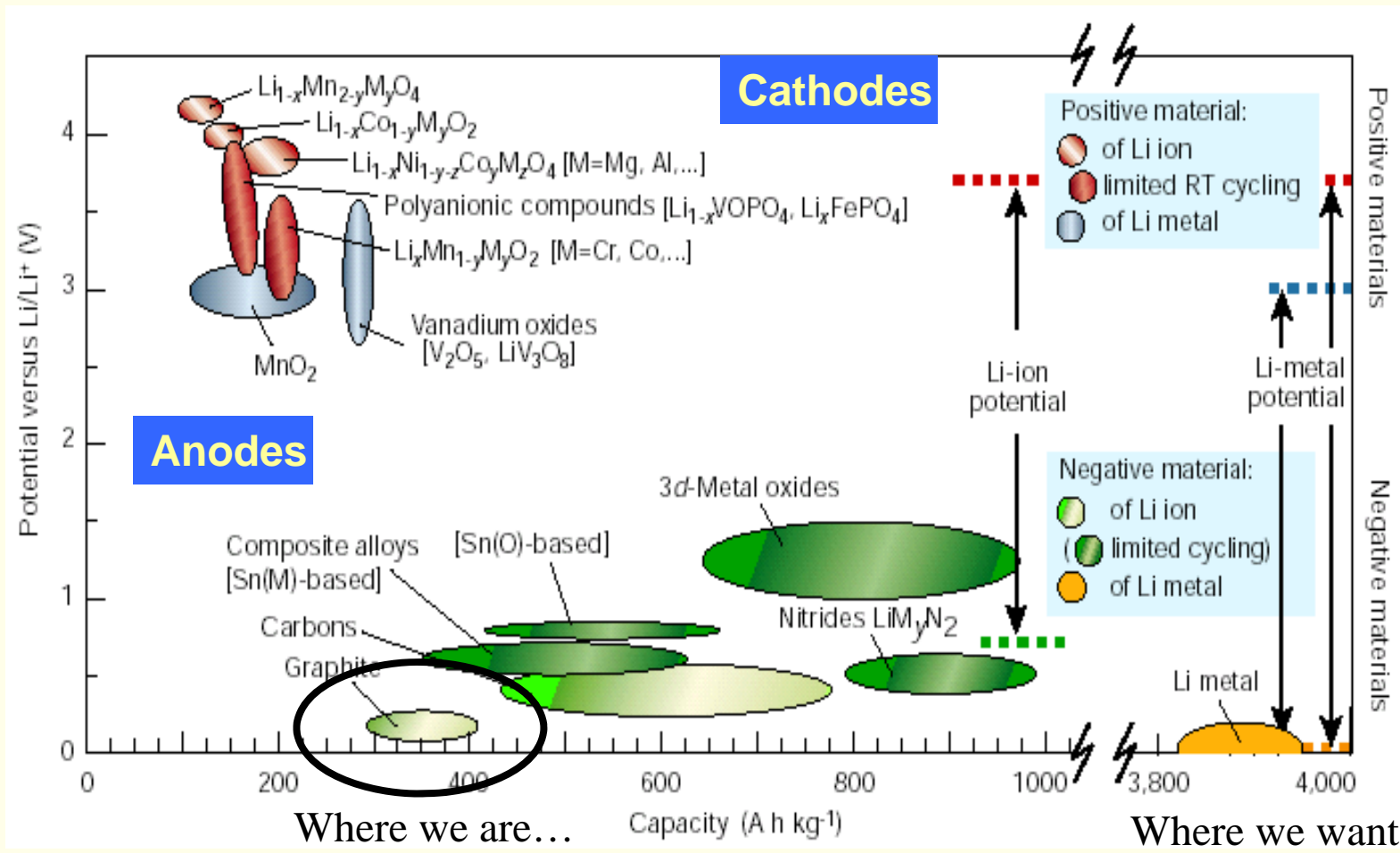# Ion Conducting Glasses for Use in Batteries 2: Glassy Solid Electrolytes
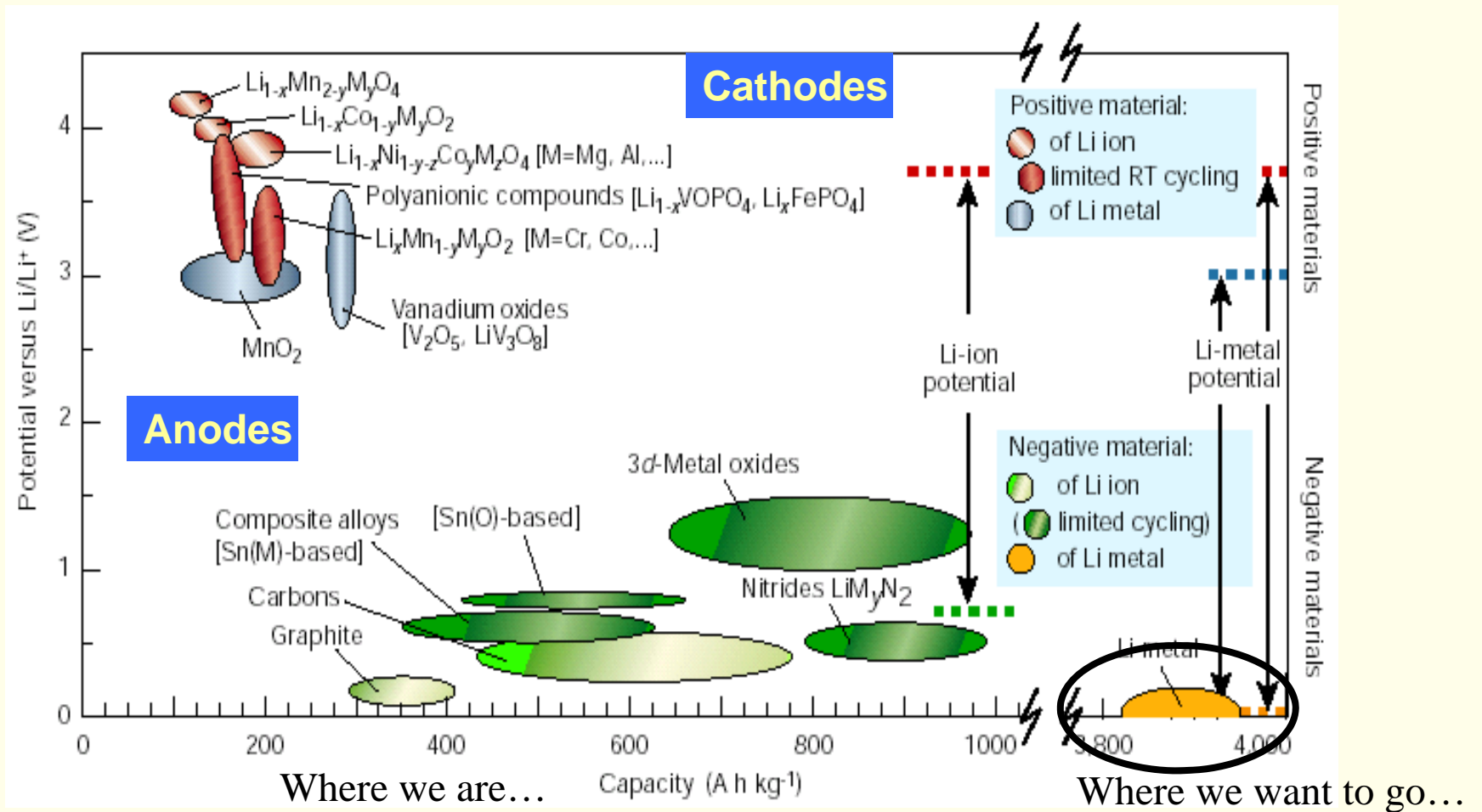
Steve W. Martin

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Anode and Cathode Combinations Determine the Voltage and Energy Density of Lithium Batteries

J.M. Tarascon, M. Armand, Nature, 414, 15 (2001) 359

Anode and Cathode Combinations Determine the Voltage and Energy Density of Lithium Batteries
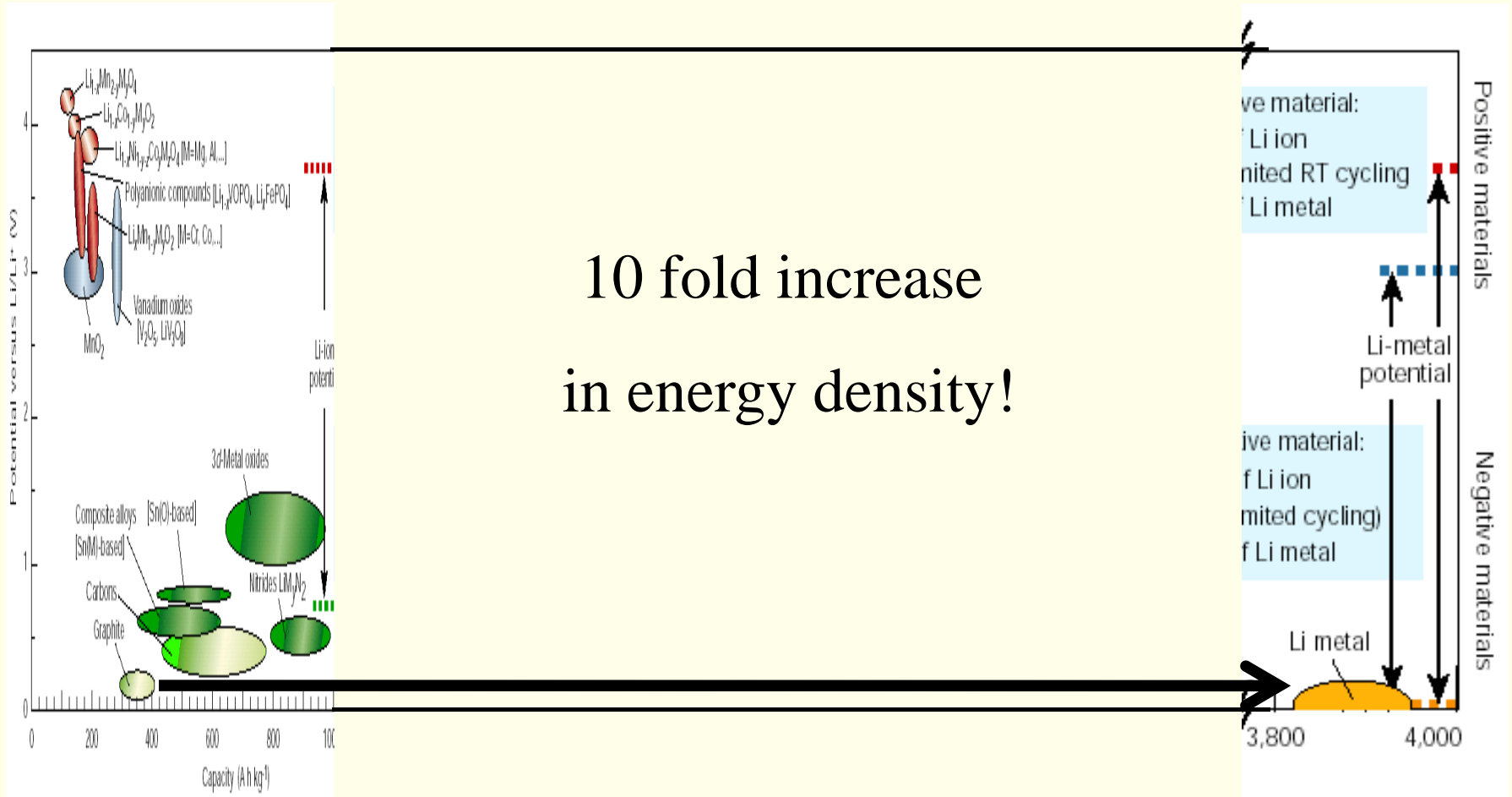

J.M. Tarascon, M. Armand, Nature, 414, 15 (2001) 359

Just for comparison…

Where we are…

Where we can go…

10 fold increase

in energy density!

Anode and Cathode Combinations Determine the Voltage and Energy Density of Lithium Batteries
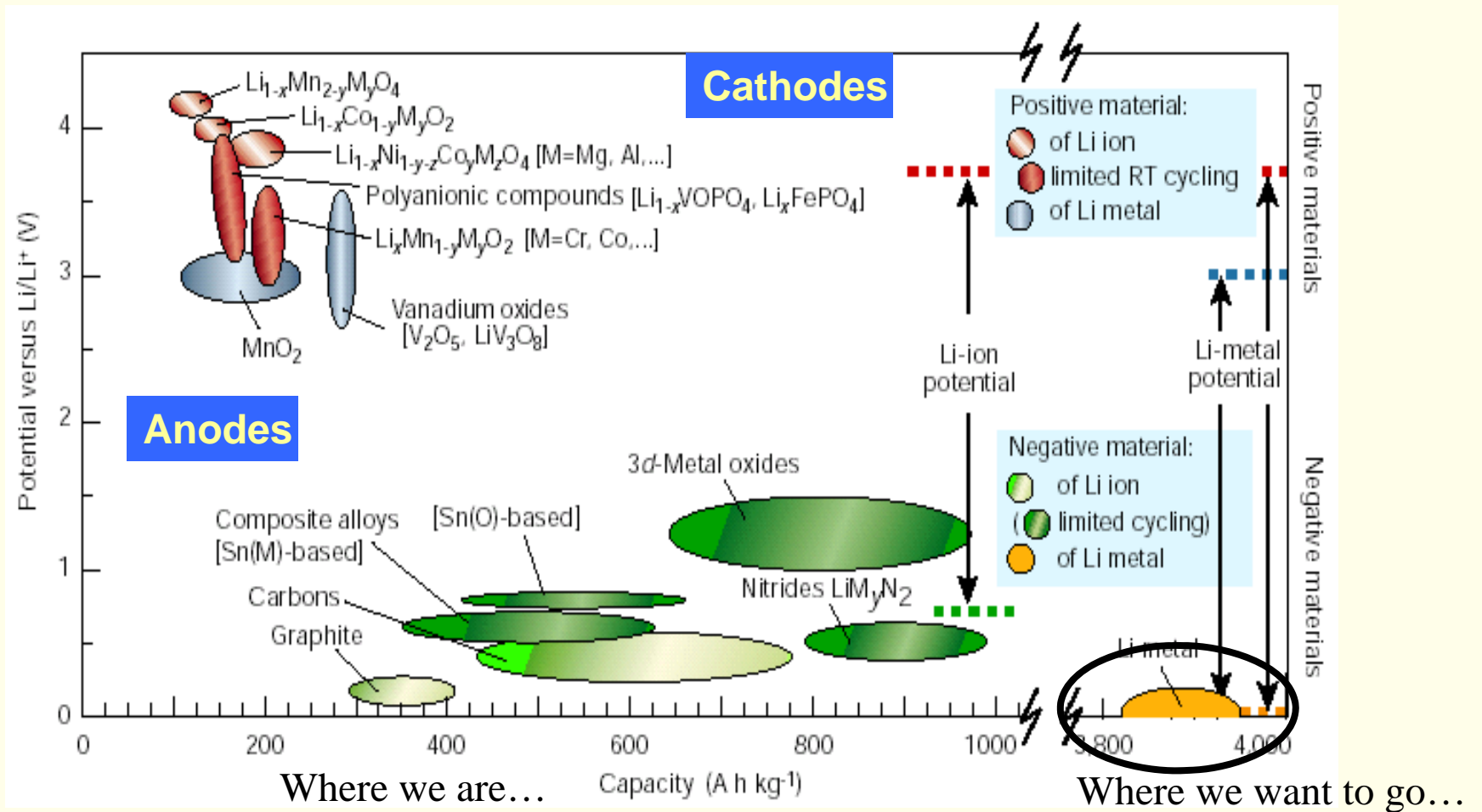

J.M. Tarascon, M. Armand, Nature, 414, 15 (2001) 359

So… Why Li-Air Batteries?

