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

Mentimeter

Classify these defects

NaCl Schottky

Skip

Effect on Stoichiometry

0

0 | 4
None (intrinsic) | Changes (Extrinsic)

Effect on density

0

0 | 4
Decrease | Increase

AgCl Frenkel

Skip

Effect on Stoichiometry

0

0 | 4
None (intrinsic) | Changes (Extrinsic)

Defect recap results

Go to **www.menti.com** and use the code **7793 2358**

Conductivity

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

Conductivity

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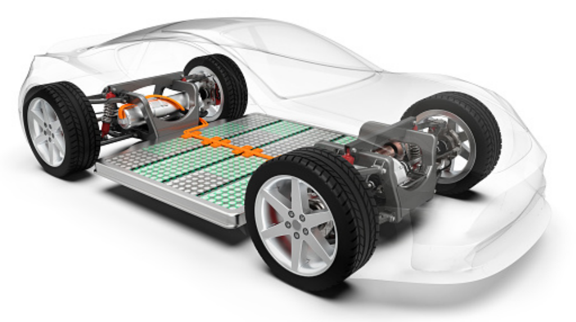
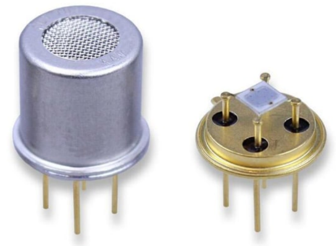
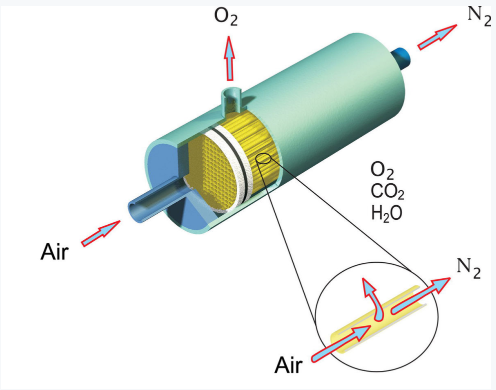
- Most ionic solids are electrically insulating/semiconducting (localised electrons)
- Ionic conductors are important!

	
Batteries (Lecture 4)	Sensors
	

Origin of ionic conduction

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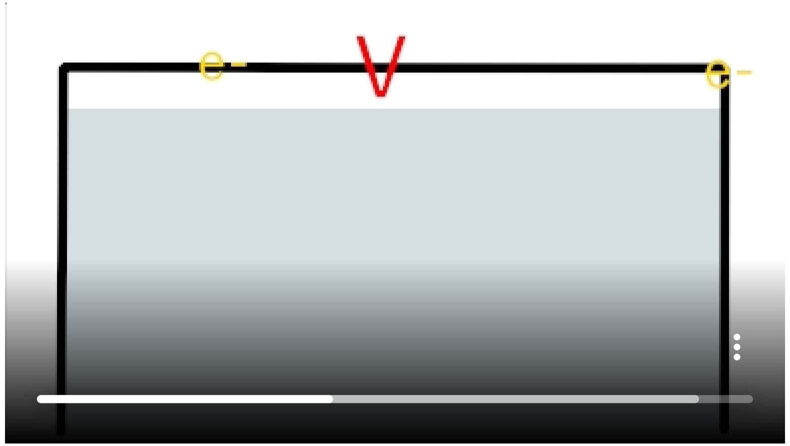
- In ionic solids, conductivity covers 10^{-16}–10^{3} $\mathrm{S\ m^{-1}}$
  - most solids are limited to around 10^{-2} $\mathrm{S\ m^{-1}}$
  - Liquid electrolytes typically 10^{-1}–10^{3} $\mathrm{S\ m^{-1}}$

