Lecture 3 - Ionic Conductivity

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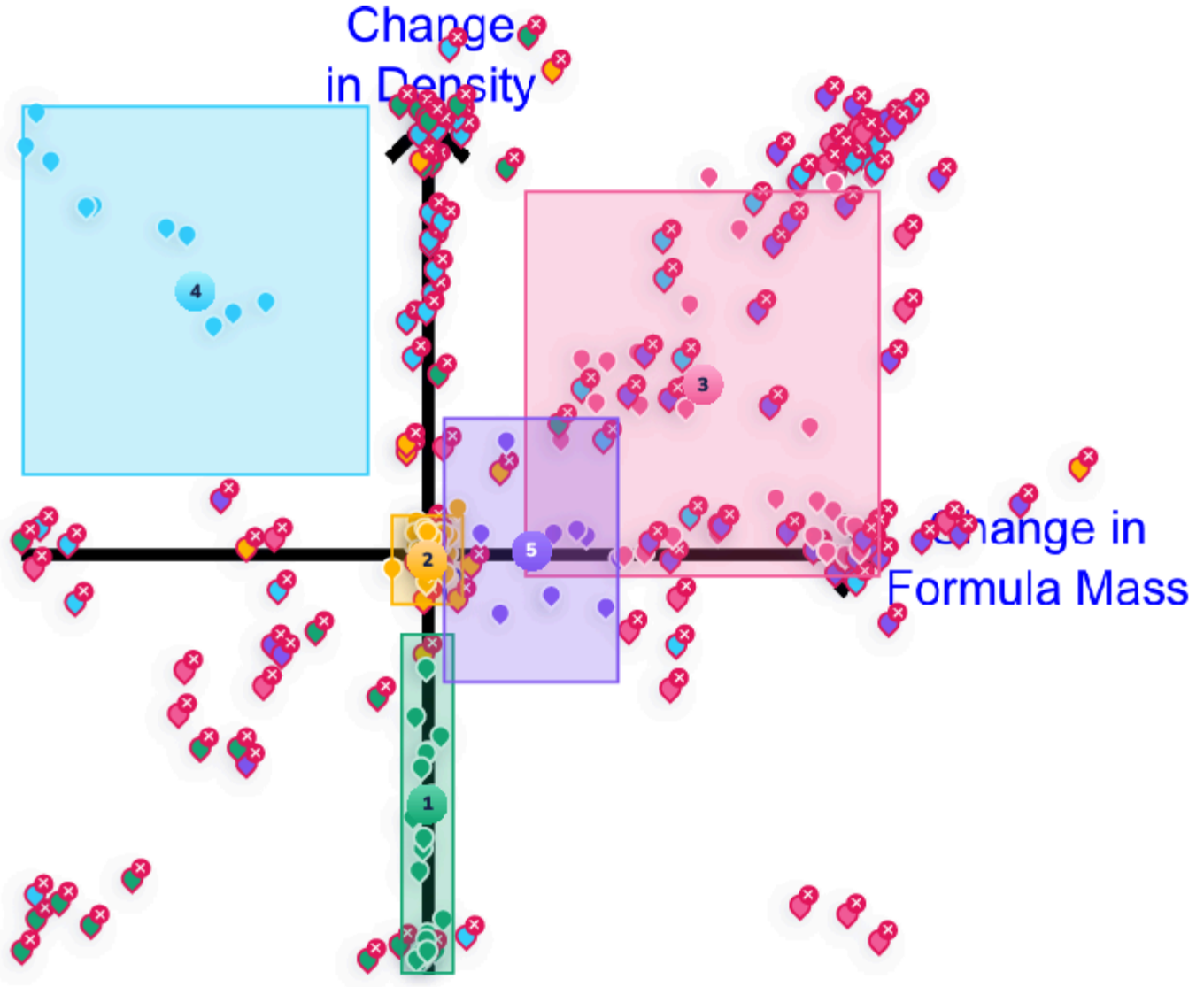
Lecture summary

- Recap of defect types
- Ionic conductivity
- Conduction mechanisms
- Ionic migration paths
- Energetics of conduction