- Because today's Li batteries use Li_1C_6 as the Anode
- And the Cathode, Li_1CoO_2, is equally less energy dense
- Comparison….
- Gasoline: C_8H_{18} + 12 ½ O_2 → 8CO_2 + 9H_2O + Energy
- 44,400 J/g C_8H_{18}
- Li: ~4,000 mAhr/g x 3,600 sec/hr x ~4 V = 57,600 J/g Li
- *Gasoline and Li are comparably energy dense*
- Compare…
- Graphite: ~ 400 mAhr/g x 3,600 sec/hr x ~ 4 V = 5,760 J/g

Safety….Lithium Dendrites in Li ion Batteries
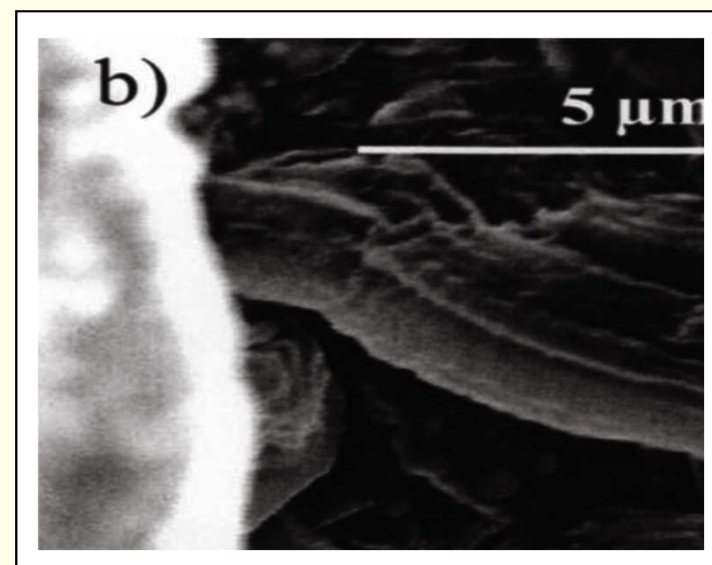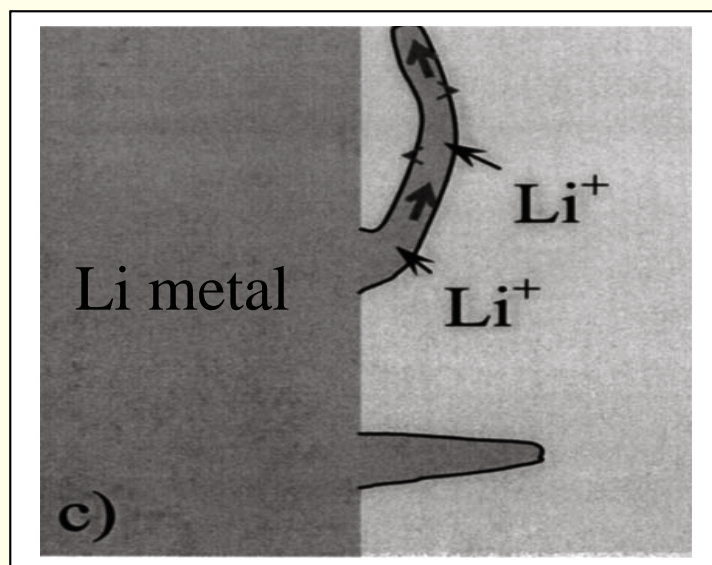
Non-epitaxial deposition of lithium after each cycle leads to the growth of uneven "fingers" or dendrites of lithium

Internal dendrites can cause short circuits of the battery

M. Dolle et al. Electrochemical and Solid-State Letters, 5(12) (2002)A286

Applications of Ion Conducting Glasses

Solid electrolytes in Lithium Batteries

- Solid state Li-cells
    - No liquids
    - Lightweight
    - High voltage
    - Wide ΔT
    - Thin film form
- Solid state electrolyte
    - High $\sigma_{d.c.}$
    - $> 10^{-3} (\Omega cm)^{-1}$
    - Stability to Li
    - Wide voltage window

Anode   Cathode

Li$^+$ →

FIC Glass
Electrolyte

→ Li$^+$

↓ e$^-$ e$^-$ ↑

Load
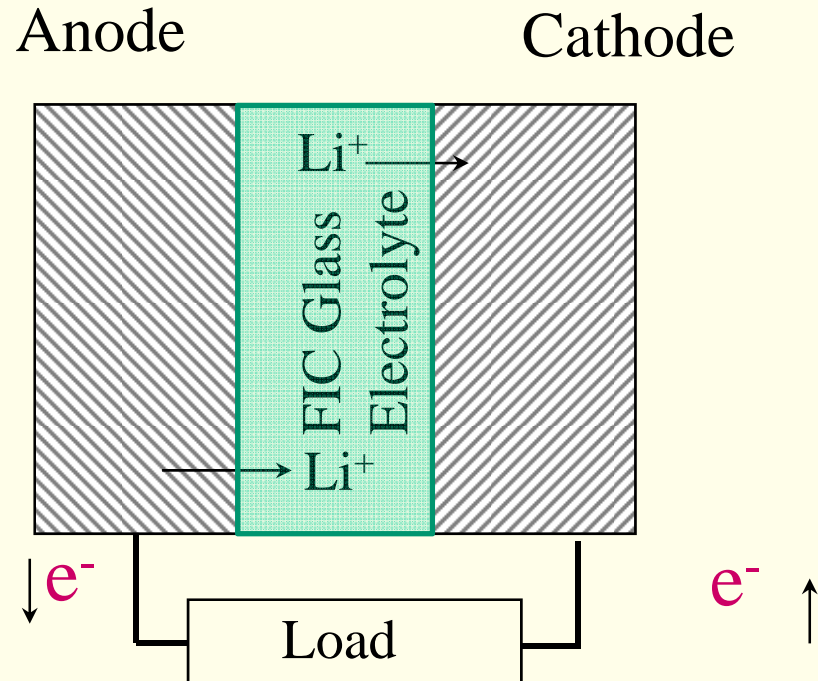
Glassy Solid Electrolytes

- Using highly conducting glasses in solid state batteries
  - Increases safety?
    - By mitigating lithium dendrite formation
  - Increases energy density?
    - By enabling lithium metal (or similar high activity) anodes
  - Reduces cost?
    - By simplifying design and using lower cost materials

Fast Ion (Li$^+$) Conducting Sulfide Glasses
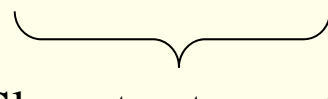
- Typical glass compositions
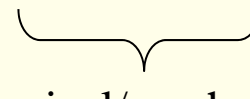 - Lithium salt +   + glass former + additives

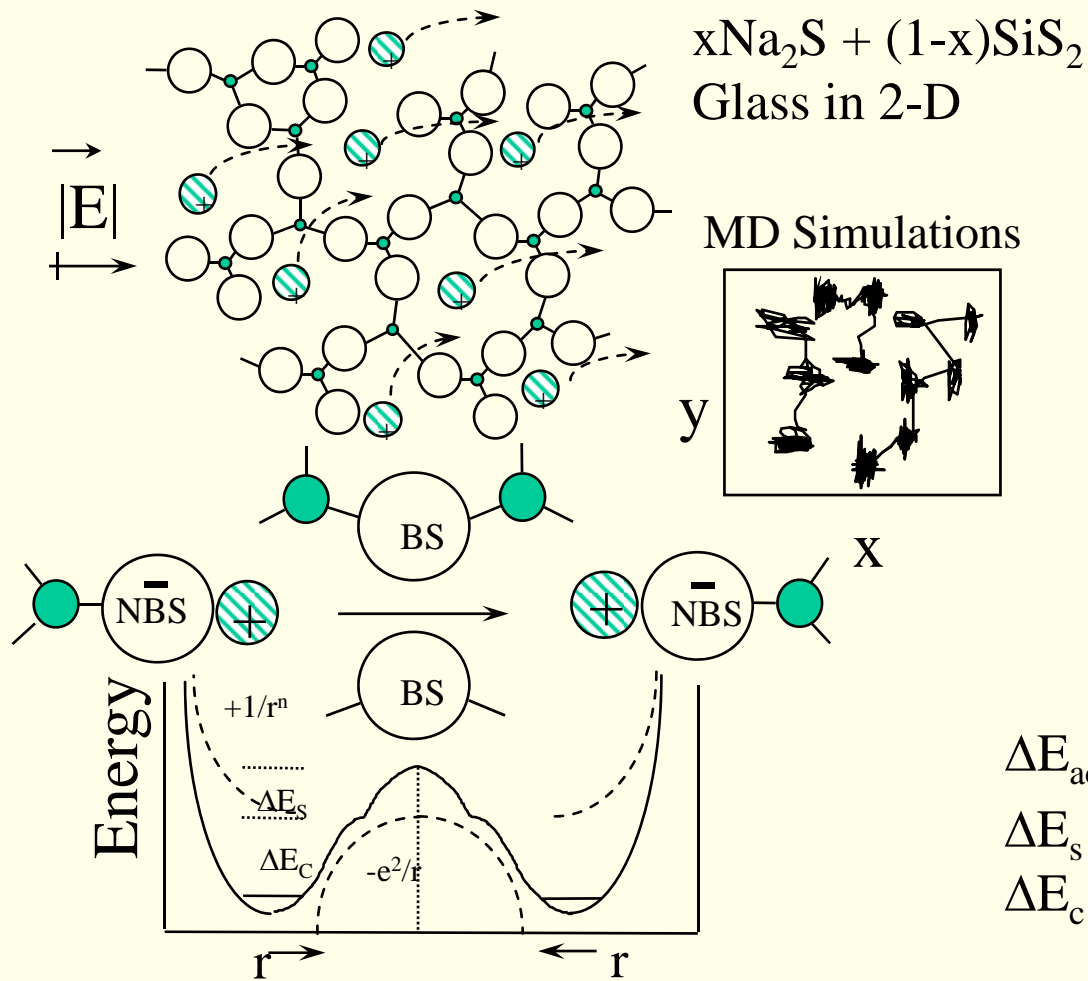   Lithium modifier

    Mobile cations   Glass structure   Chemical/mechanical/

    electrochemical durability

  - LiI + Li$_2$S + SiS$_2$, B$_2$S$_3$, GeS$_2$ …
  - LiI + Li$_2$S + GeS$_2$+ Ga$_2$S$_3$, La$_2$S$_3$, ZrS$_2$…
  - LiI + Li$_2$S + GeS$_2$ + GeO$_2$ +….

Ionic Conduction in Glass

$xNa_2S + (1-x)SiS_2$
Glass in 2-D

$|\vec{E}|$

MD Simulations

BS

NBS

BS

y

x

Energy

$+1/r^n$

ΔE_s

ΔE_c $-e^2/r$

r →   ← r
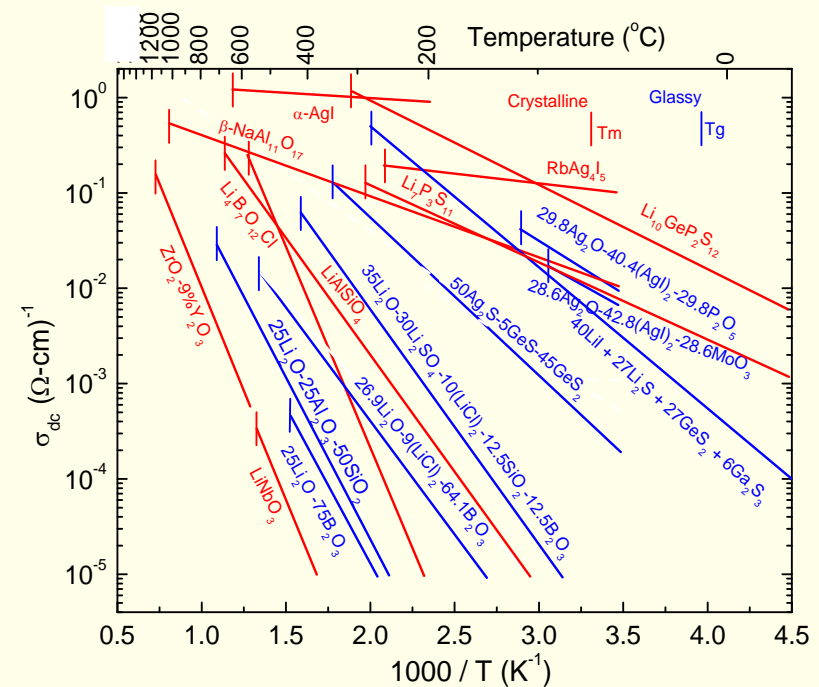
$\Delta E_{act} = \Delta E_s + \Delta E_c$

ΔE_s = Strain Energy

ΔE_c = Coulomb Energy

Ionic Conduction in Glass

- $\sigma = neZ\mu$
  - N is the number density
  - eZ is the charge, +1 most of the time
  - μ is the mobility
- Now what are common values of?
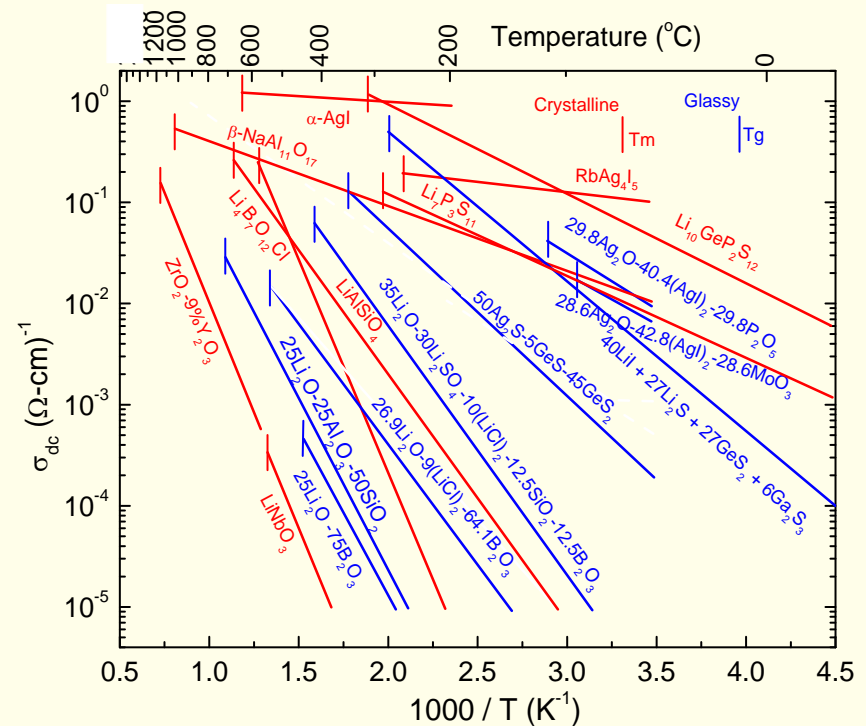 - $n \sim \# M^+/cm^3$?

Glass in Energy

Ionic Conduction in Glass

- $\sigma = neZ\mu$
  - N is the number density
  - eZ is the charge, +1 most of the time
  - μ is the mobility
- Now what are common values of?
  - n ~ 10^{22} M$^+$/cm^3
 - σ ~ # $(\Omega cm)^{-1}$?

Ionic Conduction in Glass

- $\sigma = neZ\mu$
  - N is the number density
  - eZ is the charge, +1 most of the time
  - μ is the mobility
- Common values
  - $n \sim 10^{22} \ M^+/cm^3$
  - $\sigma \sim 10^{-6} \ (\Omega cm)^{-1}$
- What does this give for
  - $\mu \sim \# \ cm^2/V\text{-}sec$

- $\sigma(T) = \sigma_o \exp(-\Delta E_a/RT)$
- The d.c. conductivity is "Arrhenius"

Ionic Conduction in Glass

- $\sigma = neZ\mu$
  - N is the number density
  - eZ is the charge, +1 most of the time
  - μ is the mobility
- Take
  - $n \sim 10^{22}$ M^+/cm^3
  - $\sigma \sim 10^{-3}$ $(\Omega cm)^{-1}$
  - $\mu \sim 10^{-6}$ $cm^2/V\text{-}sec$
- Compare Si
  - $\mu \sim 10^{+3}$ $cm^2/V\text{-}sec$
  - e^- are 10^9 times more mobile

- $\sigma(T) = \sigma_o exp(-\Delta E_a/RT)$
- The d.c. conductvity is "Arrhenius"

