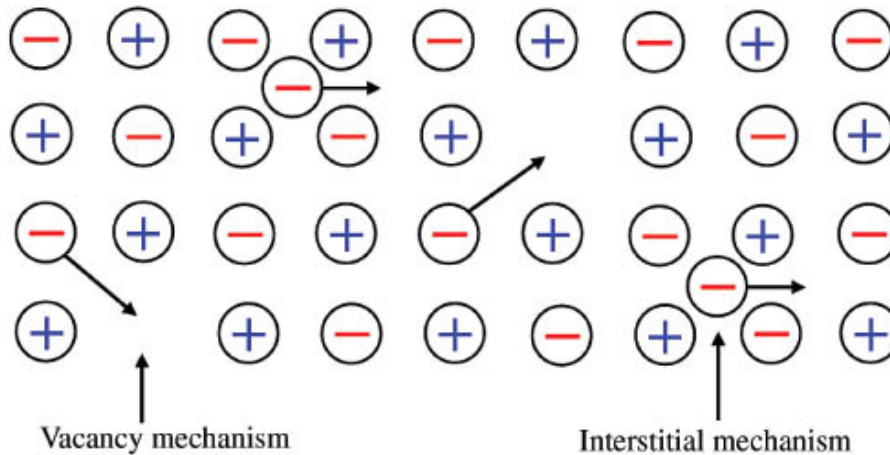


# Fuel Cells 2

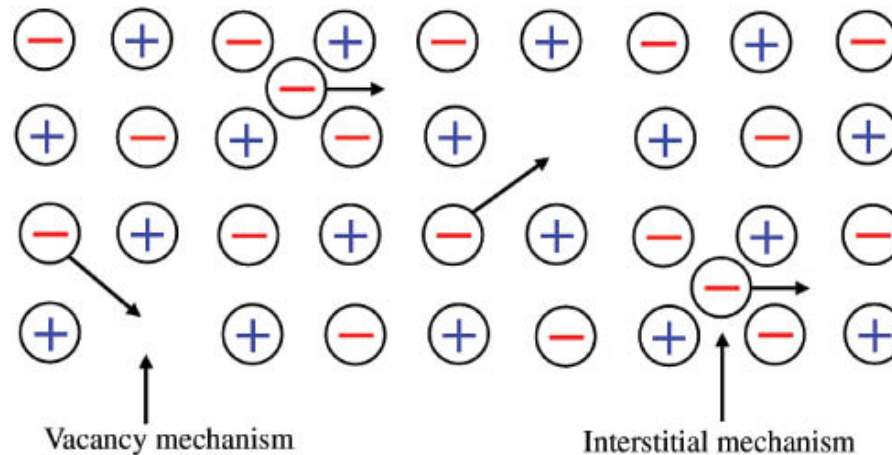
# Ionic conduction

All the technologies in this course rely on ionic motion. In the solid state, this occurs through two main mechanisms:



# Ionic conduction

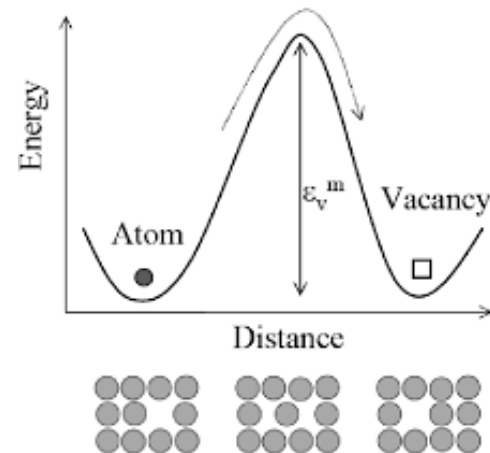
All the technologies in this course rely on ionic motion. In the solid state, this occurs through two main mechanisms:



There is an energy barrier  $E_a$  to ionic diffusion

- This can be overcome by thermal energy
- Follows an Arrhenius relationship:

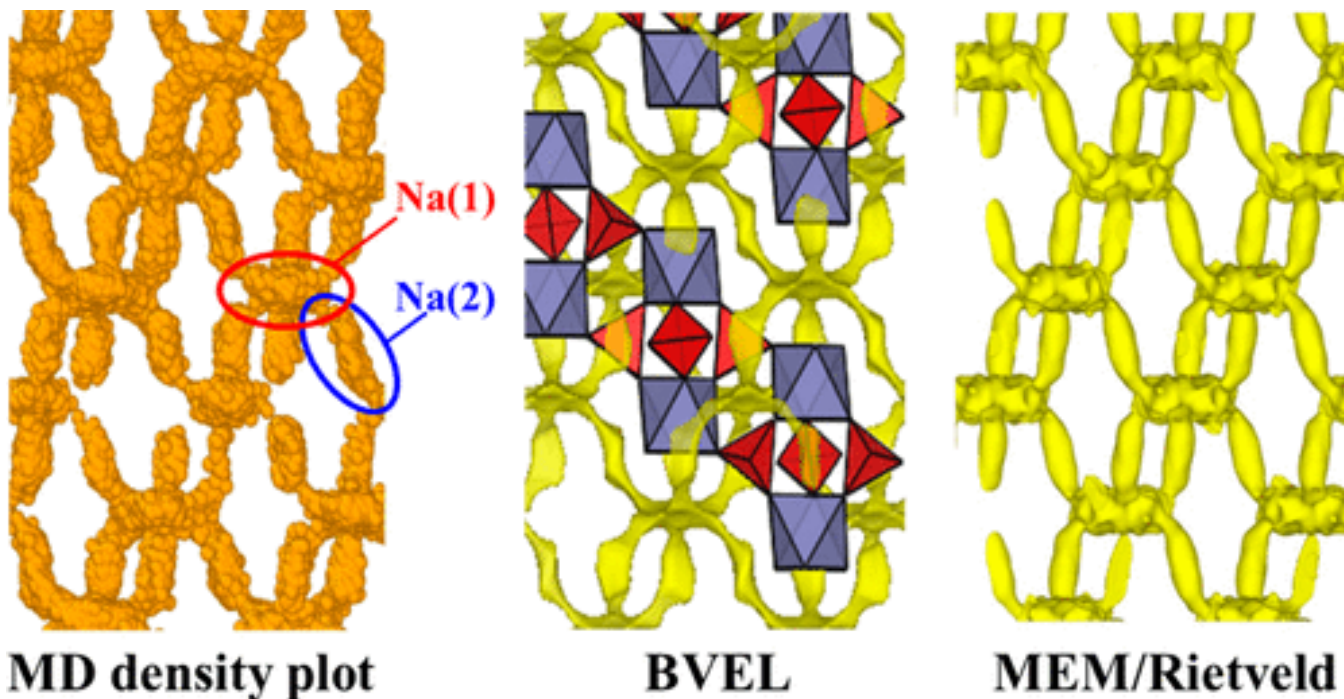
$$\sigma(T) = Ae^{\frac{-E_a}{RT}}$$



# Diffusion pathways are often complex

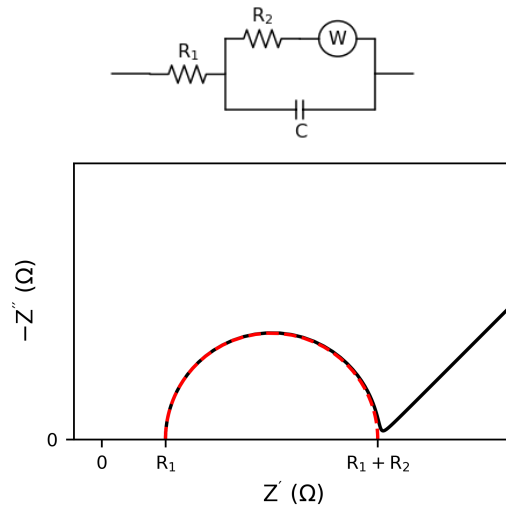
- Often there are competing pathways, with different energy barriers.
- Diffusion pathways can be calculated and/or experimentally determined

e.g. **NASICON**  $\text{Na}^+$  conductor,  $\text{Na}_3\text{Zr}_2(\text{SiO}_4)_2(\text{PO}_4)$ :



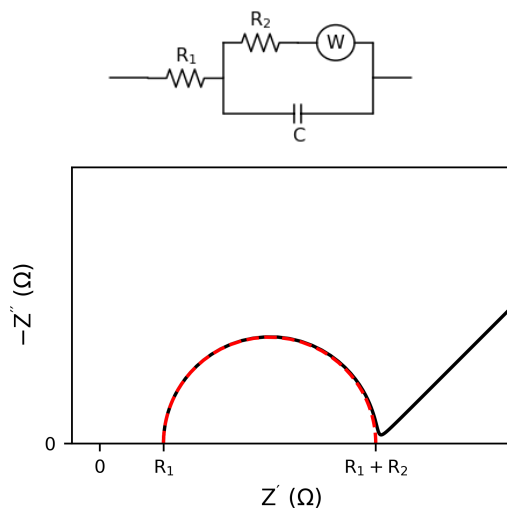
# Characterising diffusion

Impedance spectroscopy allows us to determine the conductivity at different temperatures.

