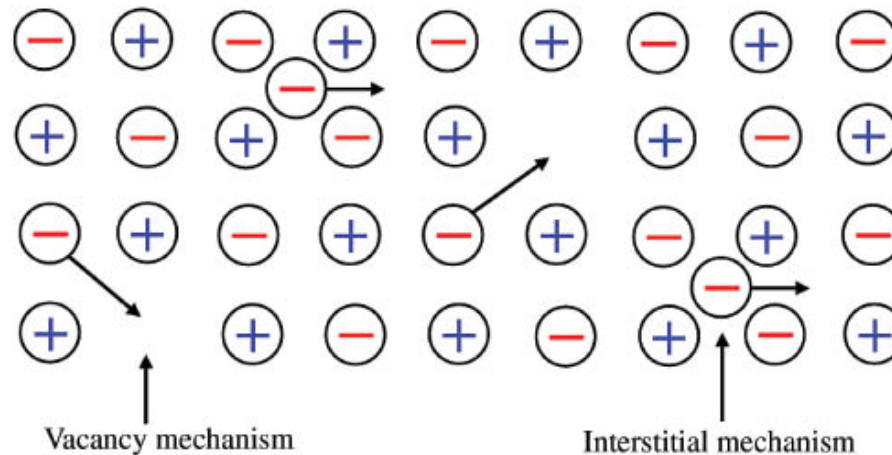


Fuel Cells 2

Ionic conduction

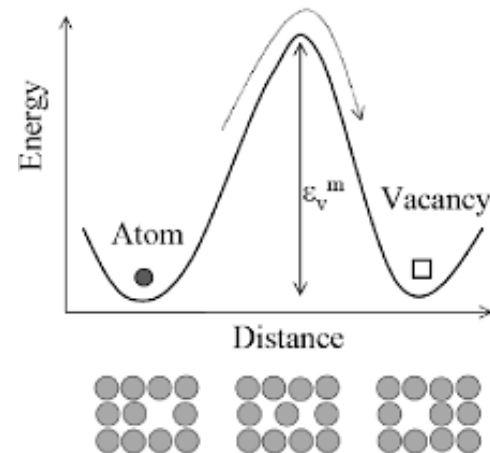
All the technologies in this course rely on ionic motion. In the solid state, this occurs through two main mechanisms:



There is an energy barrier E_a to ionic diffusion

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

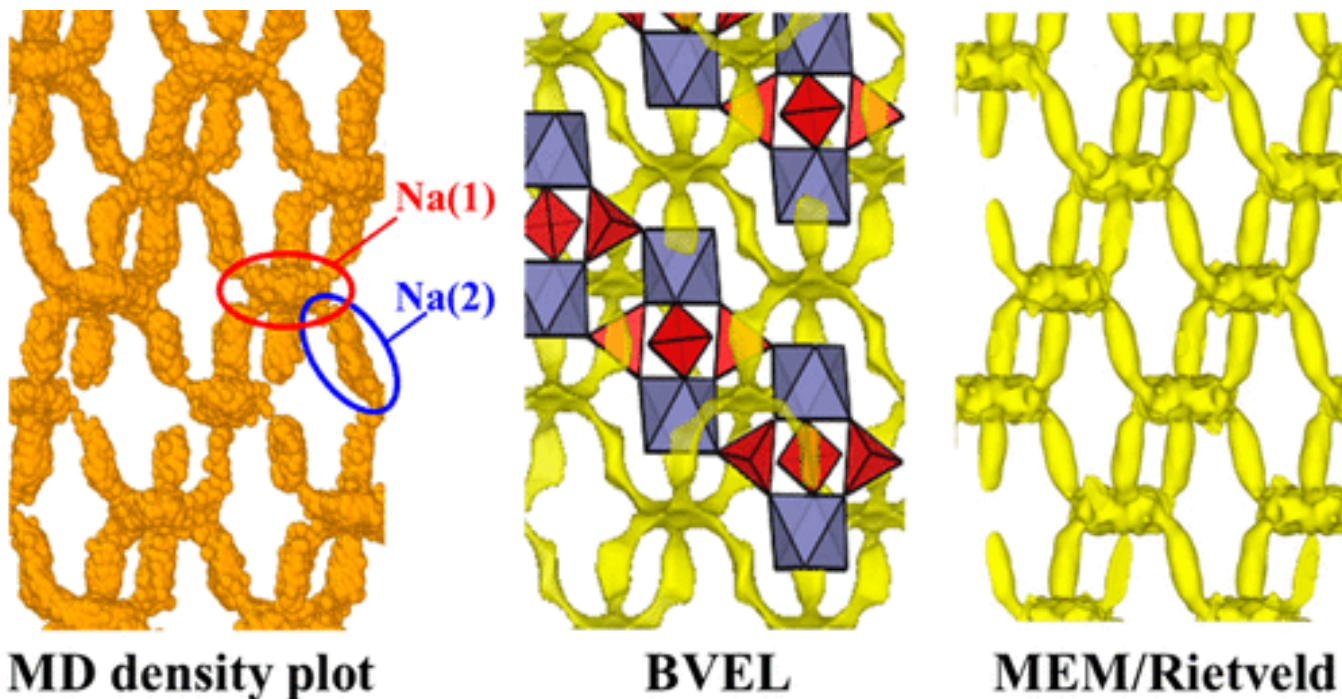
$$\sigma(T) = Ae^{\frac{-E_a}{RT}}$$



Diffusion pathways are often complex

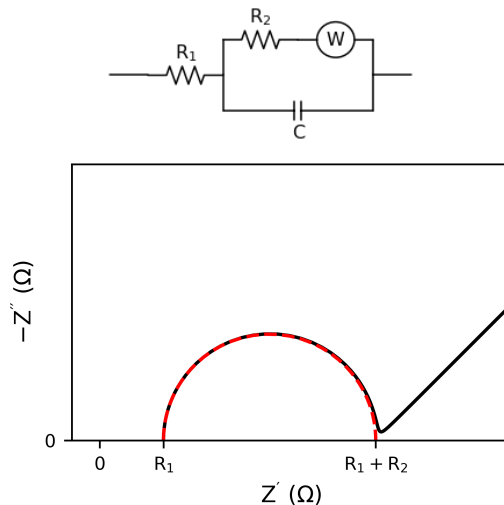
- Often there are competing pathways, with different energy barriers.
- Diffusion pathways can be calculated and/or experimentally determined

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



Characterising diffusion

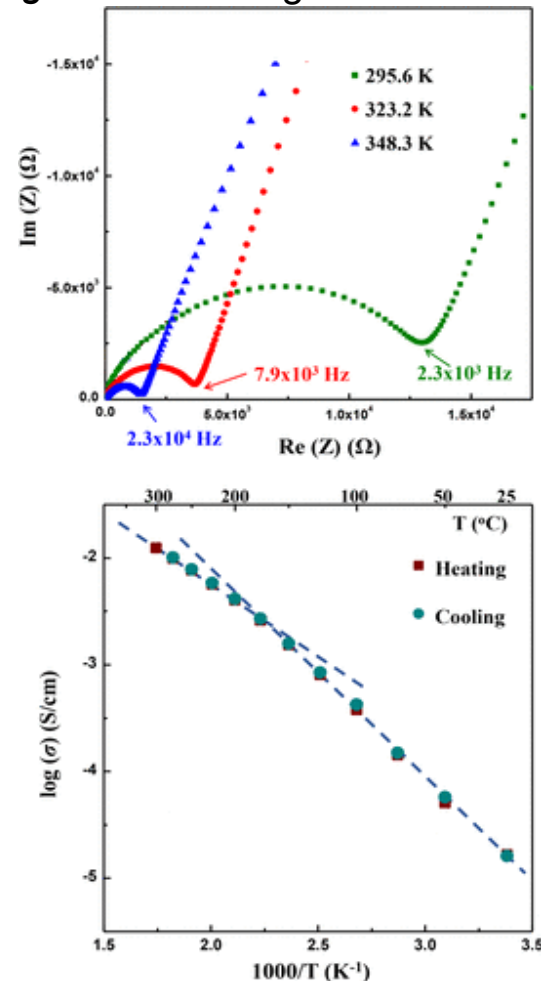
Impedance spectroscopy allows us to determine the conductivity at different temperatures.