AC versus DC ionic conductivity

$\omega\tau < 1$ $\omega\tau > 1$

10^3K/T

$\log_{10}(\sigma_{a.c.})$

$\log_{10}(f/\text{Hz})$

Energy

r
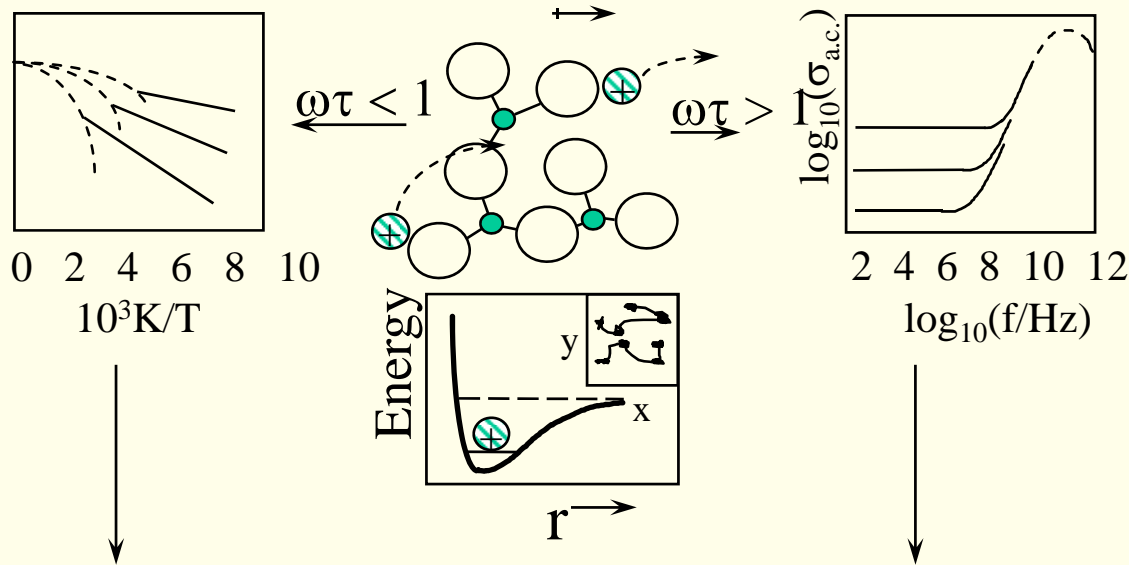
D.C. Conductivity

Charles - Polarization/Diffusion

Anderson/Stuart - Coulomb & Strain Energies

Moynihan/Macedo - Debeye &
 Faulkenhagen Theory

Ravaine/Souquet - Weak Electrolyte

Malugani- AgI Micro domains

Ingram - Cluster Pathways

Elliott - Local Structure/Diffusion
 Controlled Relaxation

A.C. Conductivity

Jonscher - Universal Response

Ngai - Coupling Theory

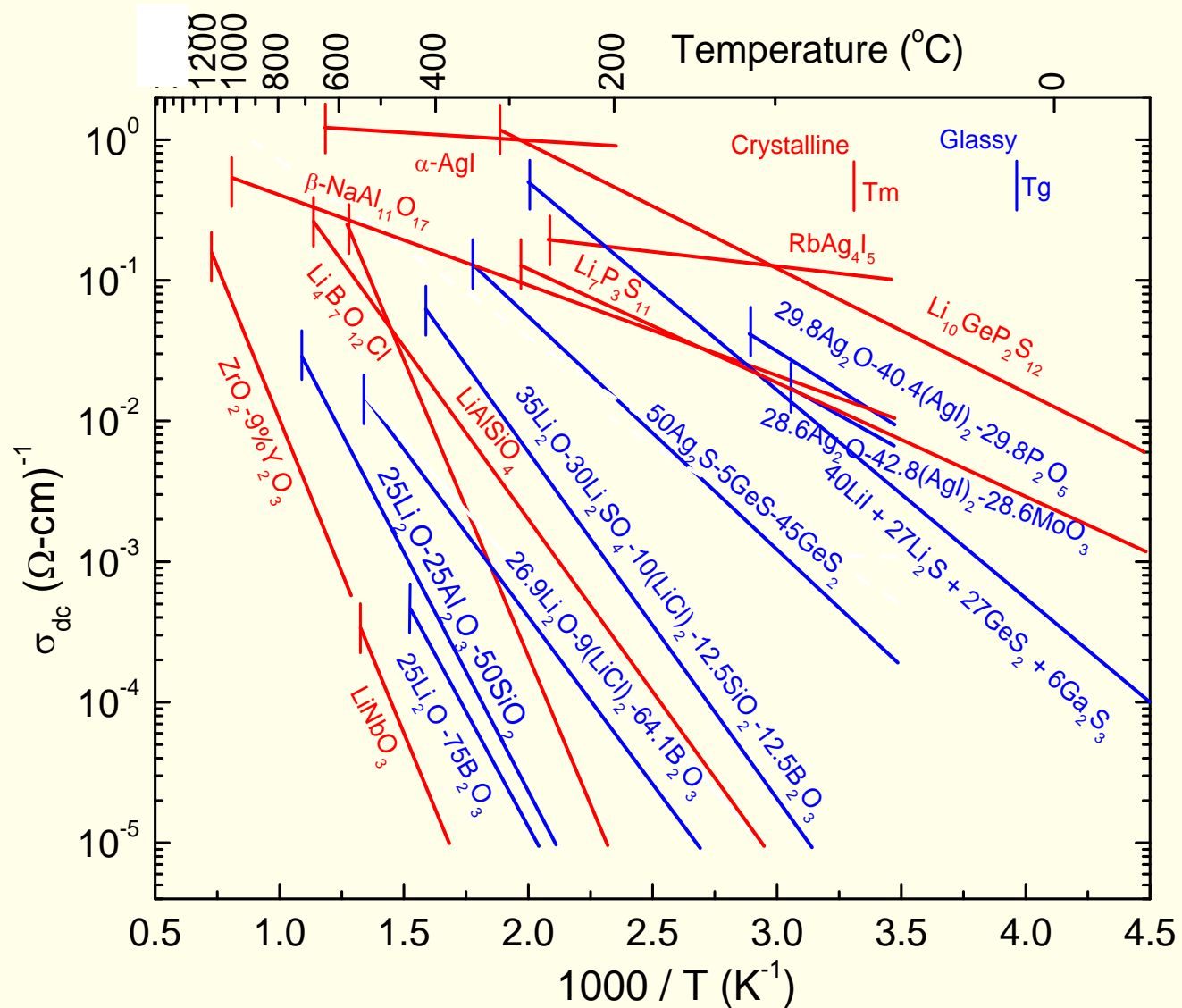*Moynihan - Modulus*

Dyre - Power Law

Funke - Jump Relaxation

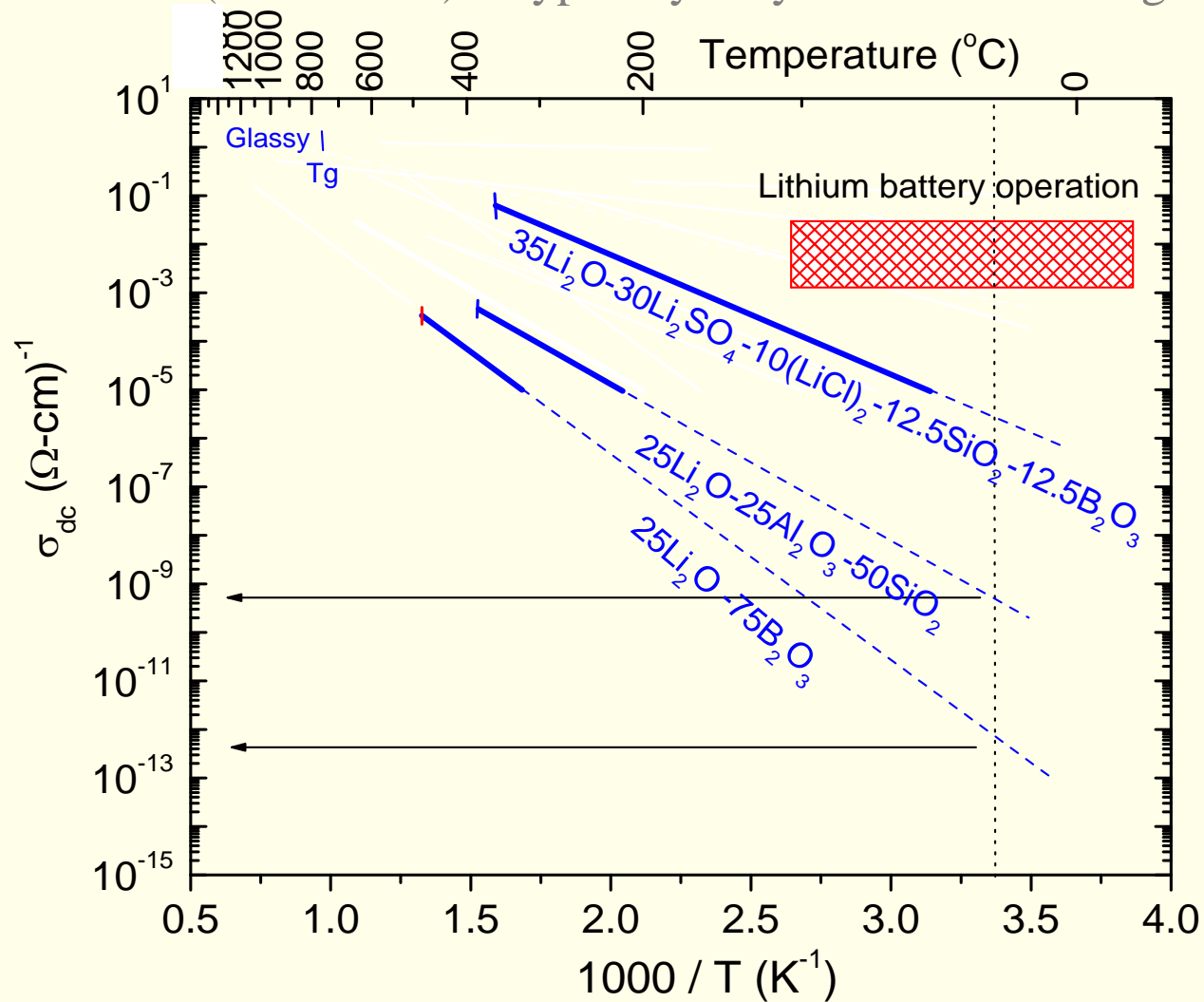*Dieterich/Bunde -*
 Coulomb Interaction

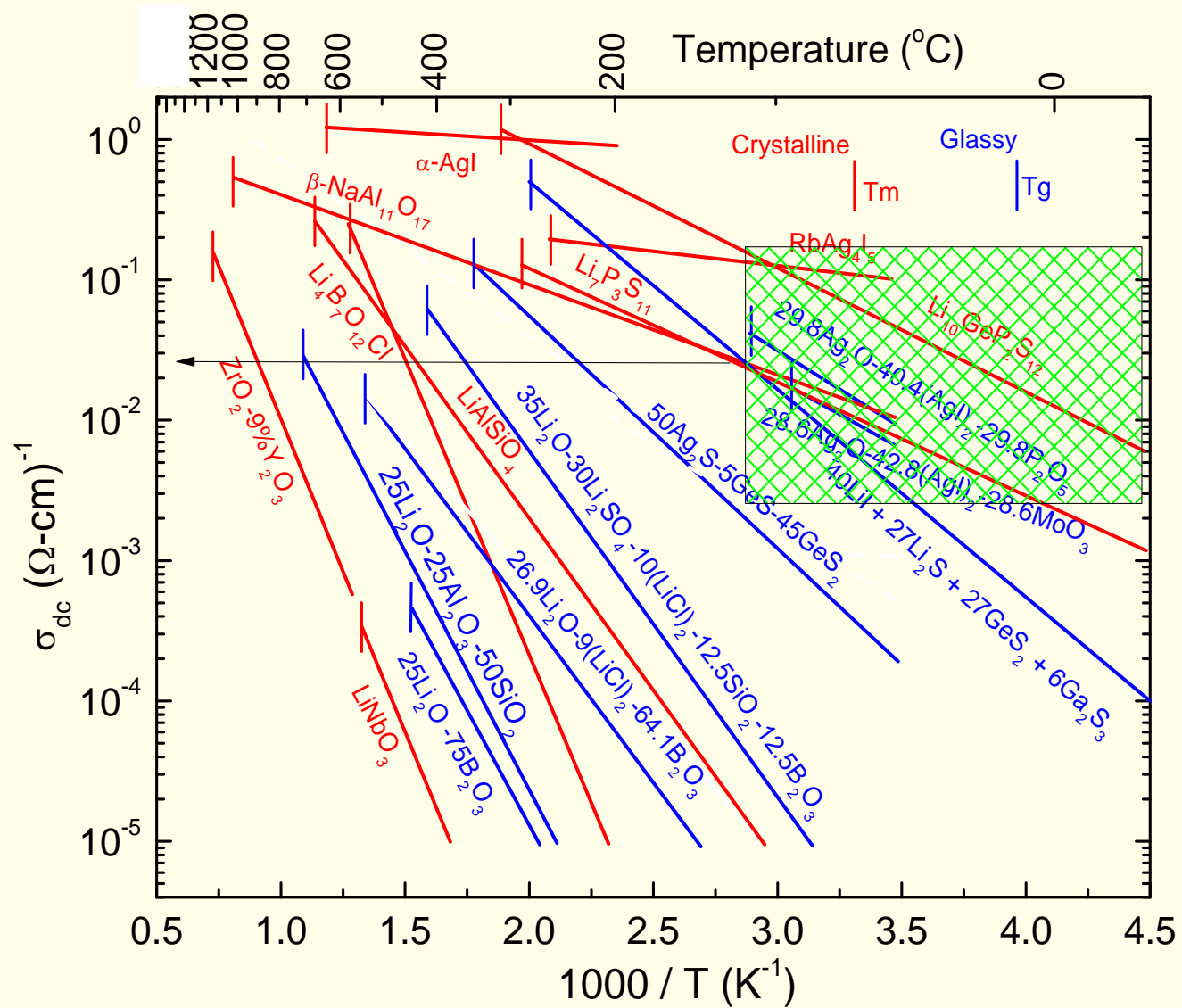*Elliott - Diffusion-Pathways*

Arrhenius Ionic Conductivity…

Ion Conduction in Glass

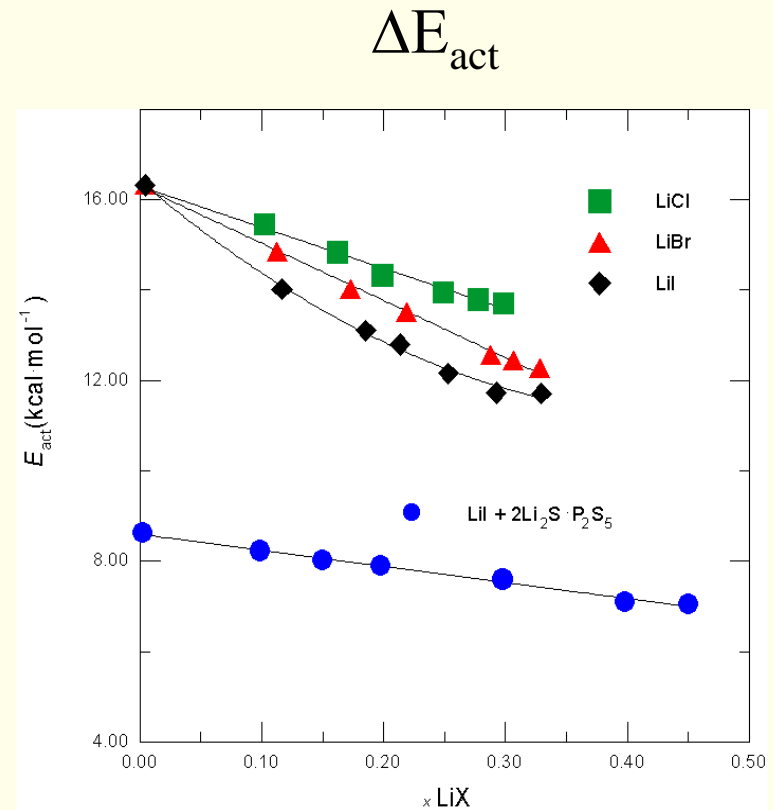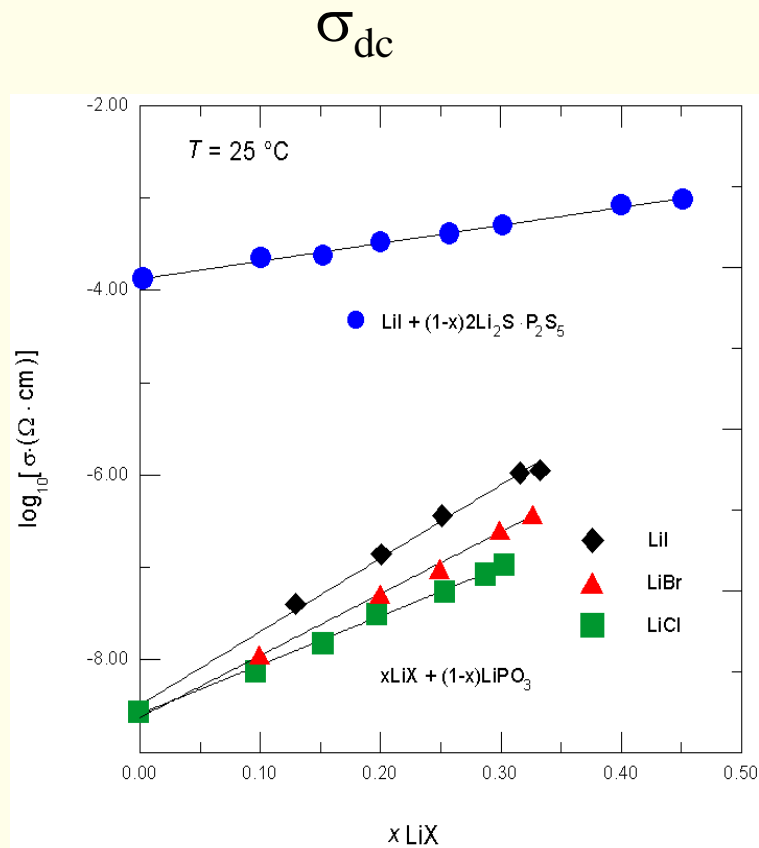Ion motion (conduction) is typically very limited in oxide glasses