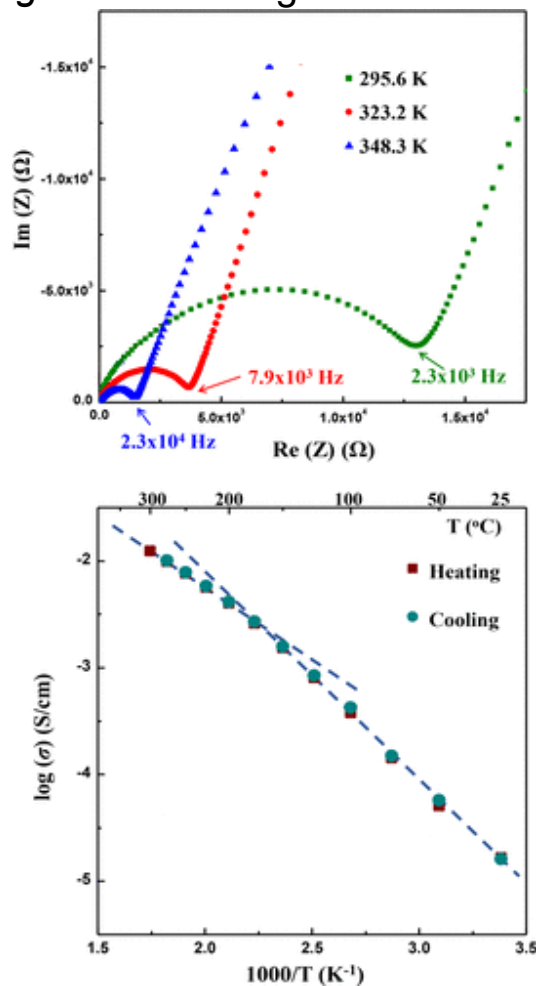


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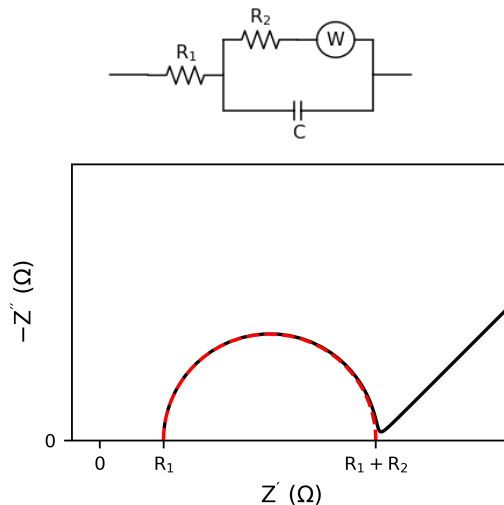


e.g. NASICON again:



# Characterising diffusion

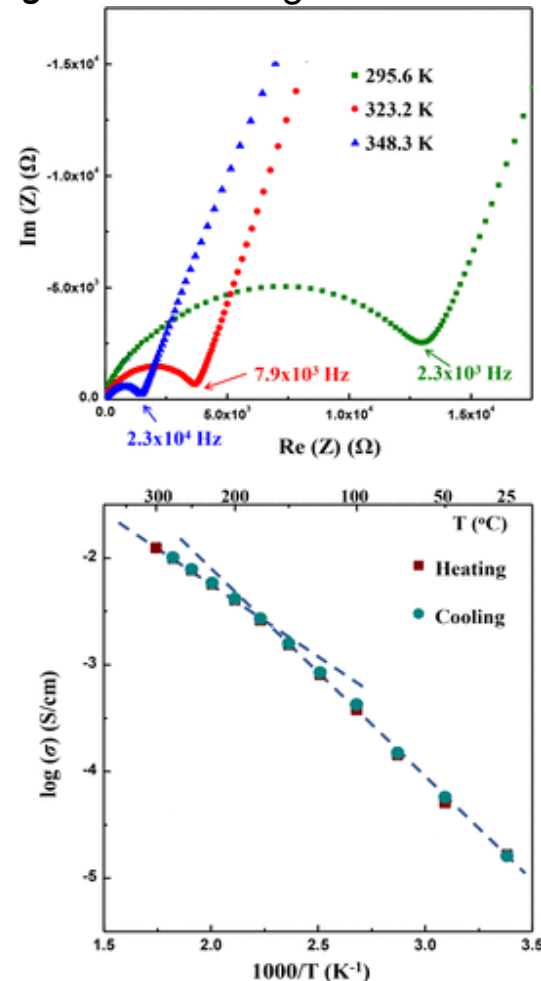
Impedance spectroscopy allows us to determine the conductivity at different temperatures.



$$\sigma(T) = Ae^{\frac{-E_a}{RT}}$$

- A plot of  $\ln \sigma(T)$  versus  $1/T$  has slope  $= \frac{-E_a}{R}$ .
- We usually plot  $\log_{10} \sigma$  then slope  $= \frac{-E_a}{2.303R}$

e.g. NASICON again:



# Ionic conduction

$$\sigma(T) = Ae^{\frac{-E_a}{RT}}$$

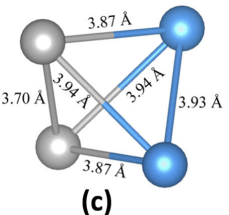
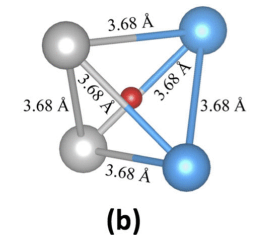
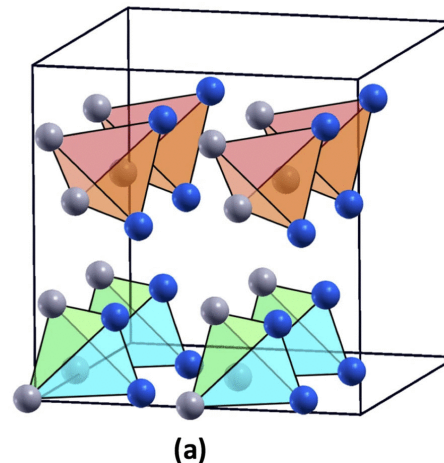
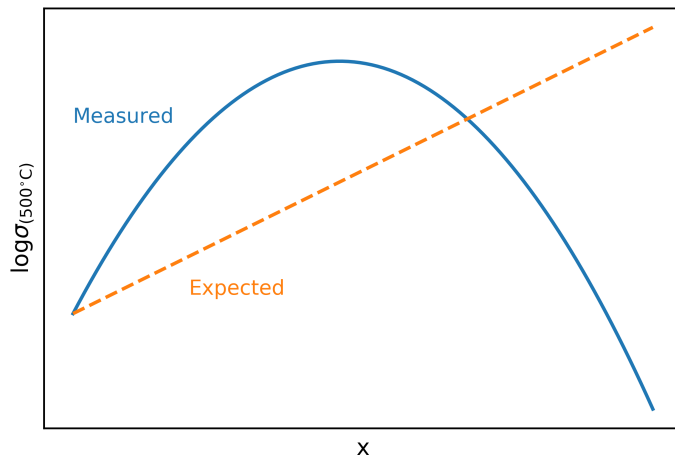
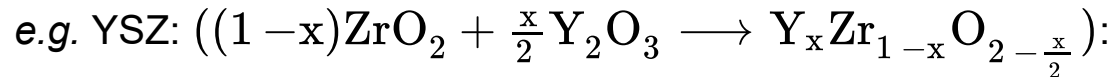
- Normally,  $A \propto$  the number of charge carriers
  - (conductivity should increase with more charge carriers)



# Ionic conduction

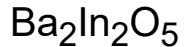
$$\sigma(T) = Ae^{\frac{-E_a}{RT}}$$

- Normally,  $A \propto$  the number of charge carriers
  - (conductivity should increase with more charge carriers)
- *However*, at high defect concentrations we can get **defect clusters**
  - Local ordering of vacancies (or other defects) reduces conduction

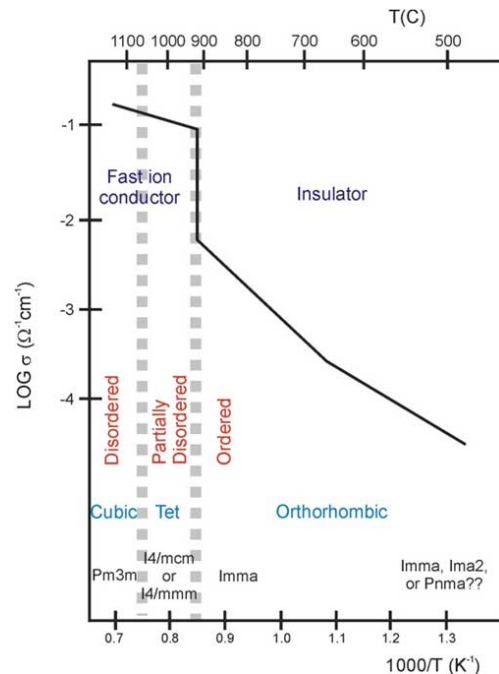
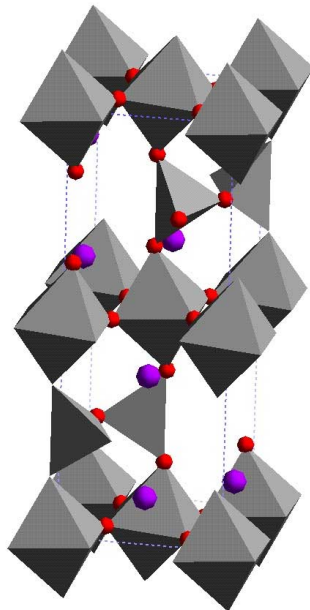


# Long-range ordering

In some cases, long-range ordering of anions or cations can influence conductivity.



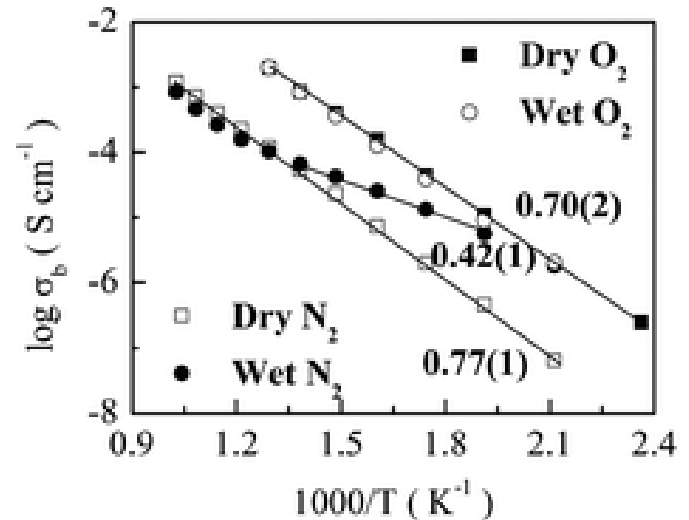
- Brownmillerite structure (essentially  $\text{ABO}_{2.5}$  perovskite with ordered vacancies)
- Low conductivity at low T due to anion ordering
- Large increase in conductivity as vacancies disorder