Defect recap

Defect recap results



NaCl Schottky

- Intrinsic defect (composition doesn't change) so formula mass change is 0
- Vacancies essentially create a hole in the structure, so density decreases

AgCl Frenkel

- Intrinsic defect
- Vacancies and interstitials created at the same rate, so density doesn't change significantly

TiO2 substitution with Zr

- Zr is heavier than Ti (91.224 vs 47.867) so formula mass will increase
- Zr^{4+} is slightly larger than Ti^{4+} so we might expect volume to increase slightly, but overall the density will increase
    - NOTE: I *wrongly* said Zr^{4+} was smaller than Ti^{4+} in the lecture - sorry!

Shear phase in WO_3

- $\mathrm{WO_3} \longrightarrow \mathrm{WO_{3-x}}$, so the formula mass will decrease
- Shear phase formation is a substantial rearrangement which is driven by reducing the overall volume. The result is that decrease in volume far outweighs the decrease in formula mass, so density will increase.

Replacing O by F in CeO_2

- $\mathrm{CeO_2} \longrightarrow \mathrm{CeO_{2-x}F_x}$
- F is slightly heavier than O (18.998 vs 15.999) so formula mass will increase slightly
- Charge balance requires us to reduce some Ce^{4+} to Ce^{3+}. There are a few ways to imagine this with KV notation:
  1. Replacing O^{2-} by F^{1-} occurs directly during synthesis:
     - $\mathrm{O_O} + \mathrm{Ce_{Ce}} + \mathrm{H_2} + \frac{1}{2}\mathrm{F_2} \longrightarrow \mathrm{F_O^{\bullet}} + \mathrm{Ce_{Ce}^{'}} + \mathrm{H_2O}$
     - (H_2 and F_2 are used to balance the equation here, but a real experiment would use a different fluorinating reagent such as CeF_3)
  2. As-synthesised CeO_2 is fluorinated by filling existing oxygen vacancies:
     - $\mathrm{V_O^{\bullet\bullet}} + \mathrm{Ce_{Ce}^{'}} + \frac{1}{2}\mathrm{F_2} \longrightarrow \mathrm{F_O^{\bullet}} + \mathrm{Ce_{Ce}^{x}}$
     - Note that the fluorite structure is often prone to anion vacancies due to the mismatch between ionic radii and the geometry (this is particularly prevalent when the cation can be reduced). We'll see why this again in lecture 6.

Conductivity

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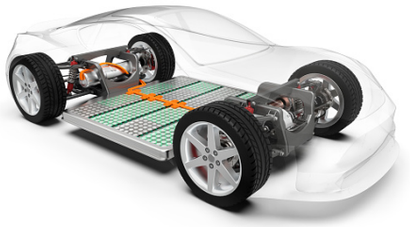
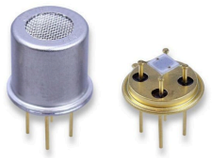
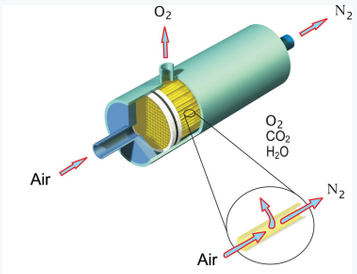
- Ionic conductors are important!

	
Batteries (Lecture 4)	Sensors
	
Separation Membranes	Fuel Cells (Lecture 6)

