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

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Quiz results will be available here
after the lecture

Conductivity

- Many ionic solids conduct electricity; due to *ionic* and/or *electronic* motion.
- Most ionic solids are electrically insulating/semiconducting (localised electrons)

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- Most ionic solids are electrically insulating/semiconducting (localised electrons)
- Ionic conductors are important!

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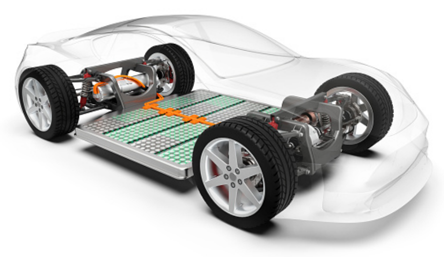
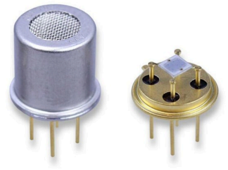
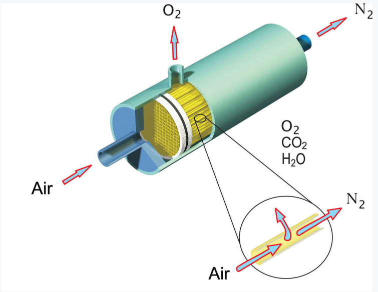
<tr><td></td><td></td></tr>
<tr><td>Batteries (Lecture 4)</td><td>Sensors</td></tr>
<tr><td>
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<tr><td>Separation Membranes</td><td>Fuel Cells (Lecture 6)</td></tr>
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Origin of ionic conduction

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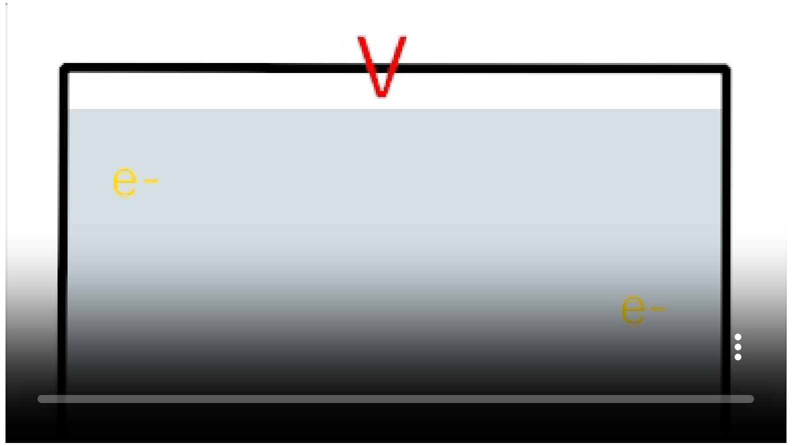
- In ionic solids, conductivity covers $10^{-16}\ \mathrm{S\ m^{-1}} - 10^{3}\ \mathrm{S\ m^{-1}}$
  - most solids are limited to around $10^{-2}\ \mathrm{S\ m^{-1}}$
  - Liquid electrolytes typically 10^{-1}–$10^{3}\ \mathrm{S\ m^{-1}}$

Measuring Conductivity

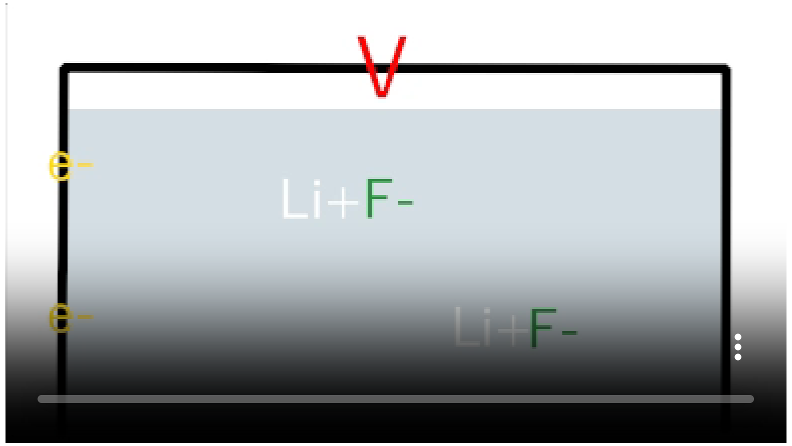
- For electronic conductors, this is simple:
  - Apply a voltage (V) and measure the resulting current (I)
  - Resistance (in Ω) is found through Ohm's law; $V = IR$
  - Resistivity (in $\Omega\ cm$) of the material calculated from geometry
- Resistivity ρ (in $\Omega\ cm$) = $\frac{1}{\text{Conductivity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



