Lecture 3 - Ionic Conductivity

Return to course contents

Lecture summary

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

Defect recap

Defect recap results

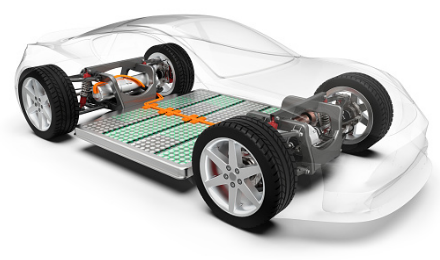
Join at menti.com | use code **4905 4669**

Conductivity

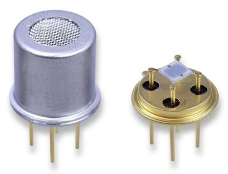
- Many ionic solids conduct electricity; due to *ionic* and/or *electronic* motion.
- Most ionic solids are electrically insulating/semiconducting (localised electrons)

Conductivity

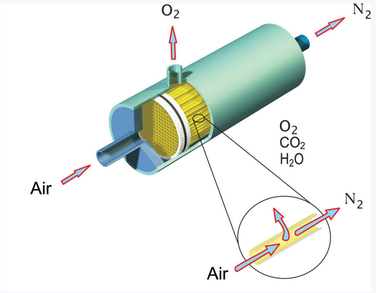
- Many ionic solids conduct electricity; due to *ionic* and/or *electronic* motion.
- Most ionic solids are electrically insulating/semiconducting (localised electrons)
- Ionic conductors are important!



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
  - vacancies and/or interstitials are the main charge carriers

Origin of ionic conduction

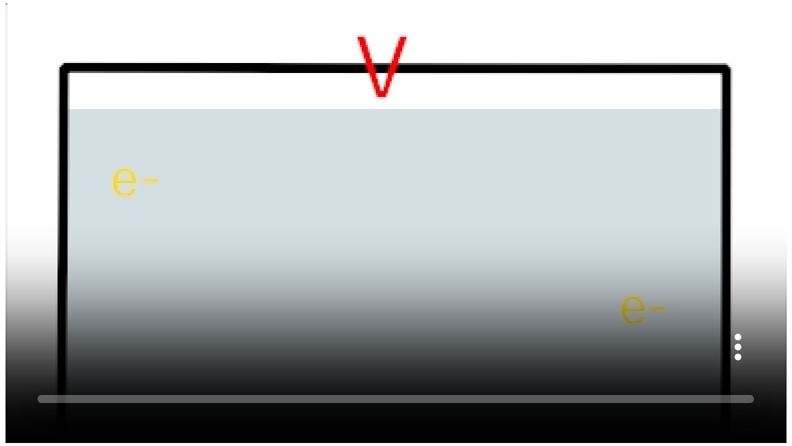
- Ionic conductivity is dominated by **defects**
  - In an ideal crystal, ions can't easily move
  - vacancies and/or interstitials are the main charge carriers
- Conductivity, $\sigma = nq\mu$, where
  - n is number of charge carriers
  - q is charge
  - μ is the mobility of charge carriers

Origin of ionic conduction

- Ionic conductivity is dominated by **defects**
  - In an ideal crystal, ions can't easily move
  - vacancies and/or interstitials are the main charge carriers
- Conductivity, $\sigma = nq\mu$, where
  - n is number of charge carriers
  - q is charge
  - μ is the mobility of charge carriers
- 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

