Lecture 12 - Ionics applications 1: Models of Ionic Conduction in Chalcogenide Glasses

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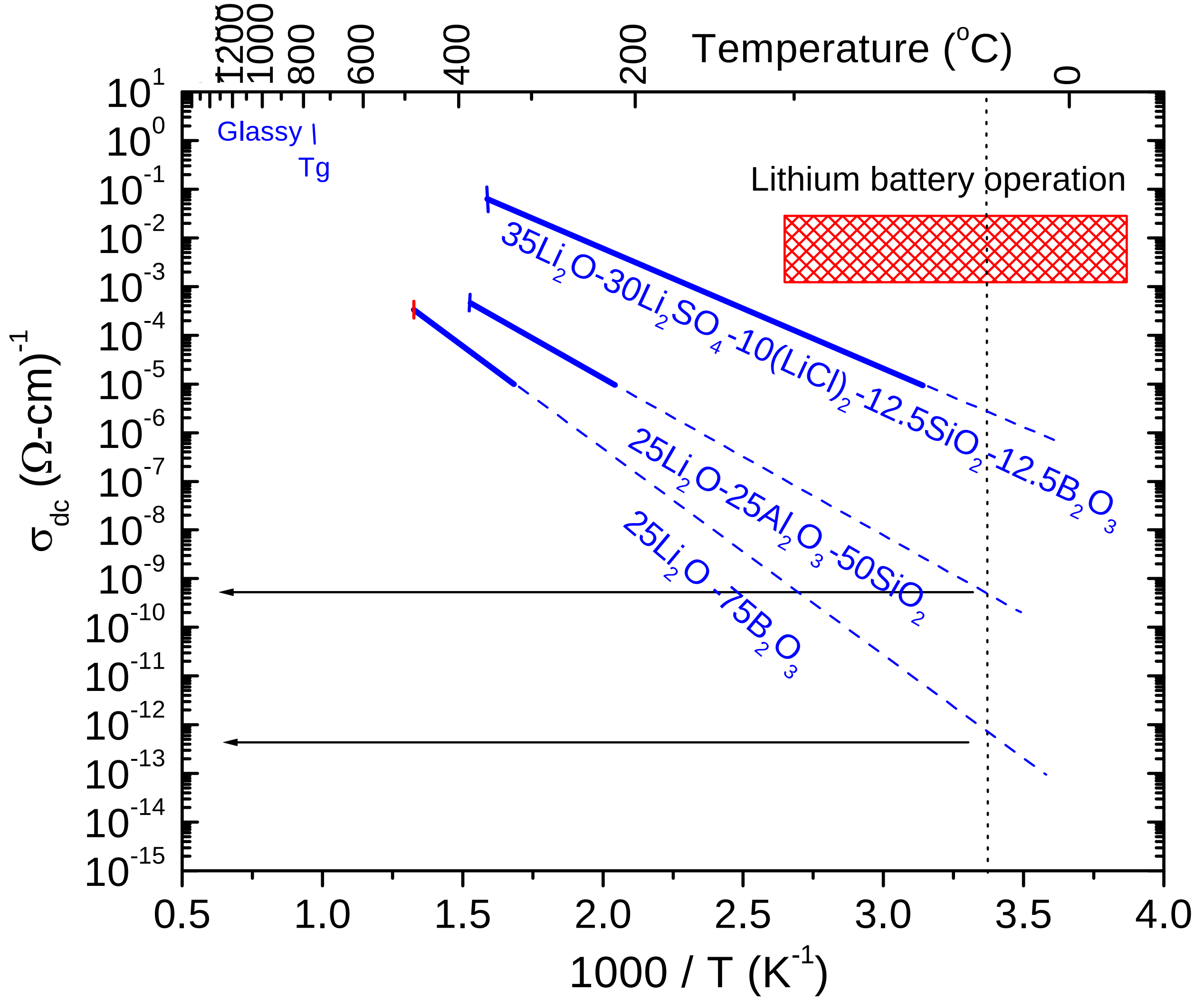
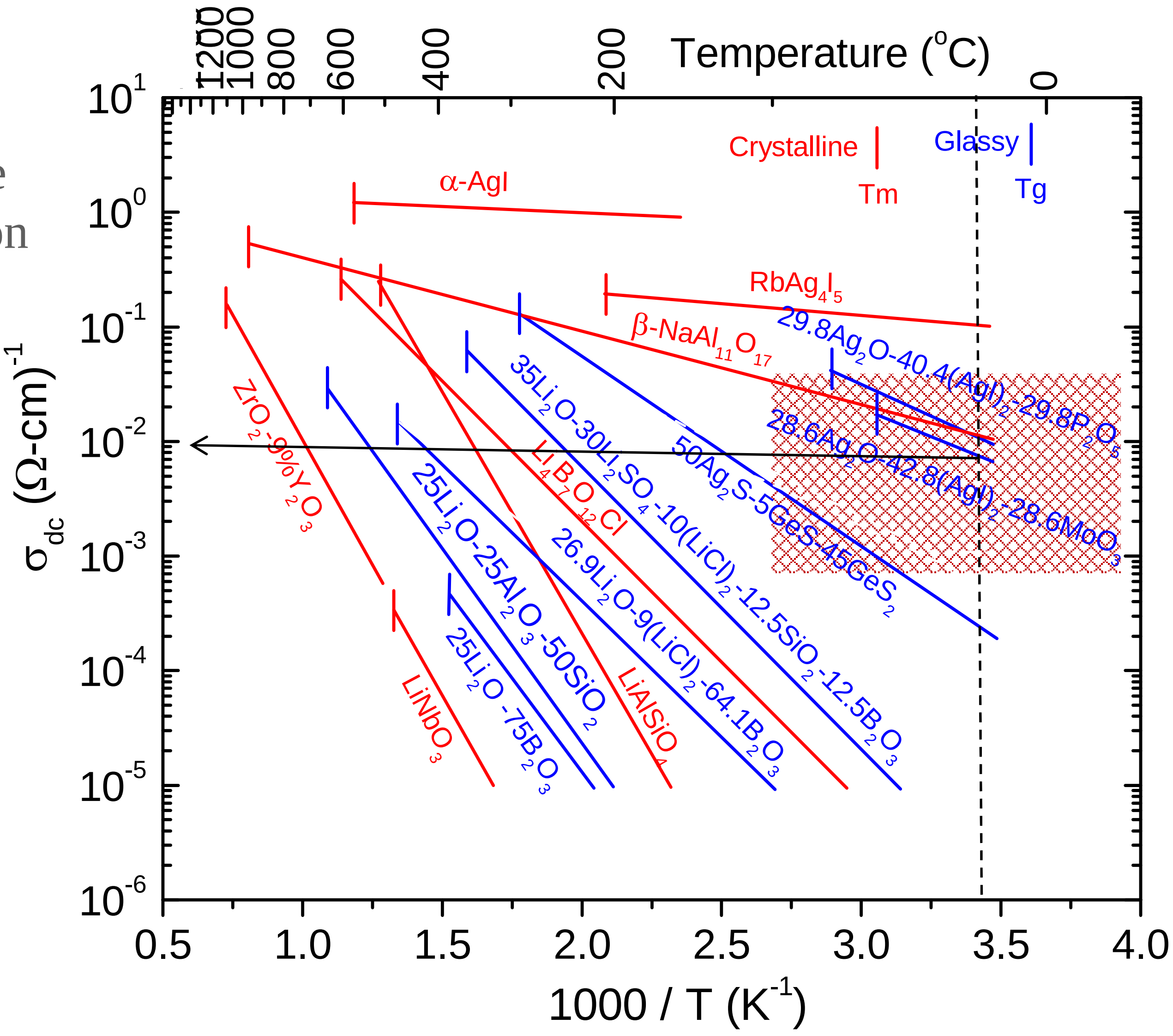
Ion Conduction in Glass

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



Fast Ion Conduction in Glass

FIC glasses can be more than 1 million times more conductive!