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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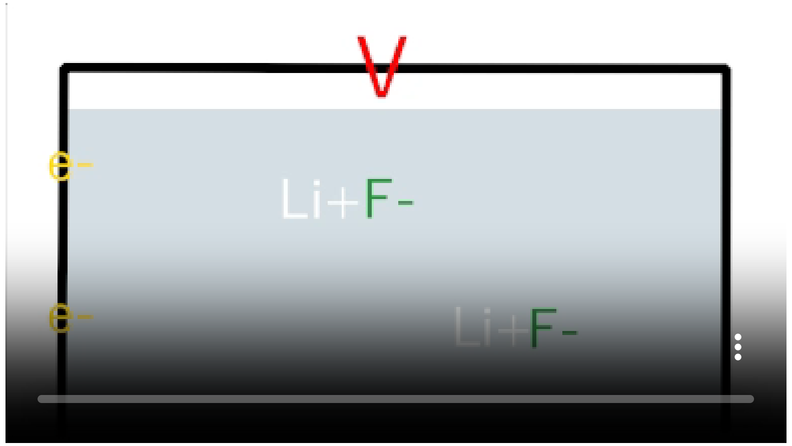
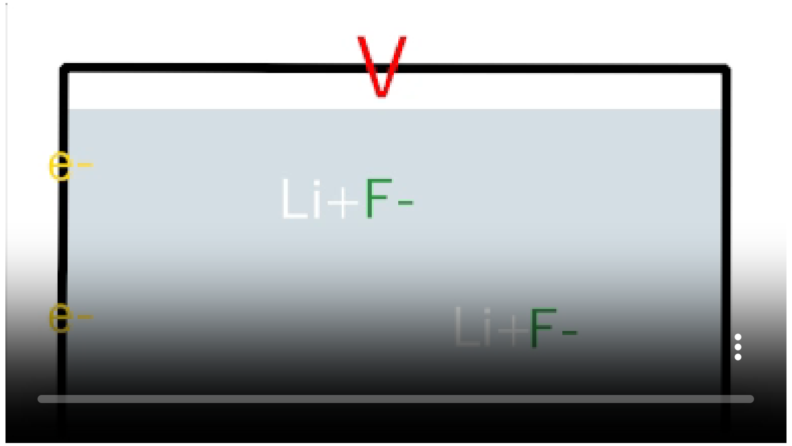


- Instead, we use an alternating voltage - this is called Impedance spectroscopy (see lecture 5)



