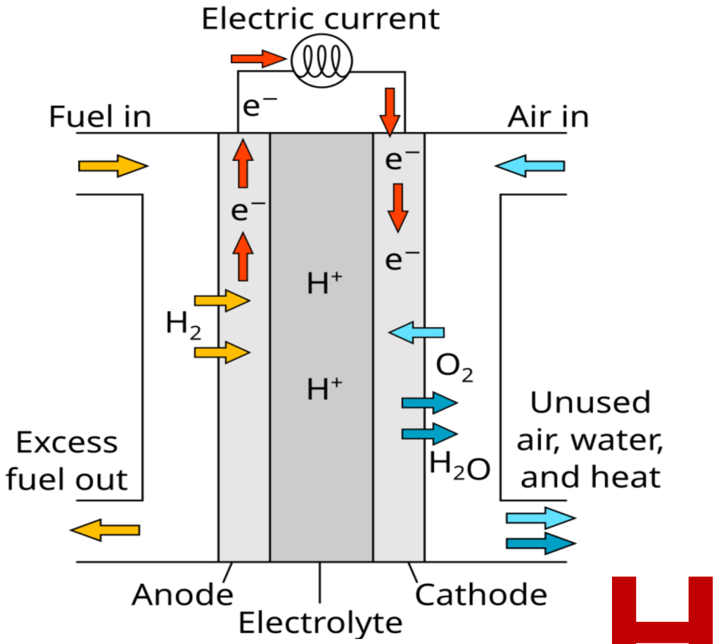


Fuel Cells & Hydrogen storage

Maria Rodrigues Pinto
&
Mohd Monis Ayyub

Lecture - Learning Objectives

At the end of this lecture, you should be able to understand:

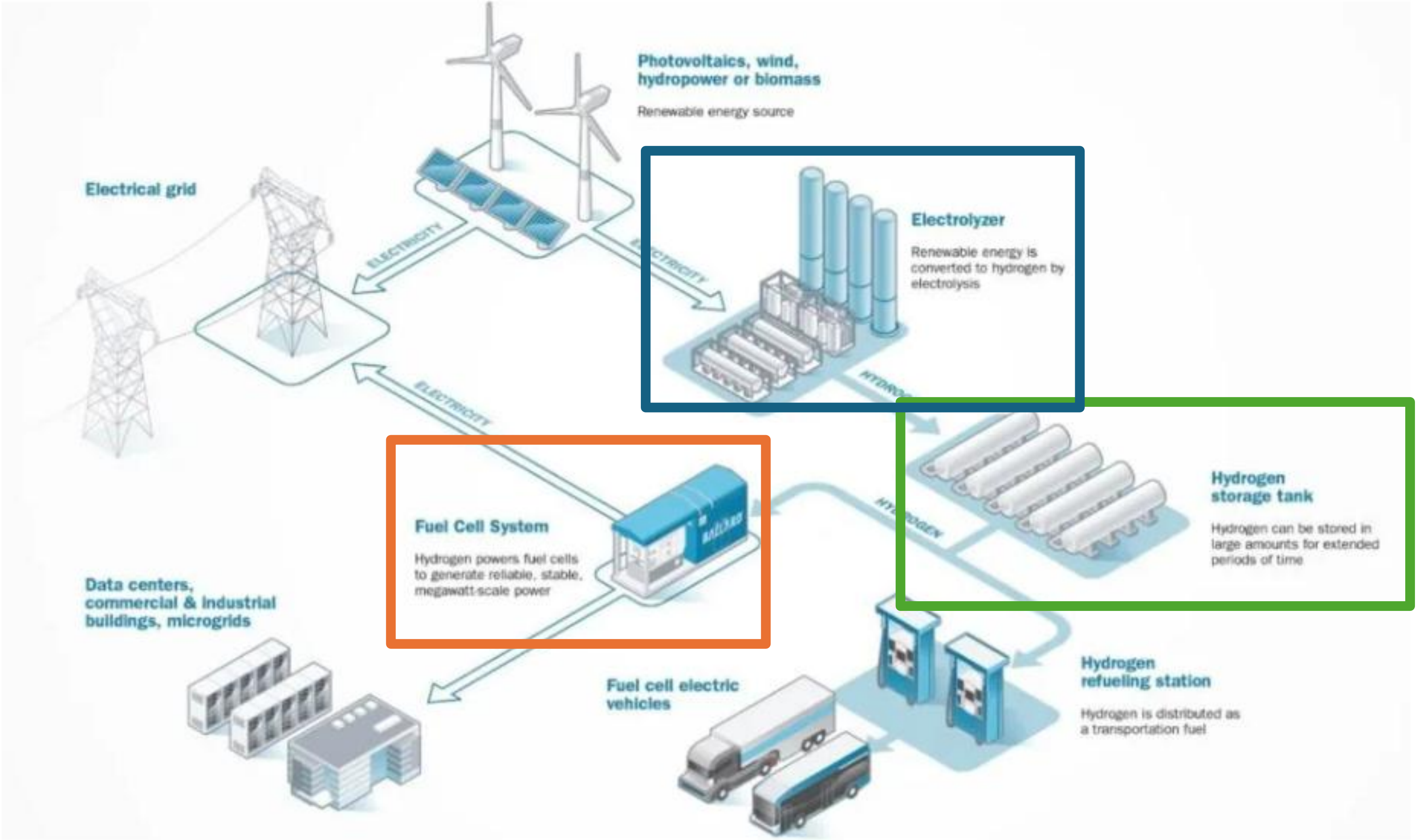
Fuel cell Fundamentals

- How it operates and main components of a fuel cell
- Thermodynamics and redox reactions in a fuel cell
- Efficiency and where the efficiency losses are in fuel cells

Hydrogen storage

- Basic principles behind different H_2 storage techniques.

Where does Fuel cell fit in a sustainable grid?



Photovoltaics, wind, hydropower or biomass

Renewable energy source

Electrical grid

Electrolyzer

Renewable energy is converted to hydrogen by electrolysis

Hydrogen storage tank

Hydrogen can be stored in large amounts for extended periods of time

Fuel Cell System

Hydrogen powers fuel cells to generate reliable, stable, megawatt-scale power

Data centers, commercial & industrial buildings, microgrids

Fuel cell electric vehicles

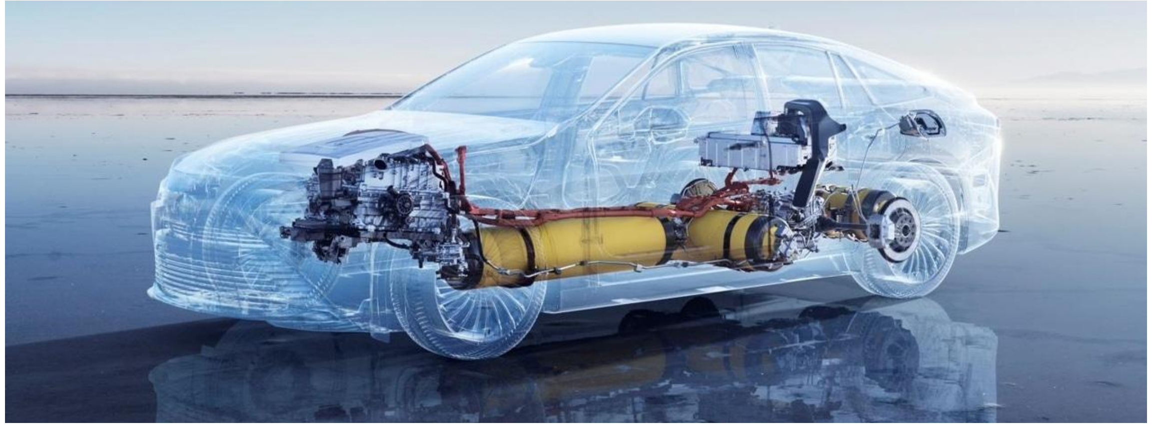
Hydrogen refueling station

Hydrogen is distributed as a transportation fuel

Application of fuel cells

Transportation

Toyota Mirai – H_2 PEM Fuel Cell Car



The first FCV to be mass-produced and sold commercially

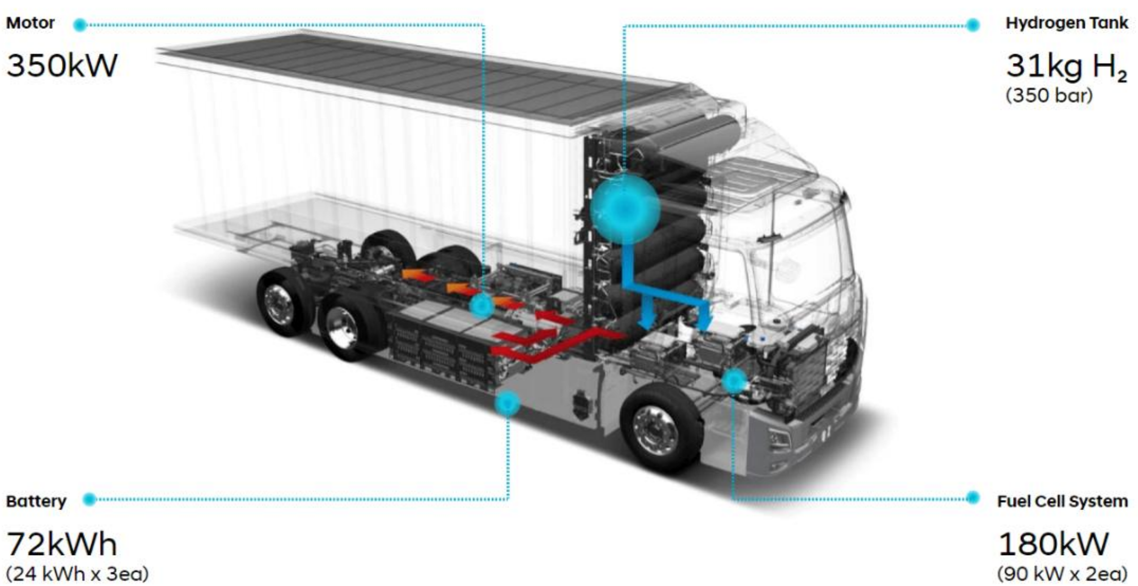
The Mirai was released in late 2014

1,360 km (845 mi) with a full tank of 5.65 kg (12.5 lb) of hydrogen

Toyota Mirai Owners file Class Action Lawsuit in California, USA *(Los Angeles Times)*

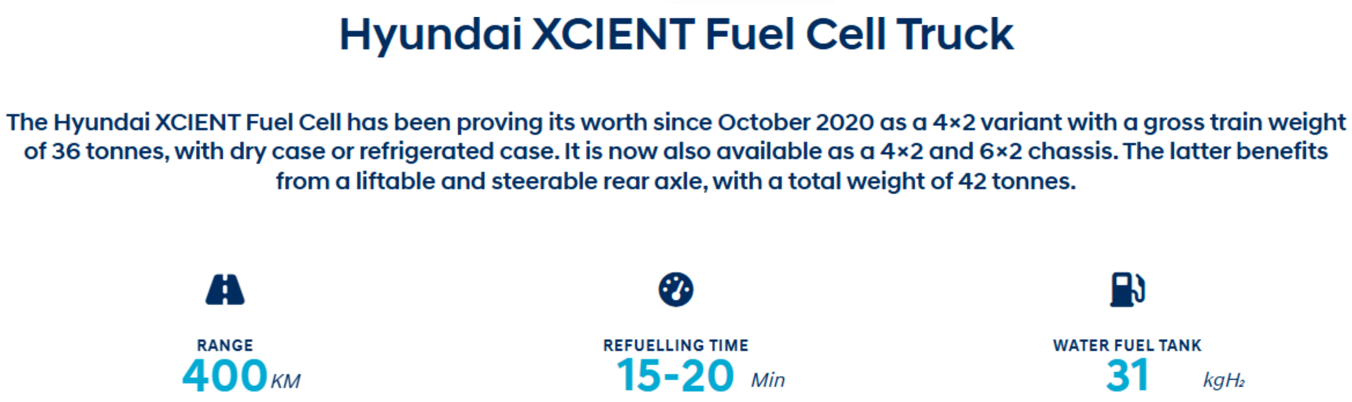
Application of fuel cells

Transportation



XCIENT Fuel Cell Trucks: actively operating in Switzerland and South Korea

In 2020, Hyundai, in a joint venture with Swiss company H2 Energy, started mass manufacturing hydrogen fuel cell-powered 34-ton cargo trucks



Hyundai XCIENT Fuel Cell Truck

The Hyundai XCIENT Fuel Cell has been proving its worth since October 2020 as a 4×2 variant with a gross train weight of 36 tonnes, with dry case or refrigerated case. It is now also available as a 4×2 and 6×2 chassis. The latter benefits from a liftable and steerable rear axle, with a total weight of 42 tonnes.

RANGE
400 KM

REFUELLING TIME
15-20 Min

WATER FUEL TANK
31 kgH₂

A 42-ton truck running on diesel would have a 2000 km autonomy

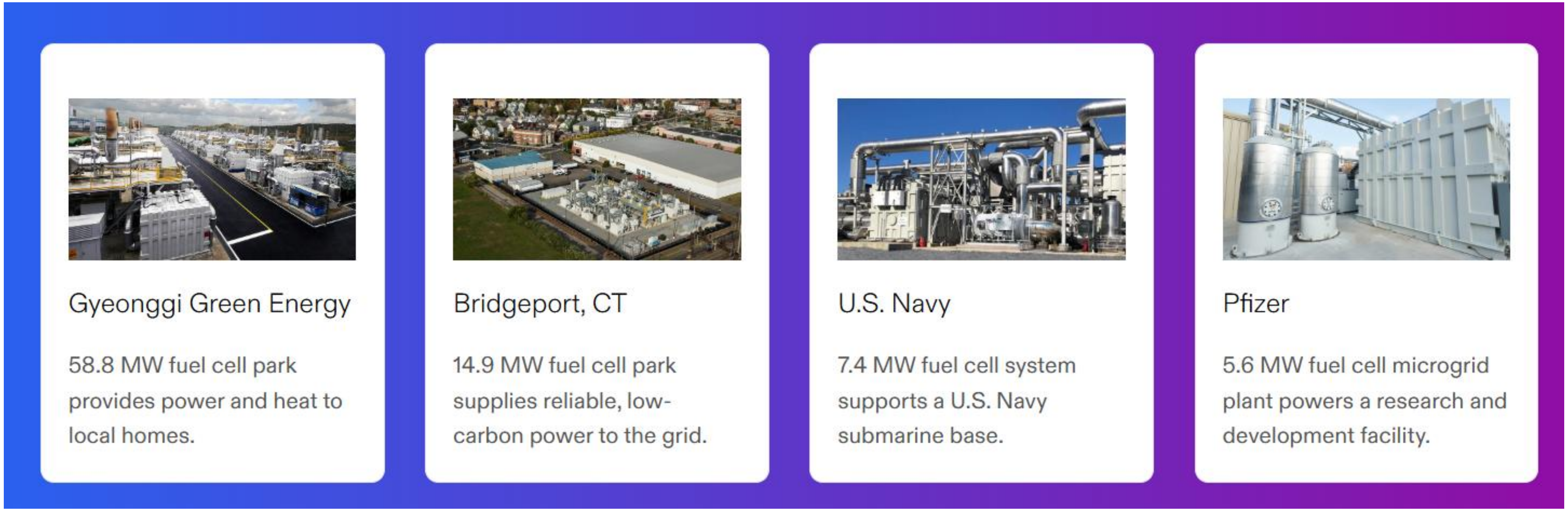
Application of fuel cells

Beyond Transportation

FuelCell Energy

- Founded in 1969 is a publicly traded company headquartered in Danbury, Connecticut.