Li-ion Battery: The Most Common Li battery

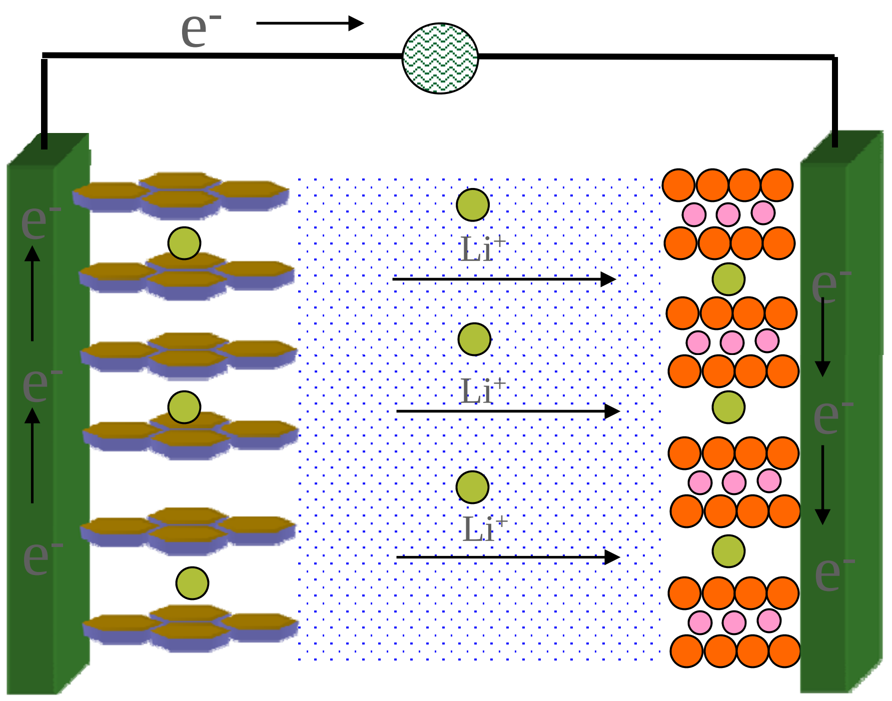
C_6 is a common anode material for Li-ion batteries