Origin of ionic conduction

- Ionic conductivity is dominated by **defects**
  - In an ideal crystal, ions can't easily move
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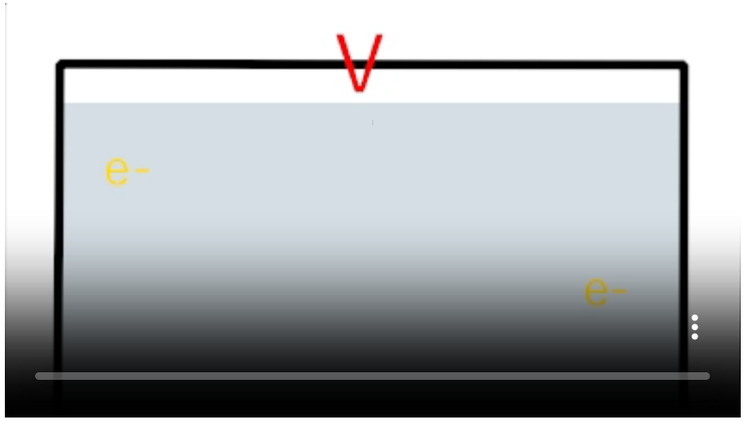
- In ionic solids, conductivity covers $10^{-16}\ \mathrm{S\ m^{-1}} - 10^{3}\ \mathrm{S\ m^{-1}}$
  - most solids are limited to around $10^{-2}\ \mathrm{S\ m^{-1}}$
  - Liquid electrolytes typically $10^{-1} - 10^{3}\ \mathrm{S\ m^{-1}}$

Measuring Conductivity

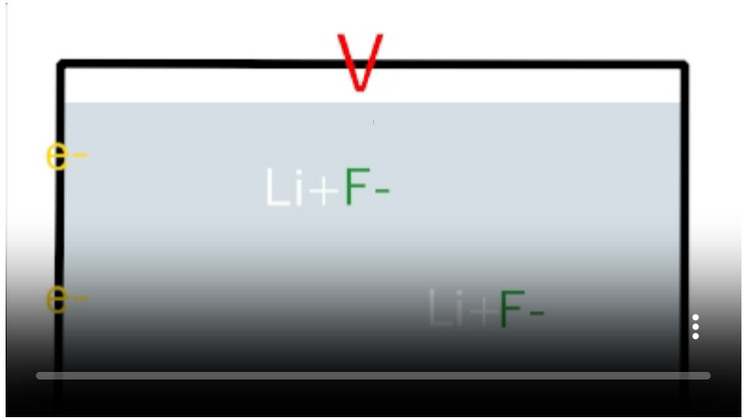
- For electronic conductors, this is simple:
  - Apply a voltage (V) and measure the resulting current (I)
  - Resistance (in Ω) is found through Ohm's law; $V = IR$
  - Resistivity (in $\Omega\ cm$) of the material calculated from geometry
- Resistivity ρ (in $\Omega\ cm$) = $\frac{1}{\text{Conductivity } \sigma \text{ (in S cm}^{-1})}$



In reality, we normally use two wires for V and two for I

Measuring Ionic Conductivity

- Ions cannot flow round a circuit, so current drops with a constant applied voltage



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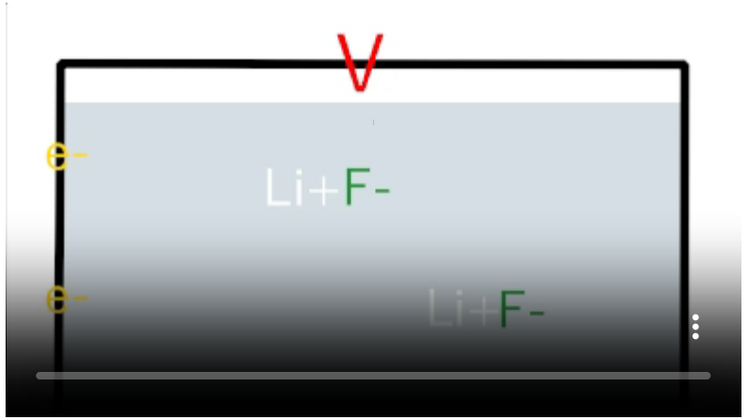
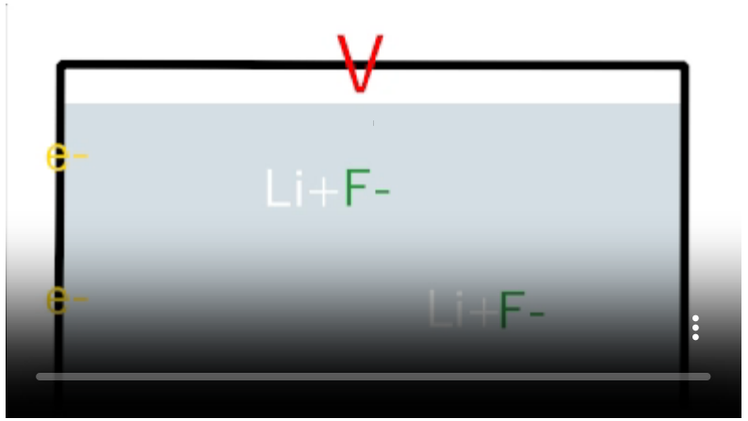