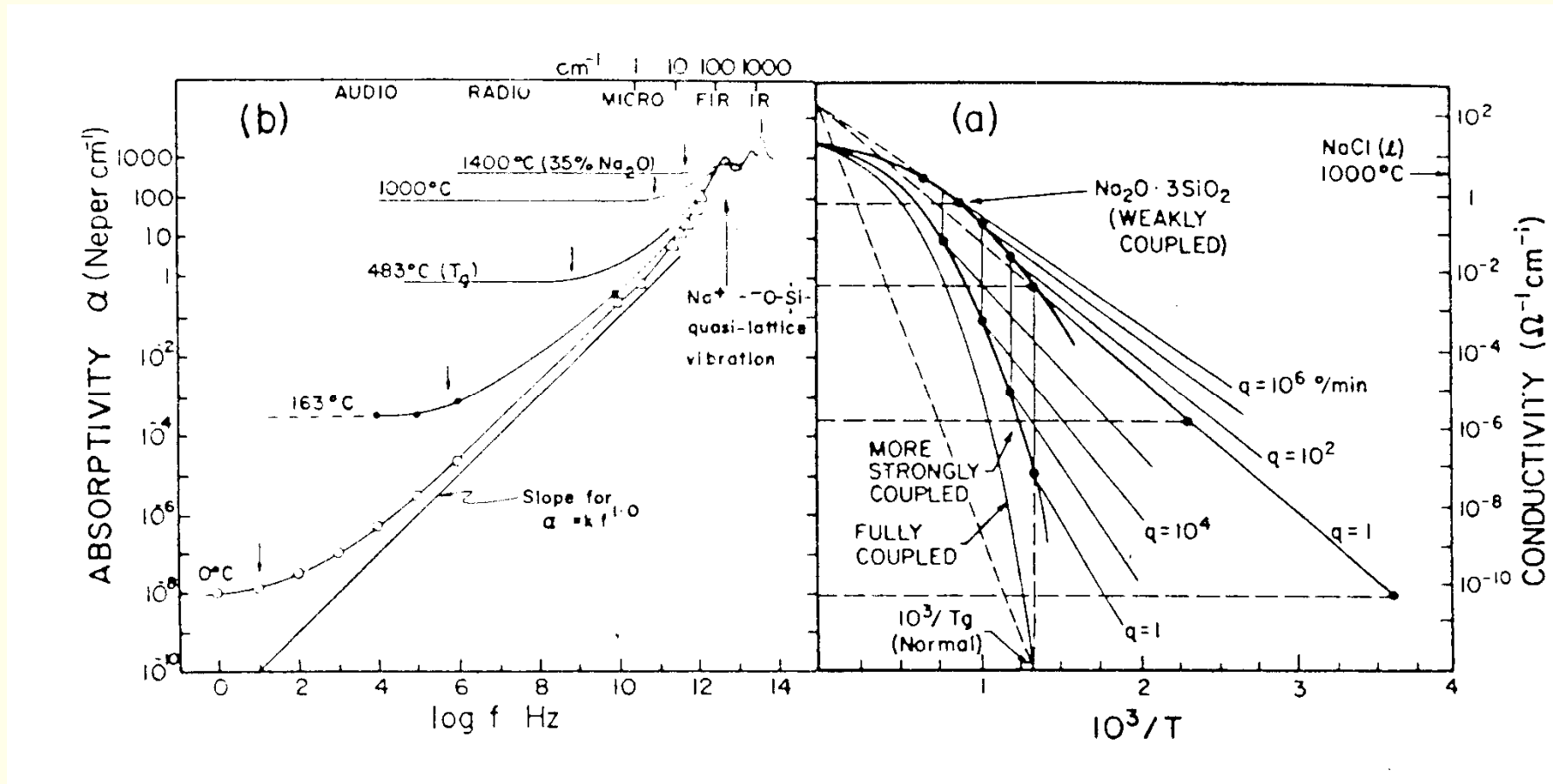# Arrhenius Ionic Conductivity…

Examples of Ion Conduction in Glass

*Salt doped lithium phosphate and thiophosphate glasses*

AC ionic conductivity in glass

- Connection to Far-IR vibrational modes, *Angell '83*

DC ion conductivity in glass

- Arrhenius temperature dependence
- $xLi_2O + (1-x)P_2O_5$
- Creation of non-bridging oxygens
- "Mobile" lithium ions
- The higher the concentration of Li_2O, the higher the conductivity
  - Lower resistivity
- Activation energy decreases with Li_2O content
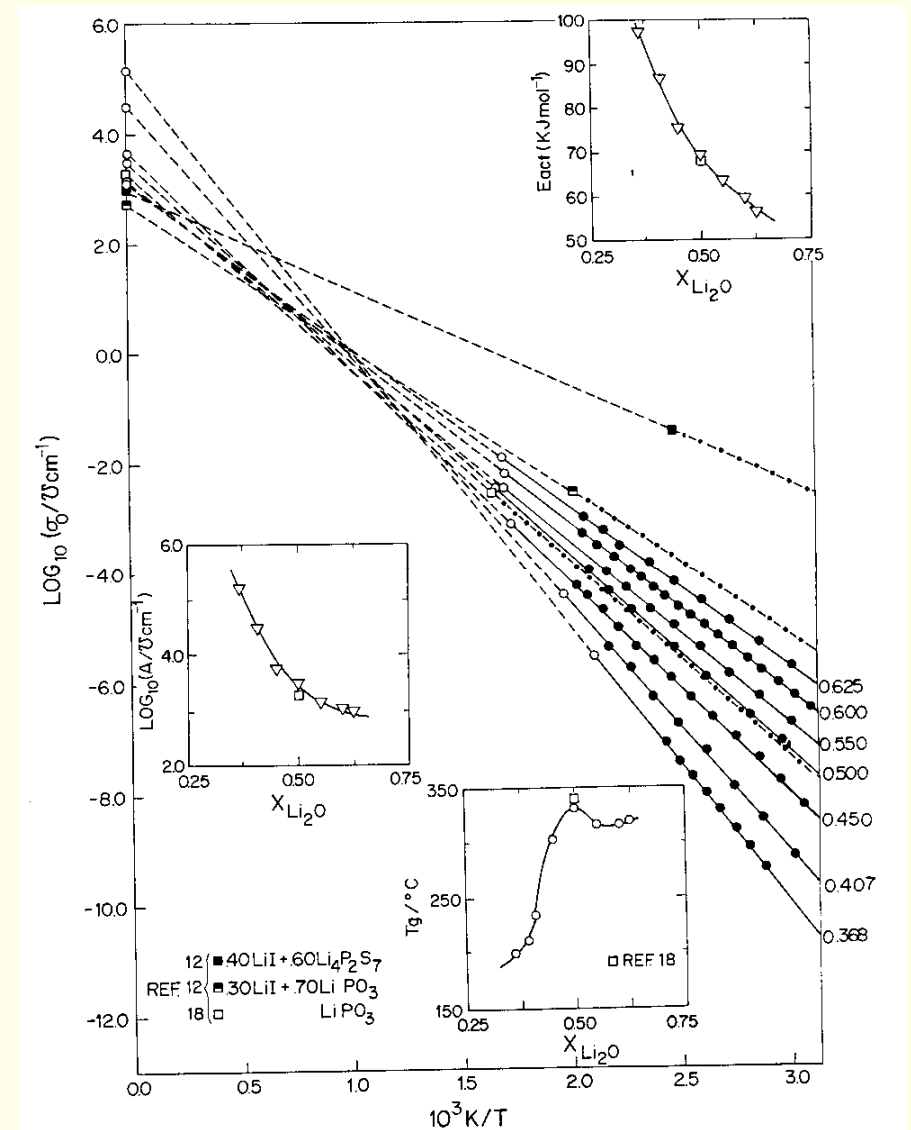
S. Martin, C.A. Angell JNCS '83

Mobility and Number Dependence of the Conductivity

$$\sigma(T) = n(T)eZ_c\mu(T) = \frac{\sigma_0}{T}\exp\left(\frac{-\Delta E_{act}}{RT}\right)$$

$$n(T) = n_o\exp\left(\frac{-\Delta E_c}{RT}\right)$$

$$\mu(T) = \frac{\mu_0}{T}\exp\left(\frac{-\Delta E_s}{RT}\right)$$

$$\sigma(T) = \frac{Z_c e n_0 \mu_0}{T}\exp\left(\frac{-\left(\Delta E_c + \Delta E_s\right)}{RT}\right)$$

Question: What are the magnitudes of $\Delta E_{S(M)}$ and ΔE_C ?

Ion Conduction in Glass: Coulombically or Structurally Constrained?

- Oxide glasses, ΔE_{act} ~100 kcal/mole
- Sulfide glasses, ΔE_{act} ~10 kcal/mole
- $\Delta E_{act} = \Delta E_s + \Delta E_c$
- Are alkali cations coulombically, ΔE_c, constrained?
  - Weak Electrolytes like HOAc, k_A ~ 1 x 10^{-5} ?
  - Cations are only weakly dissociated
- Are alkali cations structurally, ΔE_s, constrained?
  - Strong electrolytes like NaCl?
  - Completely dissociated, Na^+ Cl^- ? K ~ 10^6

Models of the Activation Energy

- Both activation energies appear to be non-zero and contribute to the total activation energy
- Anderson-Stuart[1] model calculation

$$\Delta E_C \approx \frac{C_{struct.} Z_c Z_a e^2}{\varepsilon_\infty} \left[\frac{1}{(r_c + r_a)} - \frac{2}{\lambda} \right] \qquad \Delta E_S \approx \pi G (r_c - r_d)^2 \lambda / 2$$

x Na_2O + (1-x)SiO_2	ΔE_s (calc) kcal/mole	ΔE_c (calc) kcal/mole	ΔE_{act}(calc) kcal/mole	ΔE_{act}^2 kcal/mole
11.8	11.7	66.9	78.6	68.1
19.2	10.9	62.3	73.2	63.7
29.7	10.0	56.1	66.1	59.7

- Calculation shows that the ΔE_c term is the larger of the two energy barriers.
- Coulombically constrained?

[1] Anderson, Stuart, J. Amer. Cer. Soc., 1954
[2] SciGlass 5.5, Average of many glasses

Alkali Radii Dependence of Strain and Coulomb Activation Energies
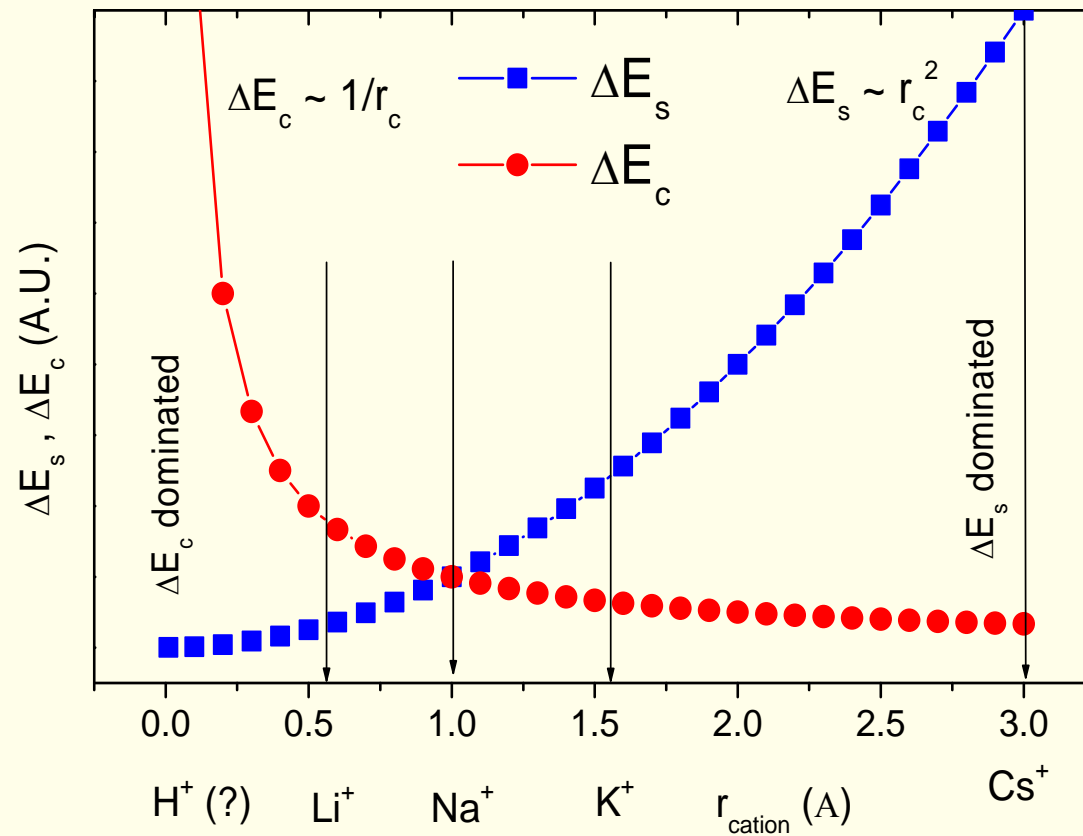
Short Range Order models

- Anderson-Stuart Model
- Assignment of Coulombic and Strain energy terms, $\Delta E_C + \Delta E_s$
- "Creation" or Concentration versus Migration energy terms, $\Delta E_C + \Delta E_m$
- Coulomb energy term, ΔE_C attractive force between cation and anion

$$\approx \frac{C_{struct.}}{\varepsilon_\infty}\left[\frac{-Z_c Z_a e^2}{\lambda/2} - \frac{-Z_c Z_a e^2}{(r_c + r_a)}\right] = \frac{C_{struct.} Z_c Z_a e^2}{\varepsilon_\infty}\left[\frac{1}{(r_c + r_a)} - \frac{2}{\lambda}\right]$$
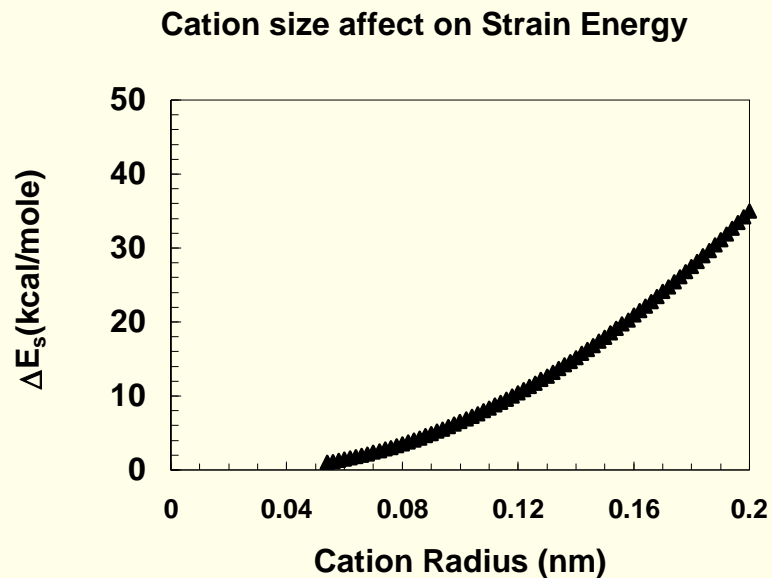
$$\lim_{\lambda \to \infty} \Delta E_{act} \to \frac{C_{struct.} Z_c Z_a e^2}{\varepsilon_\infty (r_c + r_a)} = const.$$

Short Range Order models

- Strain energy term - ΔE_s
- "Work" required to "dilate the network so large cations can migrate

$$\Delta E_S = \pi G (r_c - r_d)^2 \lambda / 2$$

G   Shear modulus

r_c Cation radius

r_d Interstitial site radius

λ Jump distance

Cation size affect on Strain Energy

Thermodynamic Models

- Glass is considered as a solvent into which salt is dissolved
- If dissolved salt dissociates strongly, then glass is considered a strong electrolyte
- If dissolved salt dissociate weakly, then glass is considered a weak electrolyte
- Coulomb energy term calculations suggest that the salts are only weakly dissociated, largest of the two energy terms
- Migration energy term is taken to be minor and weak function of composition
- Dissociation constant then determines the number of mobile cations available for conduction, dissociation limited conduction

Weak Electrolyte model, *Ravaine & Souquet*

$M_2O \longrightarrow M^+ + OM^-$
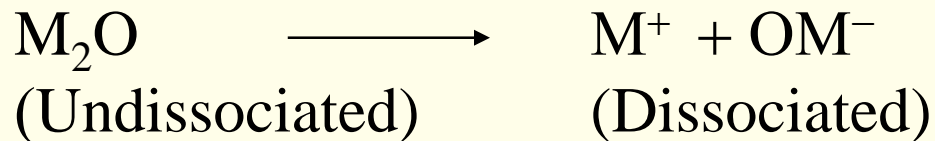
(Undissociated)   (Dissociated)