The maximum capacity of graphite (LiC_6): ~350Ah/kg

Li: ~ 4000 Ah/kg

C_6 has good cycle-life,

But low capacity for new portable devices

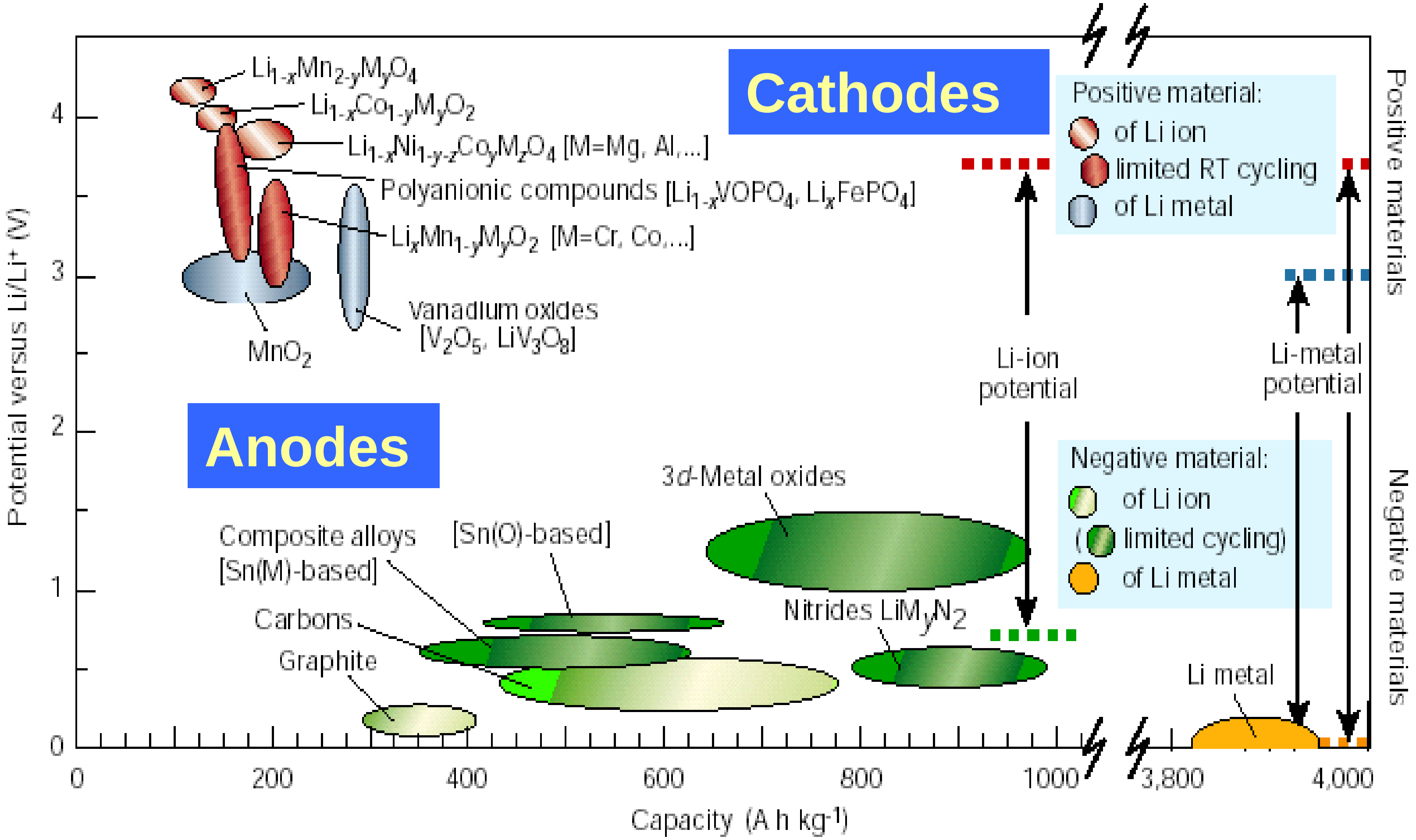


Li_xC_6 Li^+ conducting electrolyte $Li_{1-x}CoO_2$

Anode: $Li_xC_6 \longrightarrow xLi^+ + xe^- + C_6$

Cathode: $Li_{1-x}CoO_2 + xLi^+ + xe^- \longrightarrow LiCoO_2$

Anode and Cathode Combinations Determine the Energy Density of Lithium Batteries



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

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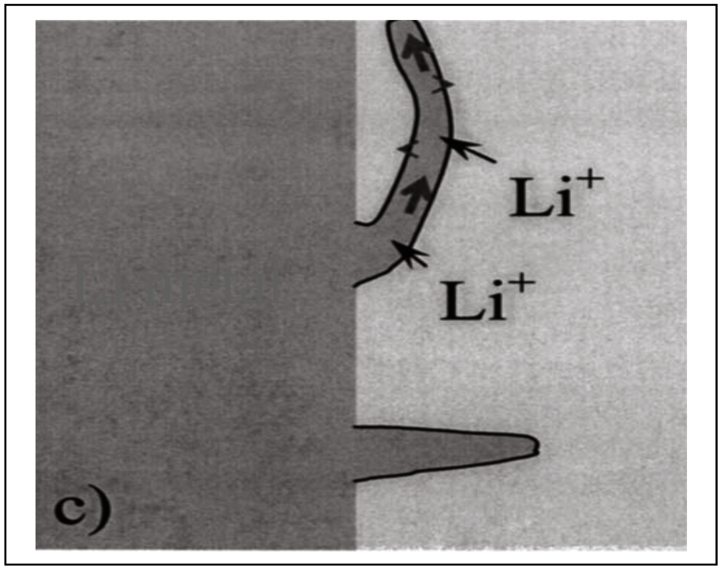
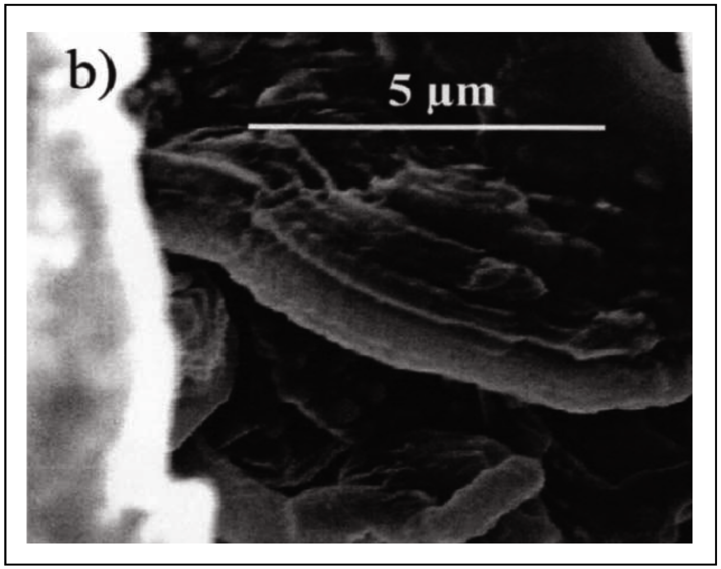
Lithium Dendrite Formation in Li ion Batteries





Non-epitaxial deposition of lithium after each cycle leads to the growth of uneven “fingers” or dendrites of lithium

Internal dendrites result in short circuits of the battery – *heat and fire*

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

Fast Ion Conduction in Glass

- Can highly conducting glasses be used in Lithium batteries
  - To increase safety?
    - By mitigating lithium dendrite formation
  - To increase energy density?
    - By enabling lithium metal (or similar high activity) anodes
  - To reduce cost?
    - By simplifying design and using lower cost materials

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Fast Ion (Li^+) Conducting Sulfide Glasses- Ionic Chalcogenide Glasses Charge Compensated Chalcogenide Glasses

- Typical glass compositions
  - Lithium salt + Lithium modifier + glass former + additives

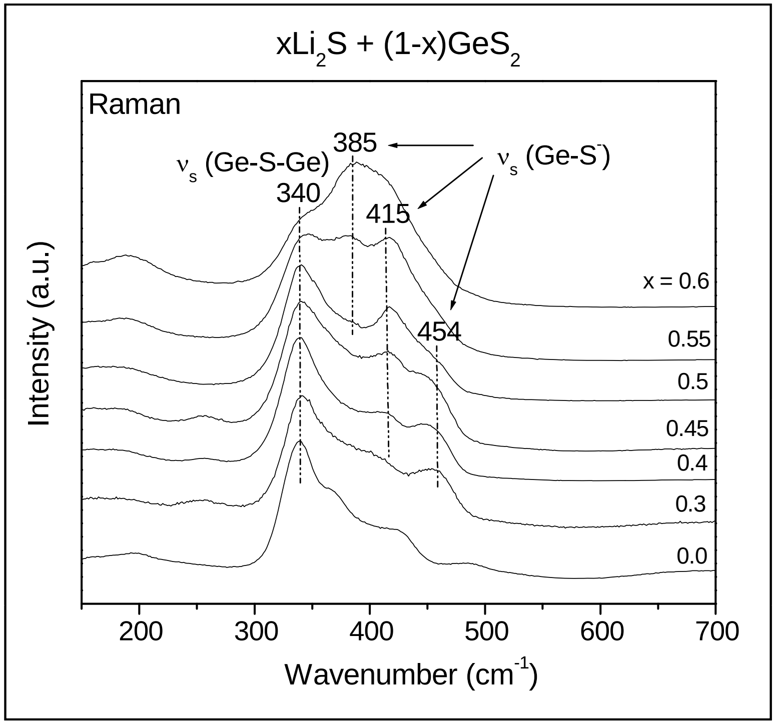
Mobile cations

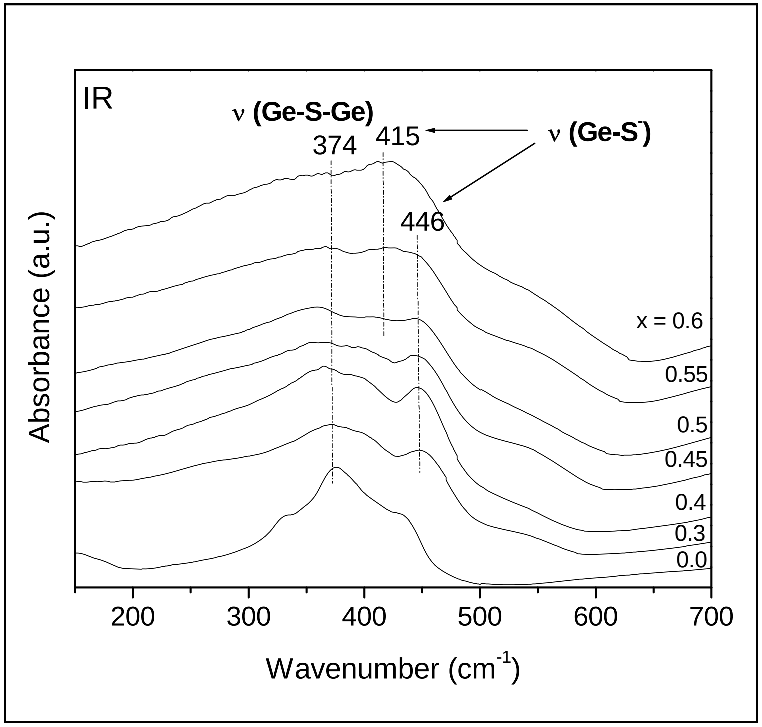
Glass structure

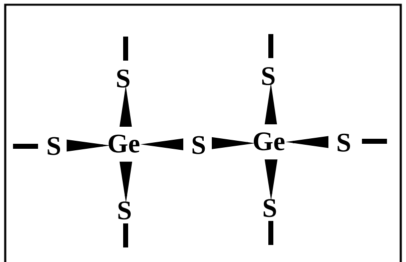
Chemical/mechanical/ electrochemical durability

  - $LiI + Li_2S + SiS_2, B_2S_3, GeS_2$ …
  - $LiI + Li_2S + GeS_2 + Ga_2S_3, La_2S_3, ZrS_2$…