- Instead, we use an alternating voltage - this is called Impedance spectroscopy (see lecture 5)



Ion migration mechanisms

Three 'main' mechanisms of ionic migration

1. Vacancy mechanism

Vacancies move throughout the lattice (atoms move into vacancy)

2. Interstitial mechanism

Ions hop between interstitial sites

3. Interstitialcy (knock-on) mechanism

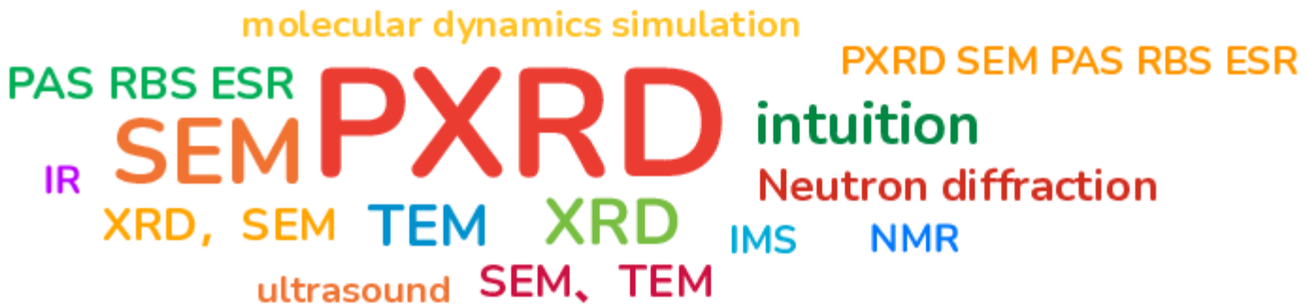
Interstitial ions 'push' into a neighbouring site

Vacancy, Interstitial or Interstitialcy?

Suggestions

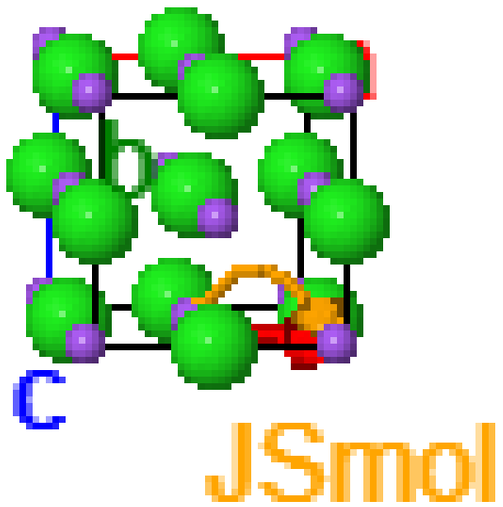
1. What technique(s) could you use to distinguish the mechanism?