# Oxide/Proton conductors

e.g. Perovskite  $\text{BaTi}_{2.98}\text{Ca}_{0.02}\text{O}_{2.98}$ :

- In dry  $\text{N}_2$  is an oxide ion conductor
- In wet  $\text{N}_2$ , shows proton conduction below 600 K, and oxide ion conduction above this



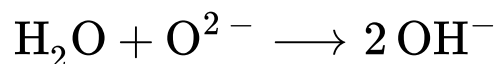
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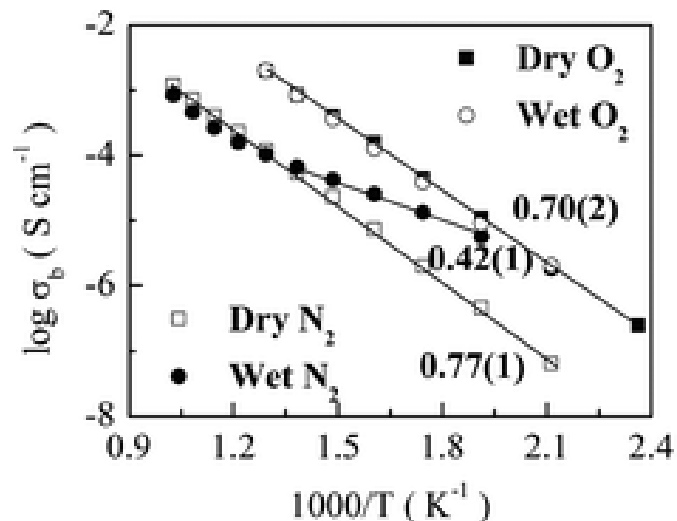
- In dry  $\text{N}_2$  is an oxide ion conductor
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Why?

- In the presence of anion vacancies:



In theory this could occur for *any* oxide-vacancy conductor, but depends strongly on the enthalpy change during water incorporation.



# How are protons transported?

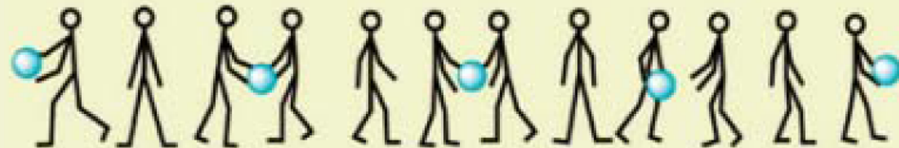
Two possible mechanisms:

- **Vehicle** mechanism
  - Direct diffusion of  $\text{OH}^-$
- **Grotthuss** mechanism
  - Exchange of  $\text{H}^+$  between neighbouring  $\text{OH}^-$

**Vehicle mechanism**



**Grotthuss mechanism (Proton hopping)**



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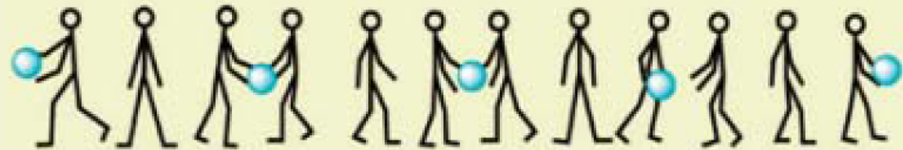
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**Vehicle mechanism**