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

- 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:

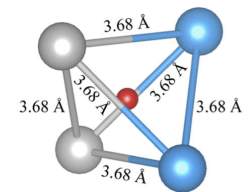
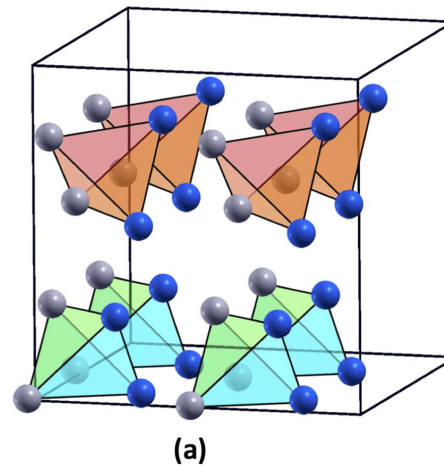
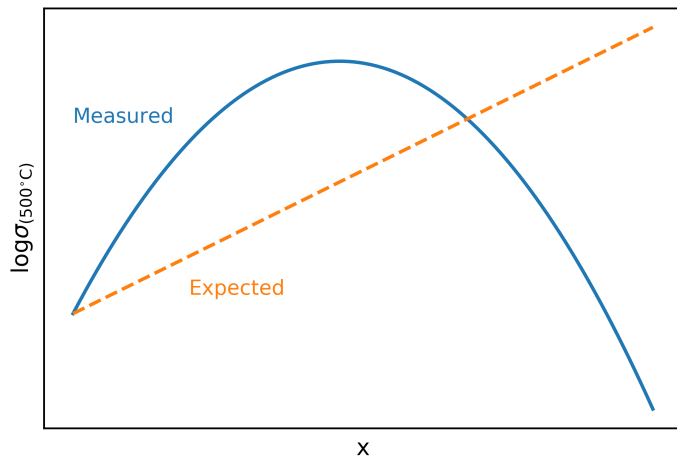


Ionic conduction

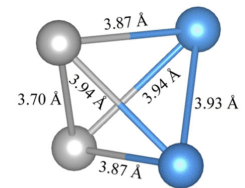
$$\sigma(T) = Ae^{\frac{-E_a}{RT}}$$

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

e.g. YSZ: $((1-x)\text{ZrO}_2 + \frac{x}{2}\text{Y}_2\text{O}_3 \longrightarrow \text{Y}_x\text{Zr}_{1-x}\text{O}_{2-\frac{x}{2}})$:



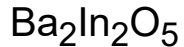
(b)