$K_{diss} = a_{M^+} a_{OM^-} / a_{M2O}$

$\sim [M^+][OM^-]/a_{M2O} = [M^+]^2/ a_{M2O}$

$[M^+] \sim K_{diss}^{1/2} a_{M2O}^{1/2} = n$

$\sigma = ze\mu n = ze\mu K_{diss}^{1/2} a_{M2O}^{1/2} \sim C \, a_{M2O}^{1/2}$

$\log K_{diss} \sim -Ne^2RT/4\pi\varepsilon_o\varepsilon_\infty (r_+ + r_-)$

As r_+, r_- increase, K_{diss} increases
As ε_∞ increases, K_{diss} increases

Strong and Weak Electrolyte models

- "Strong electrolyte" model suggests *all* cations are equally available for conduction.
  - *Each cation experiences an energy barrier which governs the rate at which it hops*
- "Weak electrolyte" model suggests only those *dissociated* cations are available for conduction
  - *Dissociation creates mobile carriers available for conduction*
- SE models suggests that $\Delta E_C + \Delta E_s$ both contribute, one could be larger or smaller than the other
- WE model suggests that ΔE_c is the dominant term
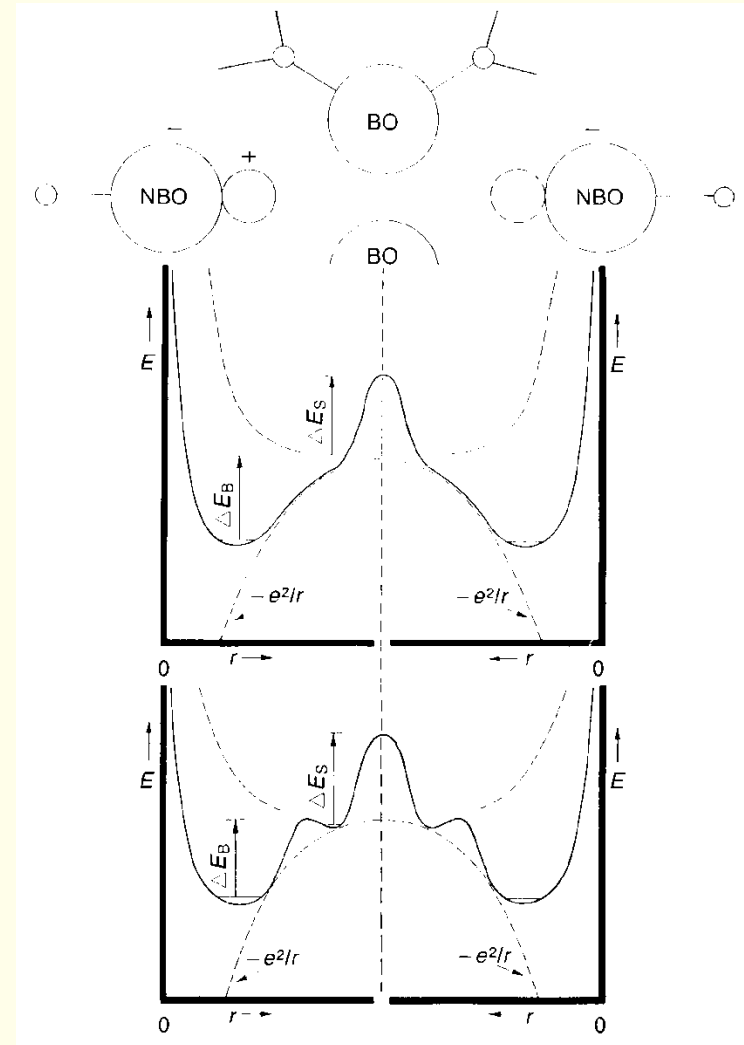
Intermediate Range Order models

- Models recognize that ion conductivity requires ion motion over relatively long length scales

- Ions must be able to move from one side of the electrolyte to the other

- Long range connectivity of the SRO structures favorable to conduction must exist

- Deep "traps" along the way must be infrequent and not severe

- Rather, low energy conduction "pathways" are thought to exist which maximize connectivity and minimize energy barriers and traps

- Cluster pathway model of Greeves '85, for example

Intermediate Range Order models

- Cluster pathway model, *Greeves et al '85*
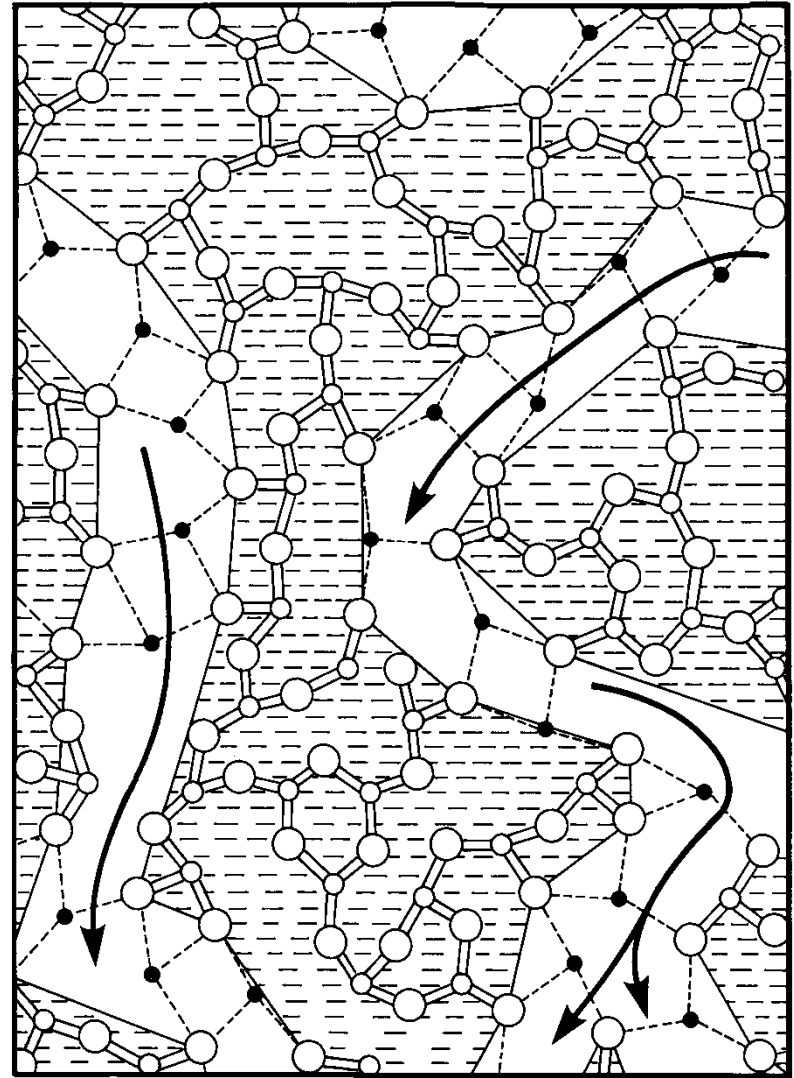
Intermediate Range Order models

- ## Proposed Percolation Models - Johari *et al.* '87
    - At low dopant concentrations
        - Cations are far separated
        - Mobile species are diluted in a non-conducting host glass
    - At intermediate concentrations
        - Cations begin to approach proximity
        - Preferential conduction paths form
        - Sites percolate
    - At high concentrations
        - Cations are fully connected
        - Conduction pathways are fully developed
    - Percolation Behavior is **NOT** observed

Failure of Conductivity percolation
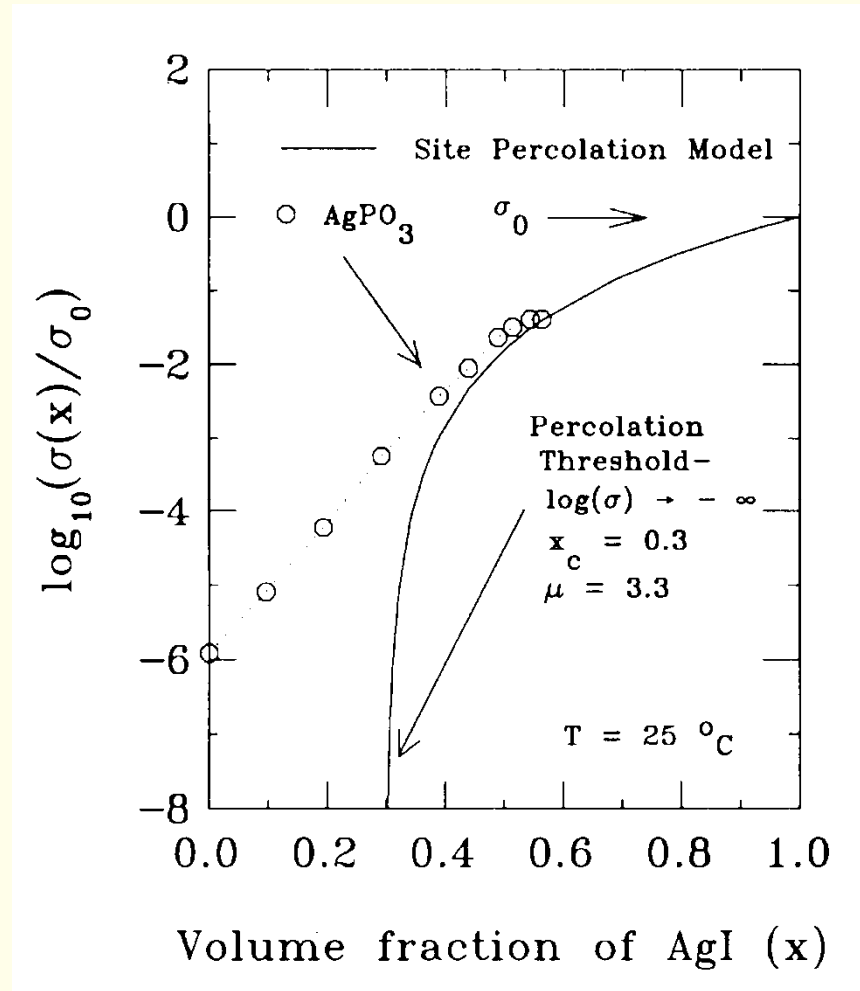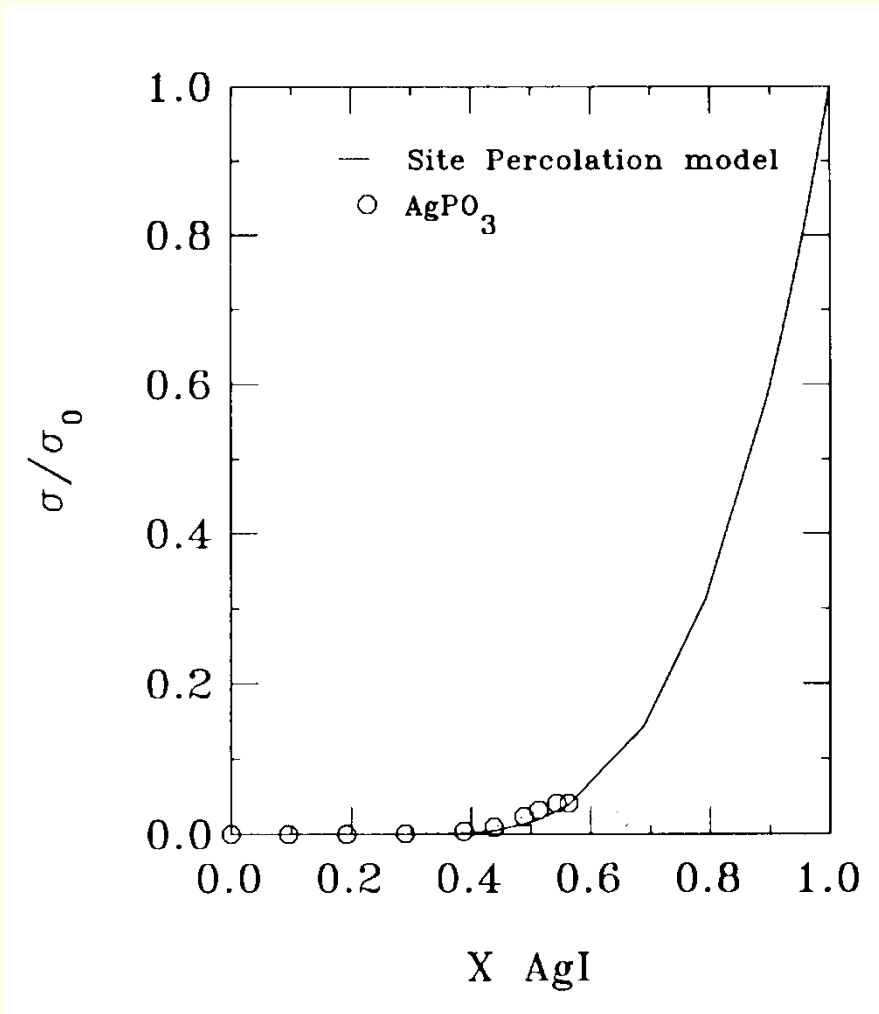
Intermediate Range Order Models

- Microdomain models of conductivity

- Dopant salts such as AgI to oxide glasses, especially $AgPO_3$, are added to increase conductivity

- AgI is itself a FIC *crystal* above 150°C

- Extrapolations of σ to xAgI = 1 give ~ σ_{AgI}(298K)

- The question then is: Does the AgI create "microdomains" of α-AgI giving rise to the high conductivity?

AgI Microdomain model

- Most well known of all glasses is $xAgI + (1-x)AgPO_3$

- $AgPO_3$ is a long chain structure of -O-P(O)(OAg)-O repeat units

- Intermediate range structure is for these long chains to intertwine and as such frustrate crystallization

- Added AgI dissolves into this liquid without disrupting the structure of the phosphate chains

- Microdomain model then suggests that this dissolved AgI creates increasingly large clusters of α-AgI between the phosphate chains

AgI Microdomain model
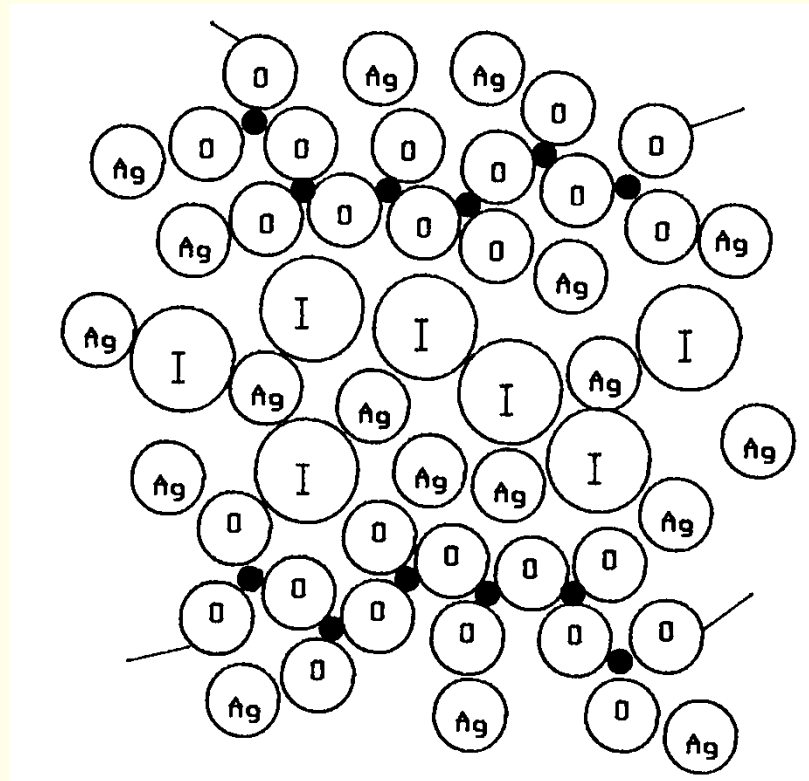
Composition Dependence of the Conductivity

- Binary lithium phosphate glasses, $Li_2O + P_2O_5$, are relative poor ion conductors

- Binary lithium borate glasses, $Li_2O + B_2O_3$, are slightly better conductors

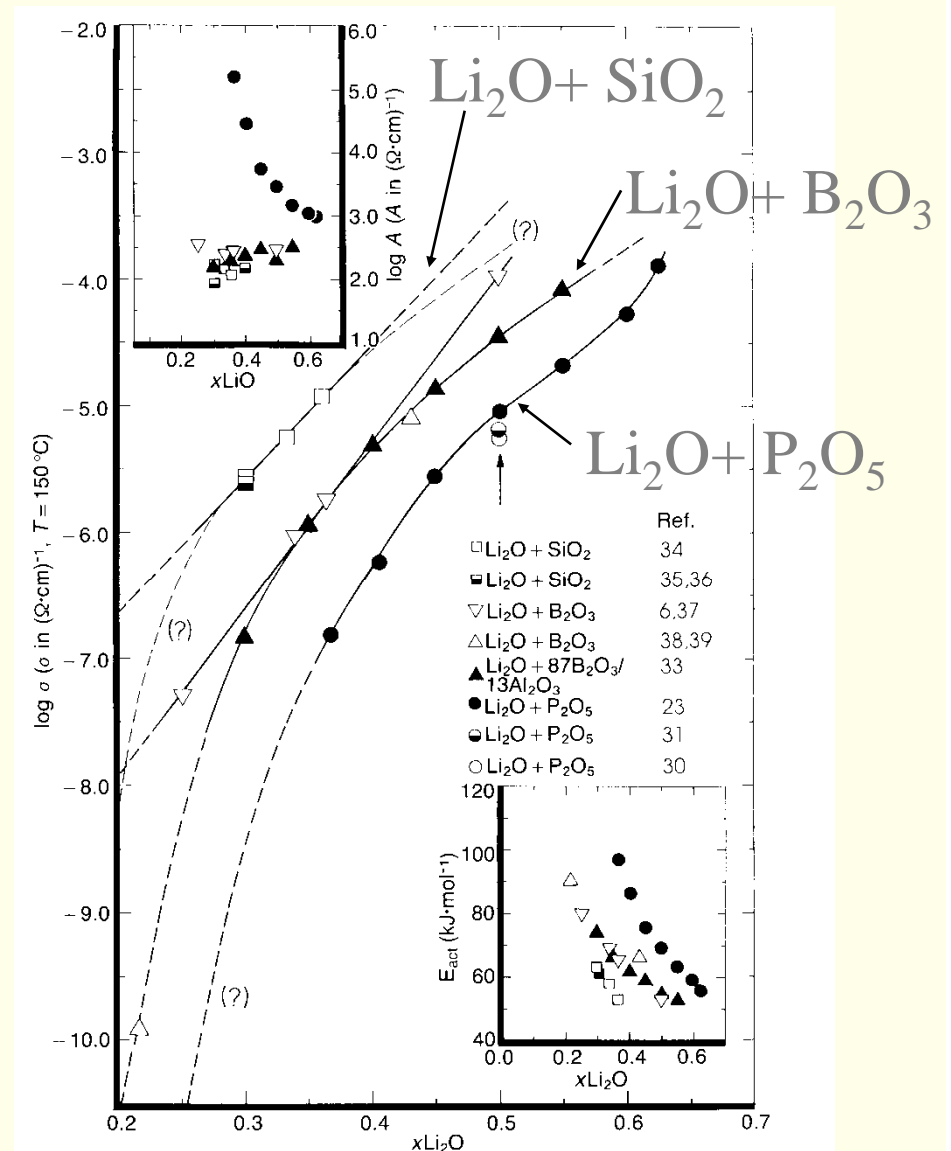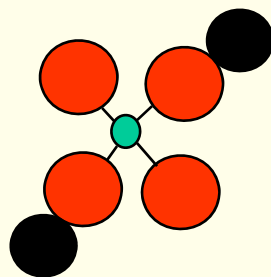- Binary lithium silicate glasses, $Li_2O + SiO_2$ are slightly better conductors yet.