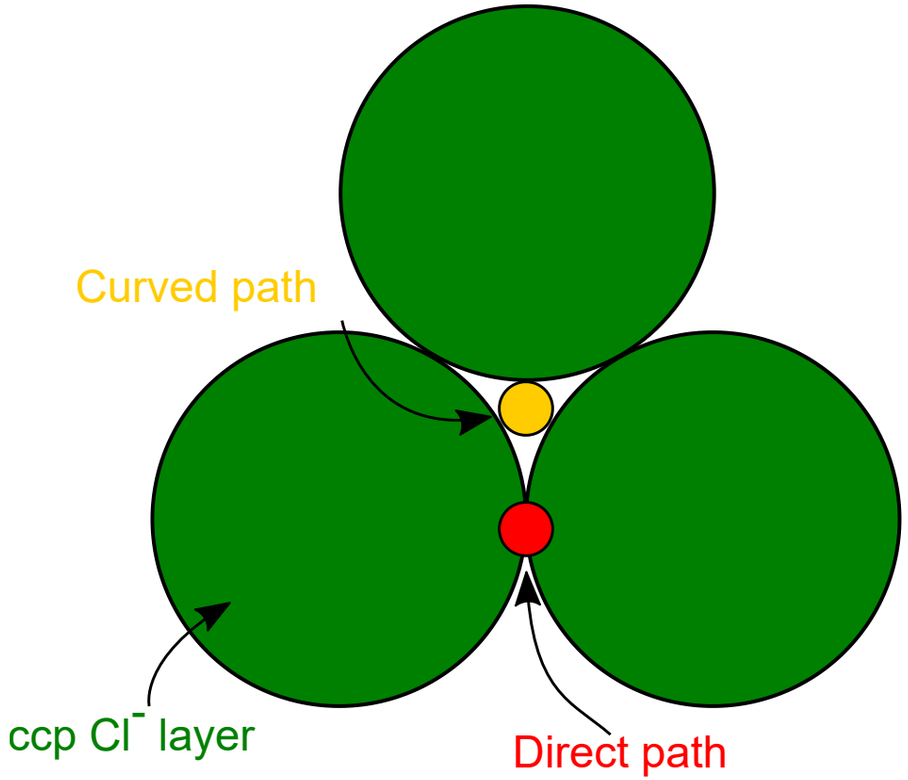
31 respondents



Migration paths

Ion paths are rarely direct, but will take the lowest energy route.