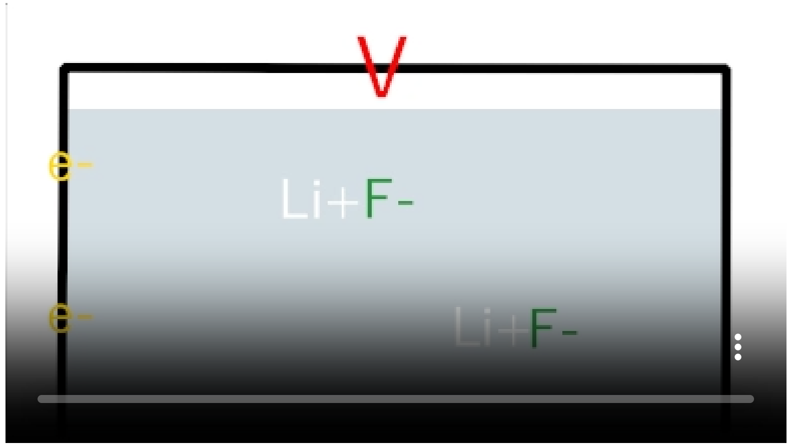
- For electronic conductors, this is simple:
  - Apply a voltage (V) and measure the resulting current (I)
  - Resistance (in Ω) is found through Ohm's law; $V = IR$
  - Resistivity (in $\Omega\ cm$) of the material calculated from geometry
- Resistivity ρ (in $\Omega\ cm$) = $\frac{1}{\text{Conductivity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