$Li_2O:P_2O_5$

$Li_2O:B_2O_3$

$Li_2O:SiO_2$

$Li_2O+ SiO_2$

$Li_2O+ B_2O_3$

$Li_2O+ P_2O_5$

	Ref.
□ $Li_2O + SiO_2$	34
▣ $Li_2O + SiO_2$	35,36
▽ $Li_2O + B_2O_3$	6,37
△ $Li_2O + B_2O_3$	38,39
▲ $Li_2O + 87B_2O_3/13Al_2O_3$	33
● $Li_2O + P_2O_5$	23
◐ $Li_2O + P_2O_5$	31
○ $Li_2O + P_2O_5$	30
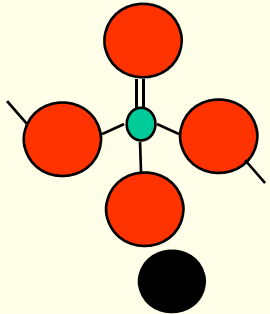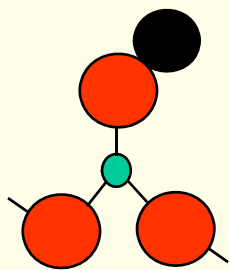
Salt doped phosphate glasses

- Halide doping strongly increases the conductivity
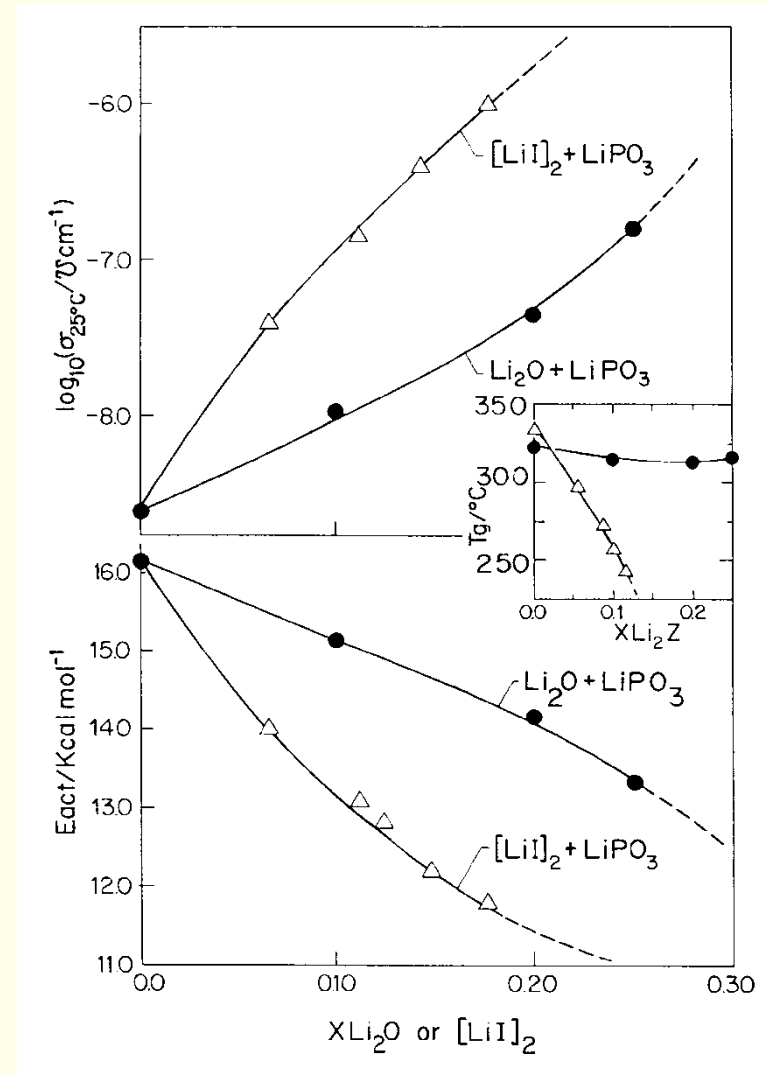
Mixed GlassFormer Cation Glasses

- $Na_2O + B_2O_3 + P_2O_5$ Glasses
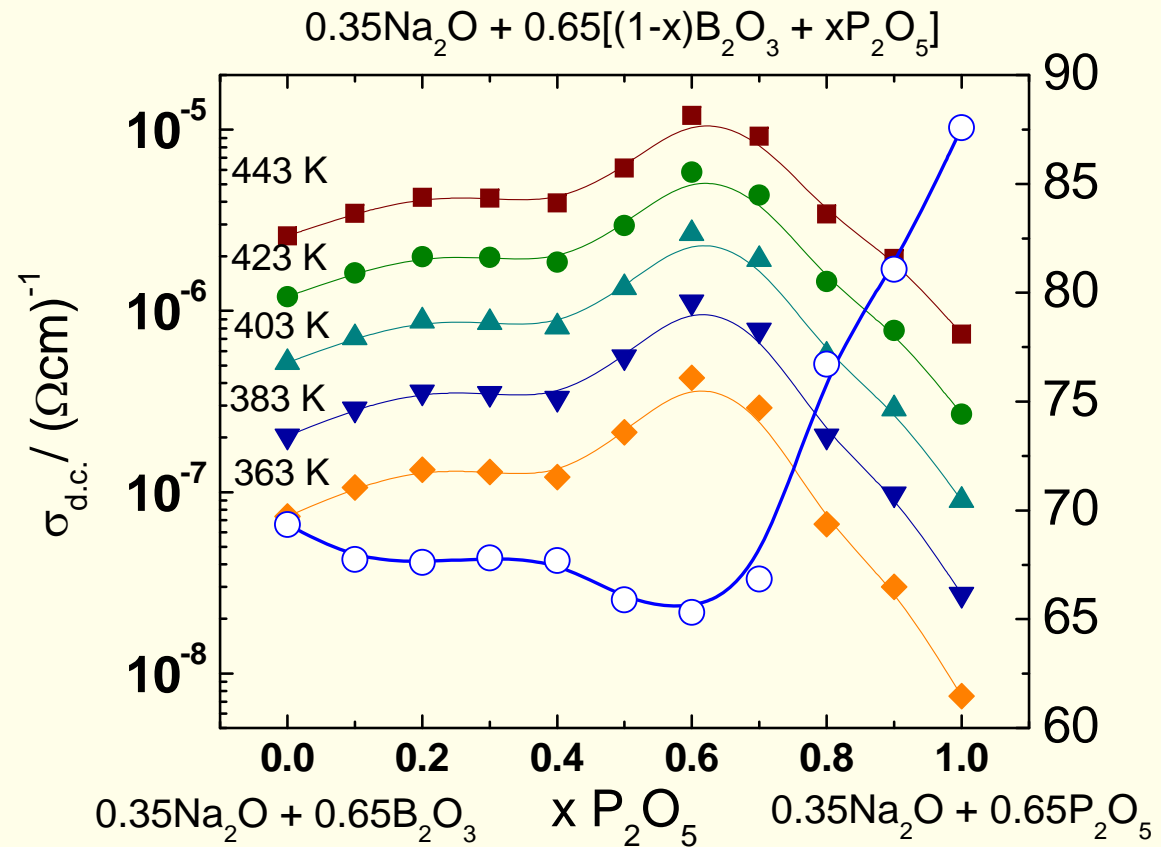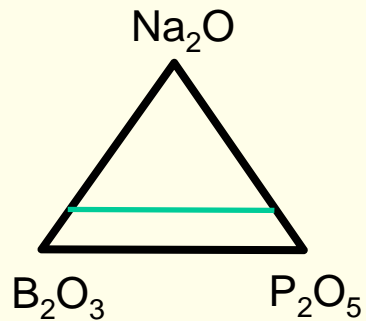- Non-Additive (+'ive) behavior in physical properties
- Increased ionic conductivity
- Increased Tg
- Improved glass forming ability
- Improved mechanical properties
- Improved chemical properties
- Overall improvement in nearly all properties required for Lithium battery applications
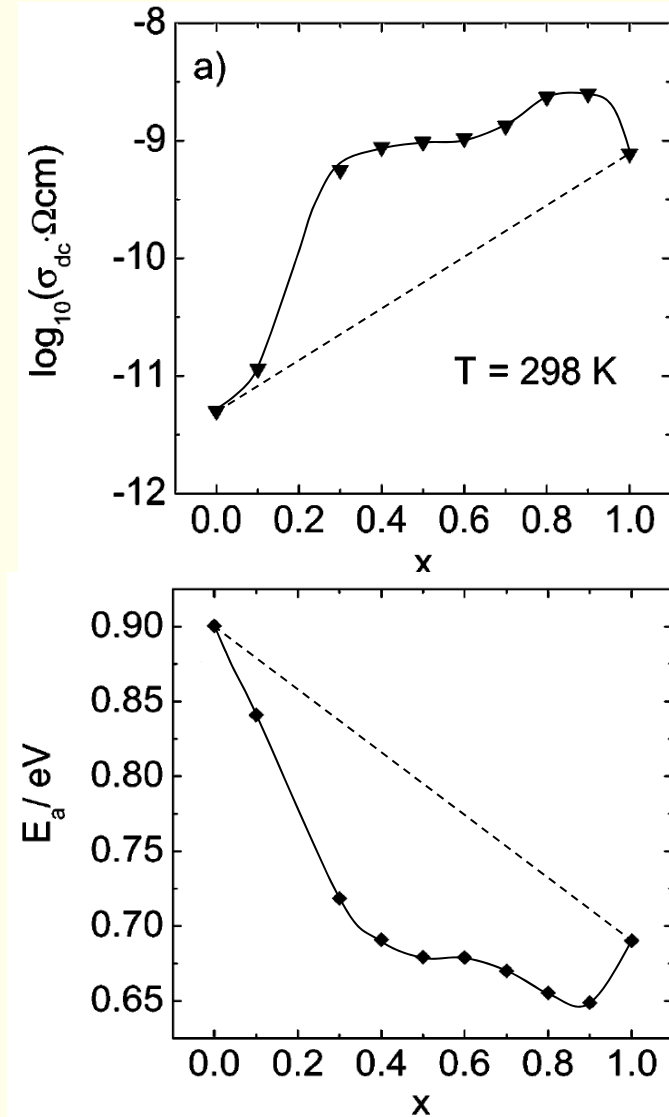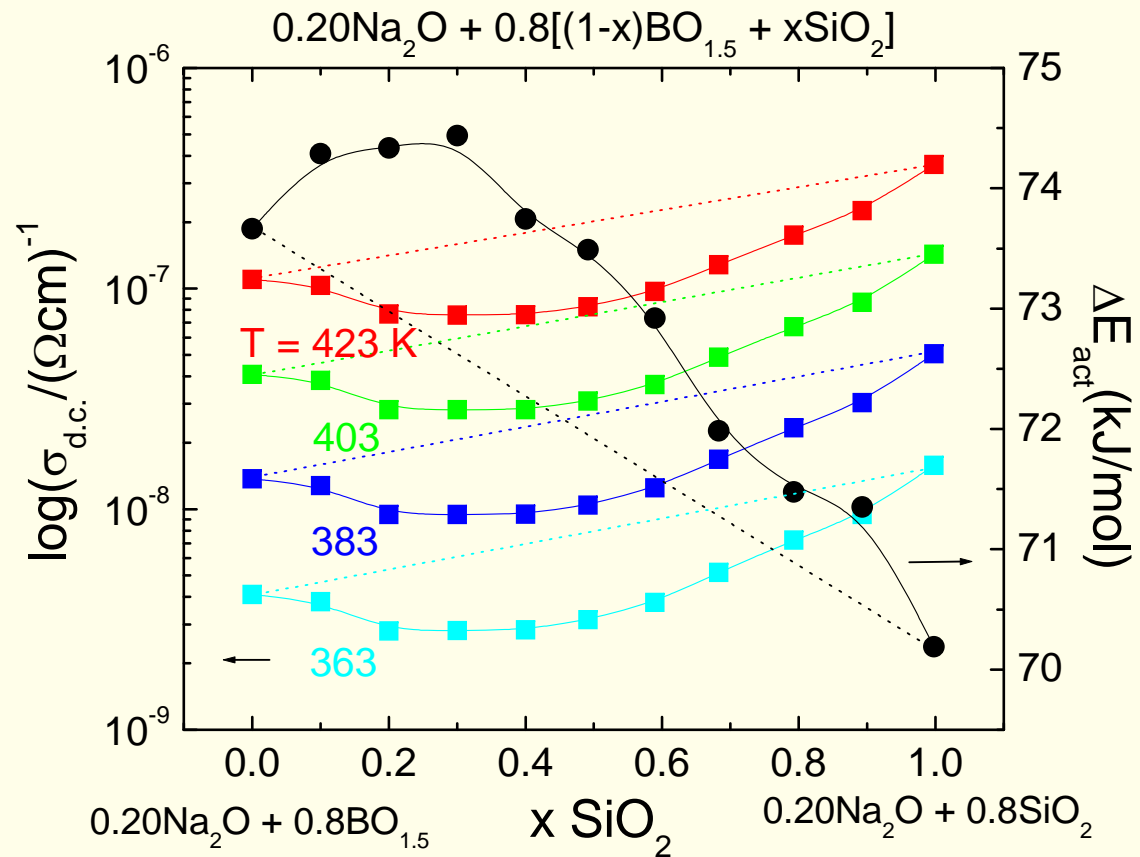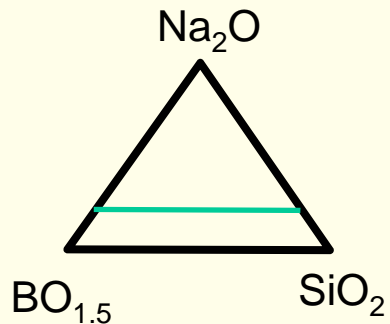