Data Centers
Food & Beverage
Manufacturing
Hospitals
Hydrogen Fueling
Universities
Utilities
Wastewater Treatment



Gyeonggi Green Energy

58.8 MW fuel cell park provides power and heat to local homes.

Bridgeport, CT

14.9 MW fuel cell park supplies reliable, low-carbon power to the grid.

U.S. Navy

7.4 MW fuel cell system supports a U.S. Navy submarine base.

Pfizer

5.6 MW fuel cell microgrid plant powers a research and development facility.

Fuel cell companies

BALLARD®

- Pioneer since 1980s, H_2 PEM
- Various Markets
- Technology, Products, R&D

Nedstack
PEM FUEL CELLS

- H_2 PEM
- Maritime Power, Stationary Power

POWERCELL

- H_2 PEM
- Various Markets
- Technology, Products, R&D

plug™

- H_2 PEM
- Various Markets – Warehouses (Mobile), Stationary Power

SFC ENERGY

- H_2, Methanol PEM
- Stationary Power

IRD
IRD Fuel Cells A/S

- H_2, Methanol PEM
- Flow Plates and MEAs

WIDEX®
HIGH DEFINITION HEARING

DANISH TECHNOLOGICAL INSTITUTE

Methanol PEM Fuel cells in Hearing Aid (Lost the market to Li Ion Batteries)

Blue World Technologies®

- H_2, Methanol PEM (high temp.)
- Maritime Power, Stationary Power

In context to what was seen previously

Solar Cells

Image Source: *https://etap.com/product/photovoltaic-array-solar-panel*

Sunlight energy into electrical energy

Wind Turbine

Image Source: *https://www.energy-uk.org.uk/publications/the-uk-offshore-wind-revolution/*

Kinetic energy of the wind into electrical energy

Energy Conversion Devices

Chemical energy into electricity (1st gen)

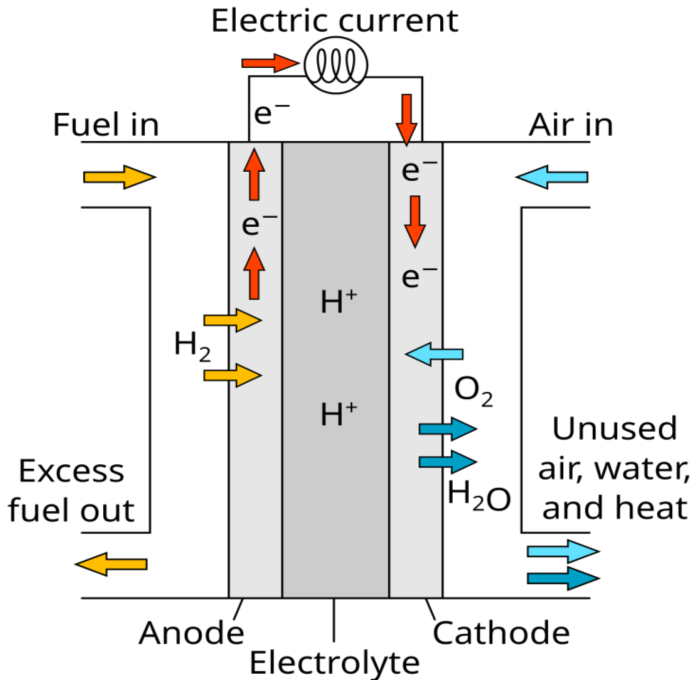
2nd generation (rechargeable) – electricity into chemical energy

Storage device

What is a fuel cell?

Energy conversion device that converts chemical energy to electrical energy

A **battery** stores energy inside itself and discharges it until depleted, while a **fuel cell** generates electricity continuously as long as it is supplied with fuel (e.g., hydrogen) and oxygen.



PEM Fuel Cell

Most relevant: H_2 and O_2 fuel cells
PEM – Proton Exchange Membrane fuel cell

Other fuels – CO, CH_3OH, CH_4, C_4H_{10}, NH_3, etc

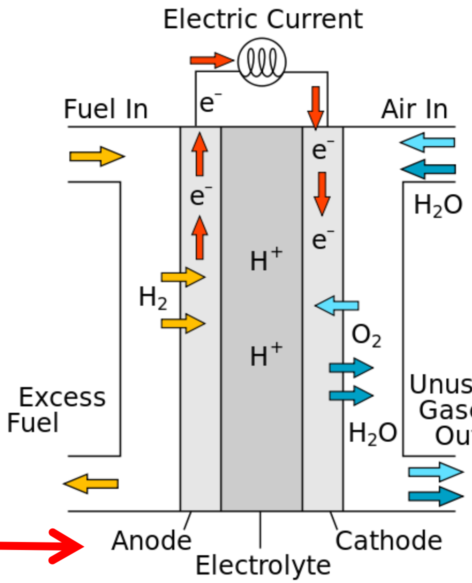
Type of fuel cells

- Alkaline fuel hydrogen fuel cells
- Phosphoric acid fuel cells
- Direct methanol fuel cells
- Molten carbonate fuel cells

The electrochemistry of a Fuel cell

- Let’s consider H_2 as a fuel
- We can break this reaction down into 2 half-reactions

Useful Mnemonic:
OIL RIG
(**O**xidation **I**s **L**osing electrons;
Reduction **I**s **G**aining electrons)



Oxidation

Anode Reaction

$$\underbrace{H_2 \rightarrow 2H^+ + 2e^-}$$

Reduction

Cathode Reaction

$$\underbrace{2e^- + 2H^+ + \frac{1}{2}O_2 \rightarrow H_2O}$$

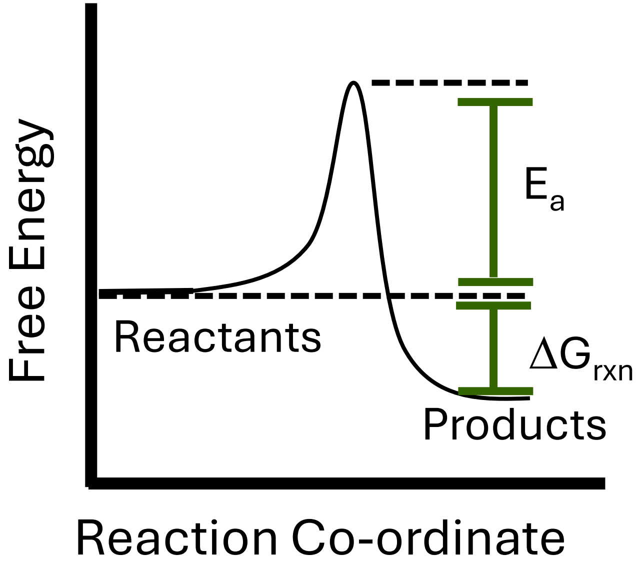
$$\overbrace{H_2 + \frac{1}{2}O_2 \rightarrow H_2O}$$

$\Delta G =$ **-237.2 kJ/mol**

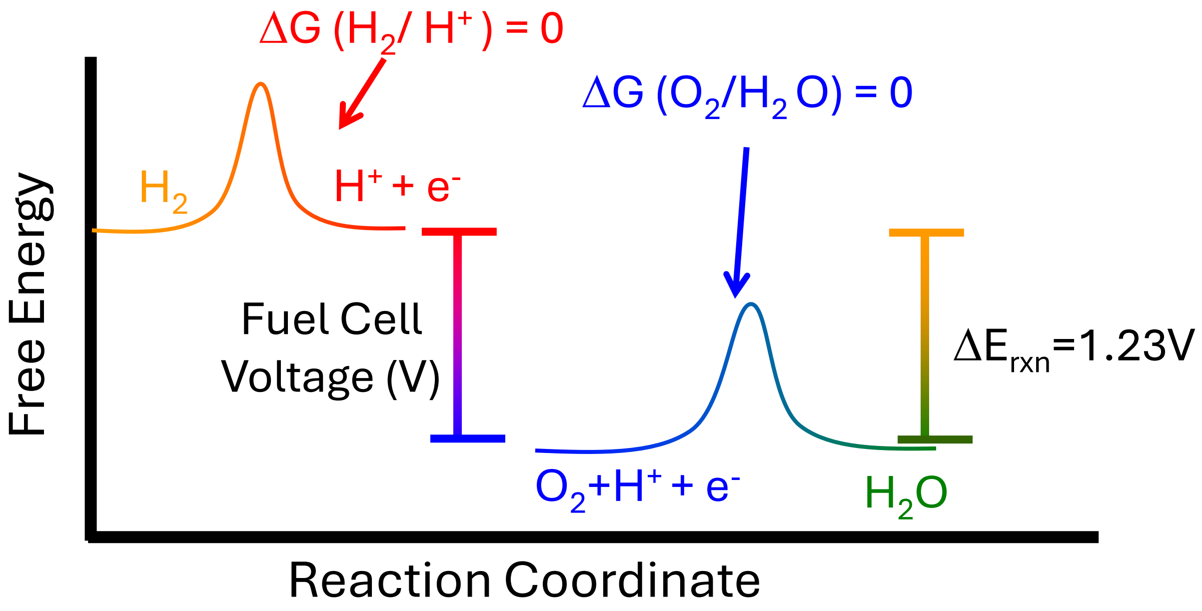
Thermal vs Electrocatalysis

- In thermal catalysis, you need to supply enough energy to overcome E_a (e.g., heat).
- The catalyst lowers E_a but doesn't change ΔG.
- The reaction releases energy as heat.

- In electrocatalysis, the driving force is an electrical potential difference rather than heat.
- ΔG is directly converted into electrical work instead of thermal energy $\Delta G = -nFE_{cell}$



Heterogeneous Catalysis



Electrochemical Catalysis

Energy efficiency of a PEM fuel cell

From previous class:

- Combust fuel chemically in a engine, produce heat and convert it to electricity.
- Electrochemically convert fuel into electricity in a fuel cell.

$\Delta G = -237.2\ \text{kJ/mol}$

- $\Delta E = \frac{\Delta G}{nF} = \frac{G_f(H_2O) - G_f(O_2) - G_f(H_2)}{2\times 96{,}485} = \frac{237{,}000 - 0 - 0}{2\times 96{,}485} = 1.23\ \text{V}$

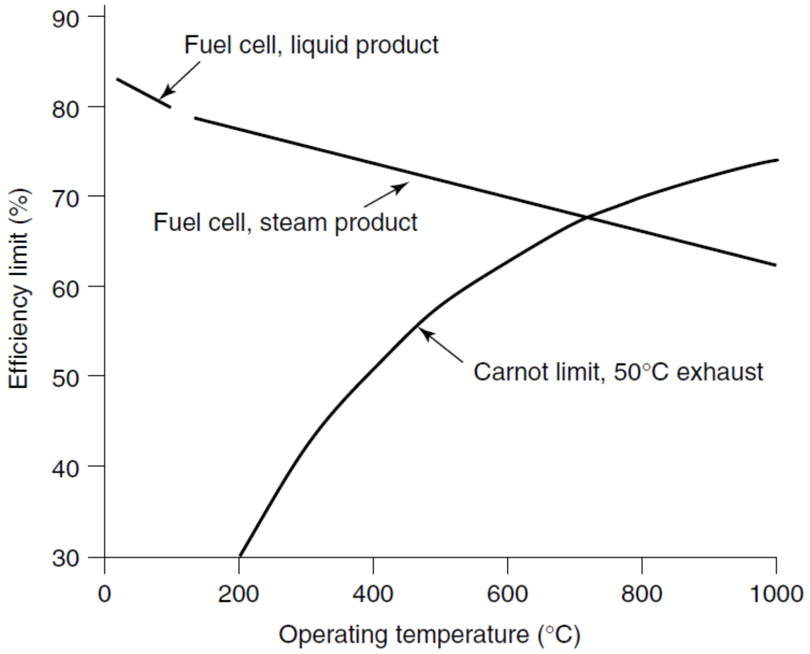
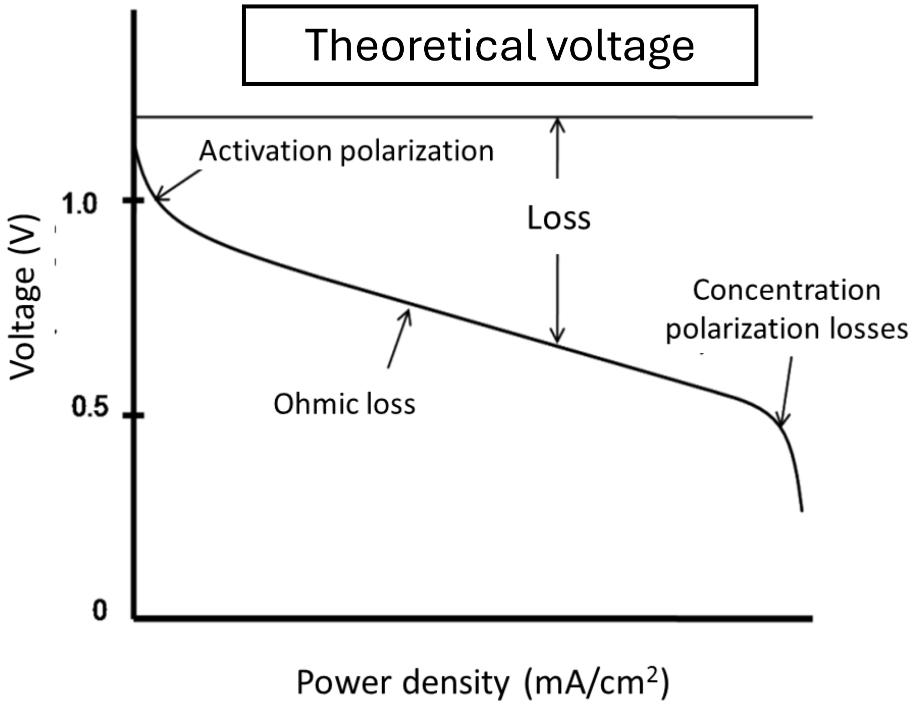


Figure 2.4 Maximum H_2 fuel cell efficiency at standard pressure, with reference to higher heating value. The Carnot limit is shown for comparison, with a 50°C exhaust temperature.



The power of a Fuel cell

- We have a voltage and a current, thus we should get power.