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

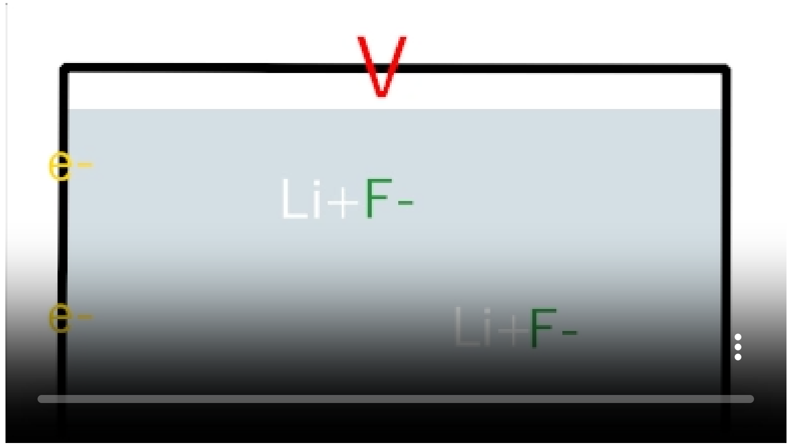
Measuring Ionic Conductivity

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

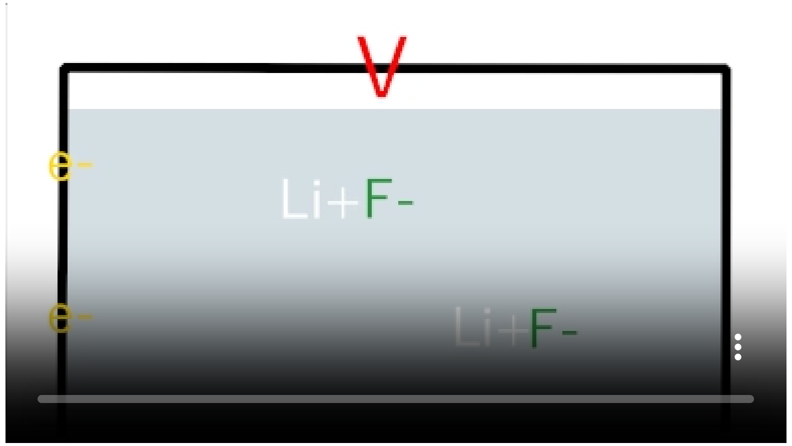


Measuring Ionic Conductivity

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



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



Ion migration mechanisms

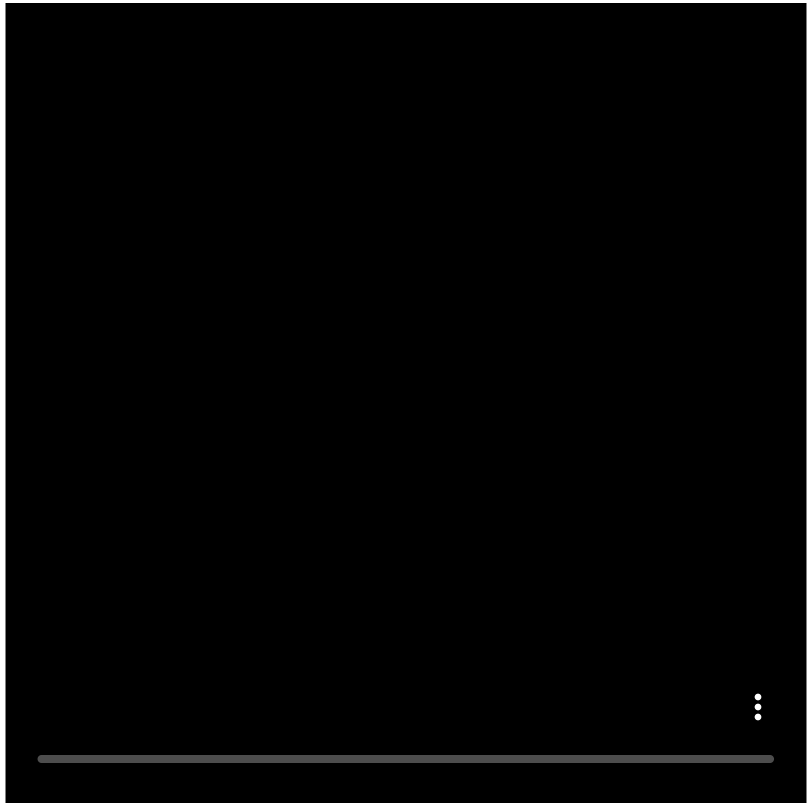