Zielniok, Cramer, Eckert . Chem. Mater. 19 (2007) 3162

Mixed Glass Former Na B P O Glasses
A Maximum in the Ionic Conductivity…

$0.35Na_2O + 0.65[(1-x)B_2O_3 + xP_2O_5]$

443 K
423 K
403 K
383 K
363 K

$\sigma_{d.c.} / (\Omega cm)^{-1}$

$0.35Na_2O + 0.65B_2O_3$ x P_2O_5 $0.35Na_2O + 0.65P_2O_5$

Na$_2$O

B$_2$O$_3$ P$_2$O$_5$

Mixed Glass Former Na B Si O Glasses
A Minimum in the Ionic Conductivity…

$0.20Na_2O + 0.8[(1-x)BO_{1.5} + xSiO_2]$

T = 423 K

403

383

363

$\log(\sigma_{d.c.}/(\Omega cm)^{-1})$

$\Delta E_{act}(kJ/mol)$

Na_2O

$BO_{1.5}$ SiO_2

$0.20Na_2O + 0.8BO_{1.5}$ x SiO_2 $0.20Na_2O + 0.8SiO_2$

R. Christensen et al., to be published

Mixed Glass Former Effect

- Phosphate additions cause a **positive** MGFE in Borate glasses
- Silica additions cause a **negative** MGFE in Borate glasses
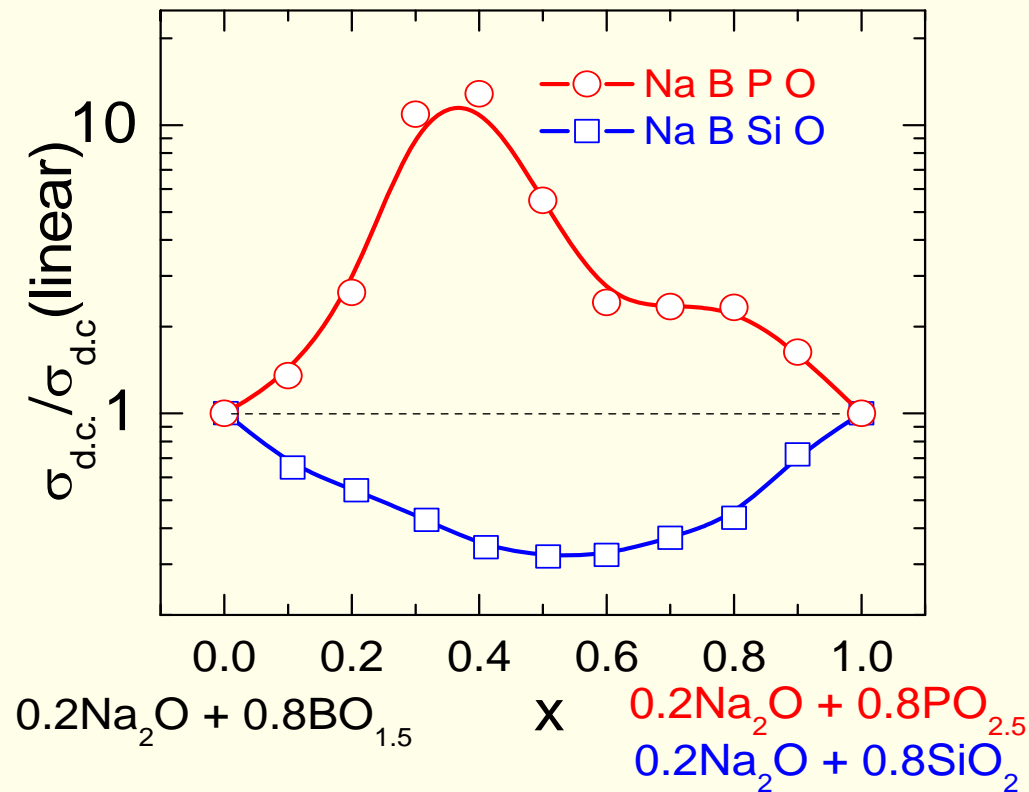
Mixed Glass Former Cation Glasses
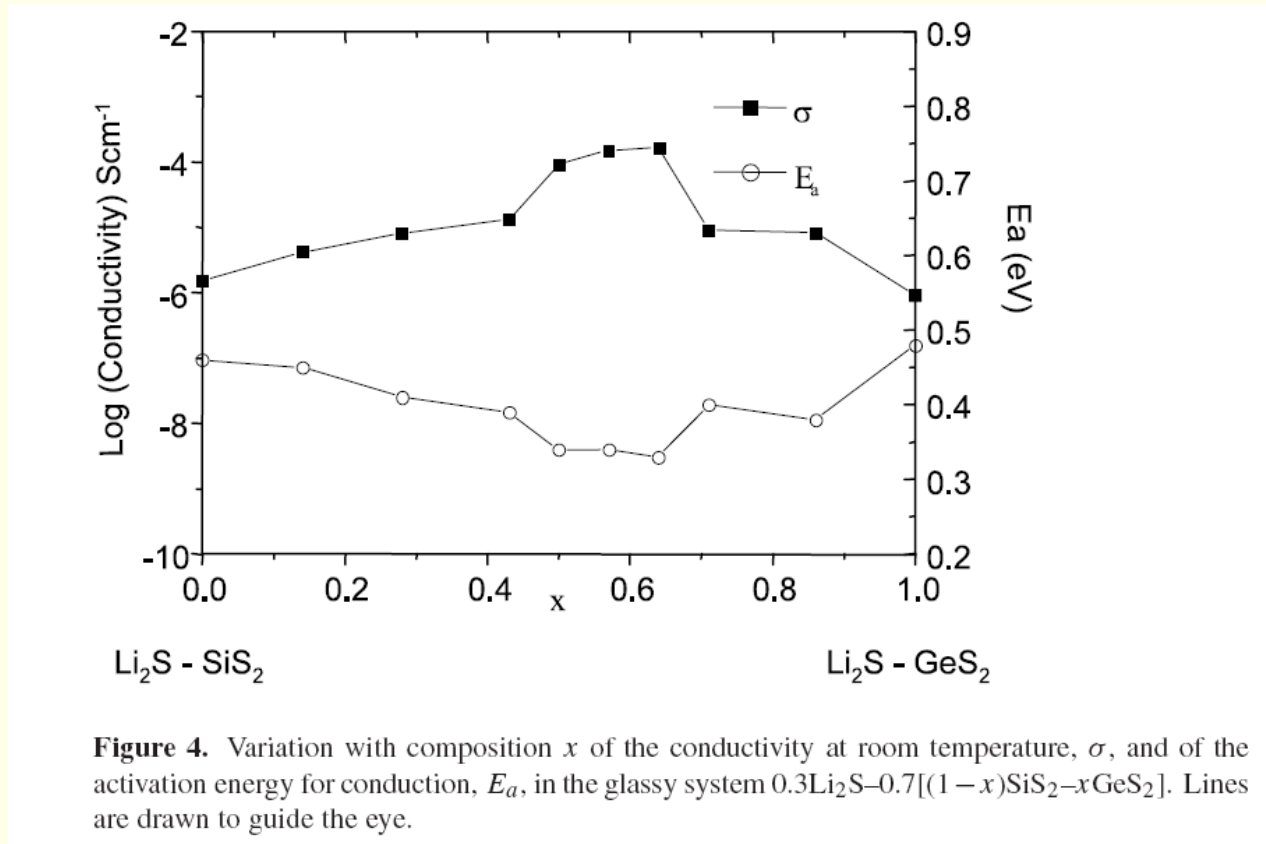
- Sulfide glasses

Figure 4. Variation with composition x of the conductivity at room temperature, σ, and of the activation energy for conduction, E_a, in the glassy system $0.3\text{Li}_2\text{S}–0.7[(1-x)\text{SiS}_2–x\text{GeS}_2]$. Lines are drawn to guide the eye.

Mixed GlassFormer Cation Glasses

- Sulfide glasses
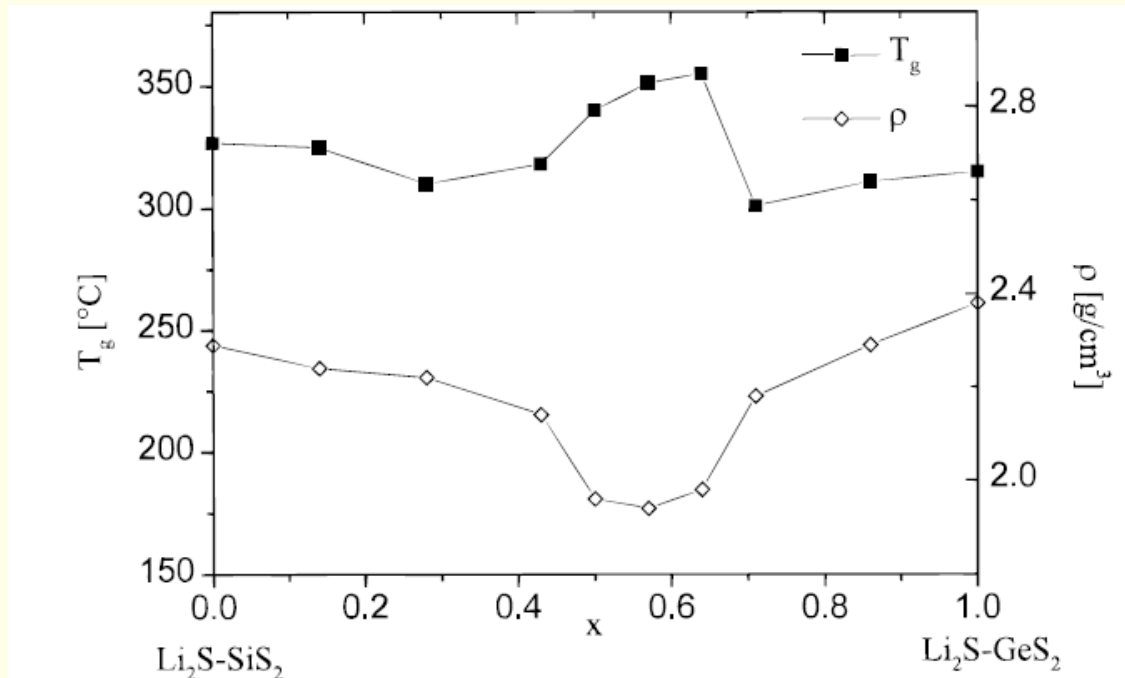
Figure 1. Variations of the glass transition temperature Tg and of the density ρ with composition x in the glassy system $0.3Li_2S-0.7[(1-x)SiS_2-xGeS_2]$.

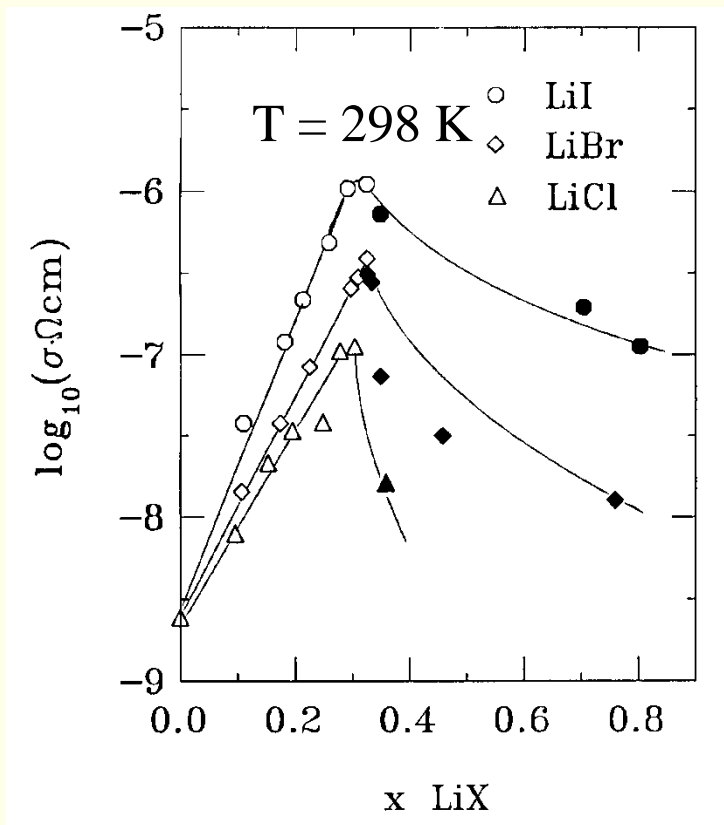# Mixed Glass Former Glasses

• AgI-Ag$_2$MoO$_4$-Ag$_3$PO$_4$ Glasses
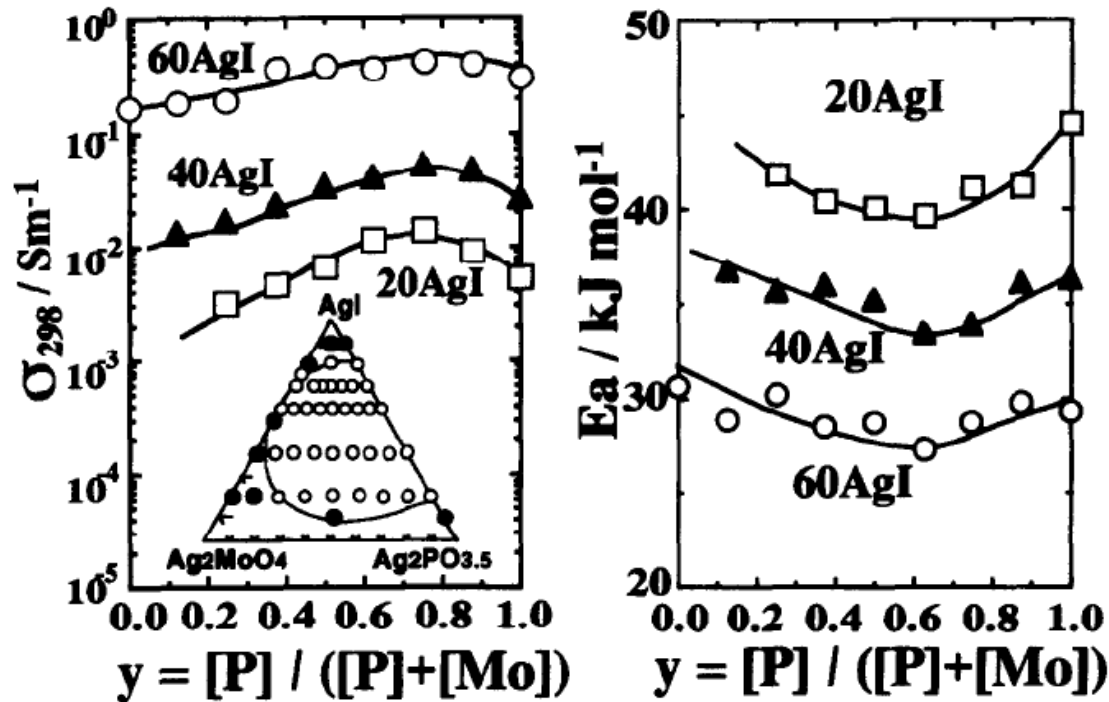
Fig. 3. (a) Conductivities at 298 K, σ_{298}, and (b) activation energies for conduction, E_a, of the glasses in the system AgI–Ag$_2$MoO$_4$–Ag$_2$PO$_{3.5}$ as a function of the composition parameter y, $y = [P]/([P] + [Mo])$.
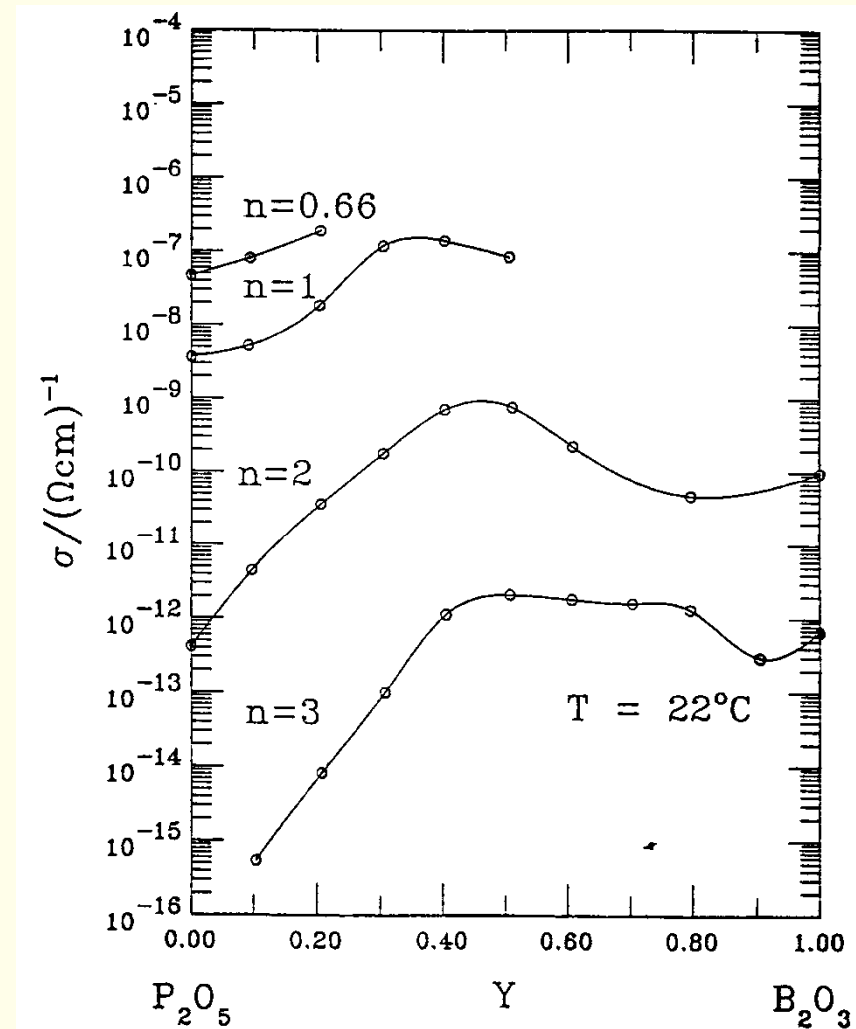
Salt doped phosphate glasses