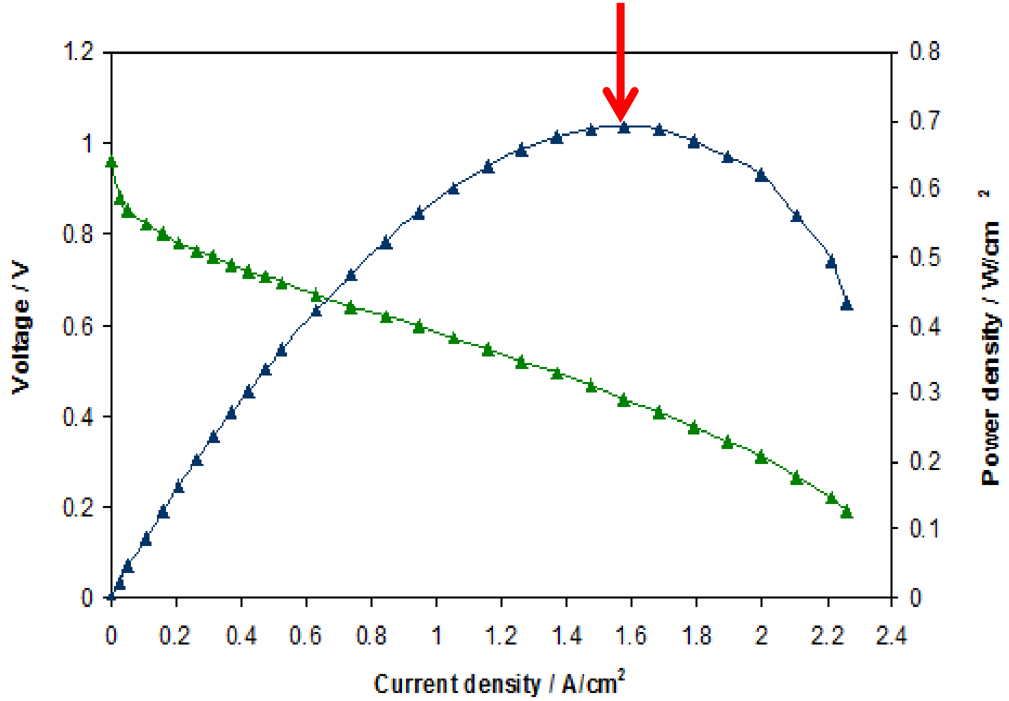
$$P = V \times i$$

Current (i) = Reaction rate x Faraday’s constant

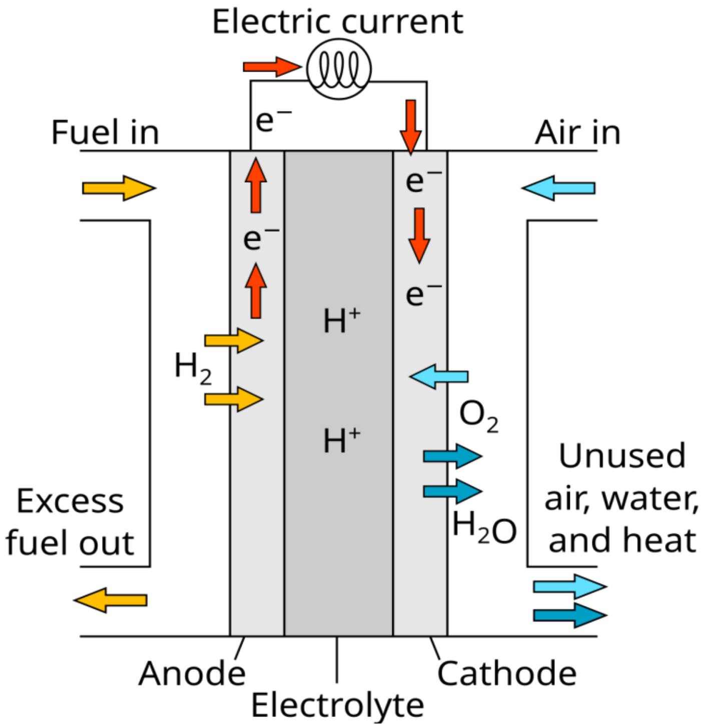
(C/s) = (mol/s) x (C/mol)

Polarization Curve Analysis
You can graphically identify the maximum power by plotting the voltage and current

The "Sweet Spot"
Maximum power doesn't occur at the highest voltage (zero current) or the highest current (near-zero voltage).


Most Power

Electrodes on a fuel cell



PEM Fuel Cell

Catalyst, Electronically Conductive Considering a H_2 PEM Fuel Cell:

Anode: $H_2 \rightarrow 2H^+ + 2e^-$

- **Platinum (Pt)** is the standard catalyst for the cathode.
- Often supported on **carbon black** (Pt/C) to maximize surface area

•**Alternatives: Pt-alloys** (Pt-Co, Pt-Ni, Pt-Fe) → higher activity and lower Pt loading

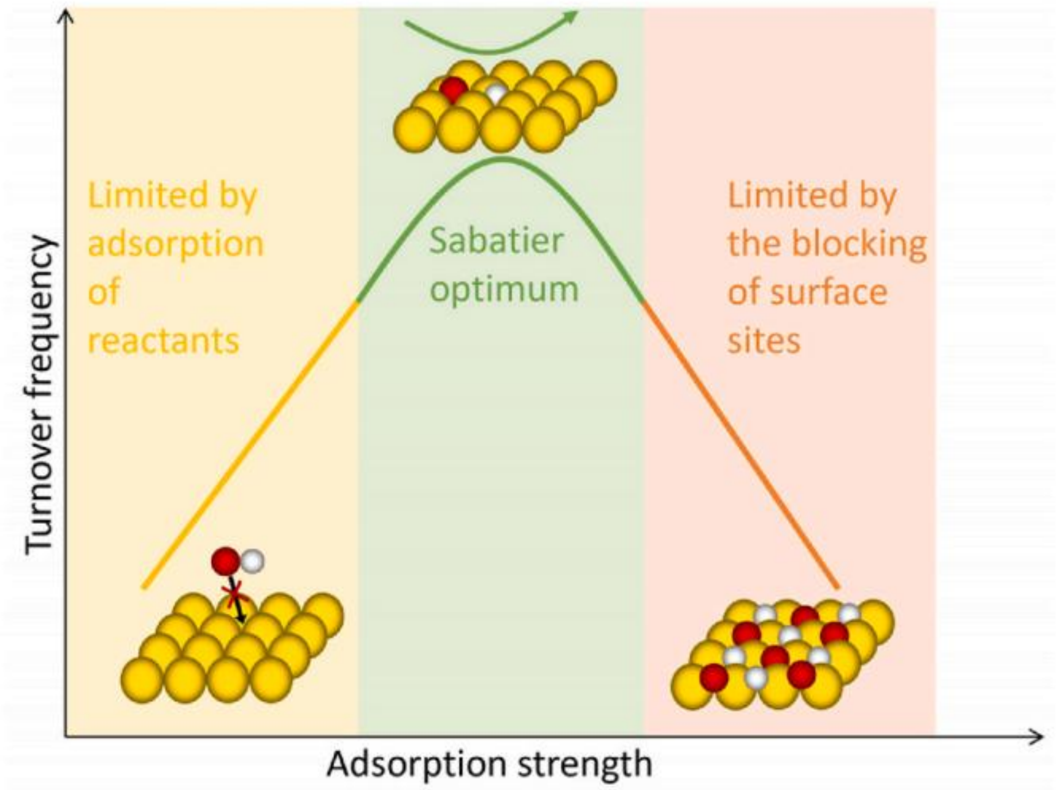
Cathode: $2e^- + 2H^+ + \frac{1}{2}O_2 \rightarrow H_2O$

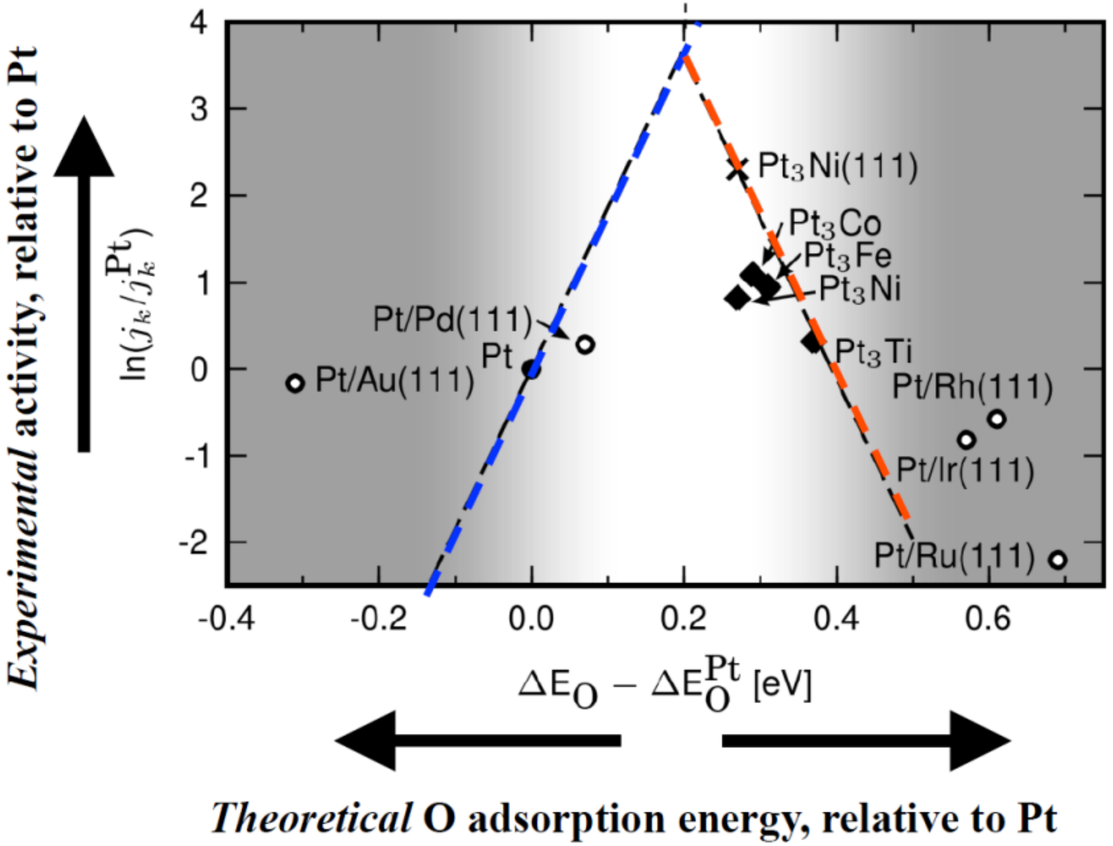
- Requires **higher Pt loadings** (0.1–0.4 mg/cm² in commercial MEAs).

- Research frontier: **non-precious metal catalysts** to replace Pt

Catalysis- Sabatier's Principle

- The Sabatier principle leads to 'volcano plots' of activity versus binding strength





Too strongly bound

Too weakly bound

Overpotential and equilibrium

$$H_2 + \frac{1}{2}O_2 \rightleftarrows H_2O \qquad \Delta E_{rxn} = 1.23V$$

H_2 Fuel cell reaction →

← Water Electrolysis

- The **overpotential (η)** is the extra voltage applied beyond the equilibrium potential.
- This accelerates the reaction rate, as described by the **Butler–Volmer equation**:

$$j = j_0\left(e^{\frac{(1-\beta)nF\eta}{RT}} - e^{\frac{-\beta nF\eta}{RT}}\right)$$

$$\mathrm{Ox} + e^- \rightleftharpoons \mathrm{Re}$$

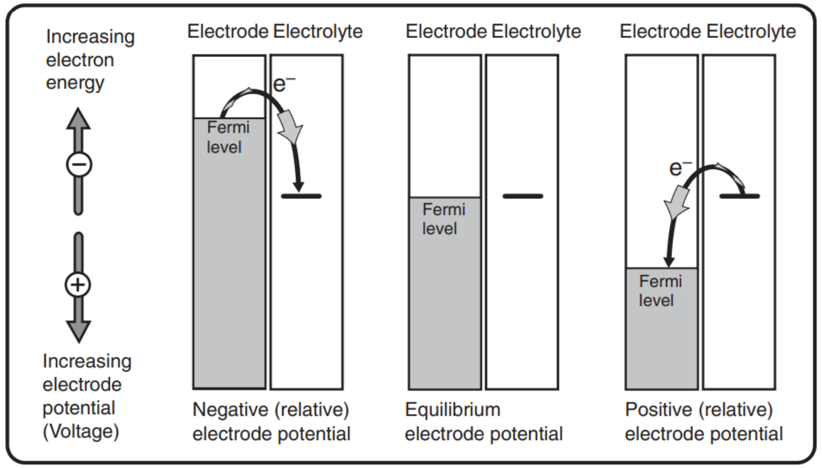
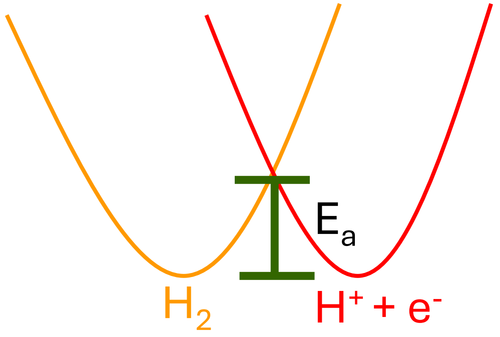
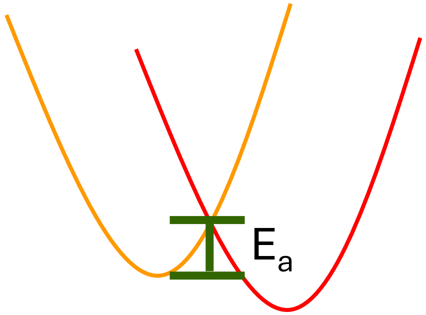


Figure 3.2. Electrode potential can be manipulated to trigger reduction (left) or oxidation (right). The thermodynamic equilibrium electrode potential (middle) corresponds to the situation where the oxidation and reduction processes are balanced.

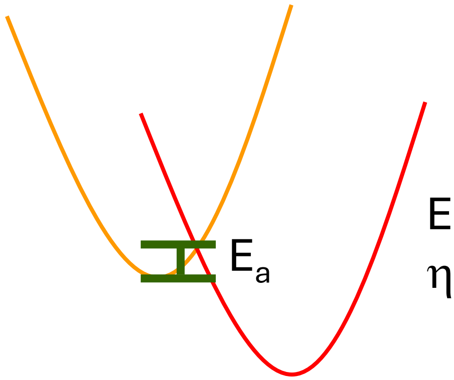


Equilibrium

E_a=200 mV
η =0 V

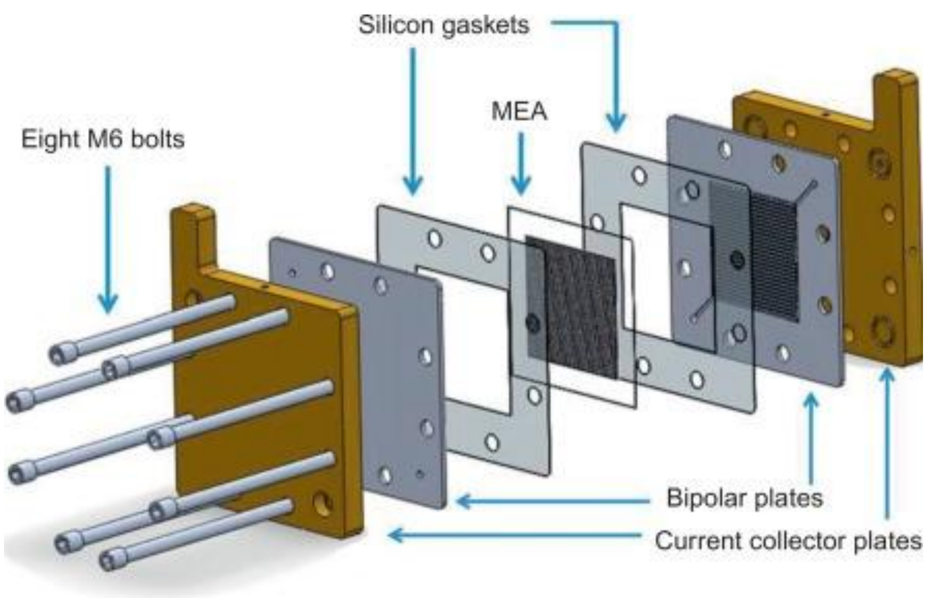


E_a=120 mV
η =100 mV

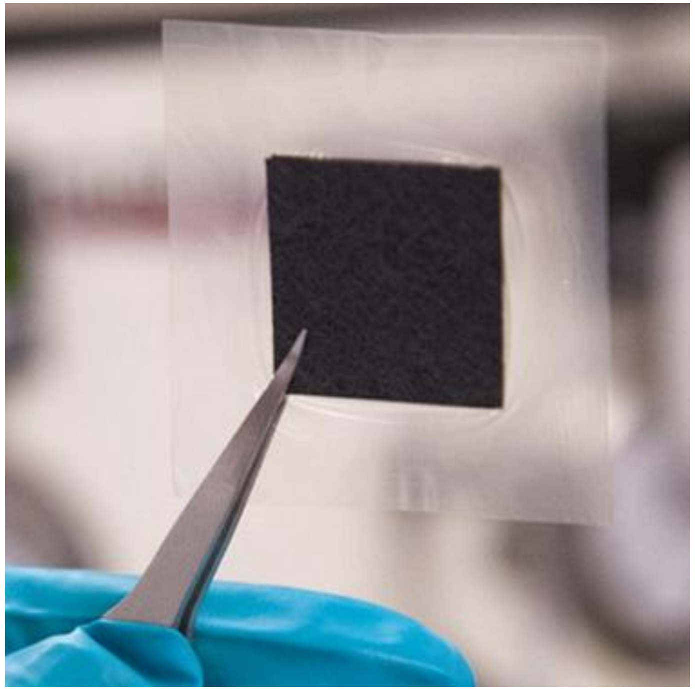


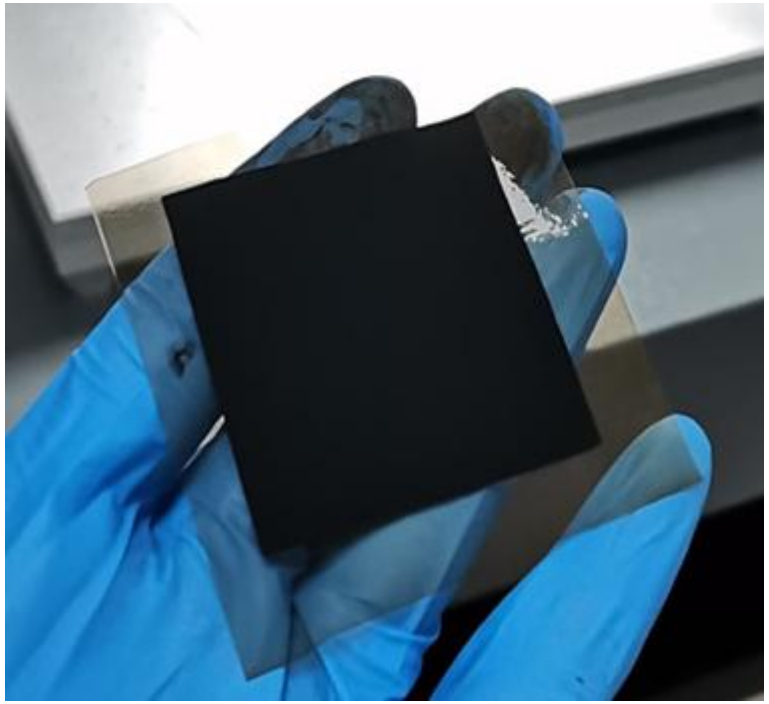
E_a=30 mV
η =300 mV

Membrane Electrode Assembly (MEA)