Three 'main' mechanisms of ionic migration

1. Vacancy mechanism

Vacancies move throughout the lattice (atoms move into vacancy)

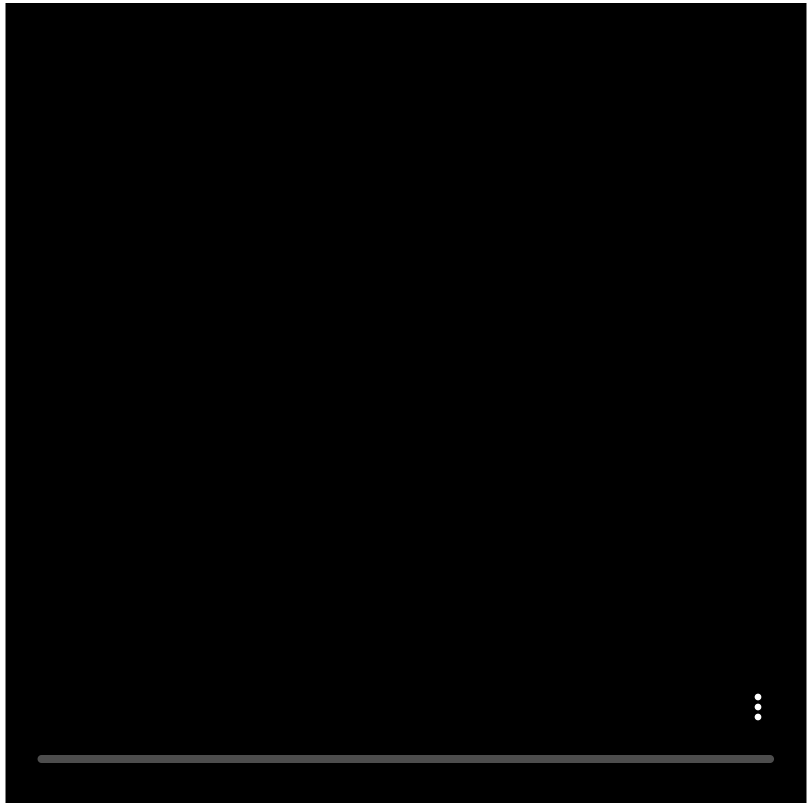
2. Interstitial mechanism

Ions hop between interstitial sites



3. Interstitialcy (knock-on) mechanism

Interstitial ions 'push' into a neighbouring site



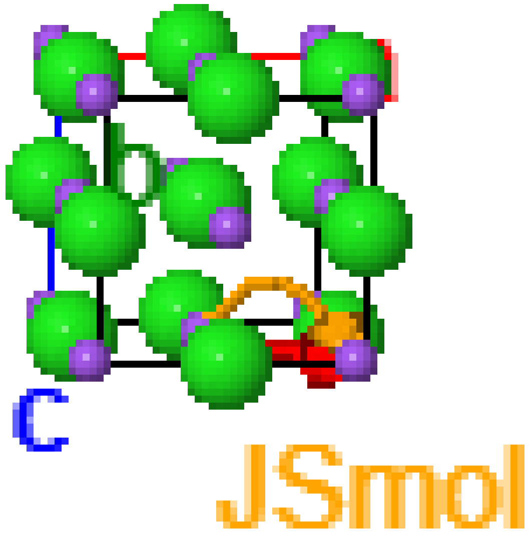
Vacancy, Interstitial or Interstitialcy?