**Grotthuss mechanism (Proton hopping)**

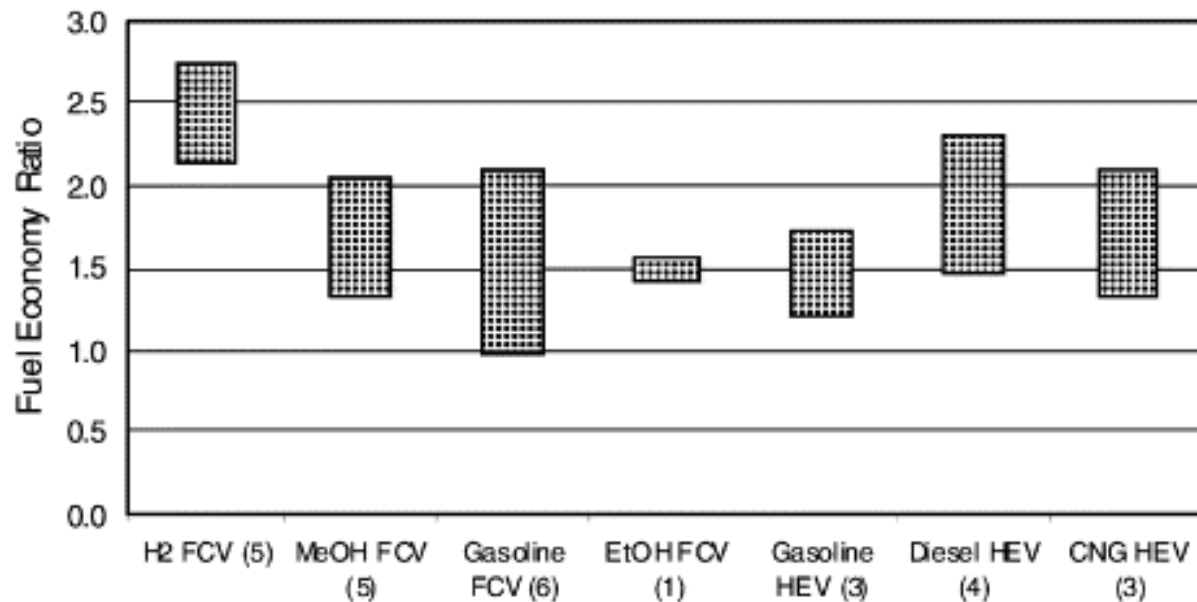


- The Grotthuss mechanism dominates
  - Water incorporation fills anion vacancies, so there is no conduction pathway for  $\text{OH}^-$

# Which fuel to choose?

Lots of economic parameters to consider. Some work has been done in relation to fuel cell vehicles

- 'Well-to-wheel' analysis



H<sub>2</sub> is the most efficient fuel (ignoring many other factors), but there are two important obstacles to a *hydrogen economy*:

- Generation
- Storage

# Hydrogen generation

## Chemical methods

- Steam reforming
  - High temperatures and pressures required
  - Requires catalyst (e.g. Ni, Pt, Rh)
  - Produces a mixture of  $\text{H}_2$ , CO,  $\text{CO}_2$  and  $\text{H}_2\text{O}$





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- Pyrolysis
  - Thermal cracking of hydrocarbons in the absence of oxygen
  - Precious-metal catalyst required
  - Produces carbon waste



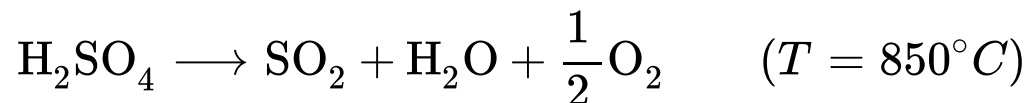
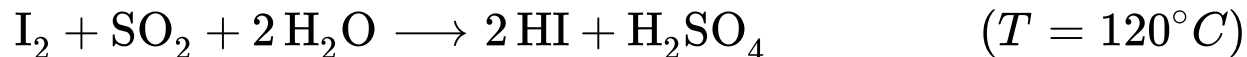
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- Iodine-sulfur cycle:



# Hydrogen generation

## Biological sources

- Fermentation
  - Enzymatic conversion of sugars to H<sub>2</sub>
  - *e.g.*  $\text{C}_6\text{H}_{12}\text{O}_6 + 2\text{H}_2\text{O} \longrightarrow 2\text{CH}_3\text{CO}_2\text{H} + 2\text{CO}_2 + 4\text{H}_2$
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## Direct water splitting

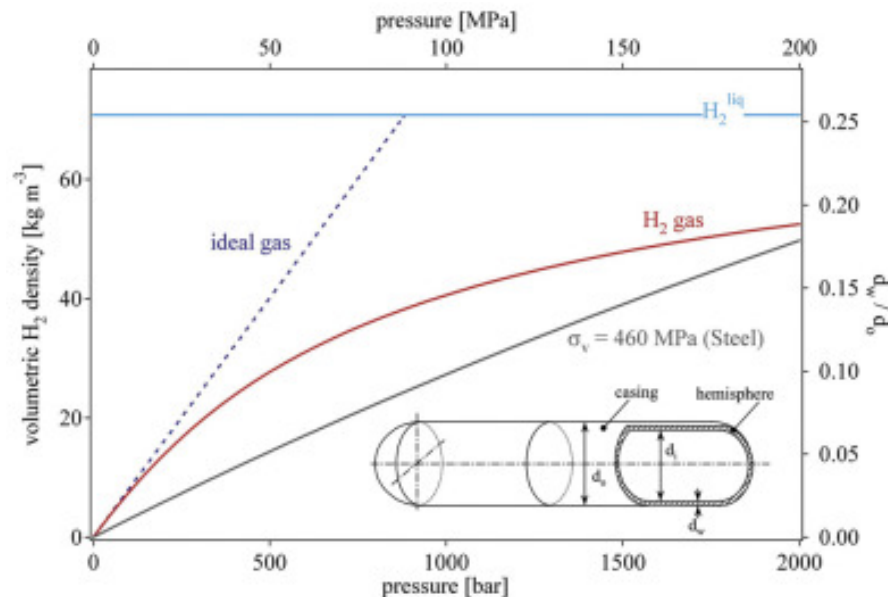
- Electrolytic splitting
  - Use electricity to split water directly
  - Can use renewable energy sources
- Direct solar splitting
  - Use solar furnace to reach the ~2000 K required to split water directly