http://dx.doi.org/10.1016/B978-1-78242-363-8.00001-3

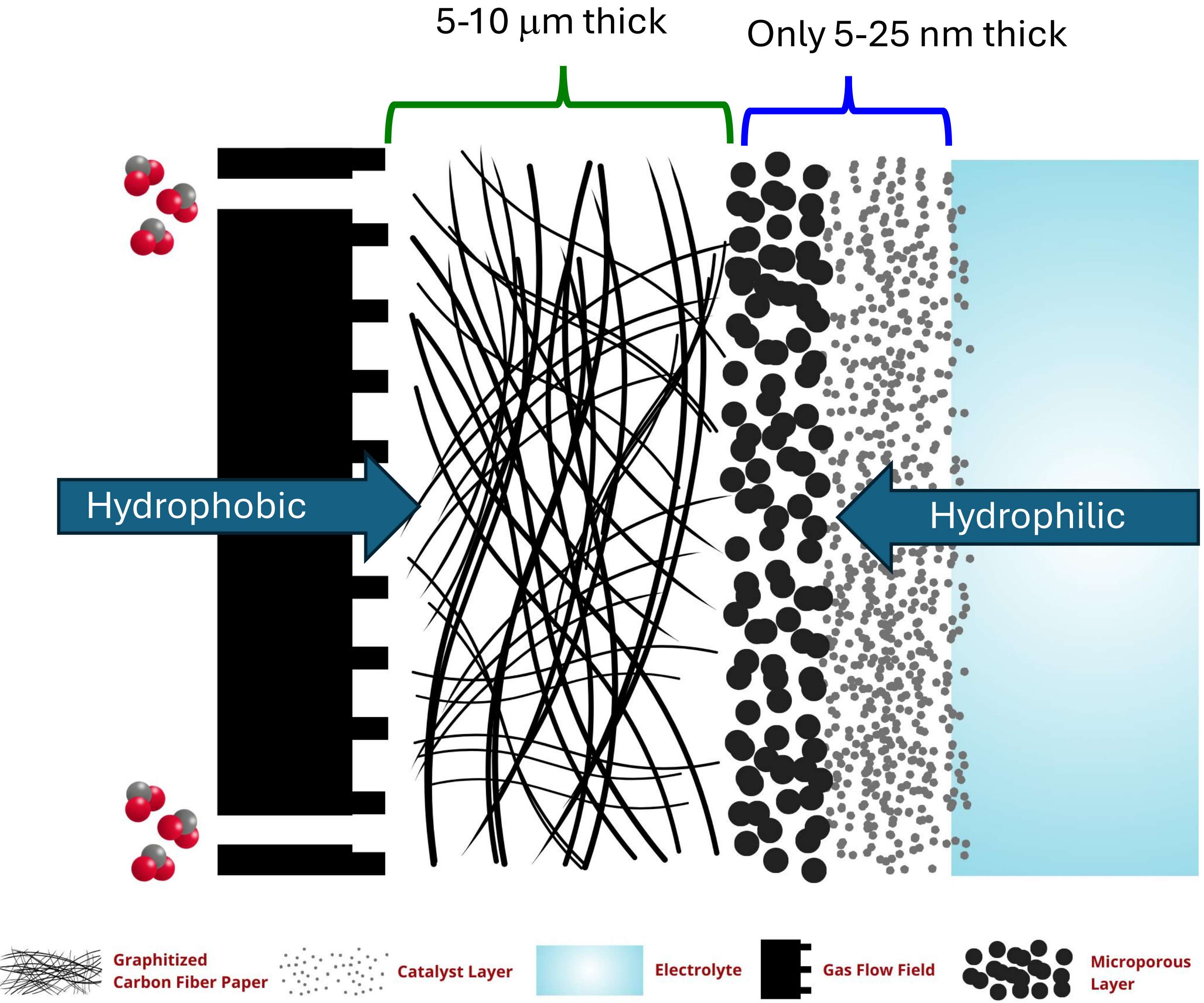




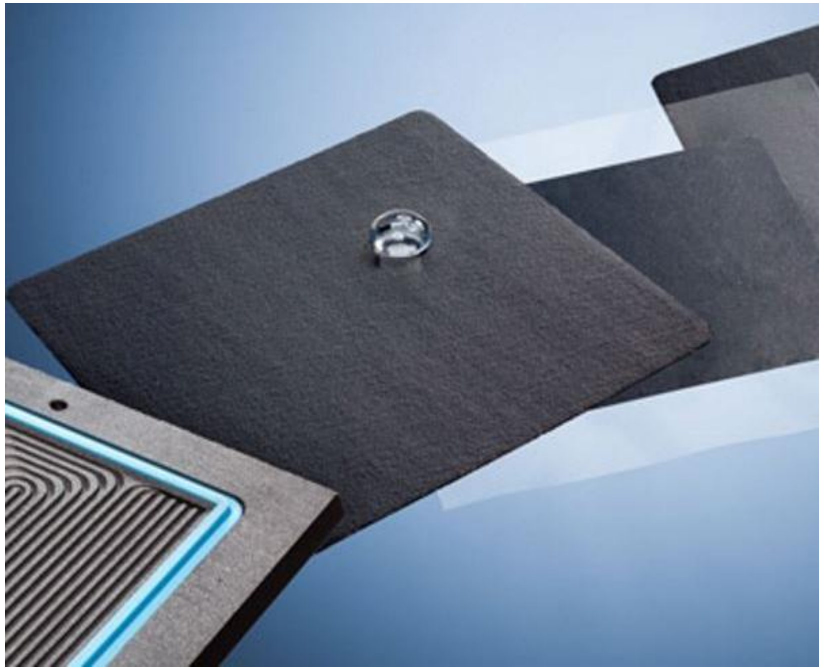
https://cheersonic-liquid.com/en/preparation-technology-of-membrane-electrode-for-pem-fuel-cell/

Contact between the membrane, catalyst, gas diffusion layer and reactants is crucial

Gas Diffusion Layers (GDL)



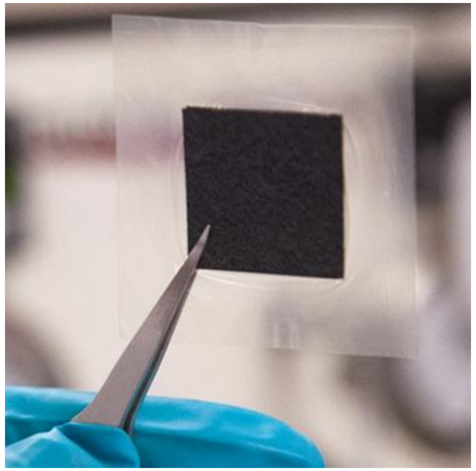
https://www.caplinq.com/renewable-energy/carbon-dioxide-electrolyzers/gas-diffusion-electrodes-for-co-electrolysis/



https://fuelcellcomponents.freudenberg-pm.com/Products/gas-diffusion-layers

Triple Phase Boundary

Reactions happen on the triple phase boundary

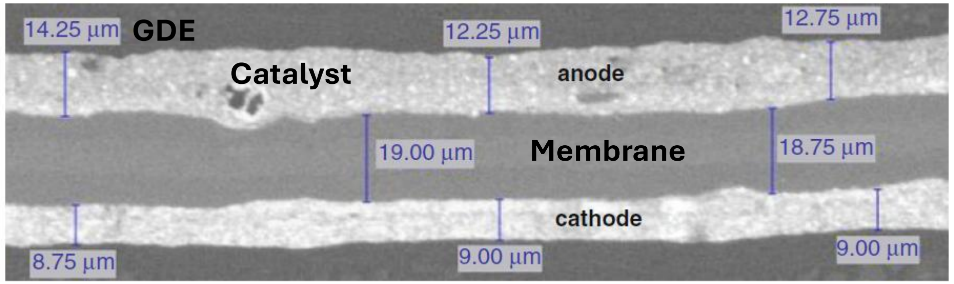


Reactants (H_2, O_2 – Gas)

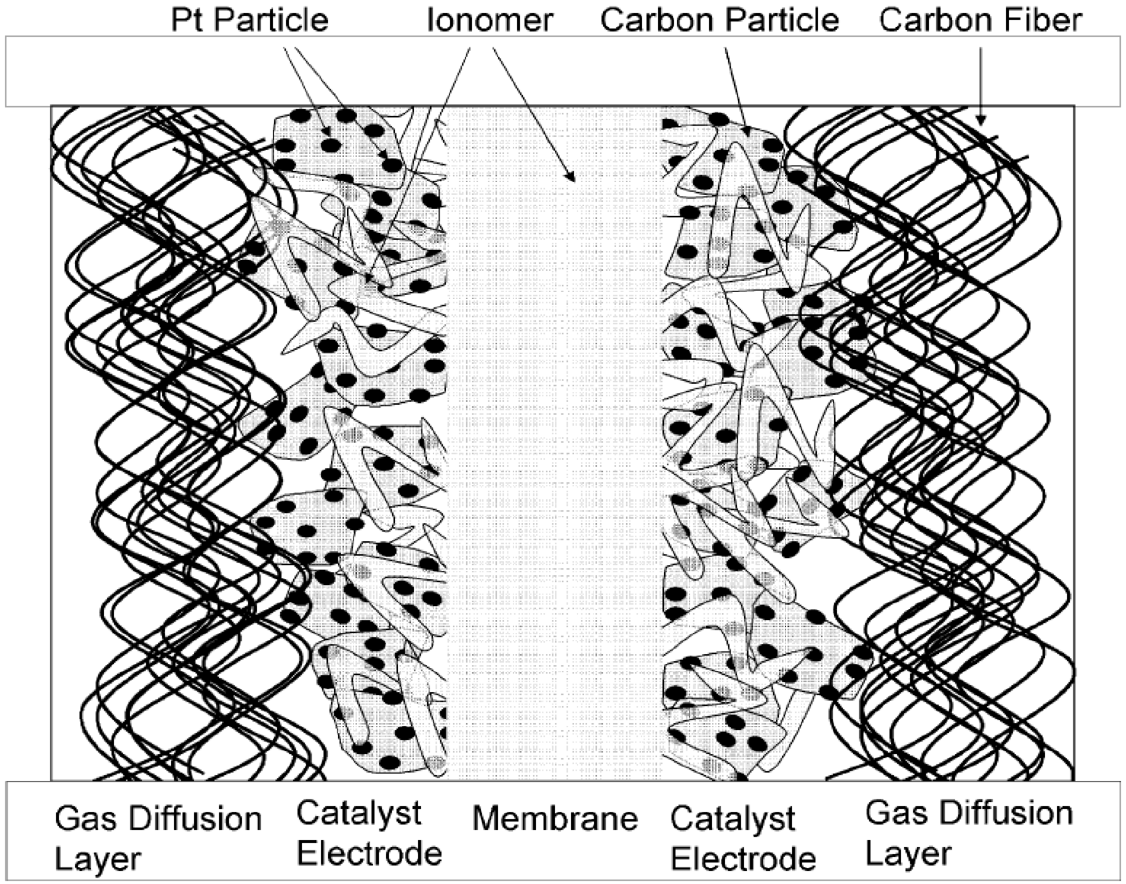
Catalyst (Pt – Solid)

Electrolyte (H^+/H_2O – Liquid)

SEM Cross section of an MEA

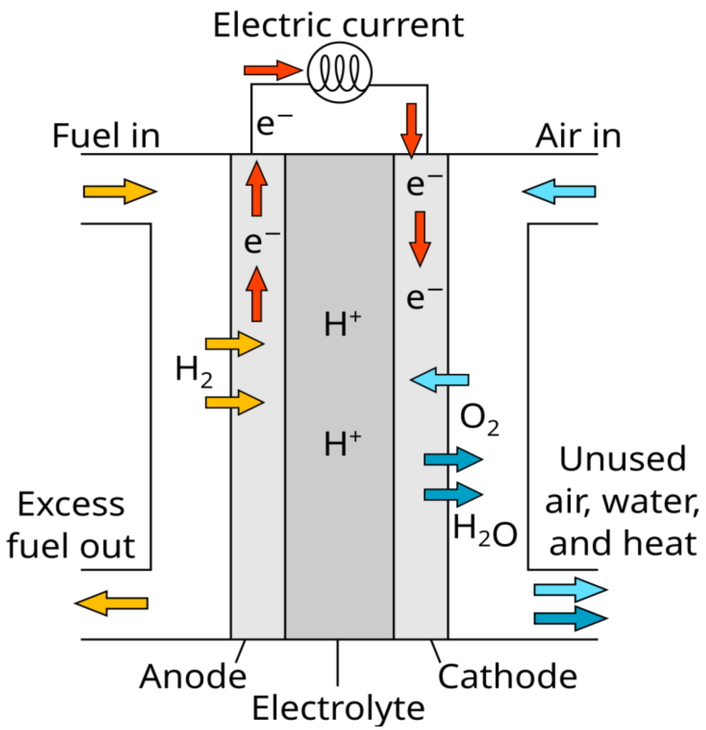


H. A. Gasteiger et al. (2008), Mini Micro Fuel Cells



S. J. Hamrock et al. (2013), Fuel Cells

Electrolytes on a fuel cell



PEM Fuel Cell

Ionically Conductive and not Electronically Conductive

“Liquid” electrolyte

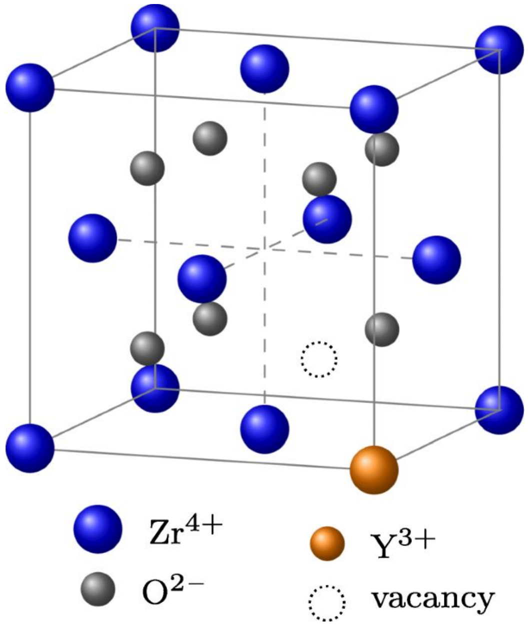
- Solid polymer membrane (e.g., **Nafion®**)
- **Ion conduction**: Protons (H^+) move from anode → cathode
- **Operating temperature**: ~60–90 °C (low-temperature system)