Measuring Conductivity

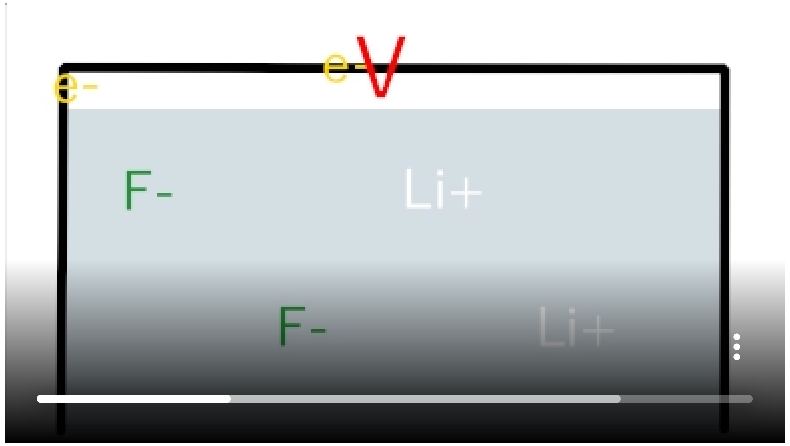
- For electronic conductors, this is simple:
  - Apply a voltage (V) and measure the resulting current (I)
  - Link by Ohm's law; $V = IR$
  - Resistivity (in $\Omega\ cm$) of the material calculated from geometry
- Resistivity ρ (in $\Omega\ cm$) = $\frac{1}{\text{Conductivity } \sigma \text{ (in S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



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

Measuring Ionic Conductivity

- Current flow is eventually restricted



Measuring Ionic Conductivity

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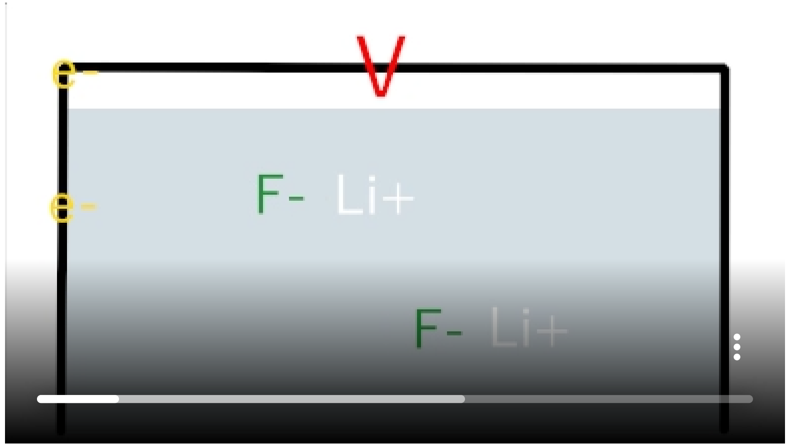
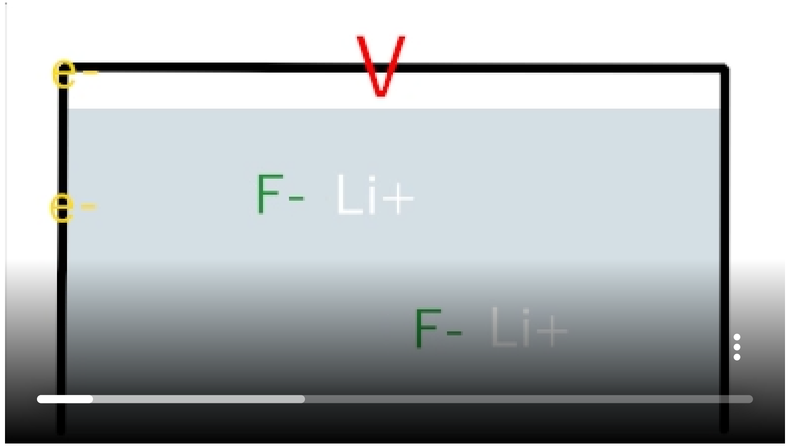


- Instead, we use alternating current
    - Impedance spectroscopy (see [lecture 5])



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?