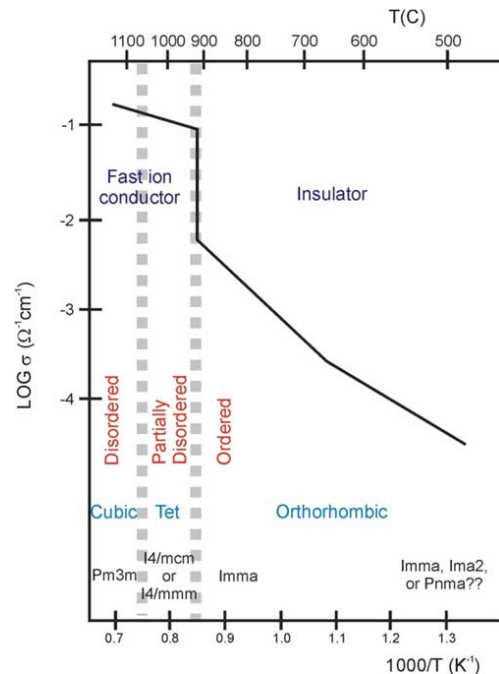
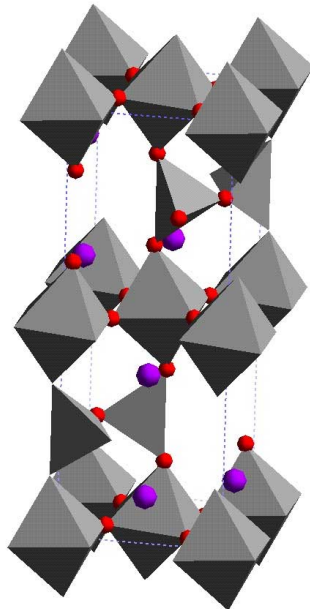
(c)

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



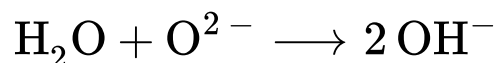
Oxide/Proton conductors

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

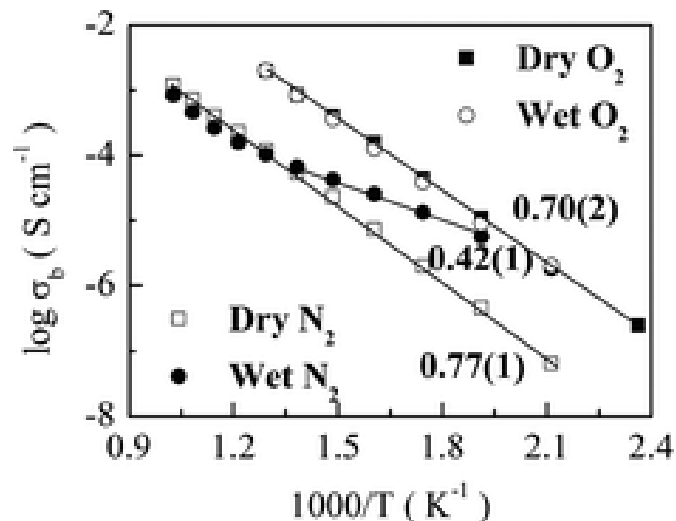
- In dry N_2 is an oxide ion conductor
- In wet N_2 , shows proton conduction below 600 K, and oxide ion conduction above this

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?

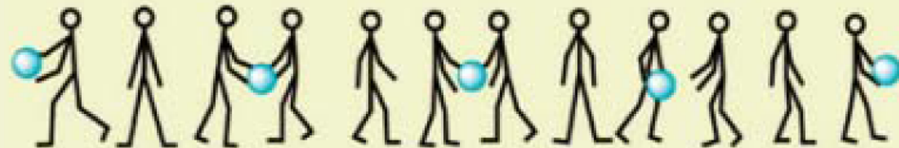
Two possible mechanisms:

- **Vehicle** mechanism
 - Direct diffusion of OH^-
- **Grotthuss** mechanism
 - Exchange of H^+ between neighbouring OH^-

Vehicle mechanism



Grotthuss mechanism (Proton hopping)