Solid electrolyte

Solid ceramic oxide: **yttria-stabilized zirconia, YSZ**

Ion conduction: Oxygen ions (O^{2-}) move from cathode → anode

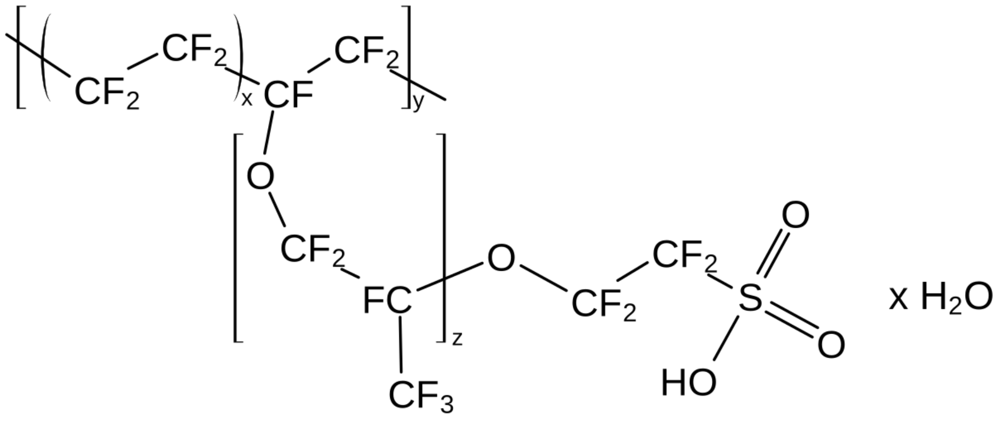
Operating temperature: 600–1,000 °C

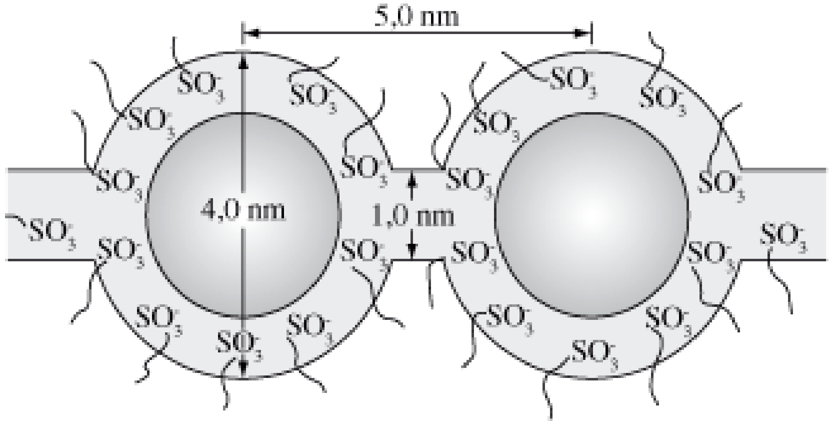


Cation exchange membrane

Nafion

perfluorosulfonic acid
(PFSA) polymer





Gierke model of Nafion

- This produces pores in the membrane, which protons can transfer through.
- Any ion has a hydration shell, thus the sulfonate won’t just take a H^+, but H^+-X H_2O where x can be from 6 to 21.

PFAS (polyfluoroalkyl substances)

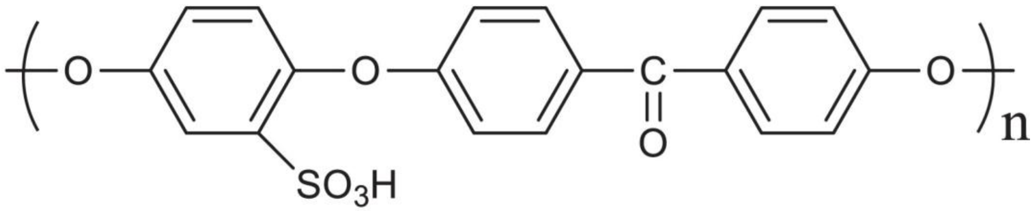
‘Forever Chemicals’

Environmentally Hazardous

EU and US are moving toward **PFAS restrictions**, which may affect Nafion’s long-term use

Alternative to Nafion

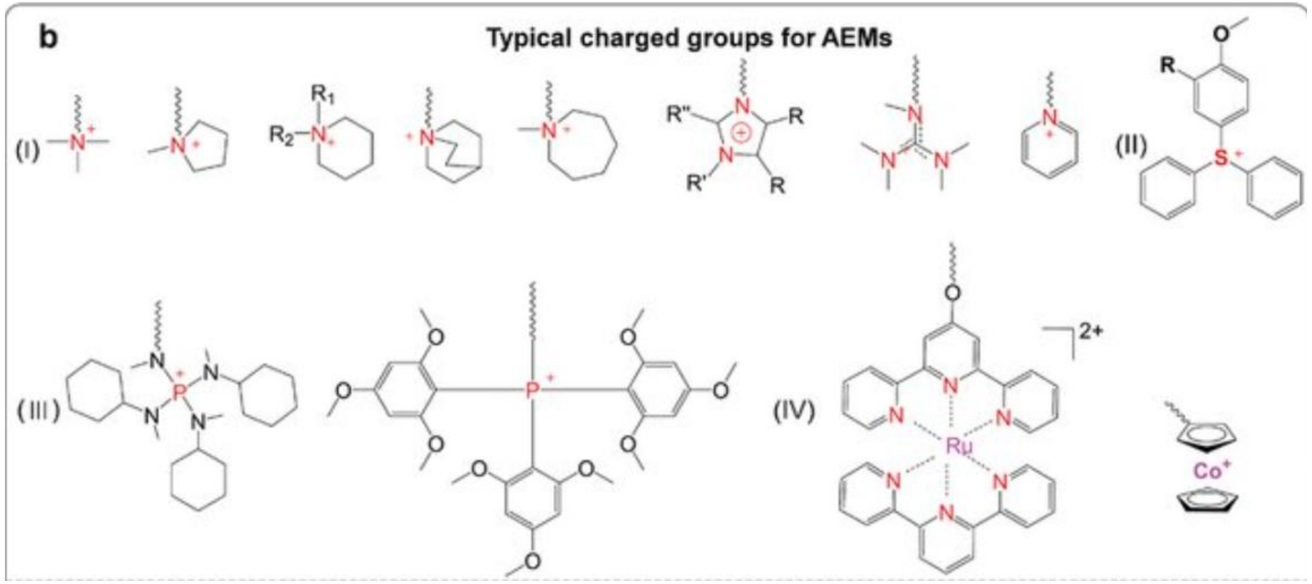
SPEEK (Sulfonated Polyether Ether Ketone)

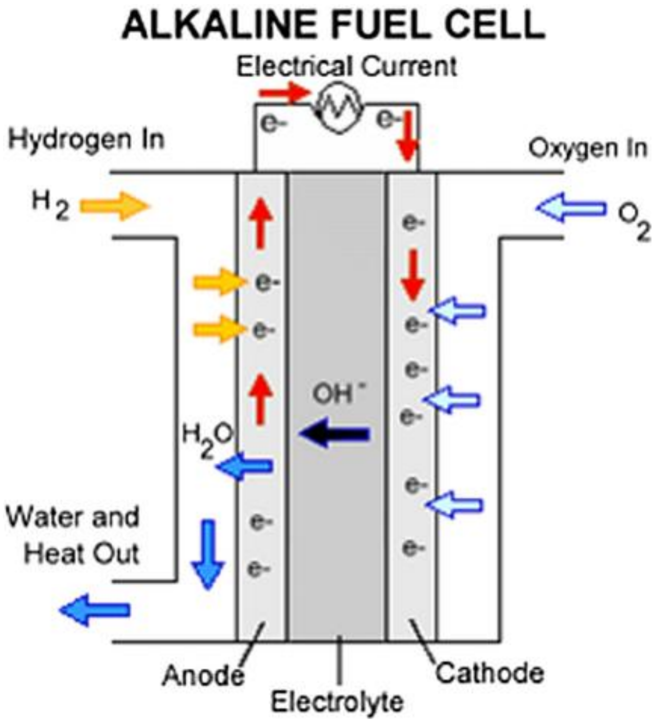


Anion exchange membrane

https://doi.org/10.1002/adfm.202207366

- Anion exchange membranes transfer OH^- instead of protons.
- They do this by having a positive nitrogen functional group attached to some form of a carbon chain





Challenges

- Lower ionic conductivity compared Nafion®-based PEMs
- Chemical stability: degradation of cationic groups in alkaline conditions

Enable alkaline fuel cells using non-precious metal catalysts

Concept check

Why can’t we use nickel (Ni) in PEM Fuel cell?

a) Nickel corrodes in the acidic environment of PEM systems

b) Nickel has poor catalytic activity for the hydrogen evolution reaction (HER)

c) Nickel requires high temperatures to function effectively

PEM electrolyzers operate in **strongly acidic conditions**, where **Ni dissolves rapidly**

That’s why **platinum group metals (PGMs)** like Pt and Ir are used - they’re stable and active in acid.

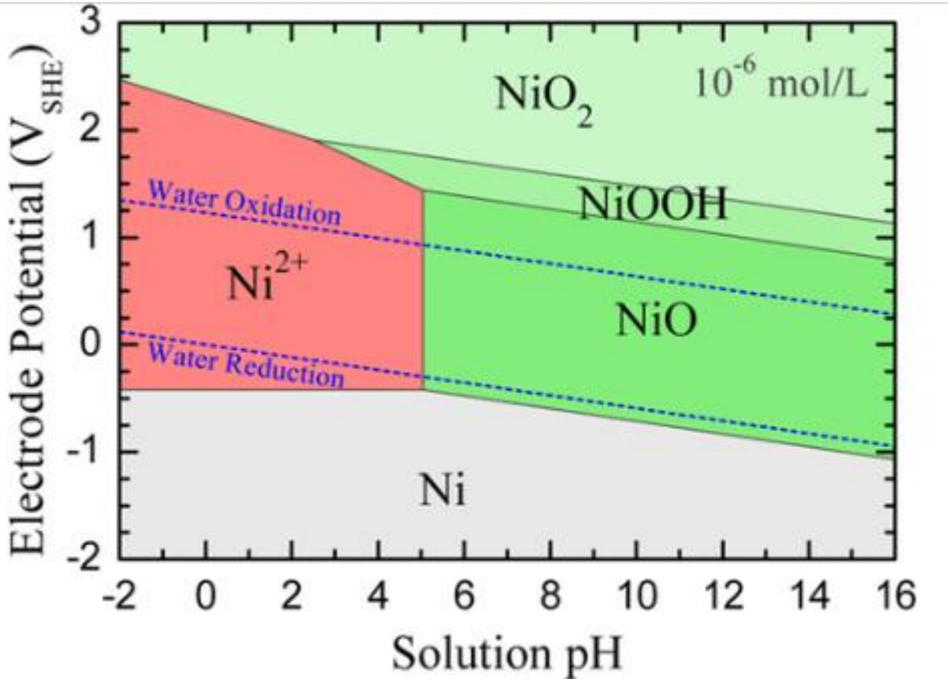
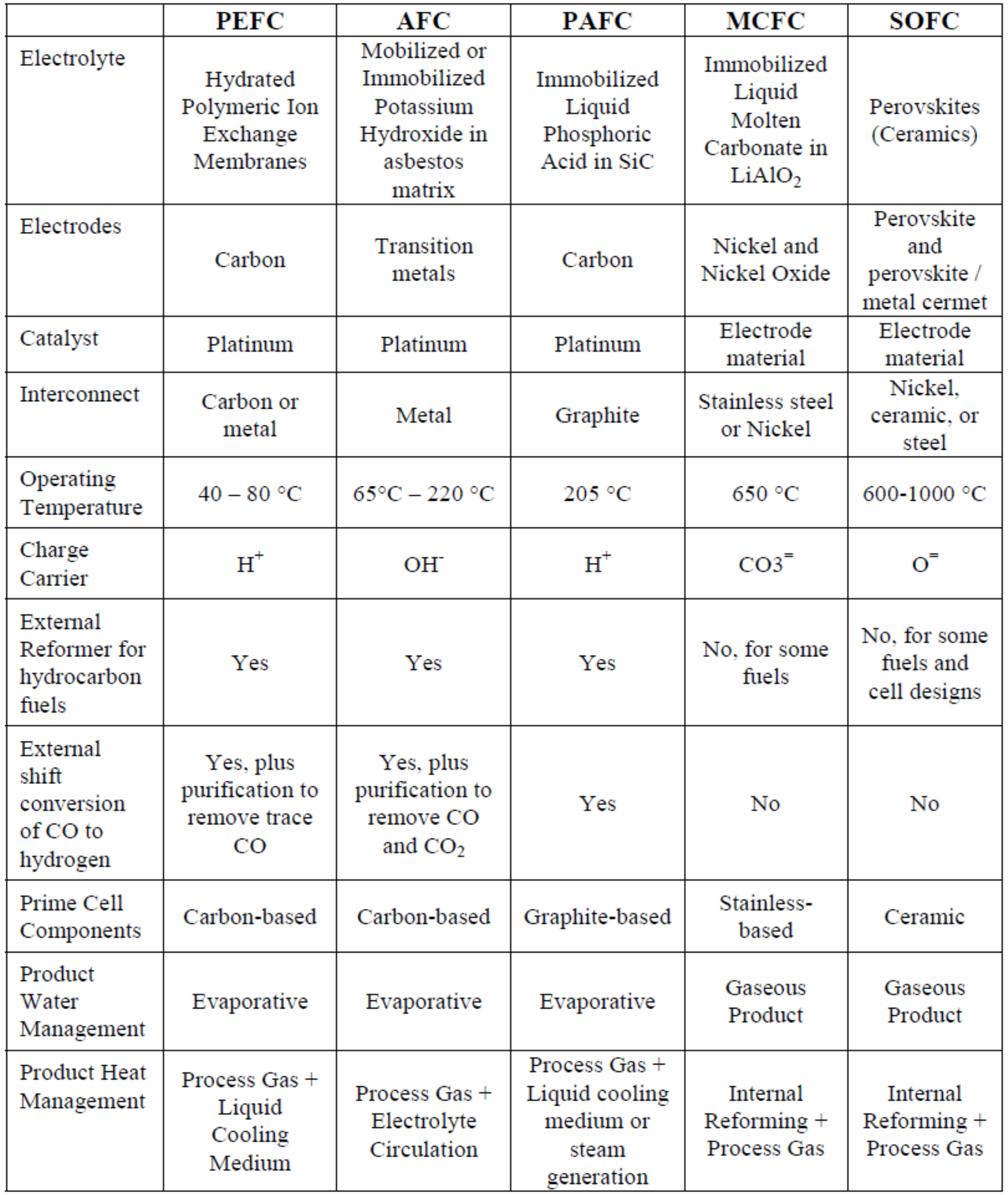