Mentimeter

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

Enter a word 25

You can submit multiple answers

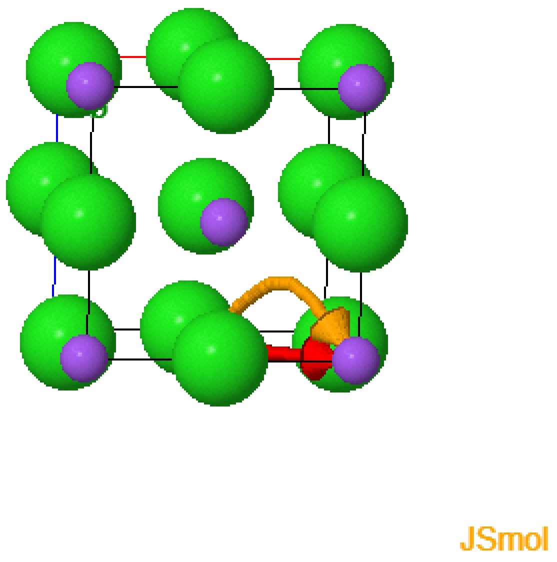
Submit

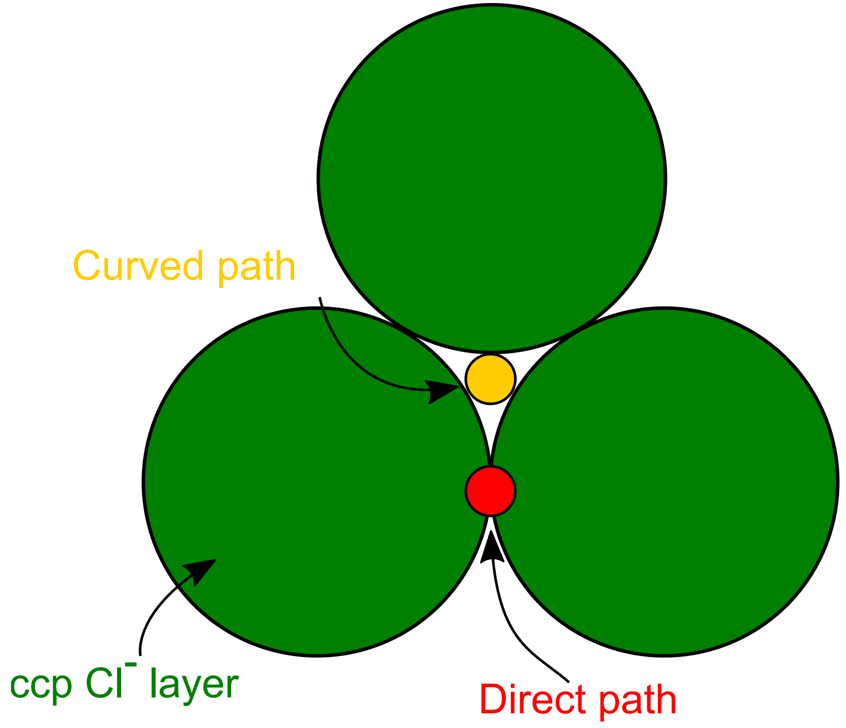
Suggestions

Go to **www.menti.com** and use the code **2129 1582**

Migration paths