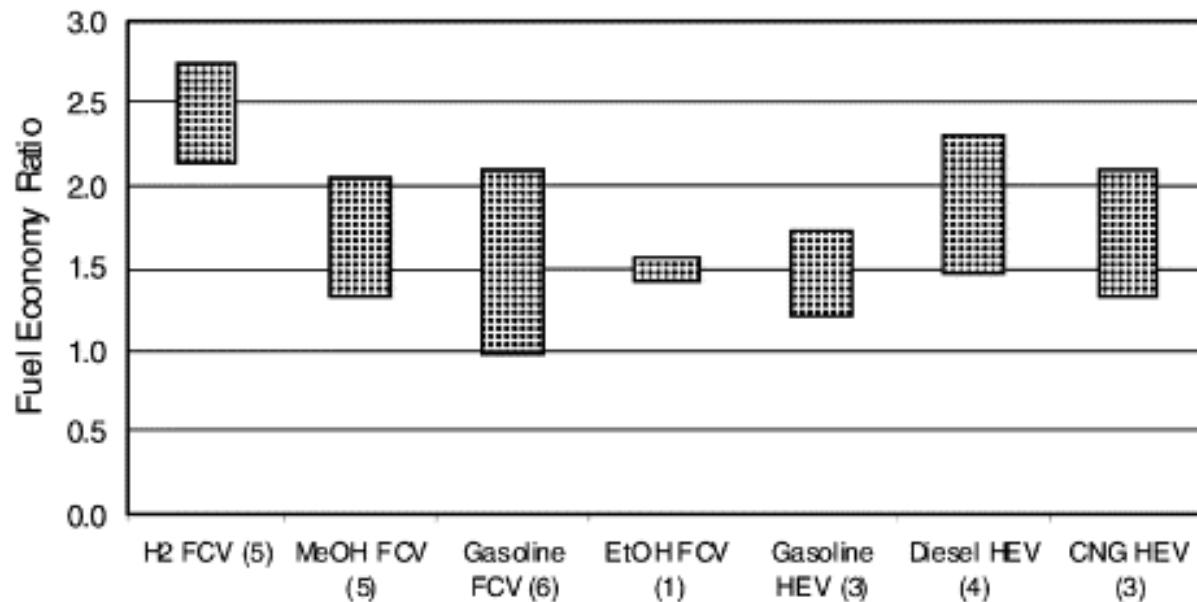


- The Grotthuss mechanism dominates
 - Water incorporation fills anion vacancies, so there is no conduction pathway for OH^-

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



H₂ is the most efficient fuel (ignoring many other factors), but there are two important obstacles to a *hydrogen economy*:

- Generation
- Storage

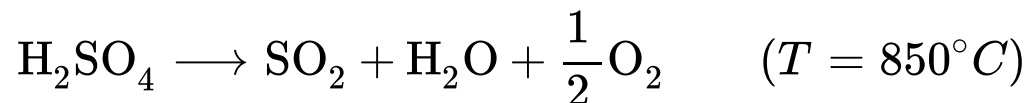
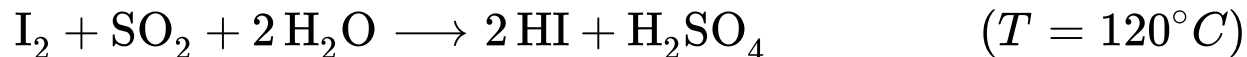
Hydrogen generation

Chemical methods

- Steam reforming
 - High temperatures and pressures required
 - Requires catalyst (e.g. Ni, Pt, Rh)
 - Produces a mixture of H_2 , CO, CO_2 and H_2O
- Pyrolysis
 - Thermal cracking of hydrocarbons in the absence of oxygen
 - Precious-metal catalyst required
 - Produces carbon waste



- Iodine-sulfur cycle:



Hydrogen generation

Biological sources

- Fermentation
 - Enzymatic conversion of sugars to H₂
 - *e.g.* $\text{C}_6\text{H}_{12}\text{O}_6 + 2\text{H}_2\text{O} \longrightarrow 2\text{CH}_3\text{CO}_2\text{H} + 2\text{CO}_2 + 4\text{H}_2$
- Photosynthesis
 - Green algae (and others) can use sunlight to generate H₂