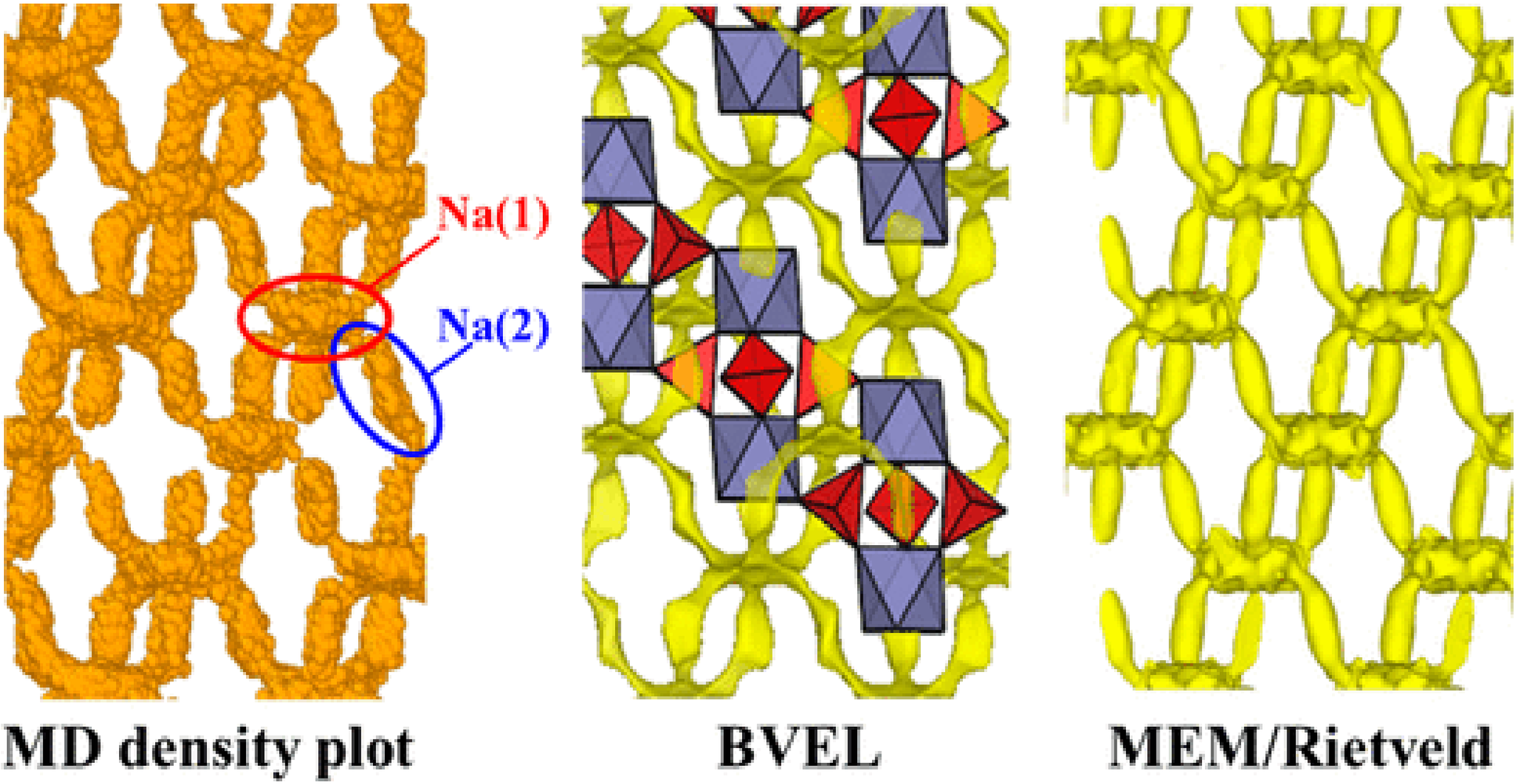




Pathways can be complex

- Migration pathways can be calculated and/or experimentally determined

e.g. **NASICON** Na^+ conductor, $Na_3Zr_2(SiO_4)_2(PO_4)$:



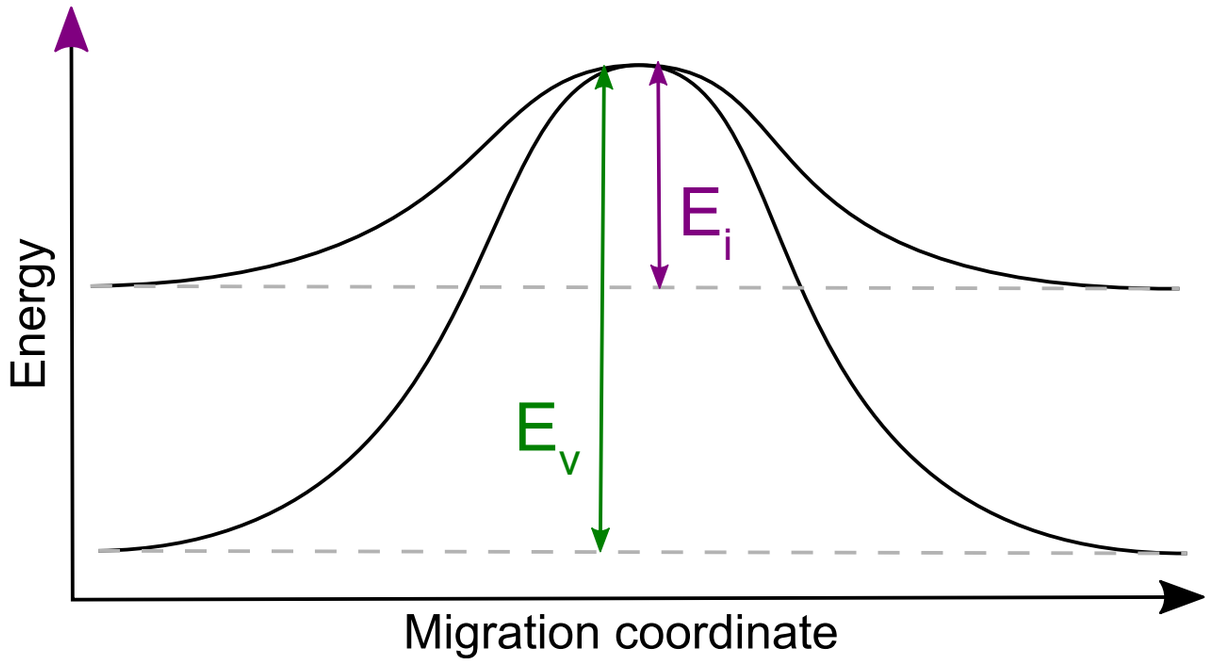
Y. Deng, *Chem. Mater.*, 2018, 2618.