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

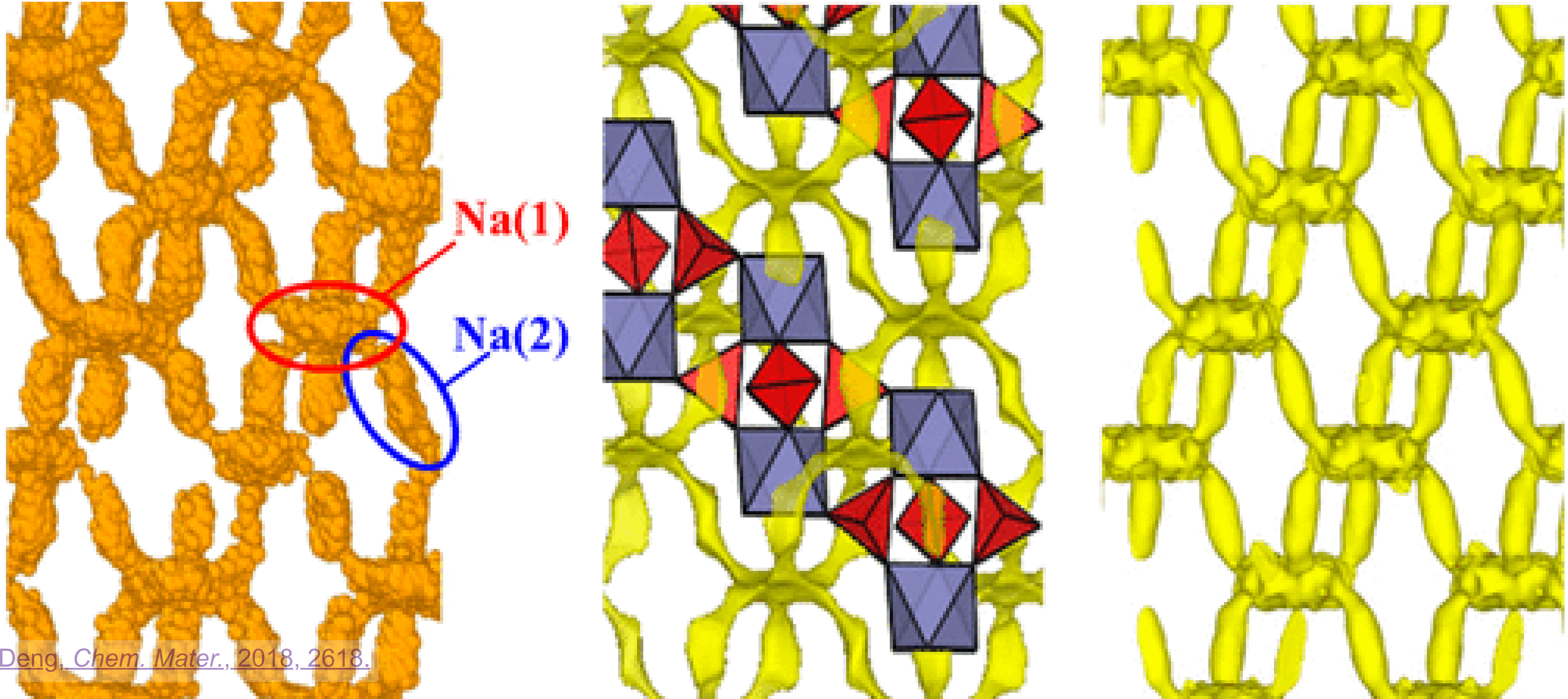




Pathways can be complex

- Migration pathways can be calculated and/or experimentally determined

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



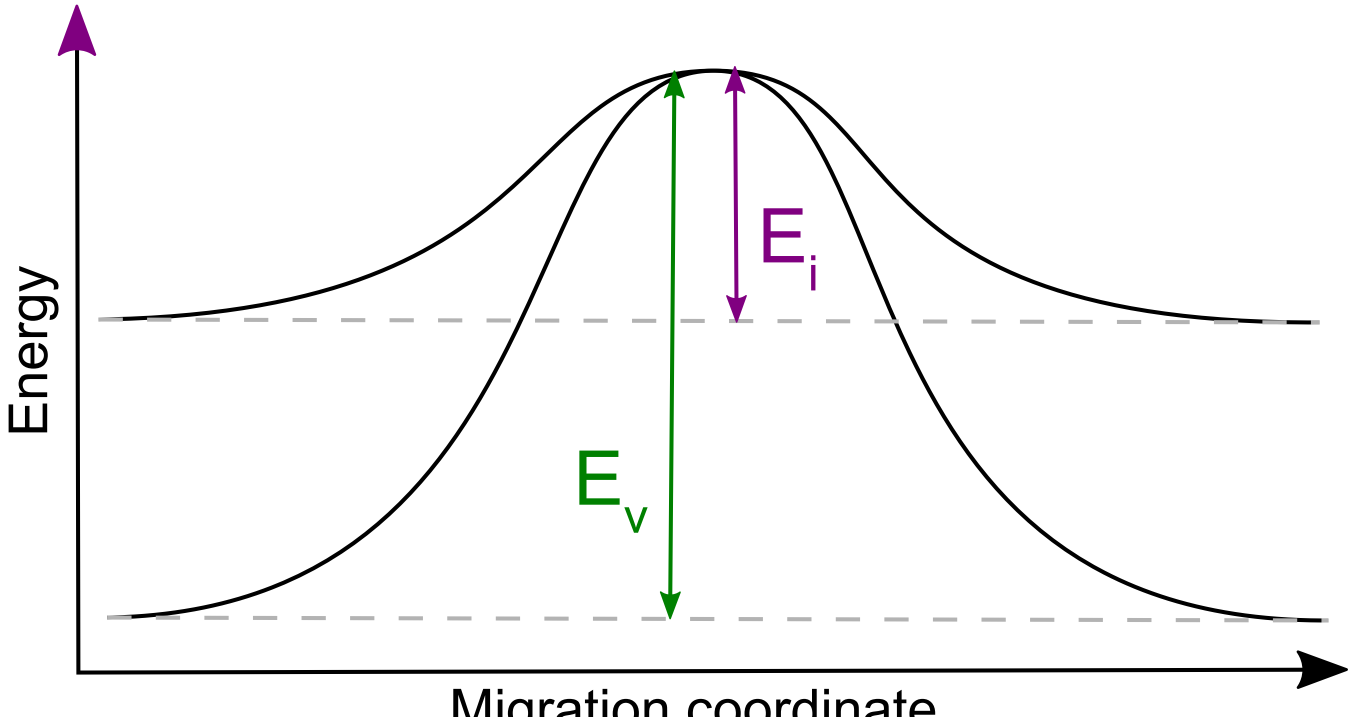
Y. Deng, *Chem. Mater.*, 2018, 2618.