Direct water splitting

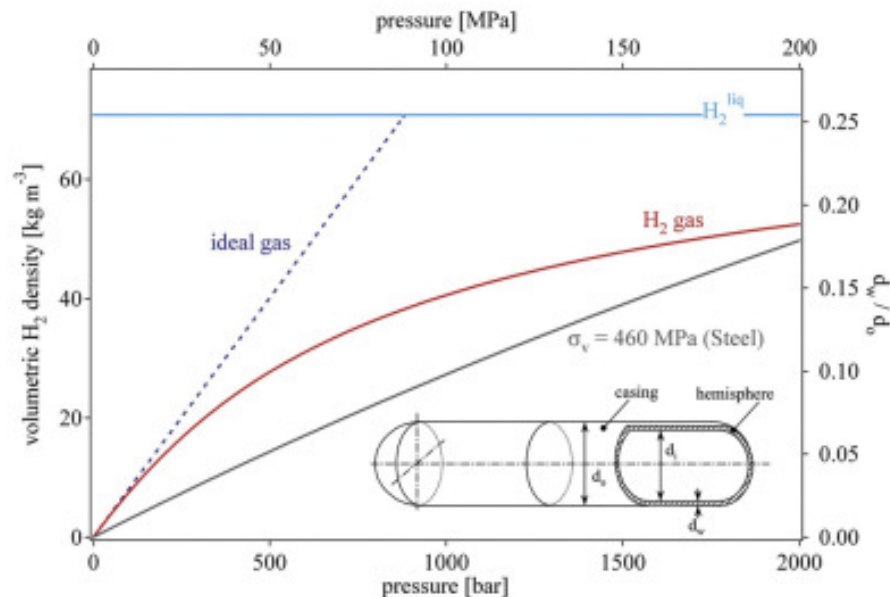
- Electrolytic splitting
 - Use electricity to split water directly
 - Can use renewable energy sources
- Direct solar splitting
 - Use solar furnace to reach the ~2000 K required to split water directly



Hydrogen Storage

Under pressure

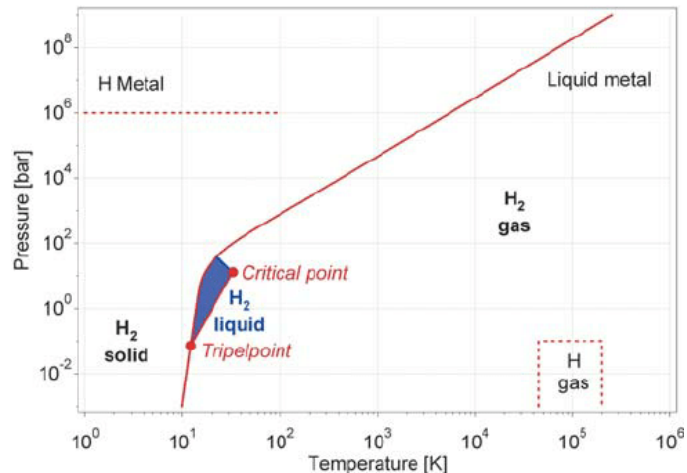
- Compressed gases are an established technology, *but*
- H_2 is not an ideal gas
 - Extremely high pressures are required to achieve a reasonable density (much higher than hydrocarbons)
- Safety concerns over compressed H_2



Hydrogen Storage

Cryogenically

- Liquid H₂ (LH₂) has a density of 70.6 kg m⁻³
- Boiling point = 21.2 K (at ambient pressure)
- *but* hydrogen liquifaction is technically challenging
 - At room temperature, H₂ **warms** on **expansion**
 - Conversion between ortho and para H₂ is exothermic
 - at RT, 75% ortho, but para is the low-temperature stable form
- Liquifaction takes ~35% of the energy stored in H₂!



Hydrogen Storage

Chemically - Physisorption

- High surface area materials (e.g. activated carbon) can adsorb H₂
- How much?