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

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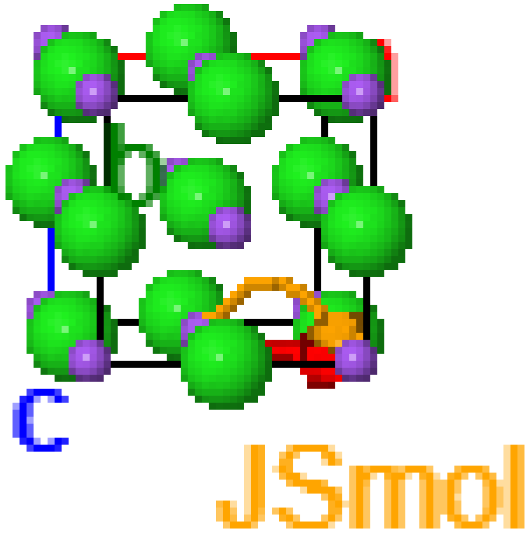
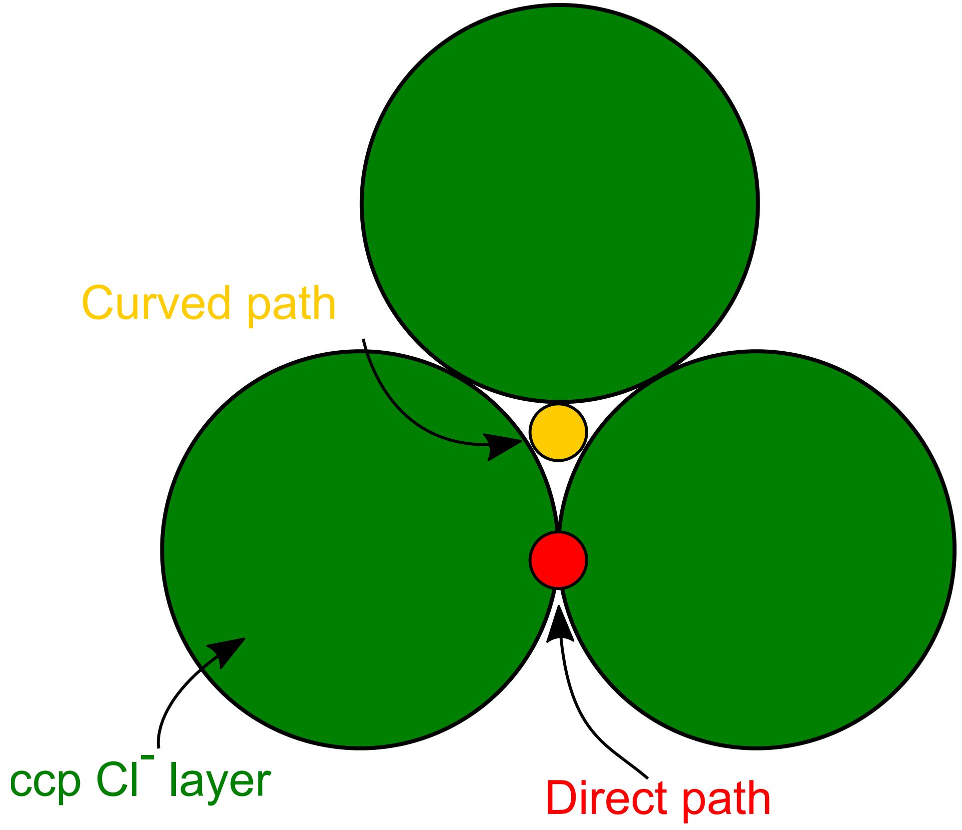
Migration paths