# Hydrogen Storage

## Under pressure

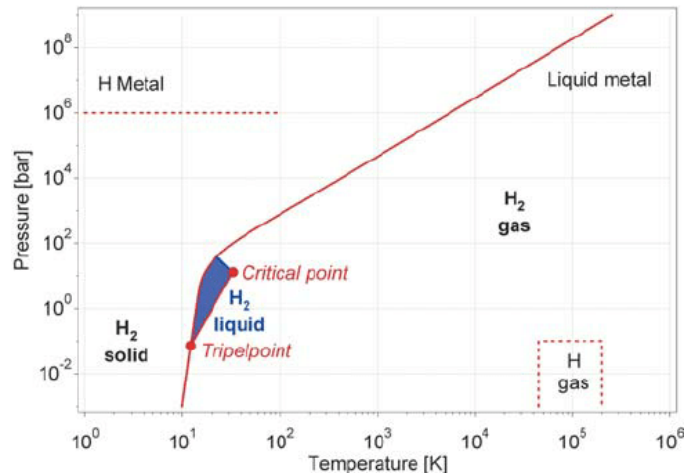
- Compressed gases are an established technology, *but*
- $H_2$  is not an ideal gas
  - Extremely high pressures are required to achieve a reasonable density (much higher than hydrocarbons)
- Safety concerns over compressed  $H_2$



# Hydrogen Storage

## Cryogenically

- Liquid H<sub>2</sub> (LH<sub>2</sub>) has a density of 70.6 kg m<sup>-3</sup>
- Boiling point = 21.2 K (at ambient pressure)
- *but* hydrogen liquifaction is technically challenging
  - At room temperature, H<sub>2</sub> **warms** on **expansion**
  - Conversion between ortho and para H<sub>2</sub> is exothermic
    - at RT, 75% ortho, but para is the low-temperature stable form
- Liquifaction takes ~35% of the energy stored in H<sub>2</sub>!



# Hydrogen Storage

## Chemically - Physisorption

- High surface area materials (e.g. activated carbon) can adsorb H<sub>2</sub>
- How much?

- $A = \left( \frac{M_{ads}}{\rho_{liq} N_A} \right)^{\frac{2}{3}}$

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- So, for a carbon with surface area of 1000 m<sup>2</sup> kg<sup>-1</sup>:
  - $A = 1.304 \times 10^{-19}$  m<sup>2</sup> per molecule, or 78240 m<sup>2</sup> mol<sup>-1</sup>
  - 1 g carbon can store 0.026 g H<sub>2</sub>, *i.e.* **2.6 wt %**



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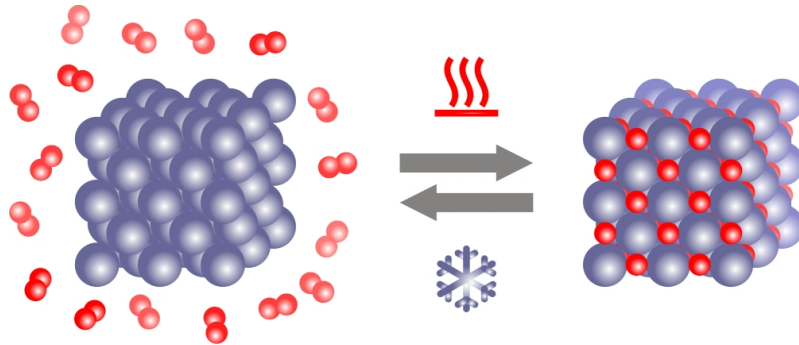
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  - 1 g carbon can store 0.026 g H<sub>2</sub>, *i.e.* **2.6 wt %**
- Relatively cheap materials
- Storage capacity depends on surface area; difficult to exceed ~4000 m<sup>2</sup> g<sup>-1</sup>
- Could be used to enhance LH<sub>2</sub> storage (as a trap for boil-off)

# Hydrogen storage

## Chemically - Hydride phases

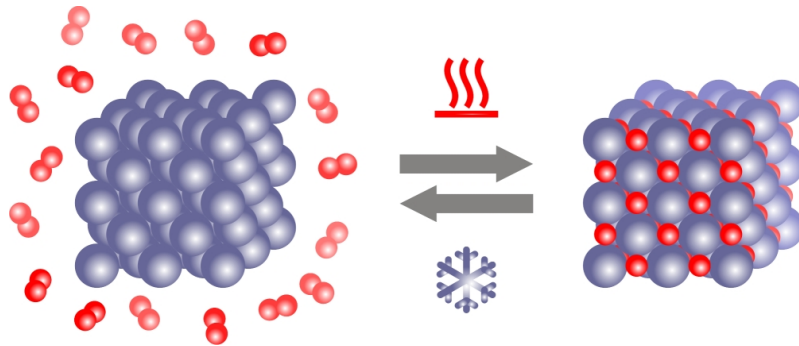
- Challenging → H-H bond is remarkably strong
  - $\text{H}_2 \longrightarrow 2 \text{H} \quad \Delta H = 436 \text{ kJ mol}^{-1}$
- Dissociation can still occur if balanced by an exothermic reaction
  - *e.g.* formation of (metal) hydride phase