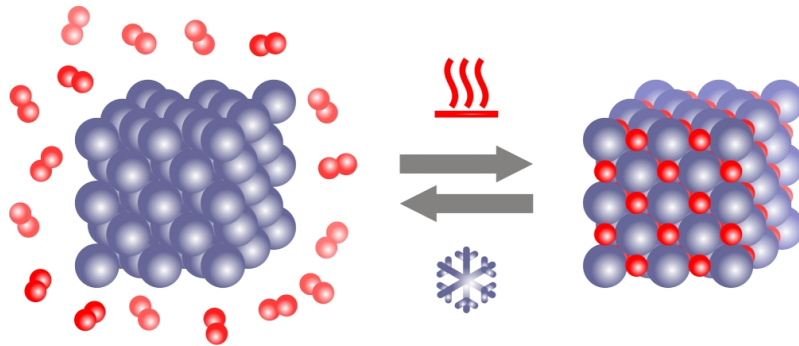
- $A = \left(\frac{M_{ads}}{\rho_{liq} N_A} \right)^{\frac{2}{3}}$

- So, for a carbon with surface area of 1000 m² kg⁻¹:
 - A = 1.304 × 10⁻¹⁹ m² per molecule, or 78240 m² mol⁻¹
 - 1 g carbon can store 0.026 g H₂, i.e. **2.6 wt %**
- Relatively cheap materials
- Storage capacity depends on surface area; difficult to exceed ~4000 m² g⁻¹
- Could be used to enhance LH₂ 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



- Good volumetric storage (up to 150 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!

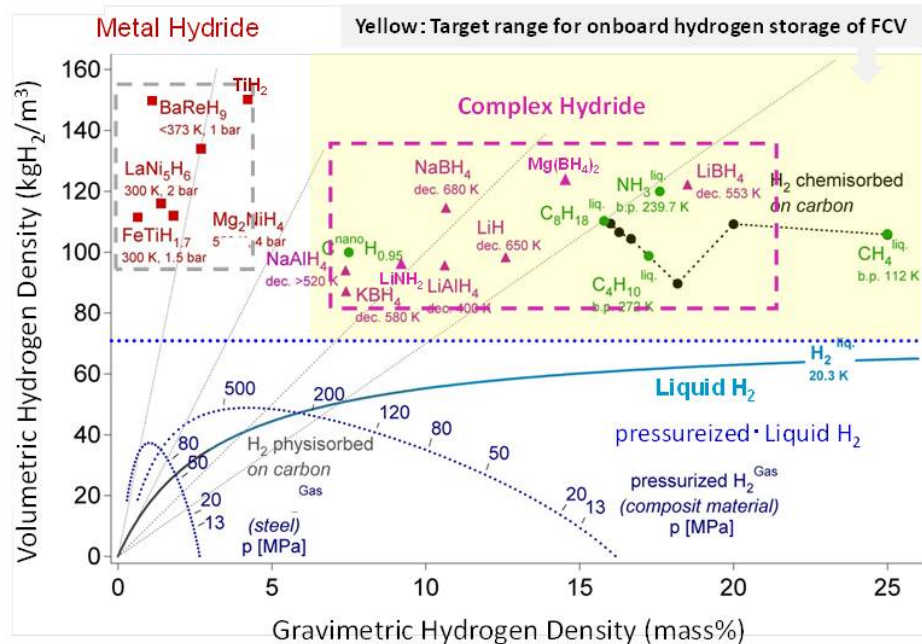
Metal	Hydride	wt%	p (bar)	T (K)
Pd	$\text{PdH}_{0.6}$	0.56	0.02	298
LaNi ₅	LaNi_5H_6	1.37	2	298
ZrV ₂	$\text{ZrV}_2\text{H}_{5.5}$	3.01	10^{-8}	323
FeTi	FeTiH_2	1.89	5	303
Mg ₂ Ni	Mg_2NiH_4	3.59	1	555

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...)