Table 1-1 Summary of Major Differences of the Fuel Cell Types



	PEFC	AFC	PAFC	MCFC	SOFC
Electrolyte	Hydrated Polymeric Ion Exchange Membranes	Mobilized or Immobilized Potassium Hydroxide in asbestos matrix	Immobilized Liquid Phosphoric Acid in SiC	Immobilized Liquid Molten Carbonate in $LiAlO_2$	Perovskites (Ceramics)
Electrodes	Carbon	Transition metals	Carbon	Nickel and Nickel Oxide	Perovskite and perovskite / metal cermet
Catalyst	Platinum	Platinum	Platinum	Electrode material	Electrode material
Interconnect	Carbon or metal	Metal	Graphite	Stainless steel or Nickel	Nickel, ceramic, or steel
Operating Temperature	40 – 80 °C	65°C – 220 °C	205 °C	650 °C	600-1000 °C
Charge Carrier	H^+	OH^-	H^+	$CO3^=$	$O^=$
External Reformer for hydrocarbon fuels	Yes	Yes	Yes	No, for some fuels	No, for some fuels and cell designs
External shift conversion of CO to hydrogen	Yes, plus purification to remove trace CO	Yes, plus purification to remove CO and CO_2	Yes	No	No
Prime Cell Components	Carbon-based	Carbon-based	Graphite-based	Stainless-based	Ceramic
Product Water Management	Evaporative	Evaporative	Evaporative	Gaseous Product	Gaseous Product
Product Heat Management	Process Gas + Liquid Cooling Medium	Process Gas + Electrolyte Circulation	Process Gas + Liquid cooling medium or steam generation	Internal Reforming + Process Gas	Internal Reforming + Process Gas

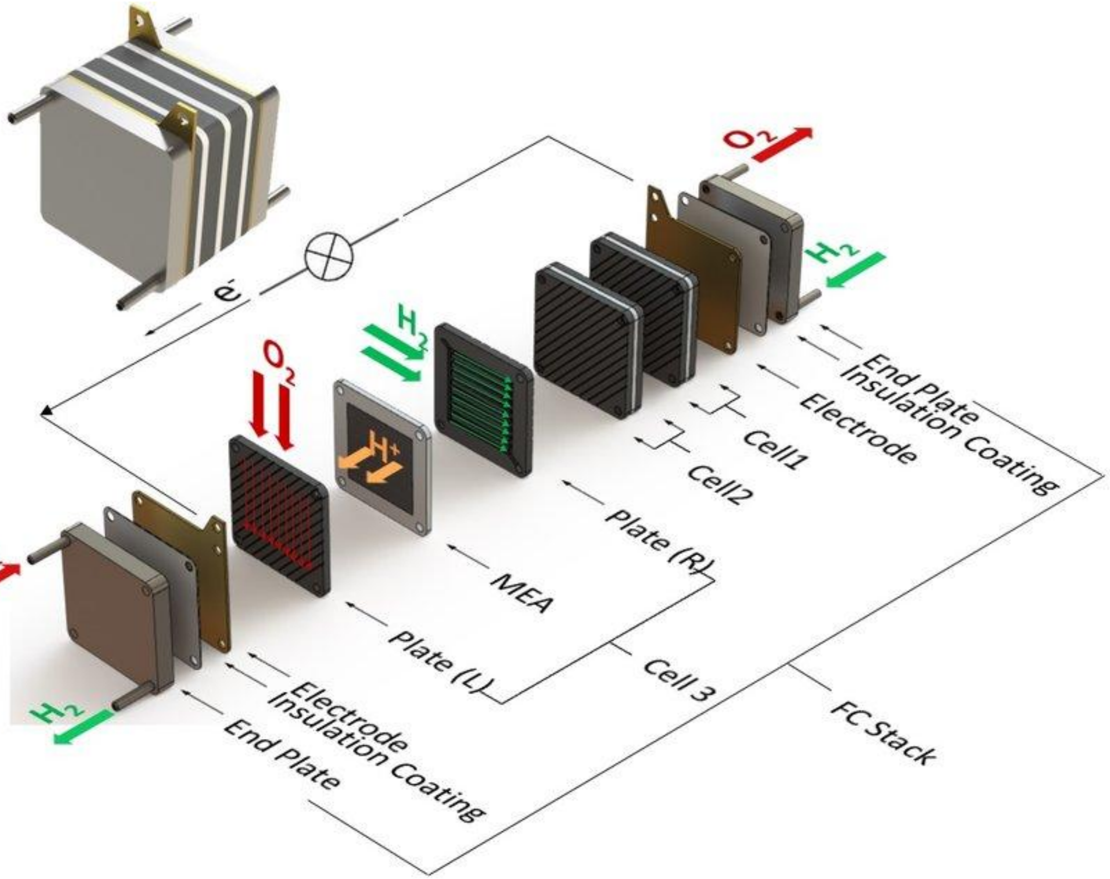
Fuel Cell Handbook, US DOE

- **PEFC → Proton Exchange Fuel Cell** (often also written as PEMFC, Proton Exchange Membrane Fuel Cell)
- **AFC → Alkaline Fuel Cell**
- **PAFC → Phosphoric Acid Fuel Cell**
- **MCFC → Molten Carbonate Fuel Cell**
- **SOFC → Solid Oxide Fuel Cell**

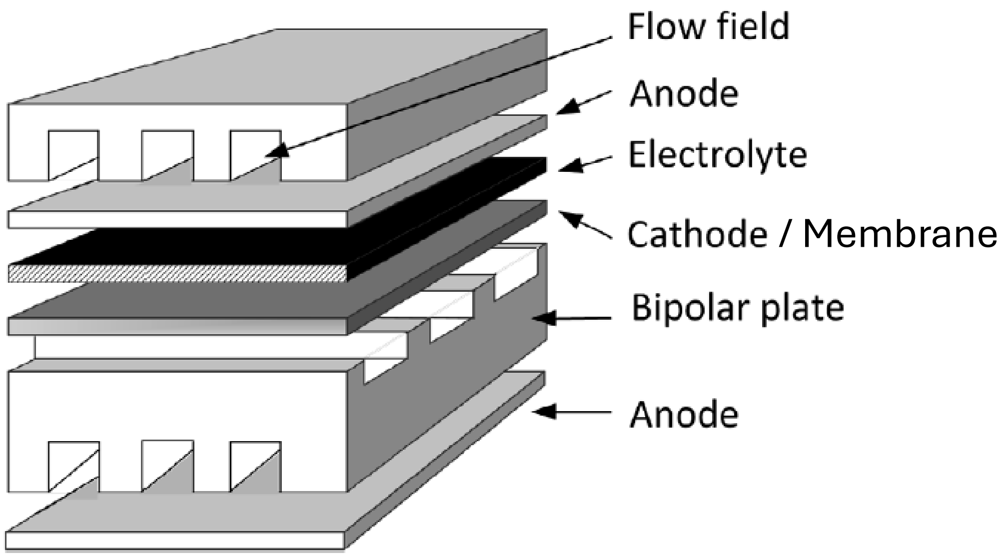
Fuel cell stack

A single fuel cell consists of a membrane electrode assembly (MEA) and two flow-field plates delivering about 0.5 and 1V voltage (too low for most applications)

The power output of a given fuel cell stack will depend on its size. Increasing the number of cells in a stack increases the voltage



- The graphite plate in between serves 2 purposes:
  - Introduces fuel into the chamber (H_2 / O_2)
  - Acts as an electrical contact. Since one side is an anode and the other a cathode, this is called a bipolar plate.



Source: *Electrochemical Engineering, T. F. Fuller and J. N. Harb*

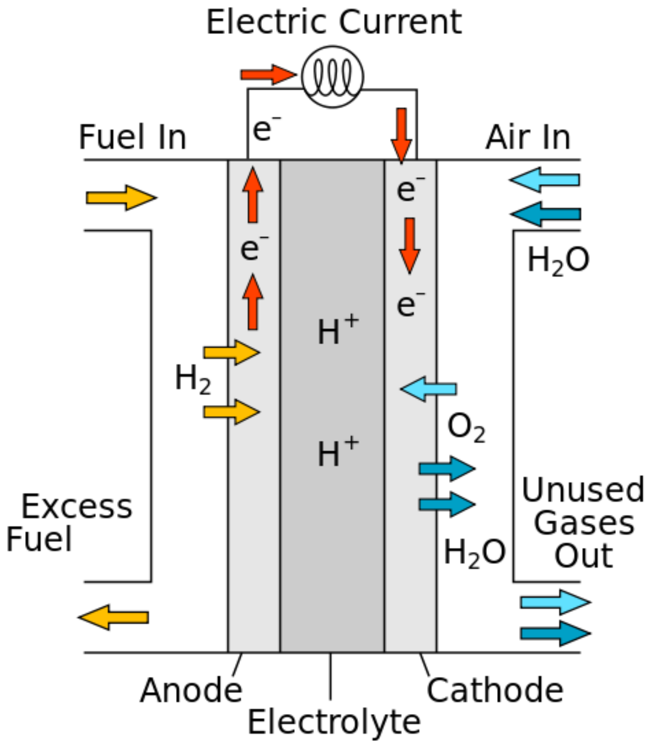
Break

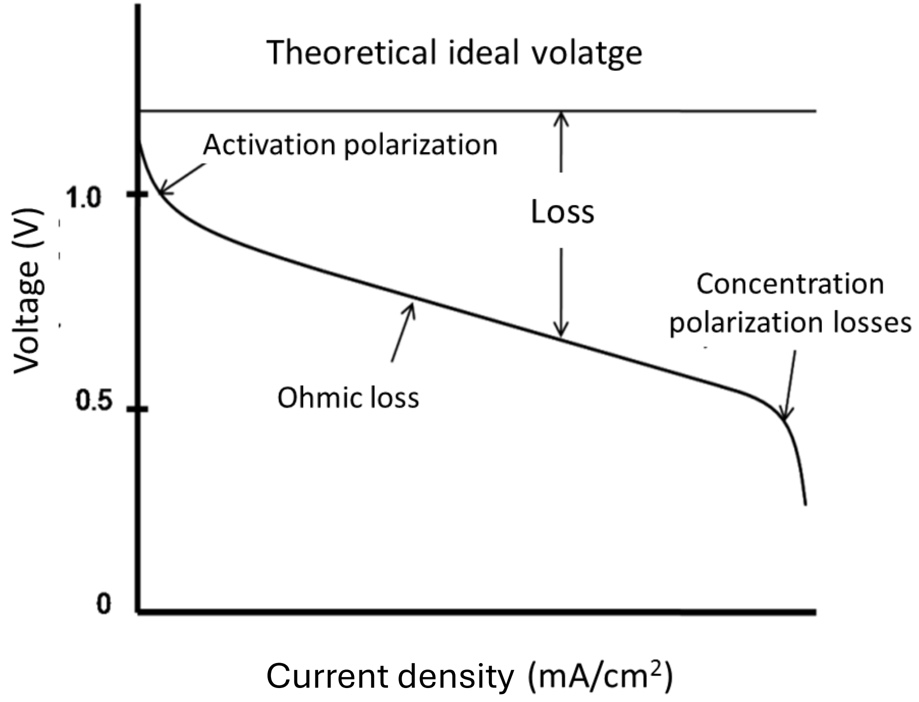
PEM Fuel cells

Places for potential energy loss

- Proton transfer
- Electron transfer
- Anode
- Cathode

- Thermodynamics
- Kinetics
- Ohmic Losses
- Mass Transfer





Thermodynamics

- Since H_2 and O_2 both are elements, their G_f, & H_f = 0 thus this is all about the H_2O. For H_2O:
  - G^f=-237 KJ/mol,
  - H^f=-286 KJ/mol (called Higher Heating Value- (HHV))

$$\eta_{Fuel\ Cell} = \frac{\Delta G}{\Delta H} = \frac{237\ kJ/mol}{286\ kJ/mol}\ or\ \frac{1.23\ V}{1.48\ V} = 83\%$$

What happens if we change the temperature?

Thermodynamics

Anode: $H_2 \rightarrow 2H^+ + 2e^-$

Cathode: $\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$$

$$\Delta G = -nFE$$

$$\Delta G^o = -nFE^o$$

$$\Delta G = \Delta H - T\Delta S$$

Nernst Equation: $E_{cell} = E^o - \frac{R.T}{n.F} \ln Q$

ΔG – Change in Gibbs Free Energy of a Reaction (kJ/mol)

ΔH – Change in Enthalpy of a Reaction (kJ/mol)

ΔS – Change in Entropy of a Reaction (kJ/mol.K)

E_{cell} – Thermodynamic Cell Potential (V)

T – Temperature (K)

R – Gas Constant (8.314 J/mol.K)

F – Faraday's Constant (96485.33 A.s/mol)

n – No. of electrons transferred in a cell reaction

Q – Equilibrium Constant $\left(\frac{\prod \text{(Activity of Products)}}{\prod \text{(Activity of Reactants)}}\right)$

For an ideal gas, Activity = Mole Fraction

o – Standard State/Reference State – Unit Activity

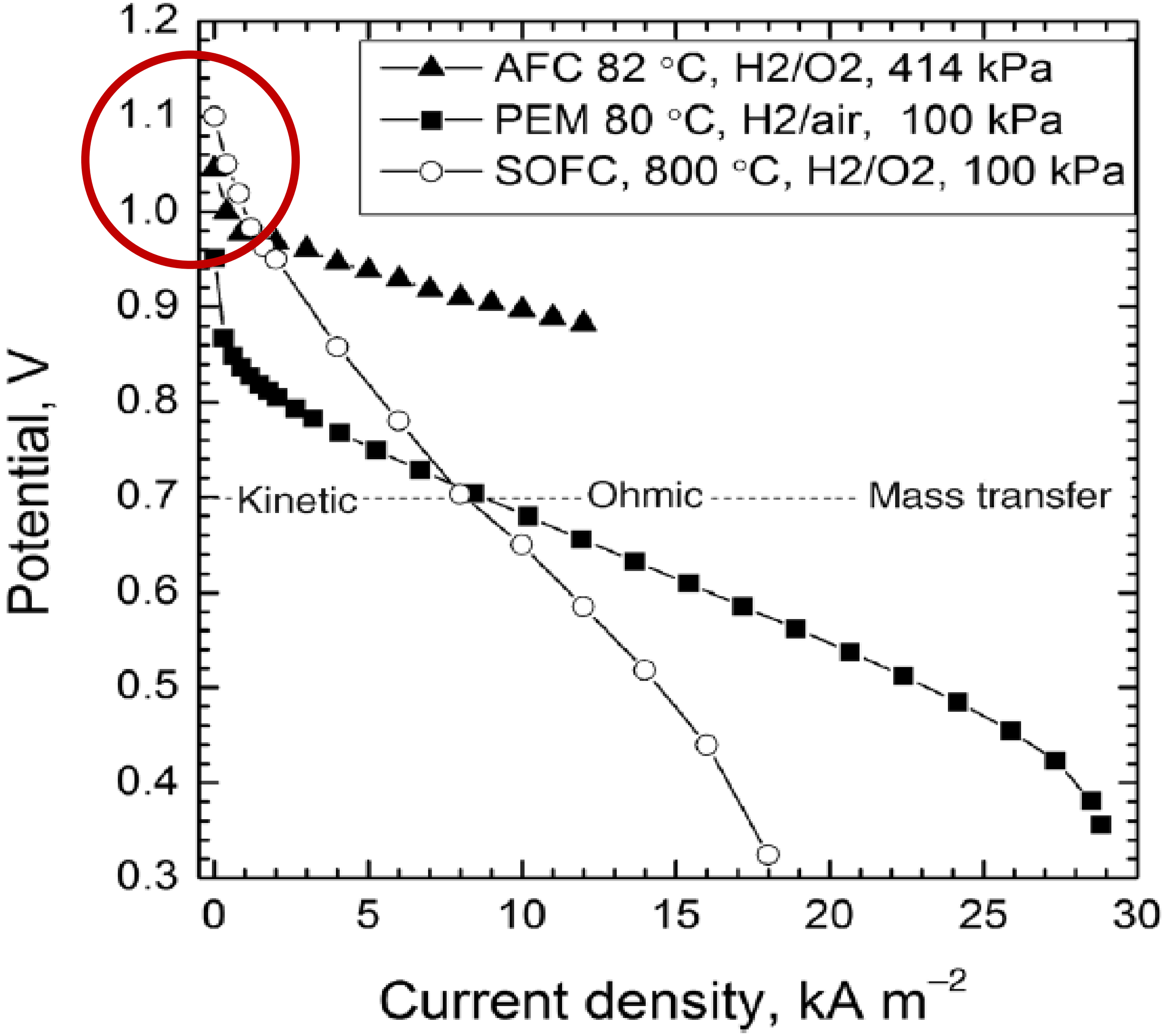
Lets assume, $Q = 1$

$$\Delta G = -nFE_{cell}$$

Temperature (°C)	ΔG (kJ/mol)
25	−237.2
80	−228.2
100	−225.2
200	−220.4
400	−210.3
600	−199.6
800	−188.6
1000	−177.4

What is the thermodynamic cell potential for a H_2 PEM fuel cell at 80 °C?