Migration energetics

- Defect mobility 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 smaller energy barrier ($E_i < E_a$) - dominates



Variation with temperature

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

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

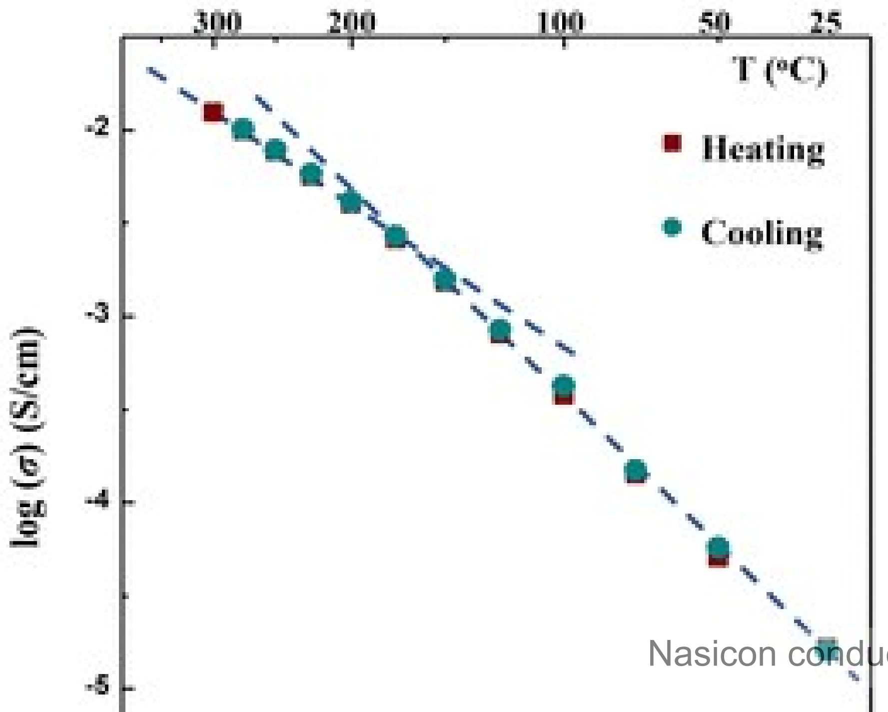
Variation with temperature

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. $\frac{1}{\mathrm{T}}$ (or more commonly $\log_{10}\sigma$ vs $\frac{1000}{\mathrm{T}}$ for high temperature measurements) should give a straight line

- gradient = $\frac{-E_a}{R}$ (or $\frac{-E_a}{2303R}$).