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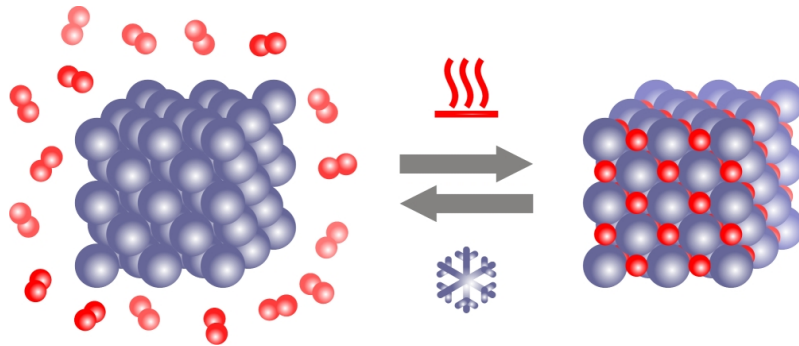


Metal	Hydride	wt%	p (bar)	T (K)
Pd	PdH <sub>0.6</sub>	0.56	0.02	298
LaNi <sub>5</sub>	LaNi <sub>5</sub> H <sub>6</sub>	1.37	2	298
ZrV <sub>2</sub>	ZrV <sub>2</sub> H <sub>5.5</sub>	3.01	10 <sup>-8</sup>	323
FeTi	FeTiH <sub>2</sub>	1.89	5	303
Mg <sub>2</sub> Ni	Mg <sub>2</sub> NiH <sub>4</sub>	3.59	1	555

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- Good volumetric storage (up to  $150 \text{ kg m}^{-3}$ )
- hydrogen is extracted at constant pressure
- Often pyrophoric in air
- Large volume changes on hydridation cause material breakdown
- Metals are typically heavy!

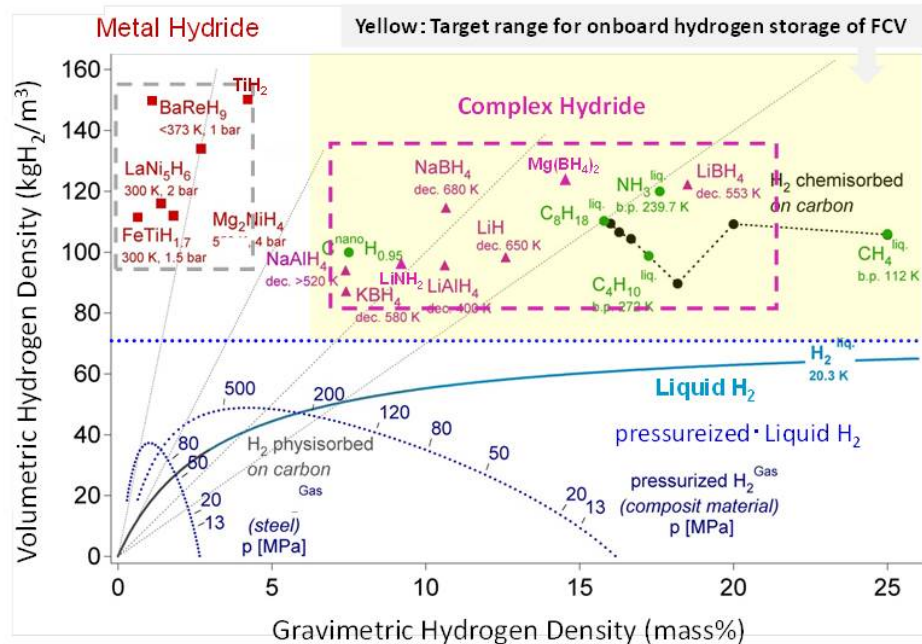
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# Hydrogen storage

## Chemically - lighter hydrides

One way to increase  $H_2$  capacity (per kg) is to use lighter elements

- e.g.  $MgH_2$  has 7.6 wt%  $H_2$
- They are often cheaper than heavier metals
- **but** formation of lighter hydrides is kinetically slow
- Often complex sequence of reactions to yield full  $H_2$  content



# Summary

Three similar energy storage technologies (batteries, supercapacitors and fuel cells) all share very similar chemistry requirements:

- High ionic conductivity at relevant temperatures
- High (or low) electronic conductivity depending on component
- Chemical stability under different operating conditions / between neighbouring materials
- Device compatibility (e.g. thermal expansion, cyclability, cost...)