Thermodynamics



Source: *Electrochemical Engineering, T. F. Fuller and J. N. Harb*

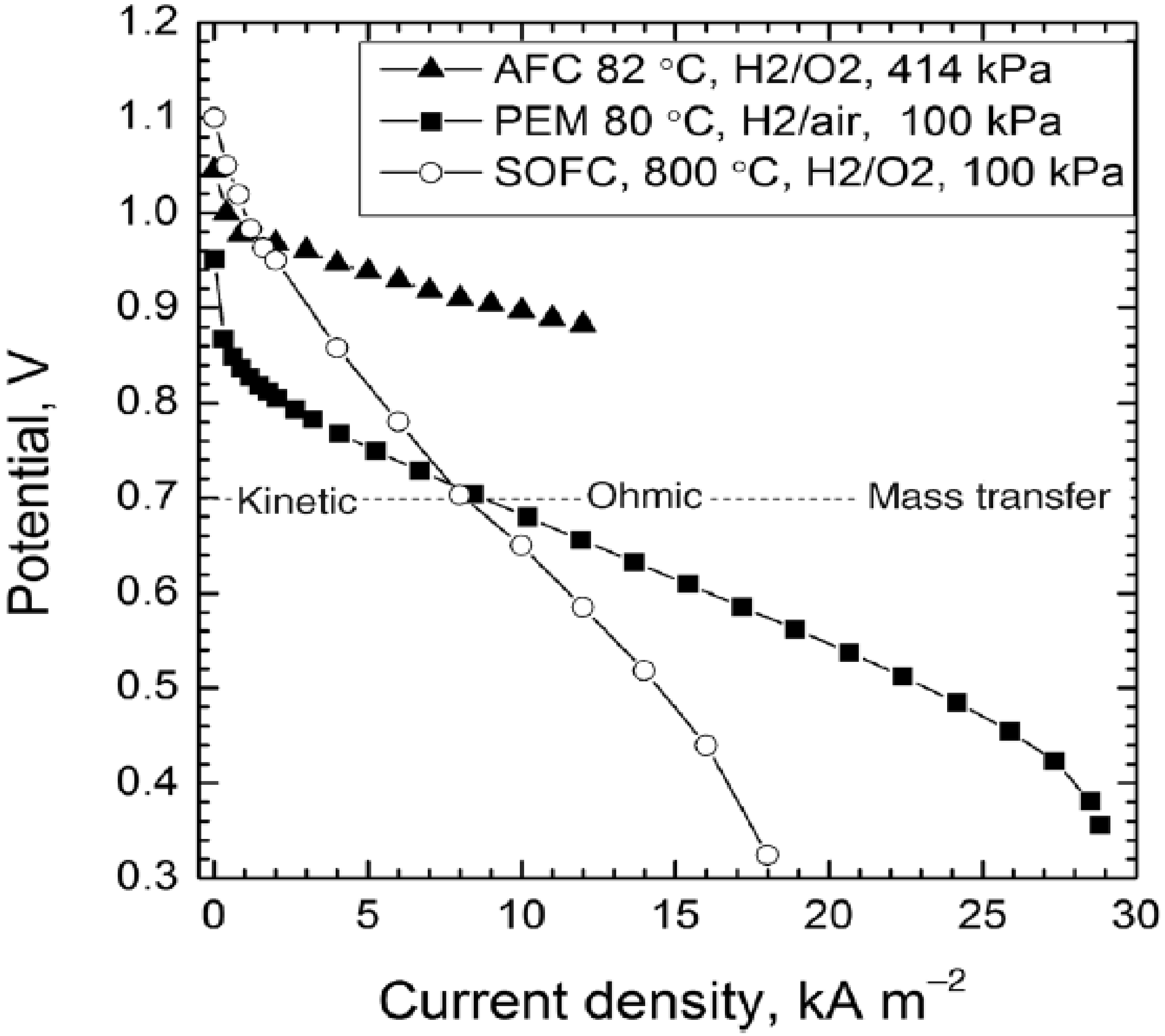
Nernst Equation: $E_{cell} = E^o - \frac{R.T}{n.F} \ln Q$

Lets assume, Q = 1

$$\Delta G = -nFE_{cell}$$

Temperature (°C)	**ΔG (kJ/mol)**	**E_{cell} (V)**
25	−237.2	1.23
80	−228.2	1.18
100	−225.2	1.17
200	−220.4	1.14
400	−210.3	1.09
600	−199.6	1.04
800	−188.6	0.98
1000	−177.4	0.92

Thermodynamics



Source: *Electrochemical Engineering, T. F. Fuller and J. N. Harb*

Nernst Equation: $E_{cell} = E^{o} - \frac{R.T}{n.F} \ln Q$

Lets assume, Q = 1

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Temperature (°C)	**ΔG (kJ/mol)**	**E_{cell} (V)**
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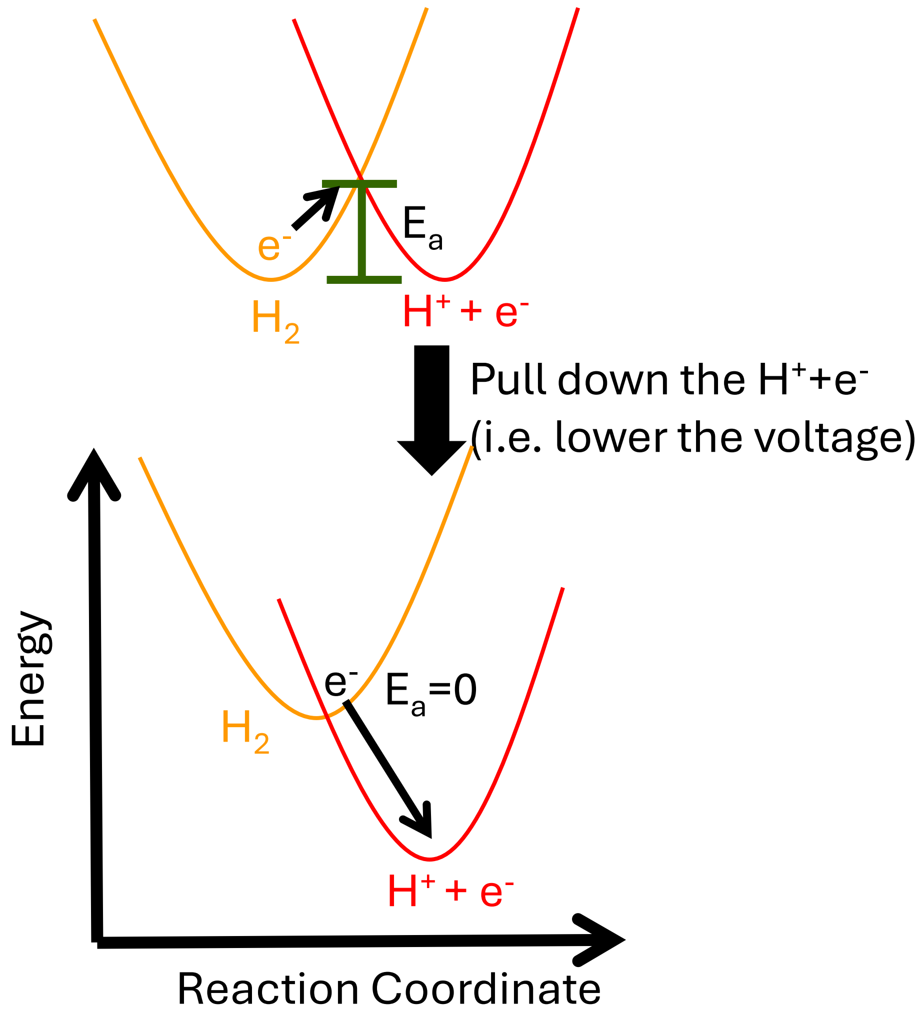
400	−210.3	1.09
600	−199.6	1.04
800	−188.6	0.98
1000	−177.4	0.92

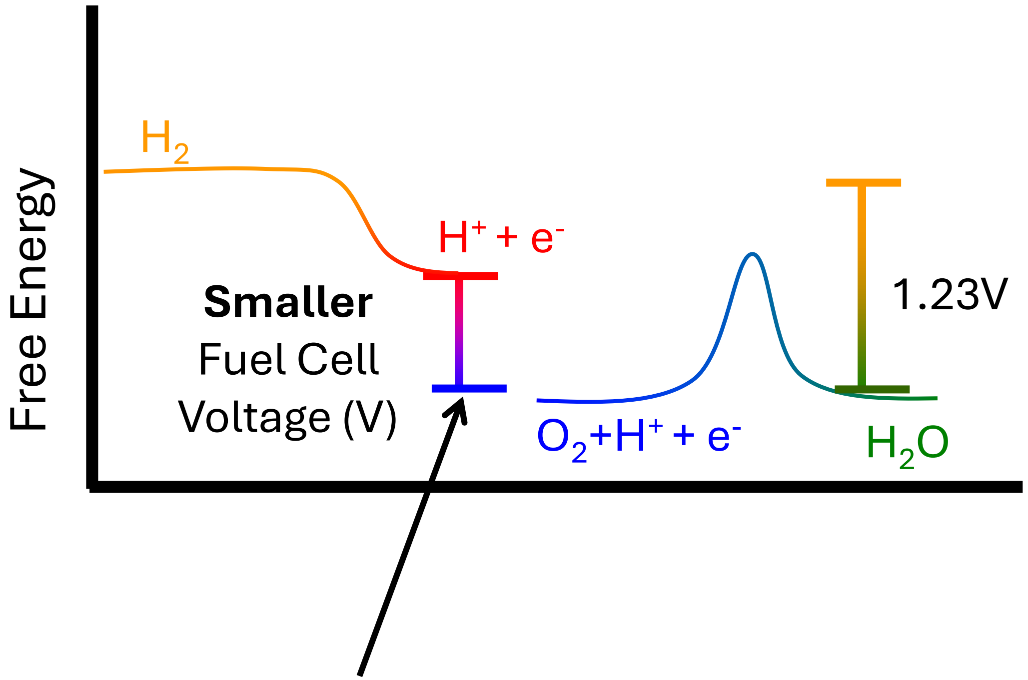
At higher temperatures the efficiency drops!

Kinetic losses: Anode and cathode catalysis

- Imagine each species as a parabolic energy state

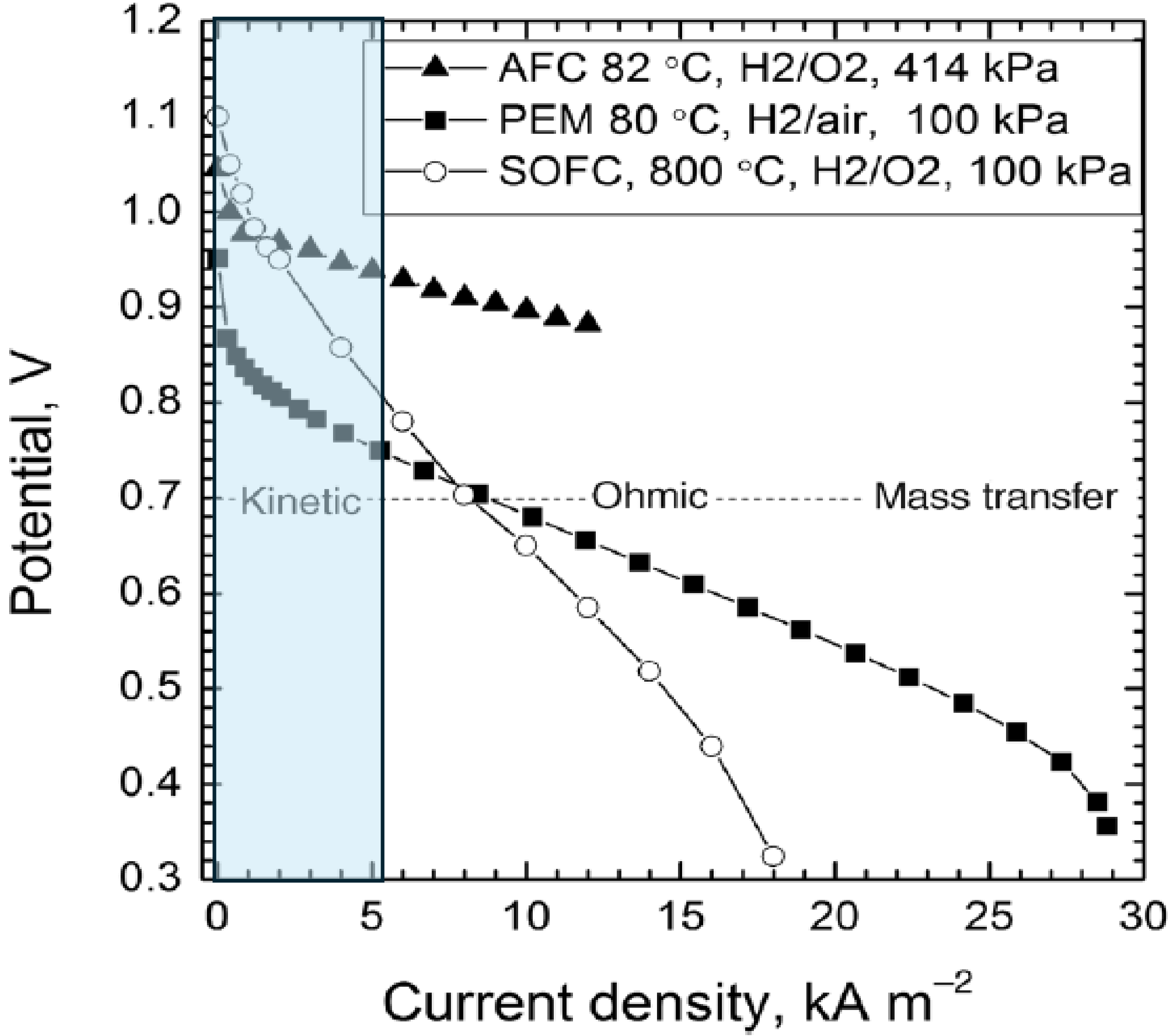
Anode: $H_2 \rightarrow 2H^+ + 2e^-$





- The fuel cell voltage needs to drop to allow for the catalysis to work.
- A similar issue occurs for the cathode reaction except the O_2 side goes up instead of H_2O side going down.