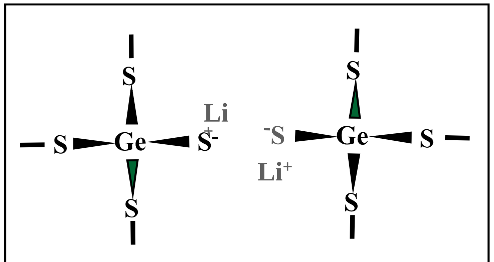
Example: Structures of $xLi_2S + (1-x)GeS_2$ Glasses



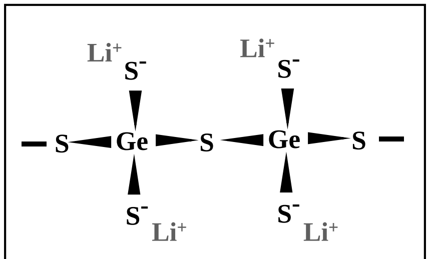




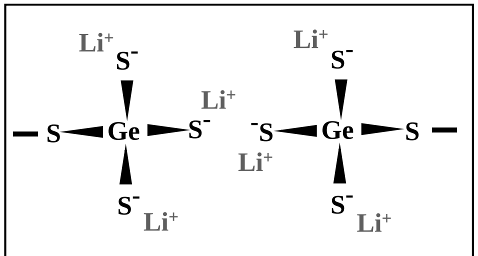
$GeS_{4/2}$



$(GeS_{3/2}S)^-$



$(GeS_{2/2}S_2)^{2-}$



$(GeS_{1/2}S_2)^{3-}$

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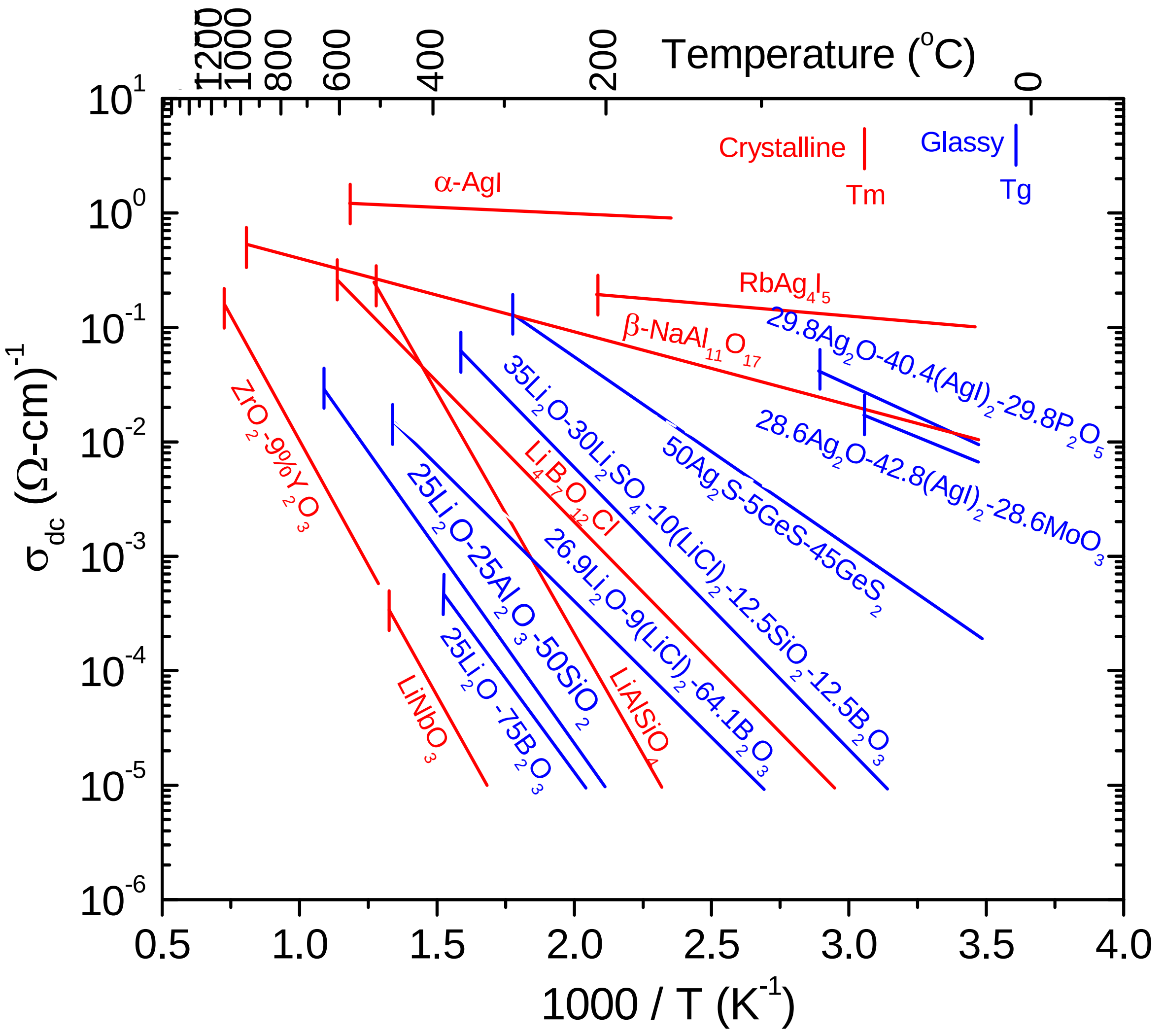
Arrhenius Ionic Conductivity



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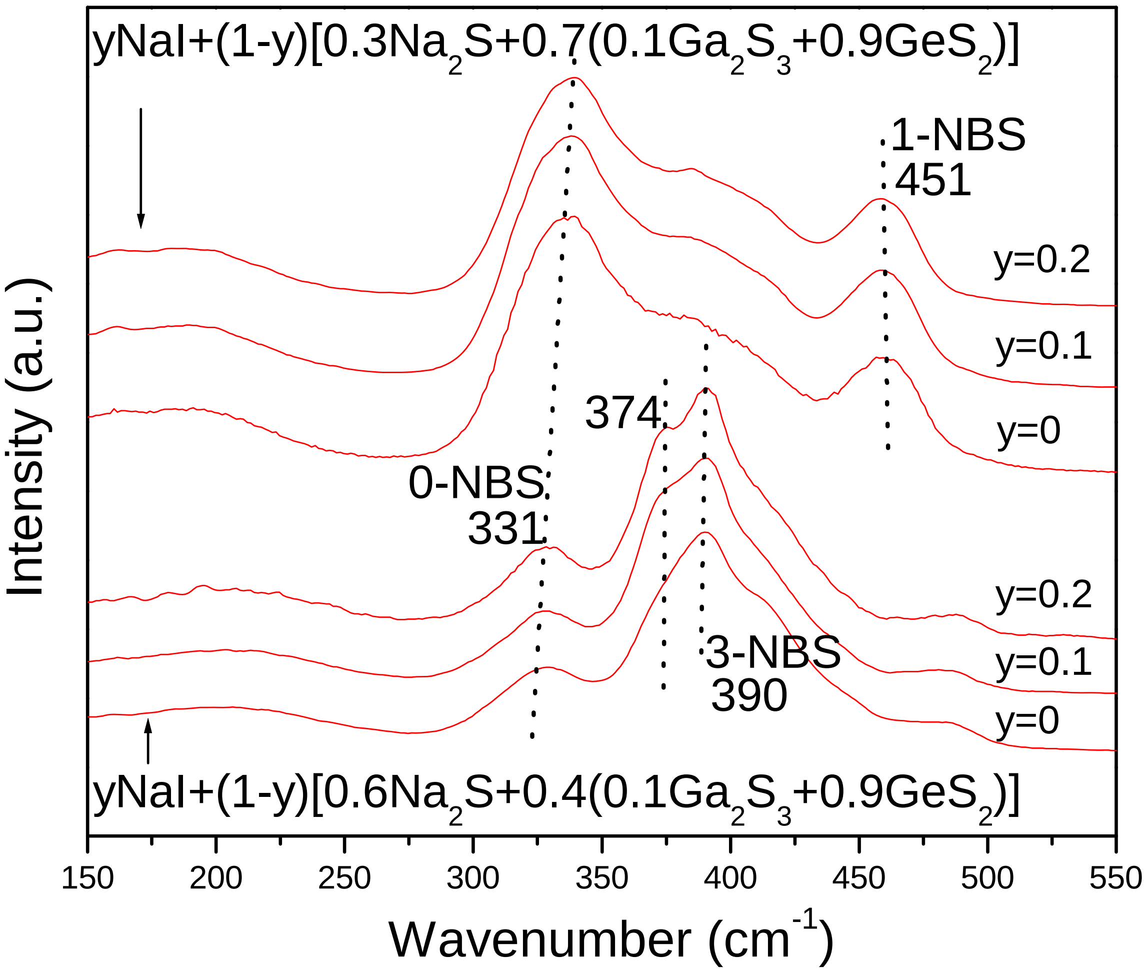
Raman Spectra of NaI doped glasses