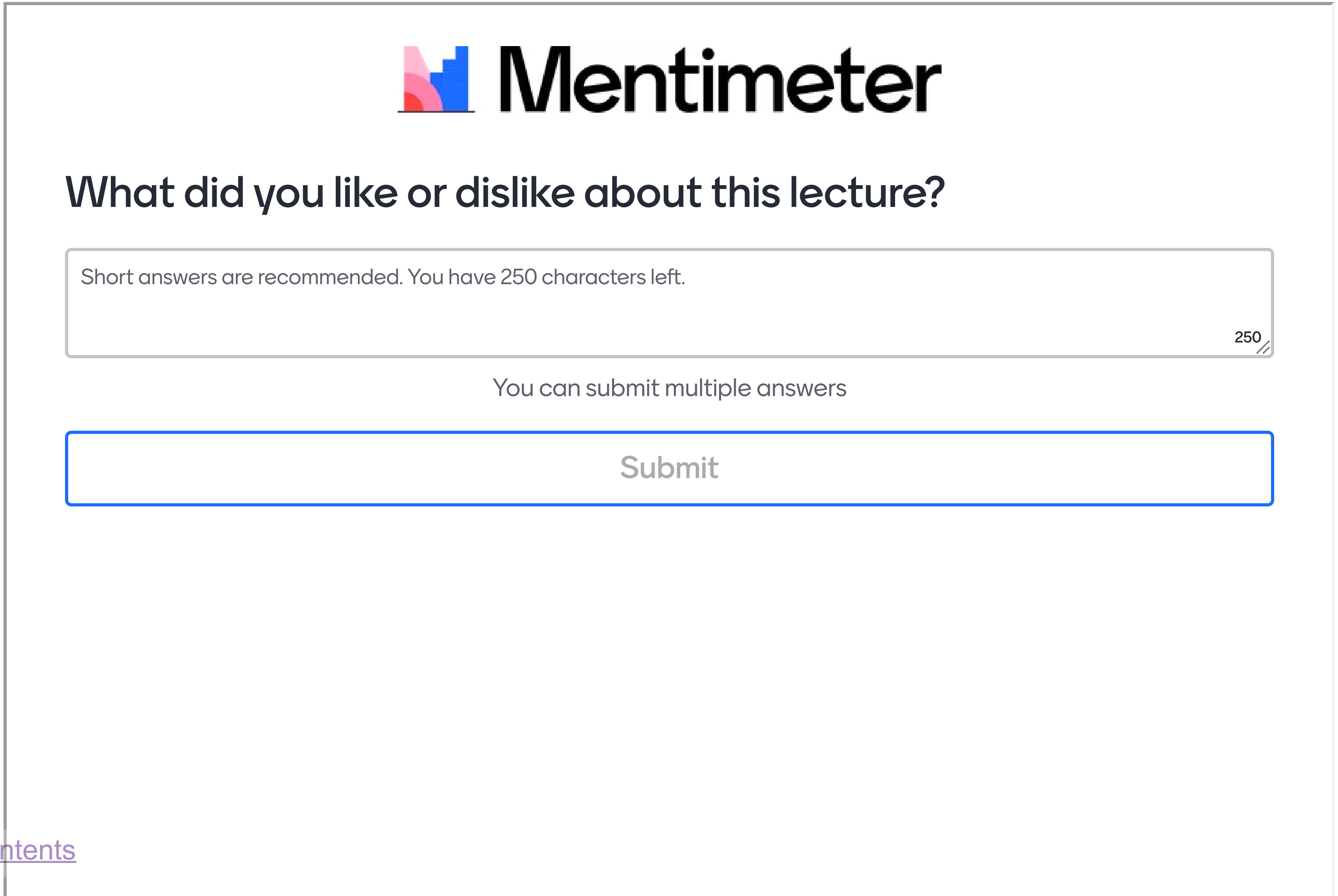


Nasicon conductivity

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


Mentimeter
What did you like or dislike about this lecture?
Short answers are recommended. You have 250 characters left.
250
You can submit multiple answers
Submit