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

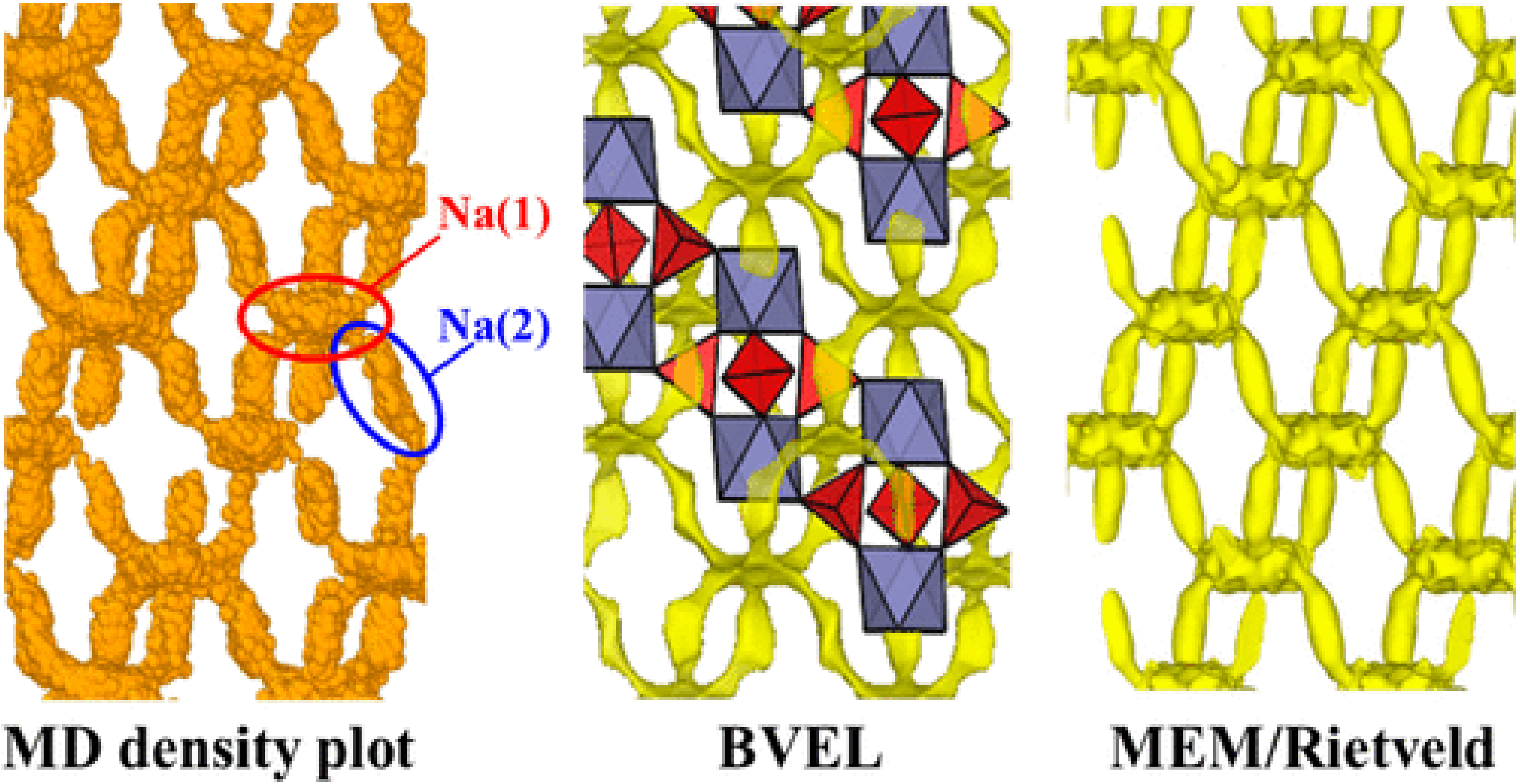




Pathways can be complex

- Migration pathways can be calculated and/or experimentally determined

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



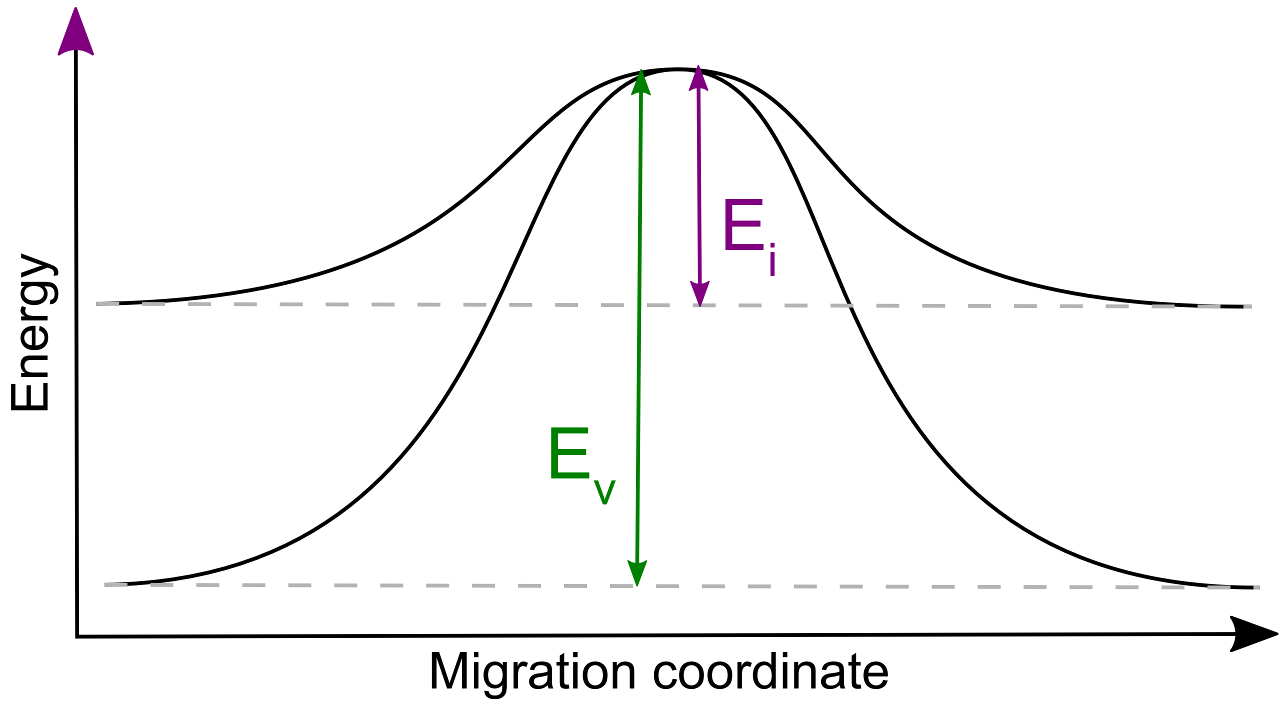
Y. Deng, *Chem. Mater.*, 2018, 2618.

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,