Usually, alkali iodide (MI) resides in the interstitials of glass structure network and causes no change in the glass network structure

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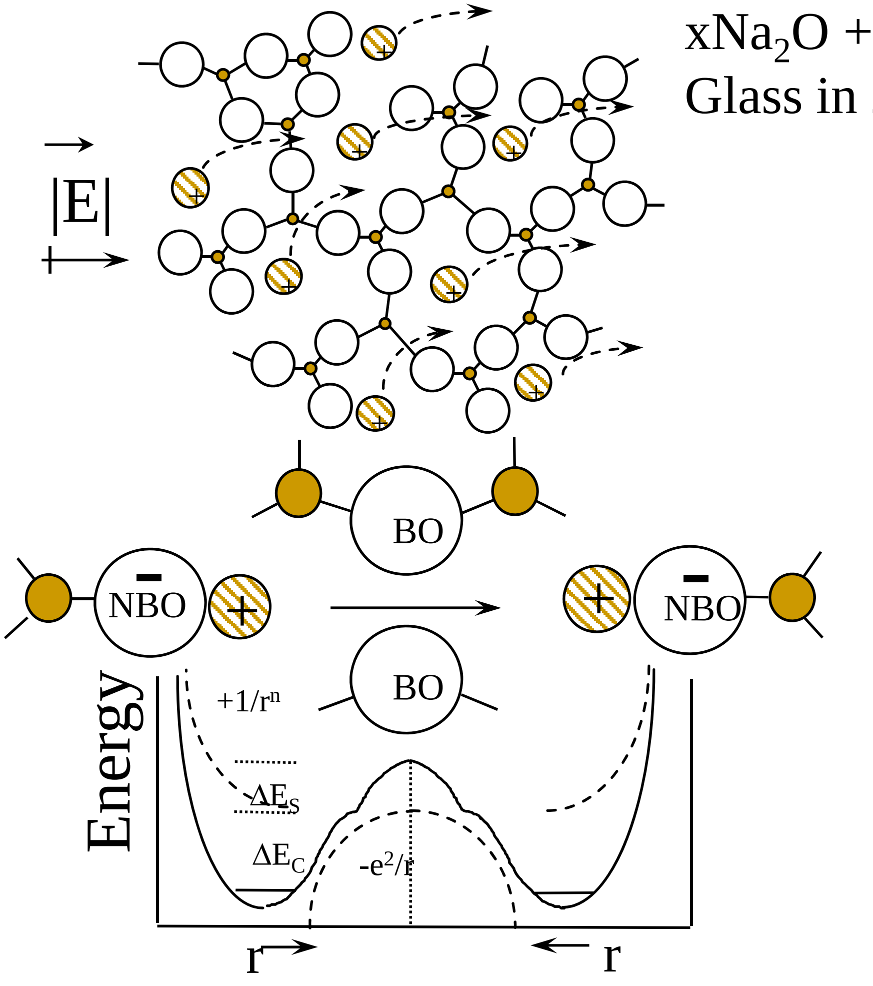
Relation of glass structure to ionic conduction



$xNa_2O + (1-x)SiO_2$
Glass in 2-D

$\Delta E_{act} = \Delta E_s + \Delta E_c$
ΔE_s = Strain Energy
ΔE_c = Coulomb Energy

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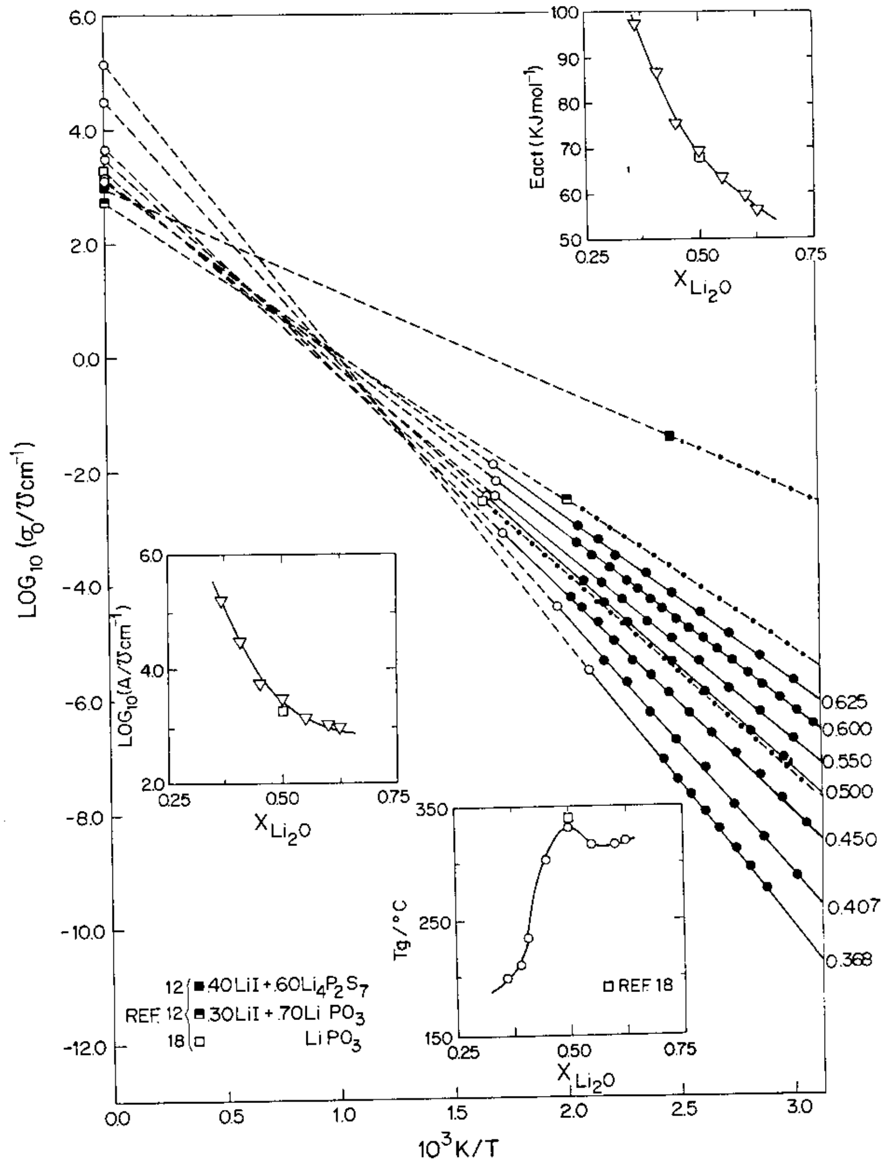
Ionic Conduction in Glass