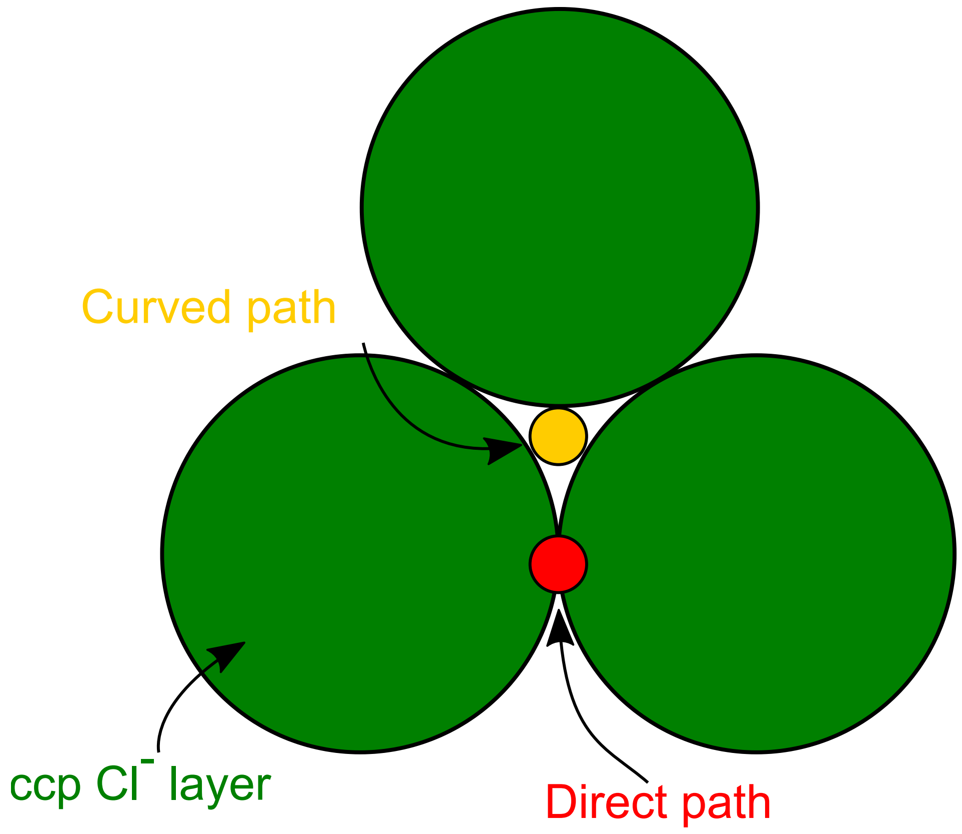
Suggestions

Join at menti.com | use code **1458 2331**

Migration paths

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

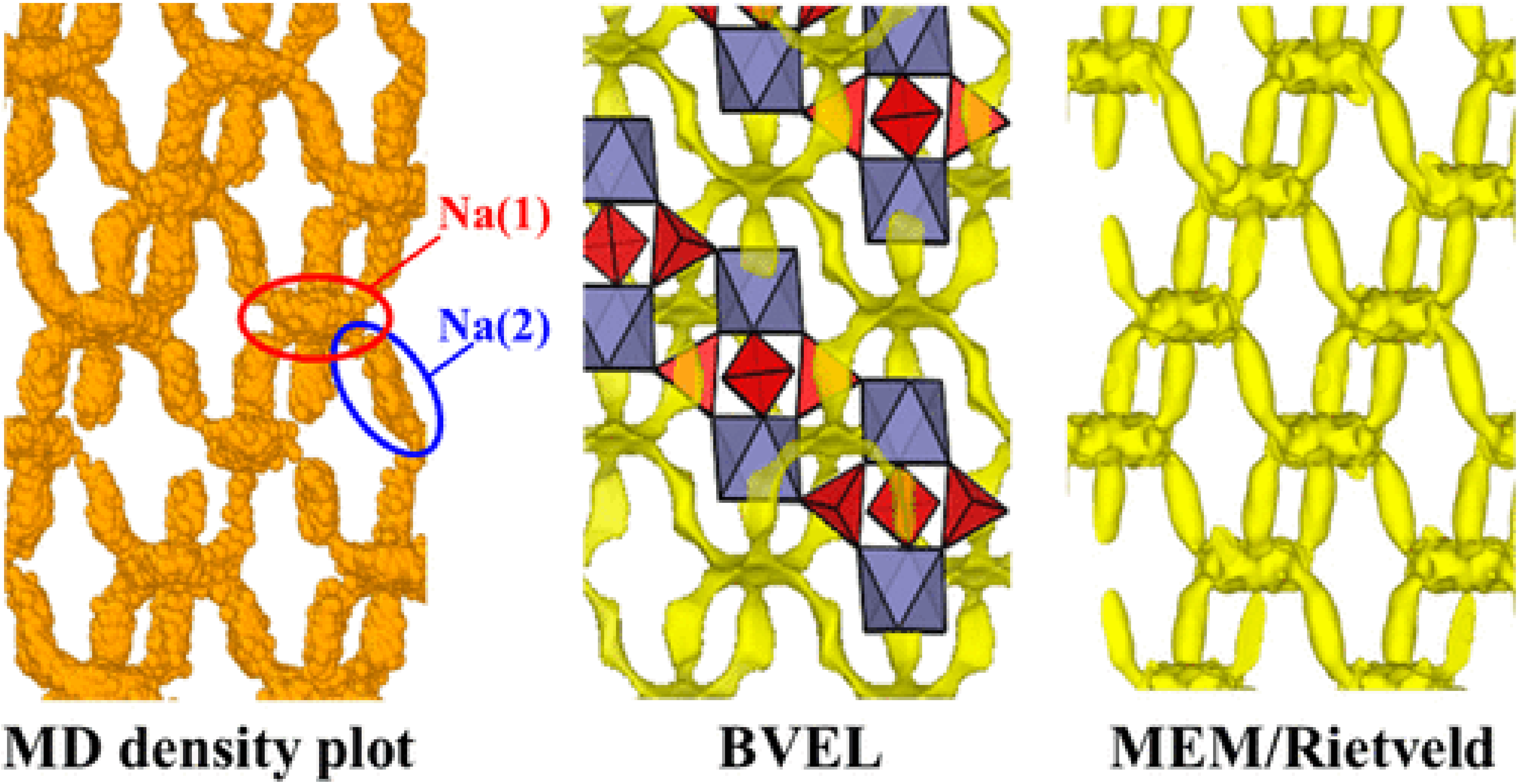




Pathways can be complex

- Migration pathways can be calculated and/or experimentally determined

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



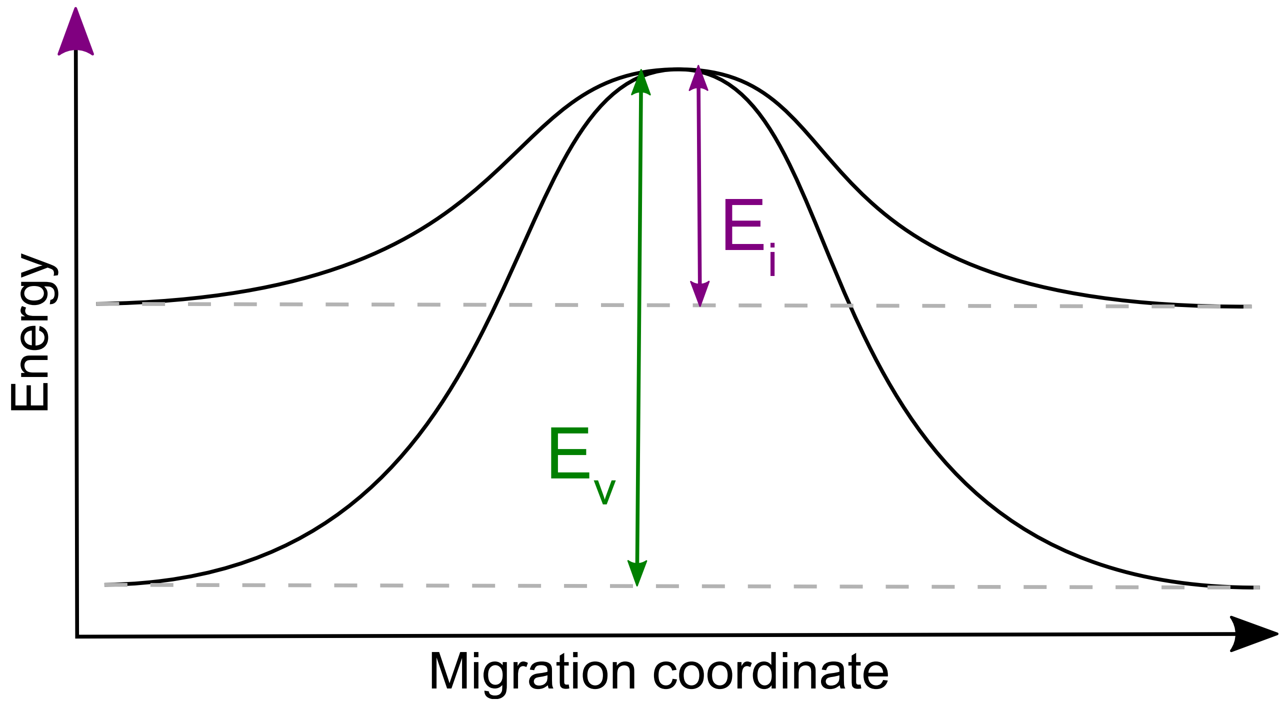