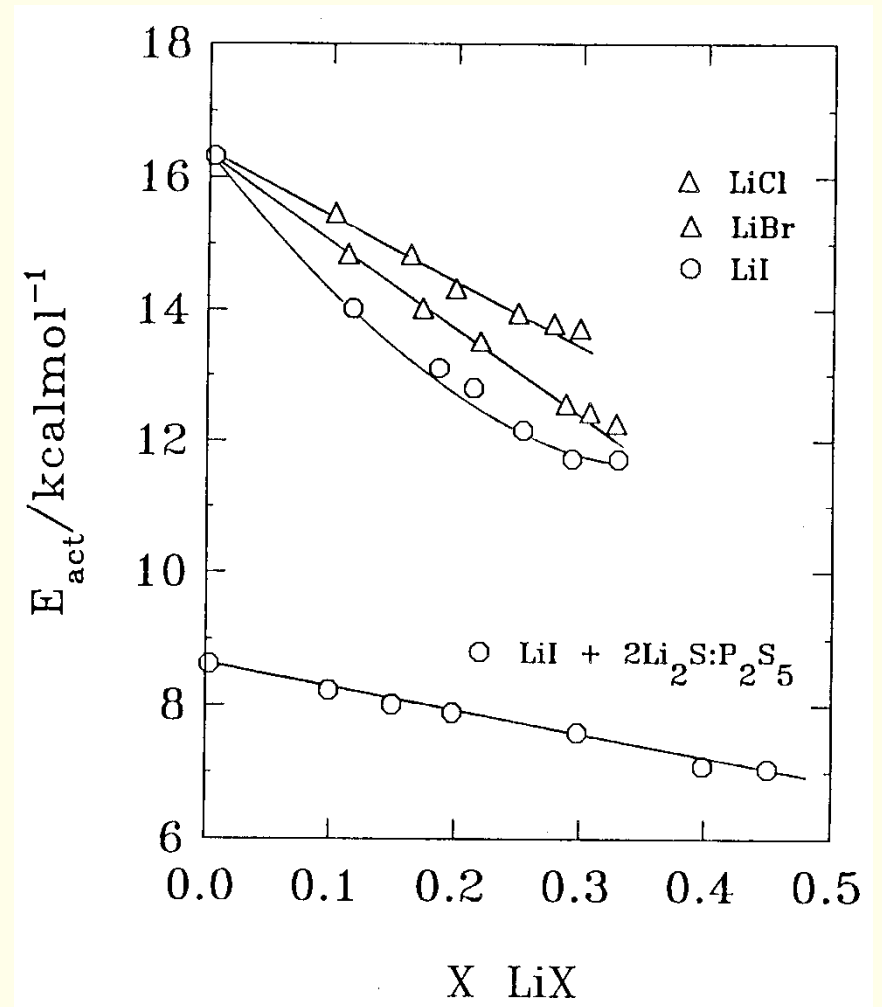- LiI doped $LiPO_3$ show highest conductivity and lowest activation energy among the halides
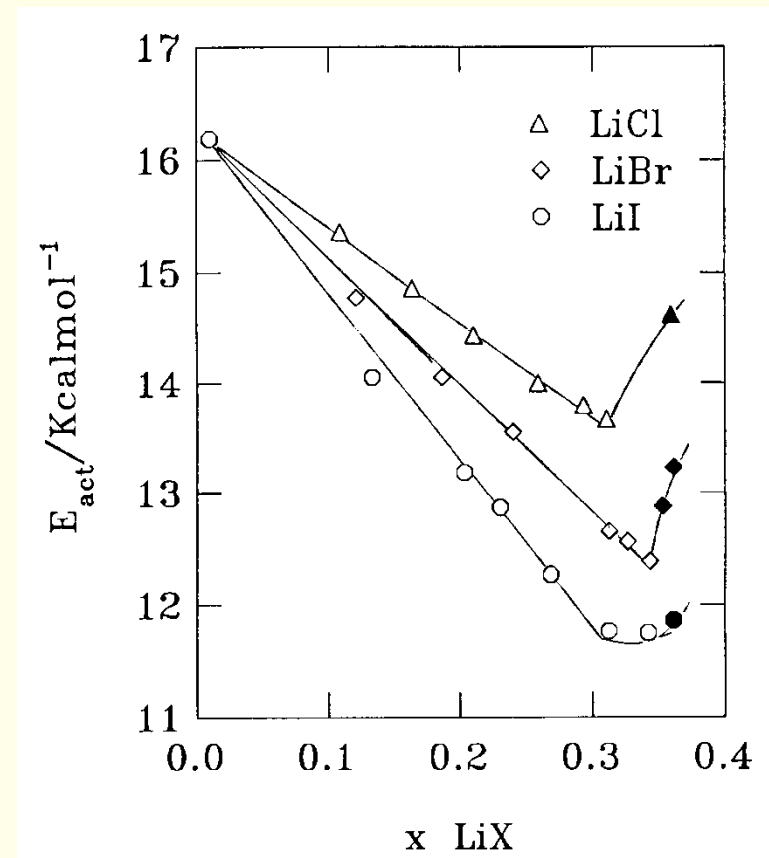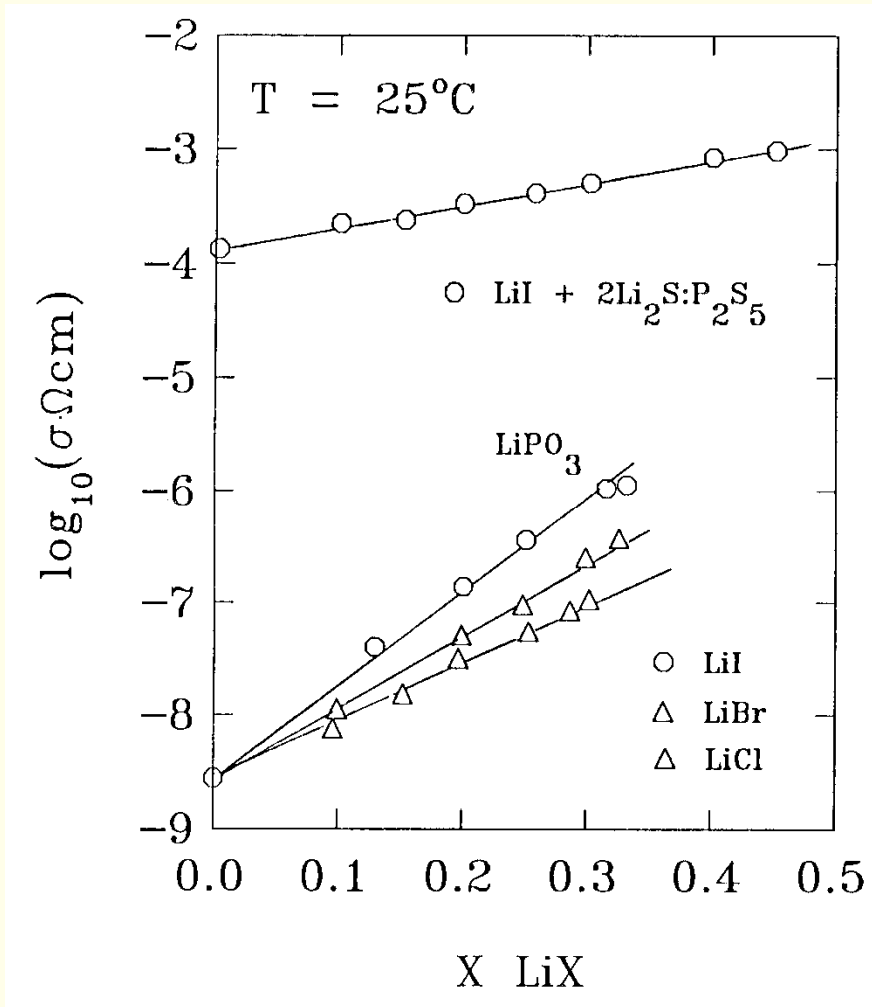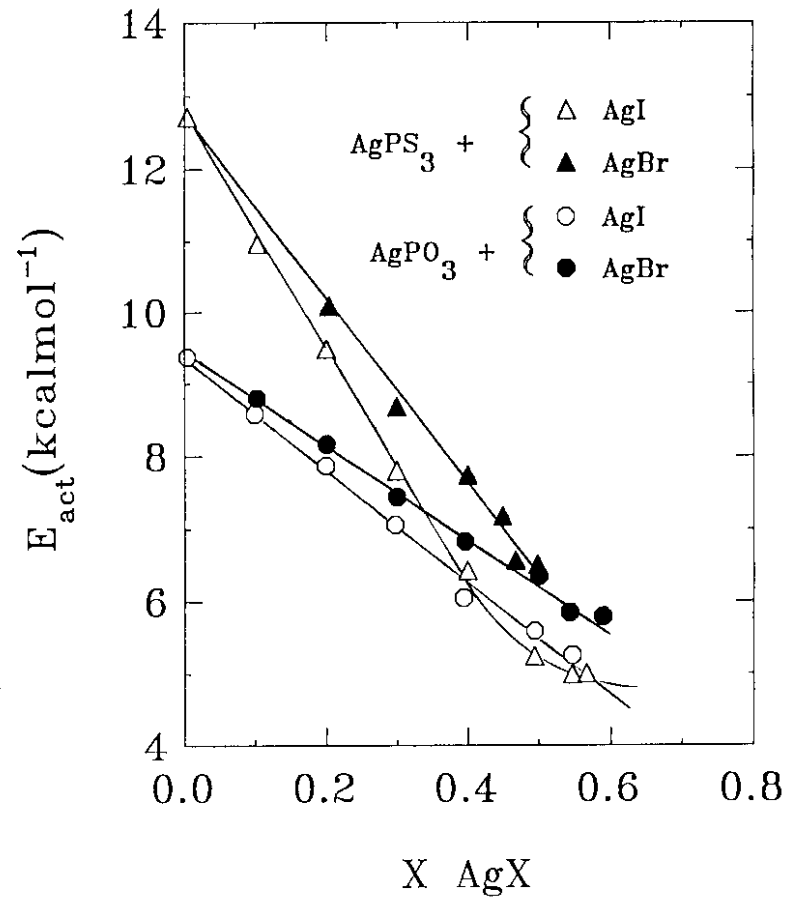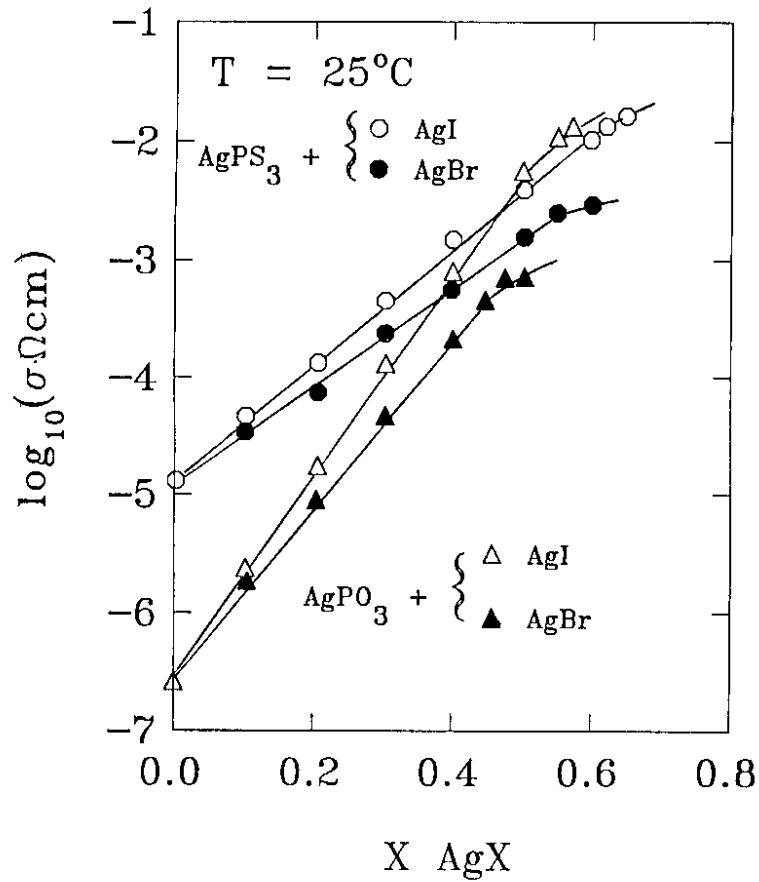
Mixed glassformer systems

- Phosphate and borate mixed glasses show non-linear "Mixed Glassformer" effect
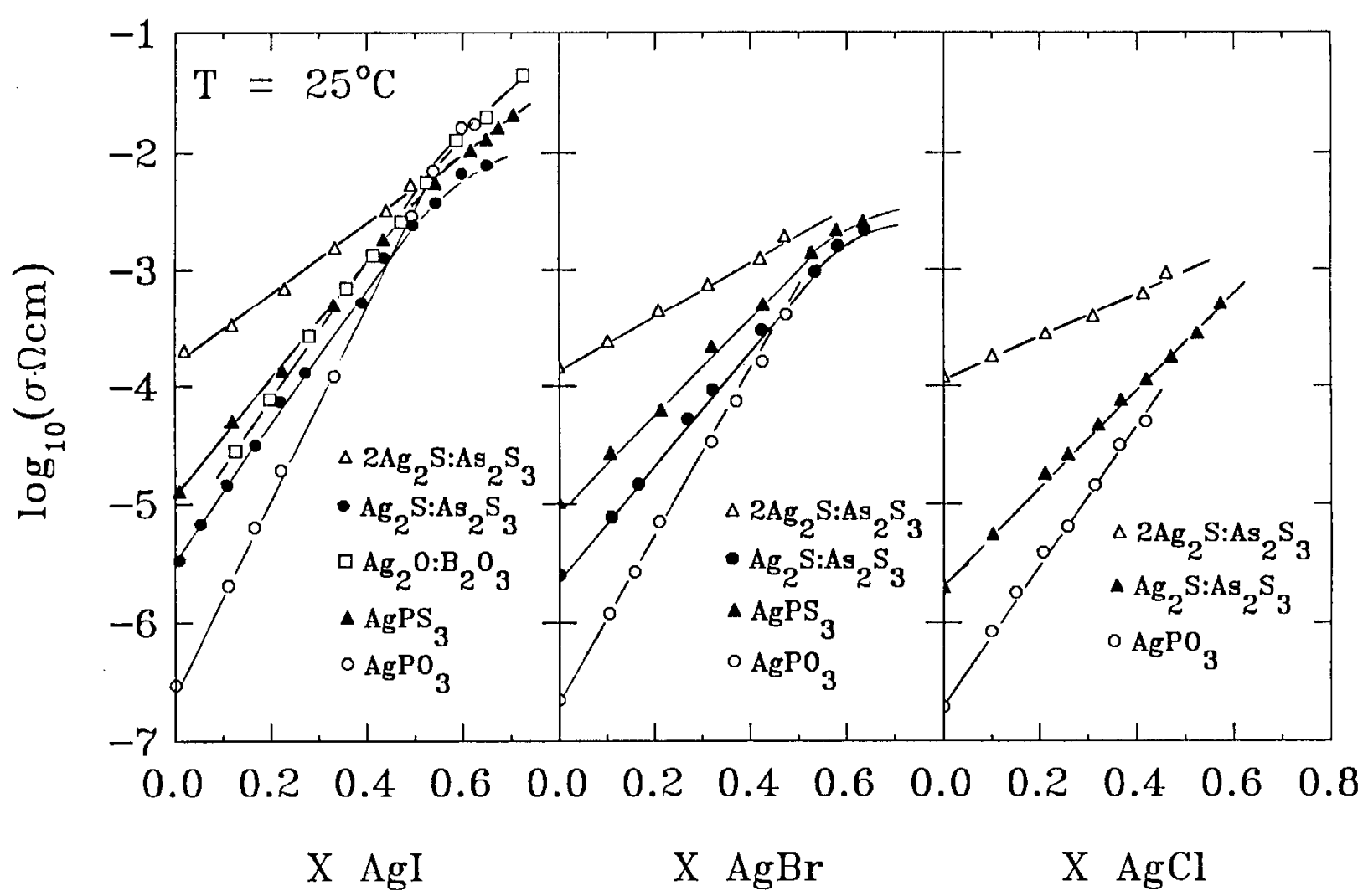
Lithium Thiophosphate Glasses

Silver Phosphate Glasses

Other Silver Sulfide Silver Halide doped glasses

Summary and Conclusions

- Fast Li^+ ion conducting glasses can be compositionally tailored
- Over wide ranges of composition and Li^+ ion conductivity
- Advantages of solid structure reduce lithium dendrites
- Improves safety of the batteries
- Simplifies battery construction
- May enable the use of metallic lithium anodes
- Dramatically and safely increasing the energy density of the batteries
- Future work will focus on cycle life time