- $\sigma = neZ\mu$
  - N is the number density
  - eZ is the charge, +1 most of the time
  - μ is the mobility
- Estimation:
  - What are the units of n?
  - What is the approximate magnitude of n for a glass?
  - What are the units of eZ?
  - What is it magnitude for Li^+?
  - What are the units of μ?
- Calculation:
- Take:
  - $n \sim 10^{22}$ M^+/cm^3
  - A-M Universities…
  - $\sigma \sim 10^{-9}$ $(\Omega cm)^{-1}$ Oxide glass
  - What is μ?
  - N-Z Universities…
  - $\sigma \sim 10^{-3}$ $(\Omega cm)^{-1}$ Sulfide glass
  - What is μ?
- Compare Si
  - What is the conductivity of a typical n doped Si?
  - What is μ?

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

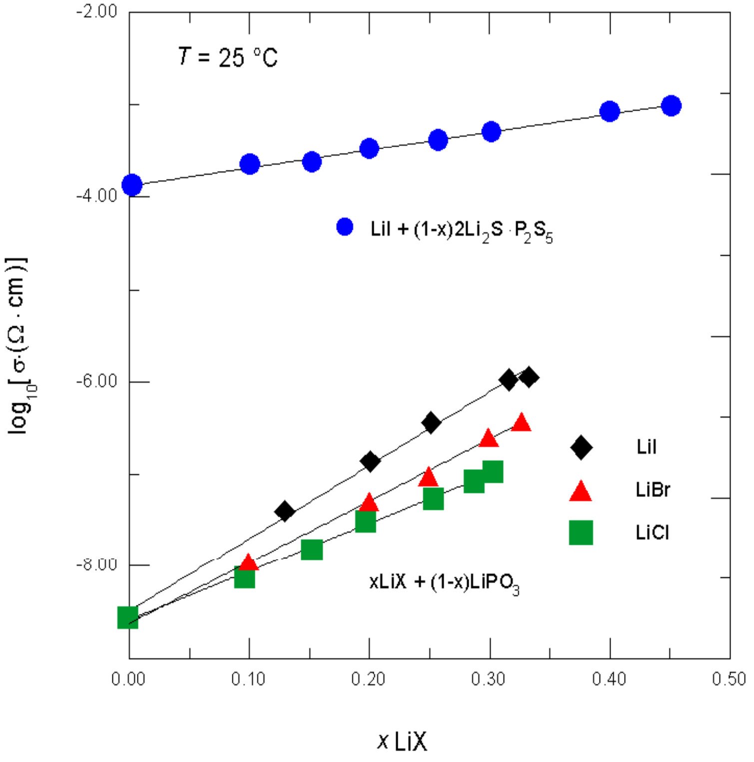


S. Martin, C.A. Angell JNCS ’83

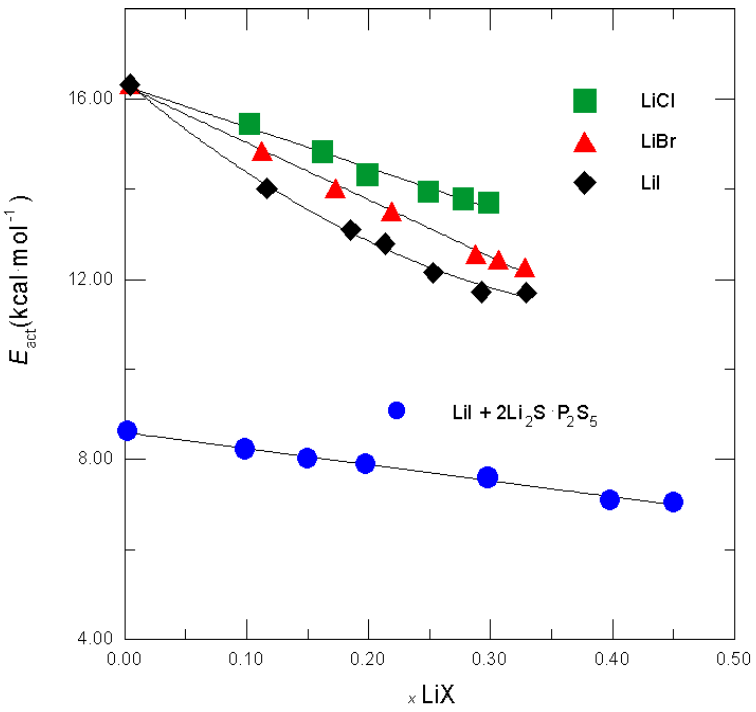
Chalcogenide Glasses have significantly higher conductivities

