_6-		
	HBOB	BOB-		
	HTFSI	TFSI-		
	HSO_3F	SO_3F-	-14	0.83
	$pFPyH^+$	**pFPy**		
	HTf	Tf^-		
Acid Electrolytes	$HClO_4$	ClO_4^-	-10	0.59
	H_2SO_4	HSO_4^-	-9	0.53
	HPO_2F_2	$PO_2F_2^-$		
	HNO_3	NO_3^-	-1.3	0.08
	CH_3SO_3H	$CH_3SO_3^-$ (MS)	-0.6	0.04
	2-Fluoropyridine H^+	**2-Fluoropyridine**	**-0.43**	**0.03**
	CF_3COOH	CF_3COO^- (TfAc)	-0.25	0.01
	H_2O^+	H_2O	0	0
	H_3PO_4	$H_3PO_4^-$	2.12	-0.13
	1,2,3-1 H-triazole H^+	1,2,4-1 H-triazole	3	-0.18
	HF	F^-	3.2	-0.19
	HCOOH	$HCOO^-$	3.75	-0.22
	CH_3COOH	$CH3COOH^-$	4.75	-0.28
Neutral Electrolytes	**α-$MePyH^+$**	**α-MEPy**	**6.99**	**-0.41**
	hydrazine H^+	hydrazine	7.96	-0.47
	NH_4^+	NH_3	9.23	-0.55
	$EtNH_3^-$	$EtNH_3$	10.63	-0.63
	Et_3NH^+	**Et_3N (TEA)**	**11.25**	**-0.67**
	$C(NH_2)_3^+$	**Guanidine**		
	H_2O	OH^-	14	-0.83
Basic Electrolytes	NH_3	NH_2^-		
Super-Bases	**H_2NC(dma)**	**HNC(dma)**		
	OH^-	$O^{2-}(Na^+)$	28	-1.660

Will any of them work?

Some indications from use of the plasticizers working as liquids:





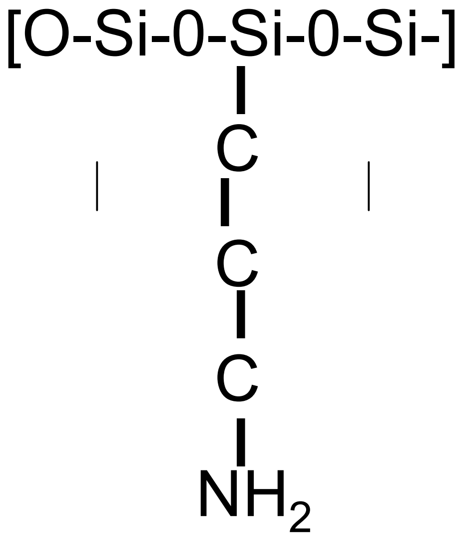
30% higher effic.

Why the drop !!!

Inorganic ionic liquids (ammonium salts) as fuel cell electrolytes!

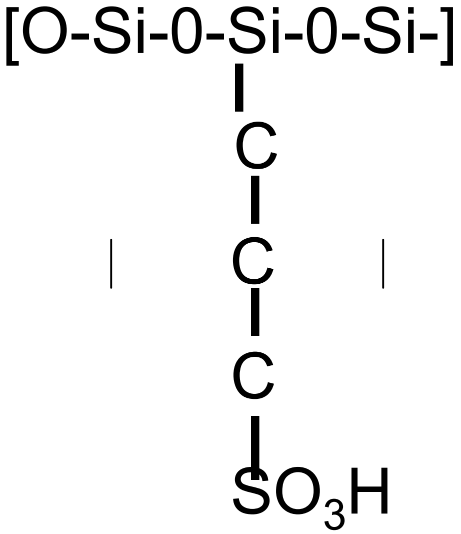
see Belieres et al Chem. Commun. Oct. (2006)