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

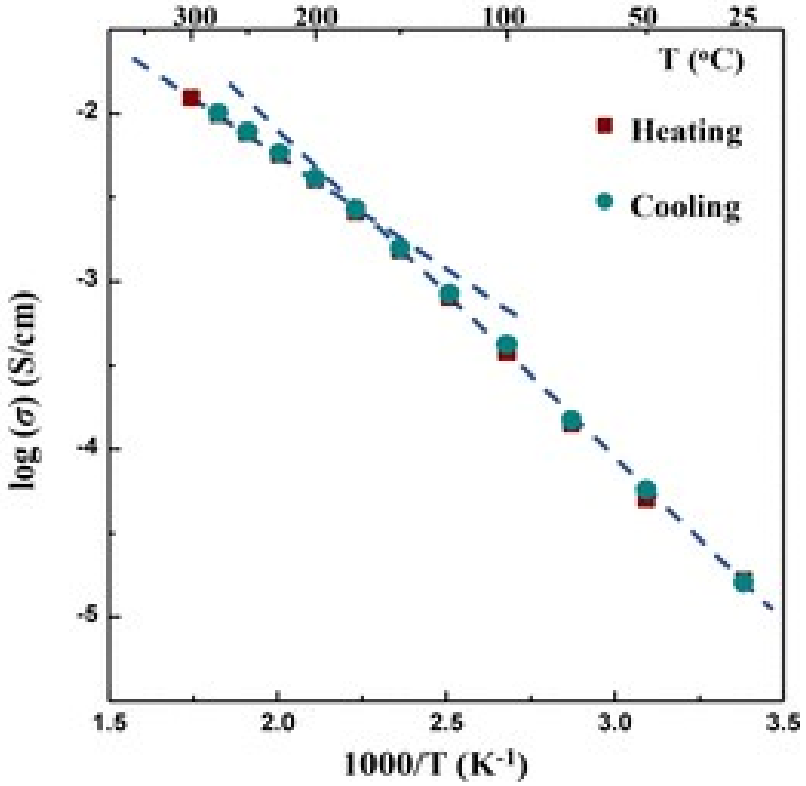
Variation with temperature

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

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

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).



Nasicon conductivity

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