Salt doped lithium phosphate and thiophosphate glasses

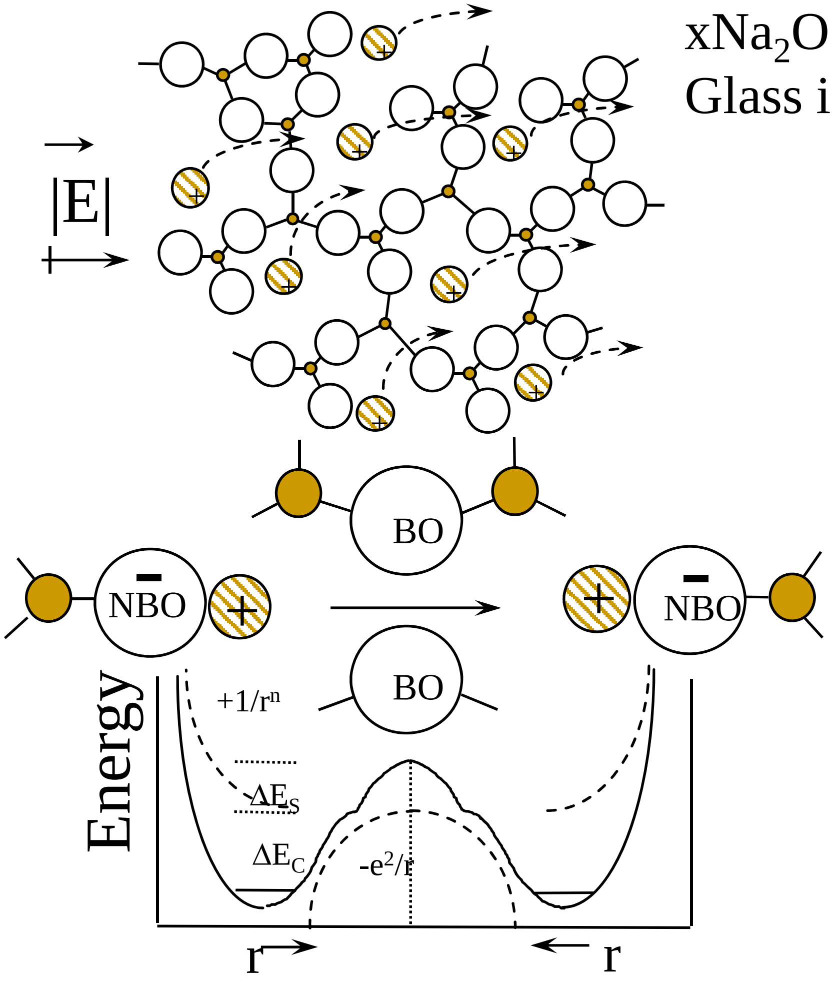
σ_{dc}



ΔE_{act}



Relation of Glass Structure to Ionic Conduction



$xNa_2O + (1-x)SiO_2$
Glass in 2-D

$\Delta E_{act} = \Delta E_s + \Delta E_c$

ΔE_s = Strain Energy

ΔE_c = Coulomb Energy

Mobility and Number Dependence of the Conductivity

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

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

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

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

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

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Short Range Order Models

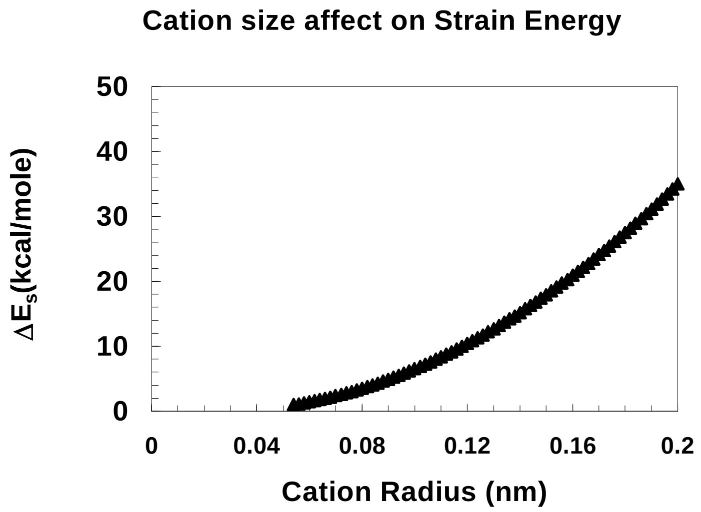
- Anderson-Stuart Model
- Assignment of Coulombic and Strain energy terms, $\Delta E_C + \Delta E_s$
- "Creation" or Concentration versus Migration energy terms, $\Delta E_C + \Delta E_s$
- Coulomb energy term, ΔE_C attractive force between cation and anion

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

- For Li^+ in a oxide and sulfide glass
- **Homework, Take $C_{struct}/\varepsilon_\infty \sim 1$**
- What are the approximate values of r_c, r_d, and λ?
- What is the approximate magnitude of ΔE_C?

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

- For Li^+ in an oxide and sulfide glass
- **Homework**
- What are the approximate values of r_c, r_d, and λ?
- What is the approximate magnitude of ΔE_s?

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, $k_A \sim 1 \times 10^{-5}$?
  - Cations are only weakly dissociated
- Are alkali cations structurally, ΔE_s, constrained?
  - Strong electrolytes like NaCl?
  - Completely dissociated, Na^+ Cl^- ?

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

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

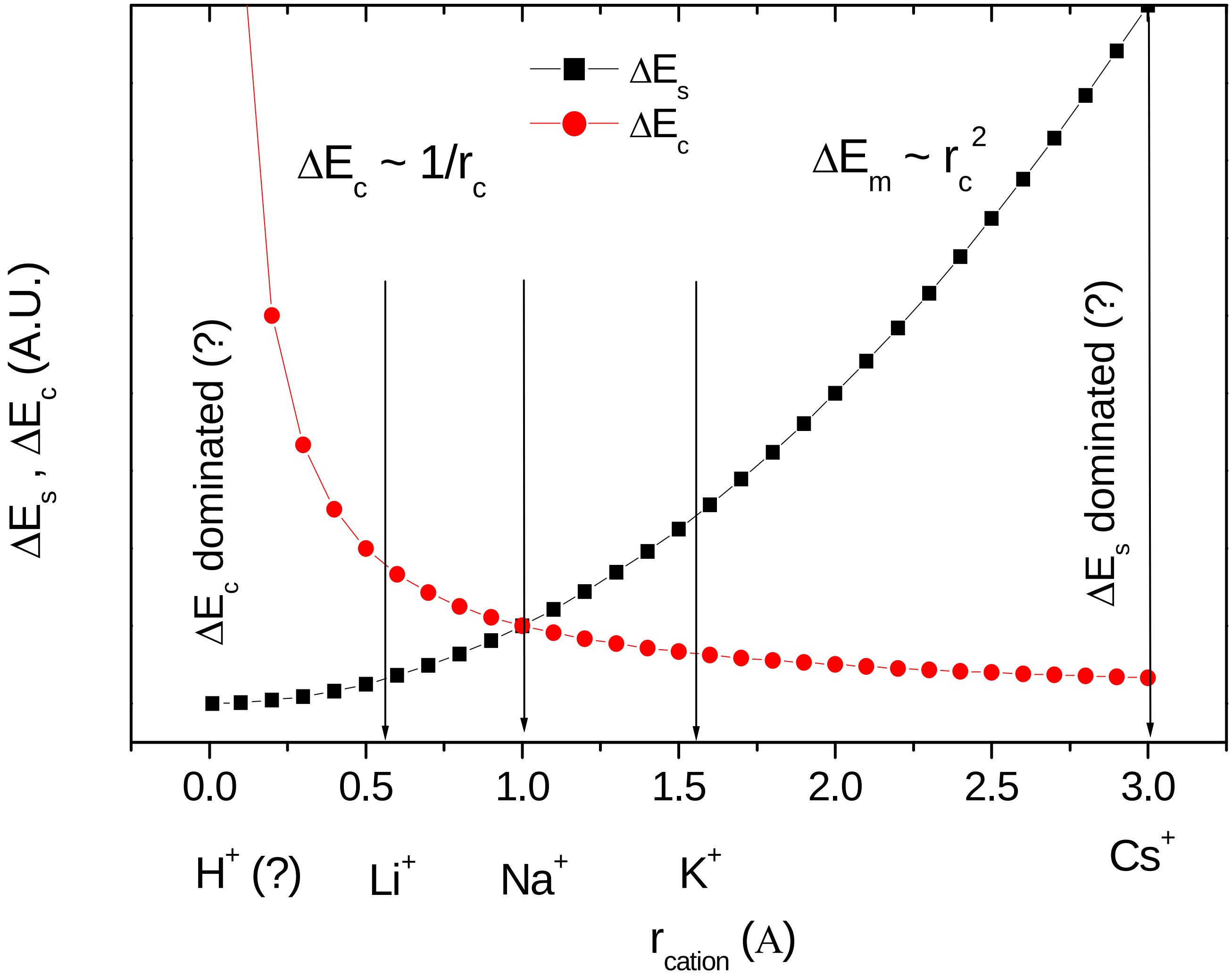
x Na_2O + (1-x)SiO_2	ΔE_s (calc) kcal/mole	ΔE_c (calc) kcal/mole	ΔE_{act}(calc) kcal/mole	ΔE_{act}[2] kcal/mole
11.8	11.7	66.9	78.6	68.1
19.2	10.9	62.3	73.2	63.7
29.7	10.0	56.1	66.1	59.7