Pendant side chain siloxane polymers


$$\text{[O-Si-0-Si-0-Si-]}\text{-C-C-C-}NH_2$$

neutralize with:
HNO_3, HTf, HSO_3CH_3, etc

Plasticize with e.g. .
1. $[EtNH_3^+][NO_3^-]$
Or2. inorganic IL eutectic mixes


$$\text{[O-Si-0-Si-0-Si-]}\text{-C-C-C-}SO_3H$$

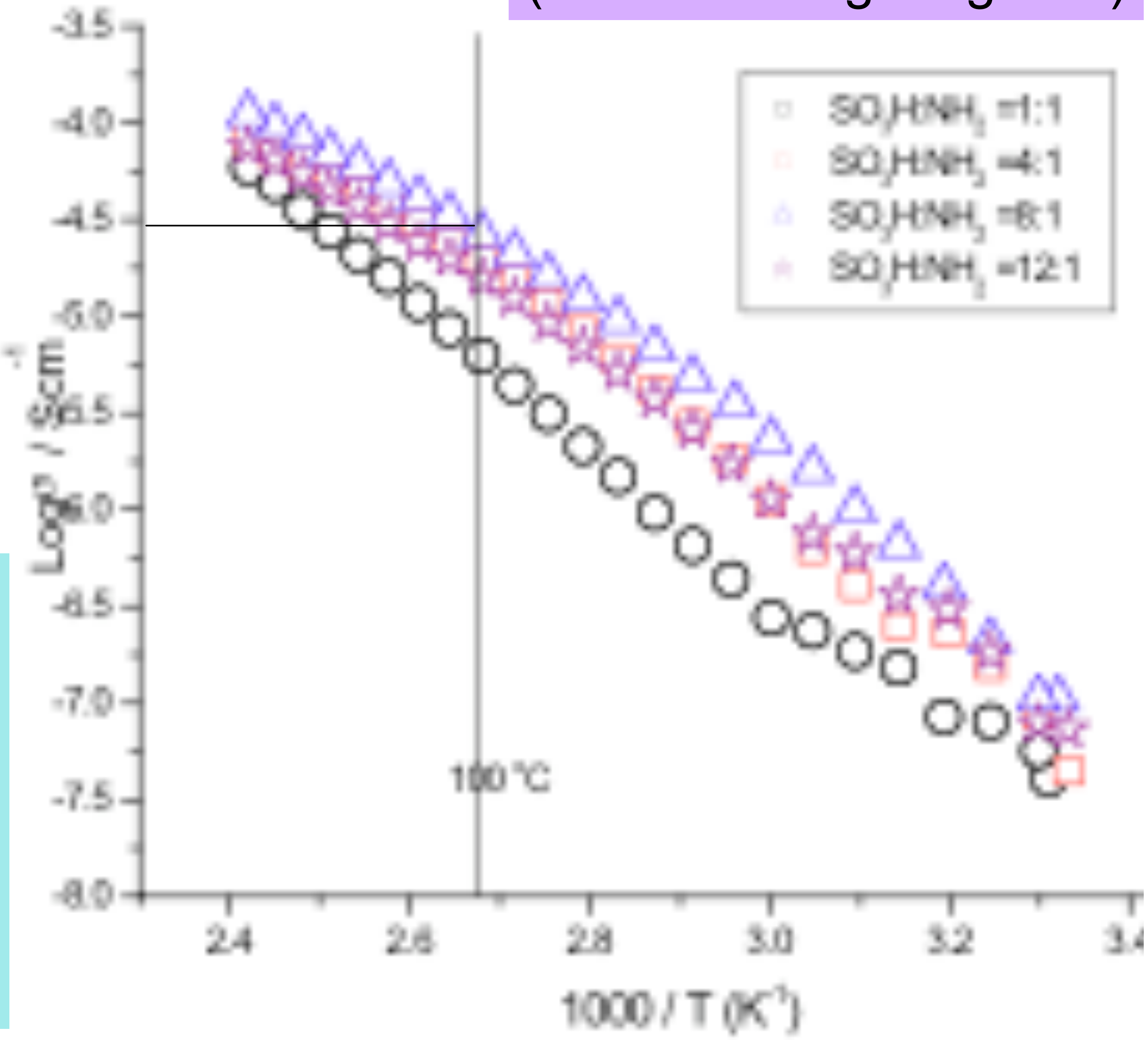
neutralize with:
NH_3, CH_3NH_2, Imidazole etc

Plasticize with $[EtNH_3^+][NO_3^-]$
Or inorganic IL (ammonium nitrate+ammonium triflate eutectic)

Pendant side chain siloxane polymers

(work of Xiaoguang Sun)

Maximum conductivity (100ºC) $10^{-4.5}$ S/cm reached at 12 % (1:8) neutralized



Is the motion of the methylaminium cations coupled to the polymer backbone, or free of it ?

Where is Tg?