Y. Deng, *Chem. Mater.*, 2018, 2618.

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 have be more mobile.



Variation with temperature

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

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

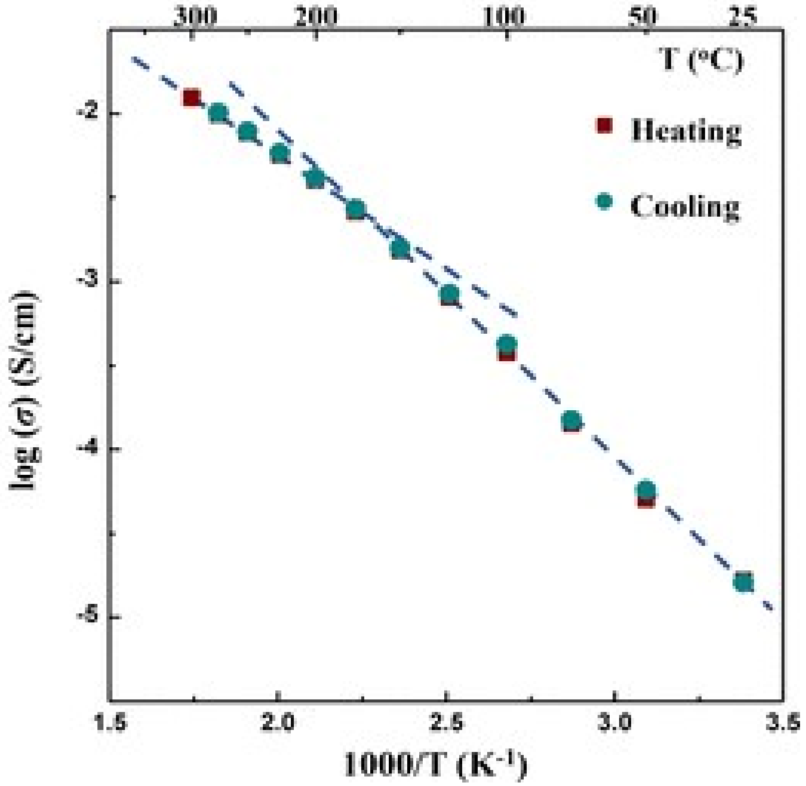
Variation with temperature

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