Migration energetics

- Defect mobility (μ) is a thermally-activated process:

$$\mu = \mu_0 \exp\left(-\frac{\mathrm{E_a}}{\mathrm{RT}}\right)$$

- interstitial sites are higher energy than vacancies, so will be more mobile.



Variation with temperature

As $\sigma = nq\mu$ and μ is thermally-activated,

$$\begin{aligned}\sigma &= nq\mu_0 \exp\left(-\frac{\mathrm{E_a}}{\mathrm{RT}}\right) \\ &= A \exp\left(-\frac{\mathrm{E_a}}{\mathrm{RT}}\right)\end{aligned}$$

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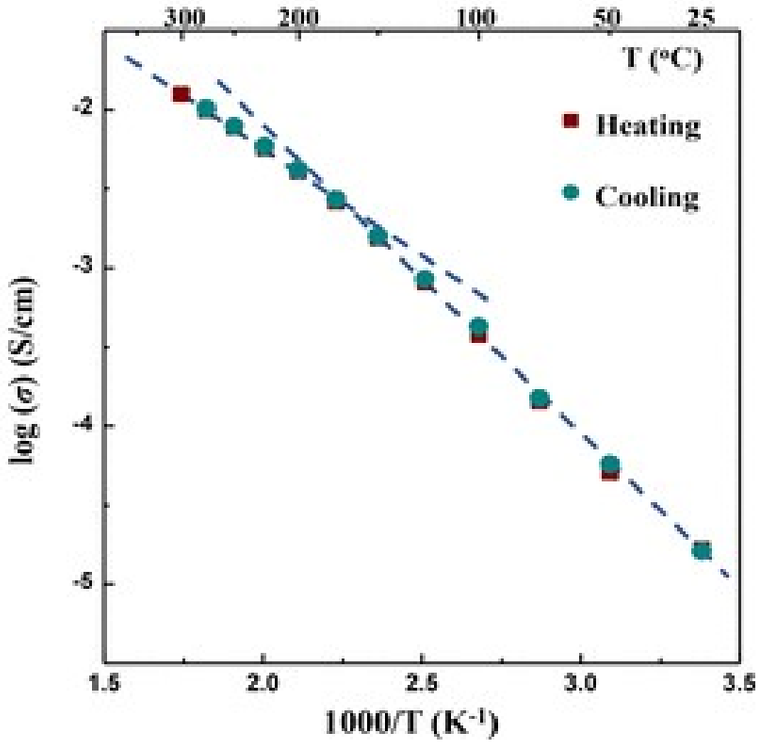
$$\sigma = nq\mu_0 \exp\left(-\frac{\mathrm{E_a}}{\mathrm{RT}}\right)$$
$$= A \exp\left(-\frac{\mathrm{E_a}}{\mathrm{RT}}\right)$$

Plotting $\ln \sigma$ *vs.* $\frac{1}{\mathrm{T}}$ should give a straight line

- more commonly we plot $\log_{10} \sigma$ *vs.* $\frac{1000}{\mathrm{T}}$ for high temperature measurements
- gradient is $\frac{-E_a}{R}$ (or $\frac{-E_a}{2303R}$ using base 10).



Lecture recap

- Defects can give rise to ionic conduction
    - Occurs by three main mechanisms:
        - Vacancy hopping
        - Interstitial hopping
        - interstitialcy (knock-on) cooperation
- Ionic conductivity is thermally-activated
    - shows Arrhenius-like behaviour
- Different defects have different conduction energetics
    - Pathways can sometimes be determined experimentally

Feedback

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