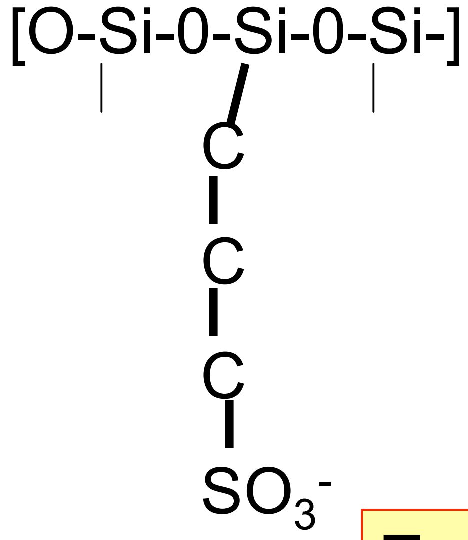
Pendant side chain siloxane polymers

(work of Xiaoguang Sun)

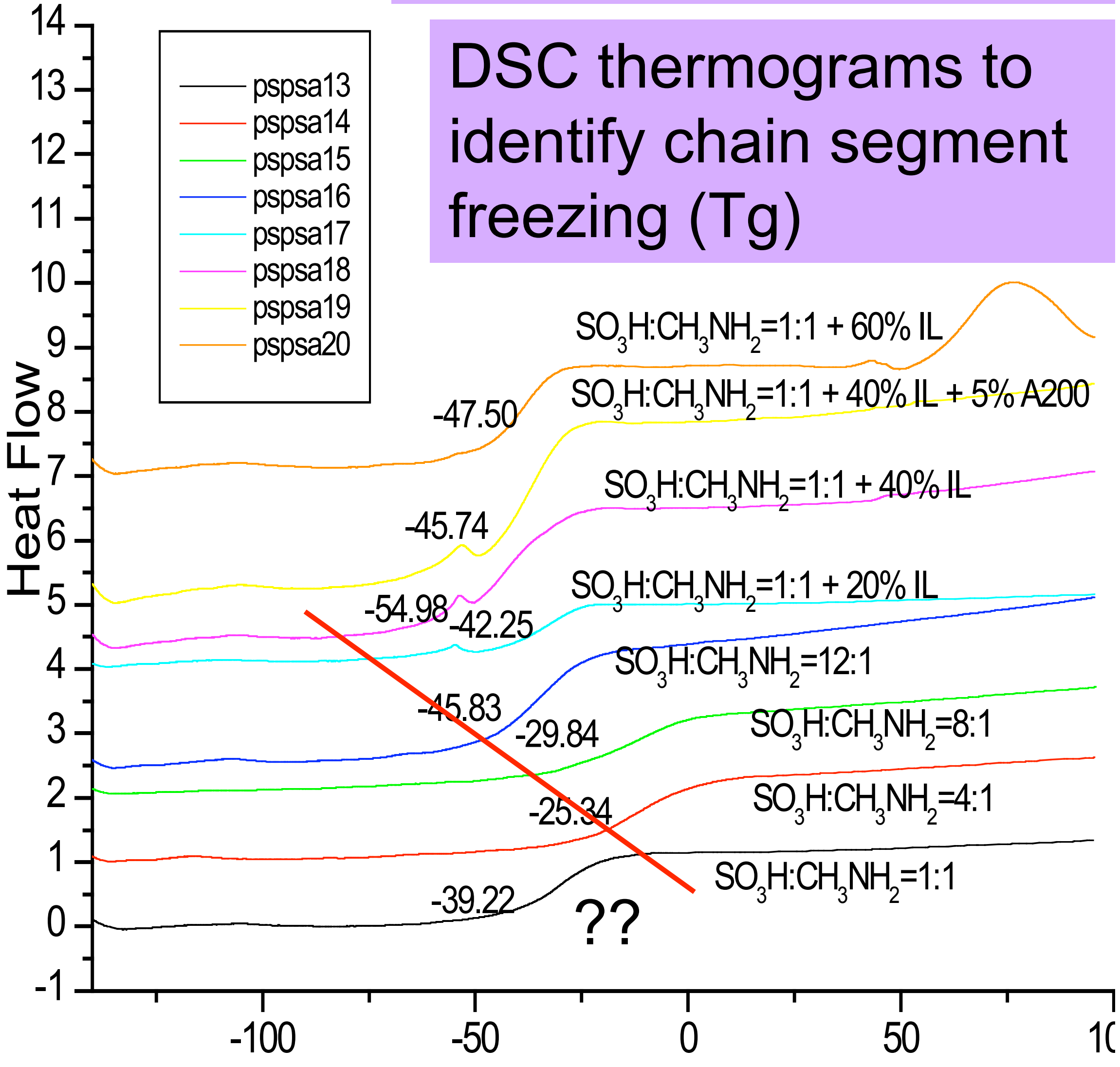
Sulfonic acid ends, neutralized with methylamine

Glass transitions

p-siloxane chain



DSC thermograms to identify chain segment freezing (Tg)



Tg is far below ambient, so evidently no decoupling