- 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



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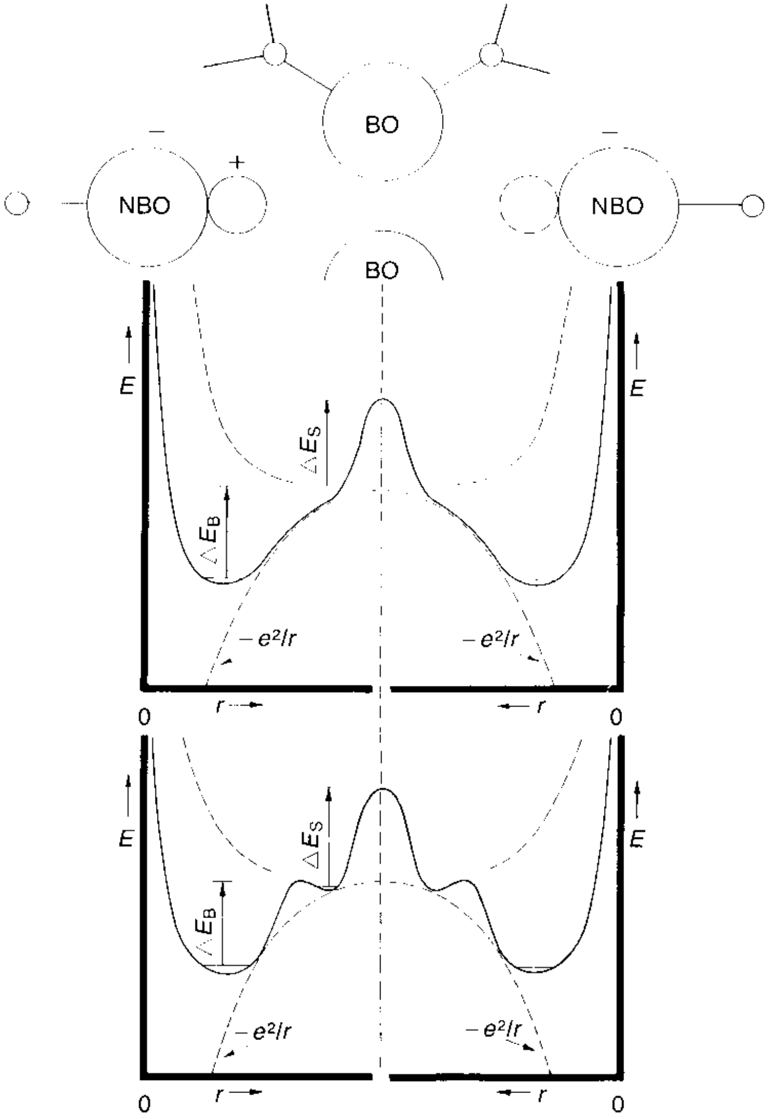
Strong and Weak Electrolyte models

- "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



Thermodynamic Models of Ionic Transport

- 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 dissociates 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 weaker function of composition
- Dissociation constant then determines the number of mobile cations available for conduction, dissociation limited conduction

Weak Electrolyte Model, *Ravaine & Souquet '80*

$$\underbrace{1/2M_2O + SiO_{4/2}}_{\text{(Unreacted)}} \rightarrow \underbrace{{}_{3/2}O\text{-}Si\text{-}O^-M^+}_{\text{(Reacted but Undissociated)}} \rightarrow \underbrace{{}_{3/2}O\text{-}Si\text{-}O^- \cdots\cdots\ M^+}_{\text{(Dissociated)}}$$

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

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

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

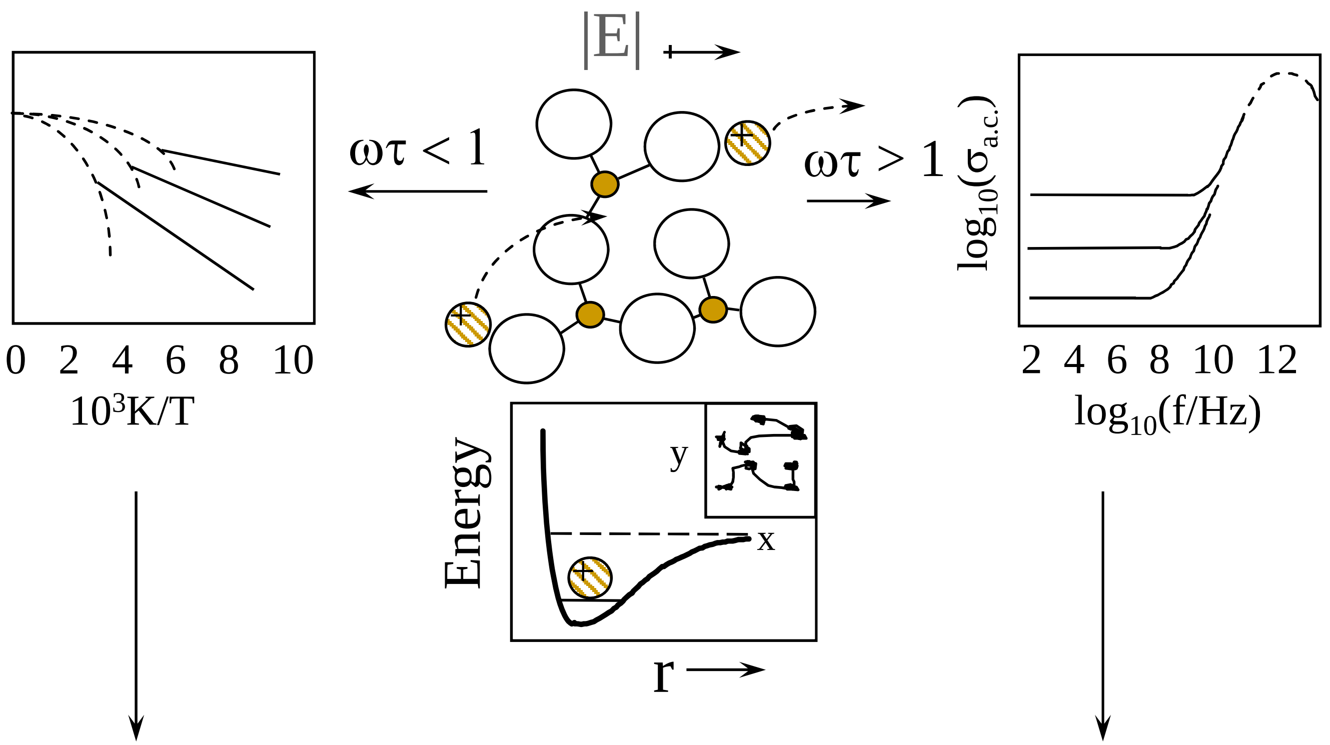
$$\sigma = ze\mu n = ze\mu K_{diss}^{1/2} a_{M2O}^{1/2} \sim C\, a_{M2O}^{1/2}$$

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

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

As ε_∞ increases, K_{diss} increases

AC versus DC Ionic Conductivity



D.C. Conductivity

Charles - Polarization/Diffusion

Anderson/Stuart - Coulomb & Strain Energies

Moynihan/Macedo - Debeye & Faulkenhagen Theory

Ravaine/Souquet - Weak Electrolyte

Malugani- AgI Micro domains

A.C. Conductivity

Jonscher - Universal Response

Ngai - Coupling Theory

Moynihan - Modulus

Dyre - Power Law

Funke - Jump Relaxation

AC ionic Conductivity in Glass

- Connection to Far-IR vibrational modes *Angell* ‘83