Kinetics



1 kA.m^{-2} = 0.1 A.cm^{-2}

Source: *Electrochemical Engineering, T. F. Fuller and J. N. Harb*

- Kinetics determine the behavior at Low current densities

Exponential relationship (J-V)

$$\boldsymbol{V = E_{cell} - \eta}$$

V – Actual/Measured Cell Potential

E_{cell} – Thermodynamic Cell Potential

η – Over Potential

Relationship between J and η in the kinetic regime is given by the

Butler-Volmer Equation

Kinetics

Butler-Volmer Equation

O + ne$^-$ ⇌ R

$$V = E_{cell} - \eta$$

V – Actual/Measured Cell Potential
E_{cell} – Thermodynamic Cell Potential
η – Over Potential

$$j = j_o\left[exp\left(-\frac{\alpha_A.n_e.F.\eta}{RT}\right) - exp\left(\frac{\alpha_c.n_e.F.\eta}{RT}\right)\right]$$

j – Current density (mA/cm^2)
j_o – Exchange Current density (mA/cm^2)
α_A, α_c – Anodic and Cathodic charge transfer co-efficients
n_e – No. of electrons transferred per half reaction (4 for ORR)
F – Faraday's Constant (96485.33 A.s/mol)
R – Gas Constant (8.314 J/mol.K)
T – Temperature (K)

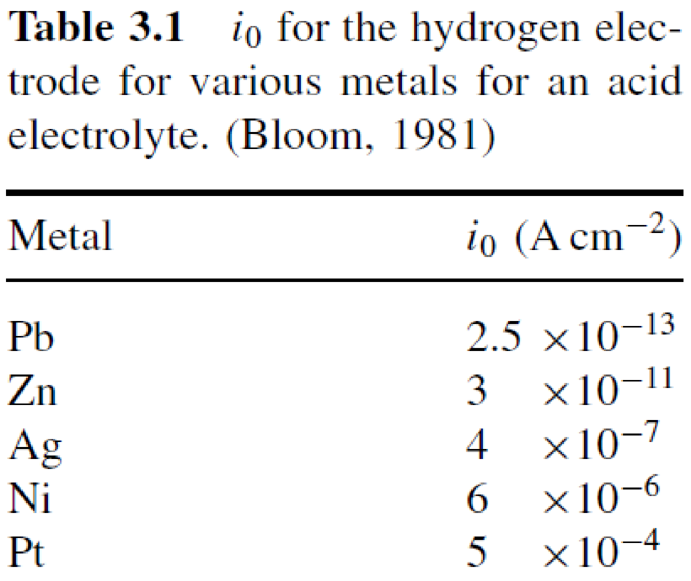


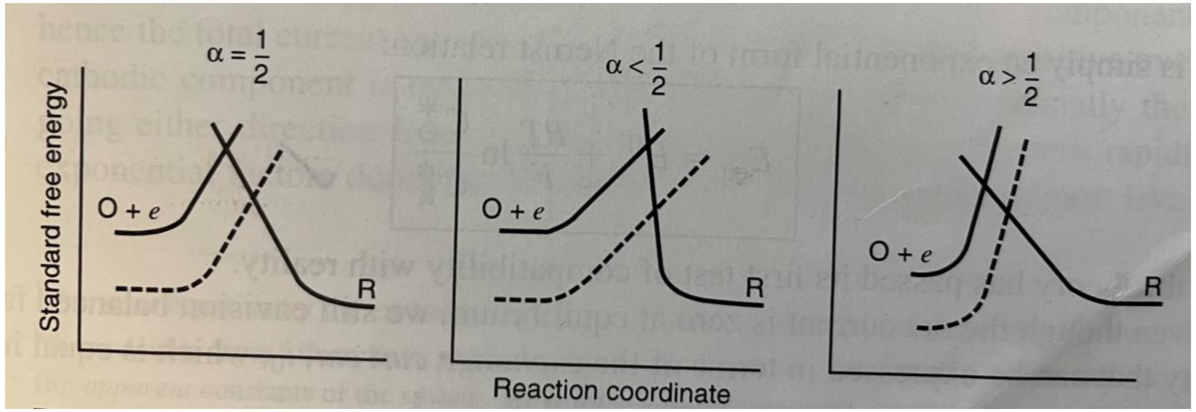
Table 3.1 i_0 for the hydrogen electrode for various metals for an acid electrolyte. (Bloom, 1981)

Metal	i_0 (A cm^{-2})
Pb	2.5×10^{-13}
Zn	3×10^{-11}
Ag	4×10^{-7}
Ni	6×10^{-6}
Pt	5×10^{-4}

Exchange Current Density

- Measure of intrinsic rate of the electrochemical reaction. Intrinsic current density at equilibrium.
- Higher exchange current density – Faster Kinetics
- Lower exchange current density – Sluggish Kinetics

Charge Transfer Co-efficient



Indicator of the symmetry of the free energy barrier for the forward and backward reactions

Kinetics

Butler-Volmer Equation

$\mathrm{O} + n\mathrm{e}^- \rightleftharpoons \mathrm{R}$

$$j = j_o\left[exp\left(-\frac{\alpha_A . n_e . F . \eta}{RT}\right) - exp\left(\frac{\alpha_c . n_e . F . \eta}{RT}\right)\right]$$

j – Current density (mA/cm^2)
j_o – Exchange Current density (mA/cm^2)
α_A, α_c – Anodic and Cathodic charge transfer co-efficients
n_e – No. of electrons transferred per half reaction (4 for ORR)
F – Faraday's Constant (96485.33 A.s/mol)
R – Gas Constant (8.314 J/mol.K)
T – Temperature (K)

$$V = E_{cell} - \eta$$

V – Actual/Measured Cell Potential
E_{cell} – Thermodynamic Cell Potential
η – Over Potential

At large overpotentials,

$$j = j_o\left[-exp\left(\frac{\alpha_c . n_e . F . \eta}{RT}\right)\right]$$

Tafel Equation

(-ve sign) - Sign Convention

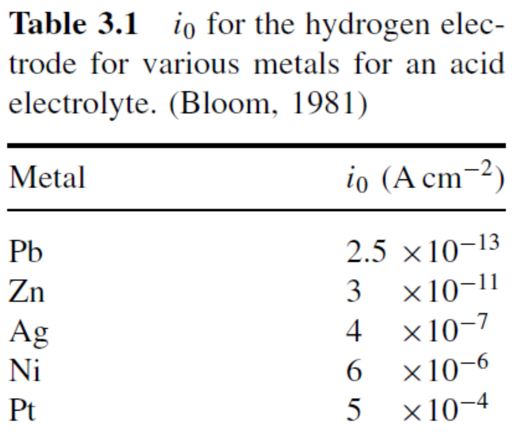
(Cathodic currents are taken as negative)

Exercise

- If you have Ni and Pt, how much more Ni would you need to achieve the same current? Assume same Tafel slope for each and each has the same surface area (i.e. same m^2/g).

Answer- If the Tafel slope is the same then it just comes down to the exchange current density (i_o). Since Ni has an i_o 100 times worse than Pt (From Table 3.1), we need 100 times more Ni than Pt.

- If you had either 1 cm^2 of Ni or Pt, how much overpotential would you need for each to produce 10 mA. Assume both have a Tafel slope of 30 mV.



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Pb	2.5×10^{-13}
Zn	3×10^{-11}
Ag	4×10^{-7}
Ni	6×10^{-6}
Pt	5×10^{-4}

Answer: Use the Tafel Equation

For Ni we have 30 mV*Ln((10 mA/ 1 cm^2)/6 x 10^{-6})= 220 mV

For Pt we have 30 mV*Ln((10 mA/ 1cm^2)/5 x 10^{-4})= 90 mV

$$\eta = ALn\left(\frac{i}{i_0}\right)$$

- Ni is not stable in acid. Why is that bad?- Answer: We transfer protons, in these fuel cells. Protons are basically acid.

KINETICS

Butler-Volmer Equation

$$O + ne^- \rightleftharpoons R$$

$$j = j_o\left[exp\left(-\frac{\alpha_A.n_e.F.\eta}{RT}\right) - exp\left(\frac{\alpha_c.n_e.F.\eta}{RT}\right)\right]$$

Tafel Equation

$$j = j_o\left[-exp\left(\frac{\alpha_c.n_e.F.\eta}{RT}\right)\right]$$

Tafel Equation is simpler and more useful

Absolute value of current densities,

$$j = j_o\left[exp\left(\frac{\alpha_c.n_e.F.\eta}{RT}\right)\right]$$

$$\eta = \frac{R.T}{\alpha_c.n_e.F}\ln(j_o) + \frac{2.303\ R.T}{\alpha_c.n_e.F}.\log(j)$$

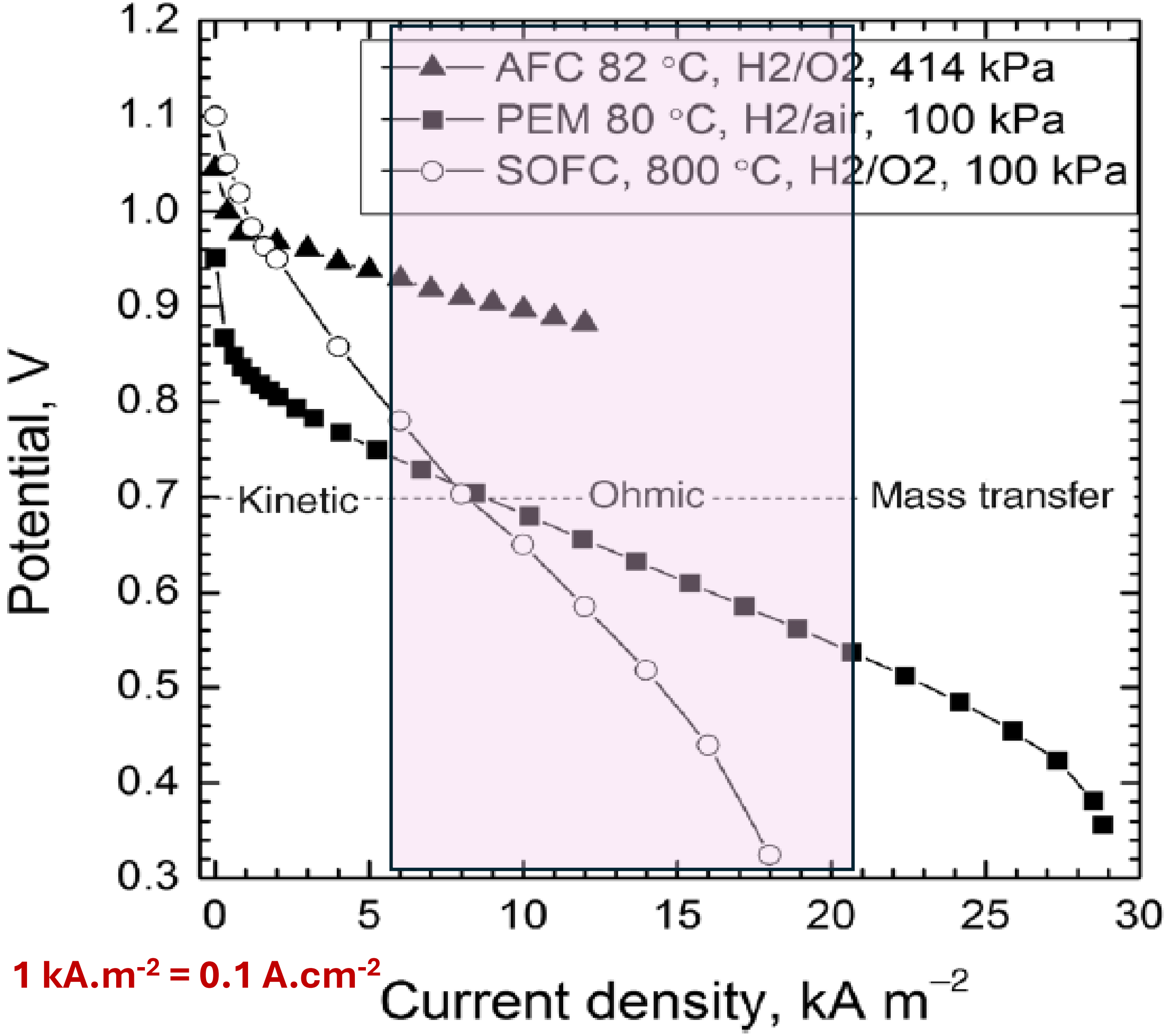
$$\text{Tafel Slope} = \frac{2.303\ R.T}{\alpha_c.n_e.F}\ \text{(mV/decade)}$$

- We can perform experiments, measure j and η
- Calculate j_o and α_c

Tafel slope indicates the change in mV that causes a 10 fold increase in current density

Lower Tafel slope indicates that the reaction is more efficient,
small increase in overpotential to achieve significant increase in current

Ohmic losses



1 kA.m^{-2} = 0.1 A.cm^{-2}

Source: *Electrochemical Engineering, T. F. Fuller and J. N. Harb*

- Dominant at moderate current densities
- "Ohmic Polarization"

- Linear I-V Response

- Ohmic Resistance determined by slope

$$R_\Omega = \frac{\Delta V}{\Delta I}$$

- Ohmic transport of species
  - Electrons through the catalyst and the current collector
  - Ions through the electrolyte

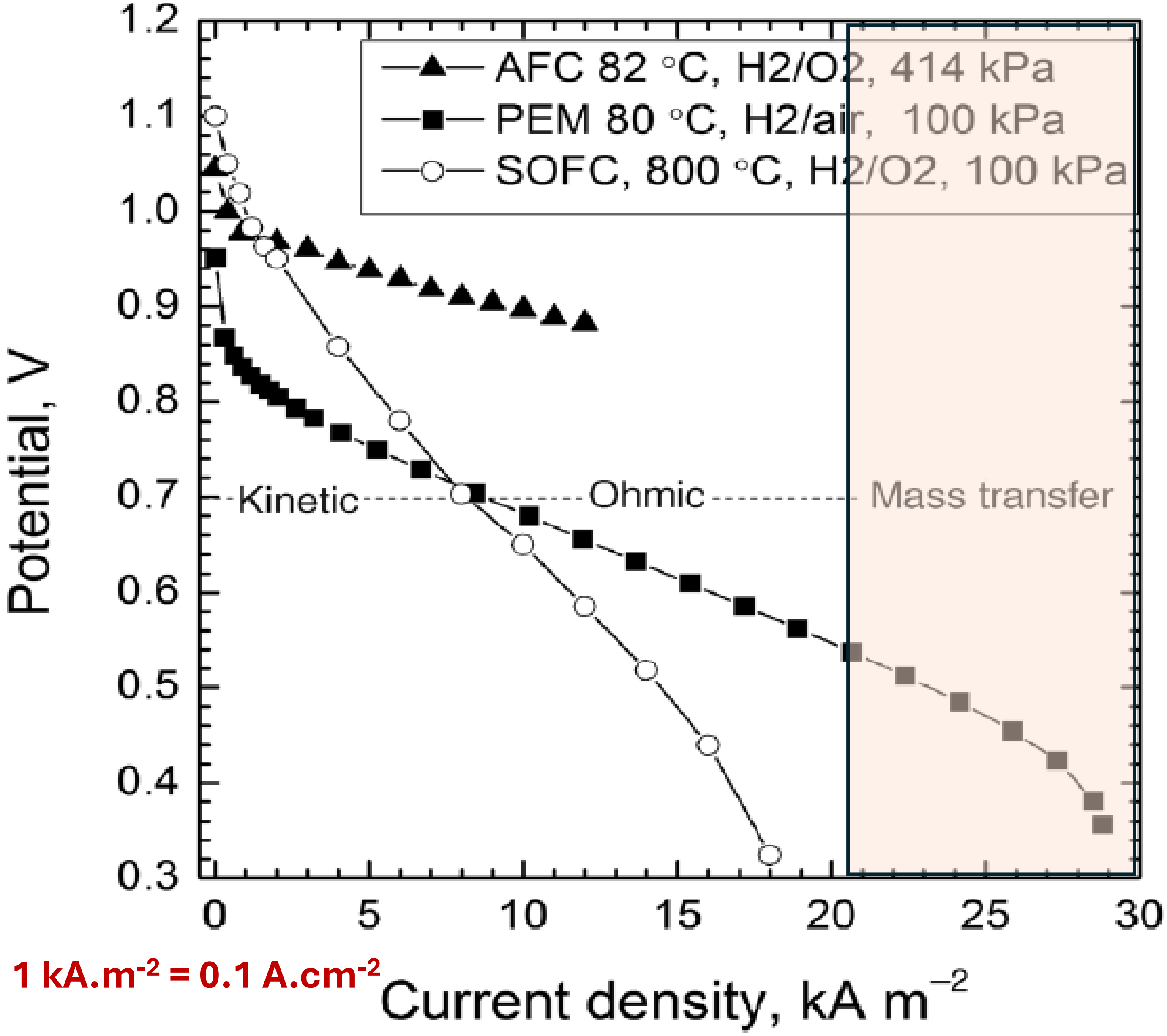
- **Contact Resistance**

(Contact between GDL, Catalyst, and membrane

- **Membrane/Electrolyte Resistance**

(Thickness and Conductivity of the electrolyte)

Mass transfer

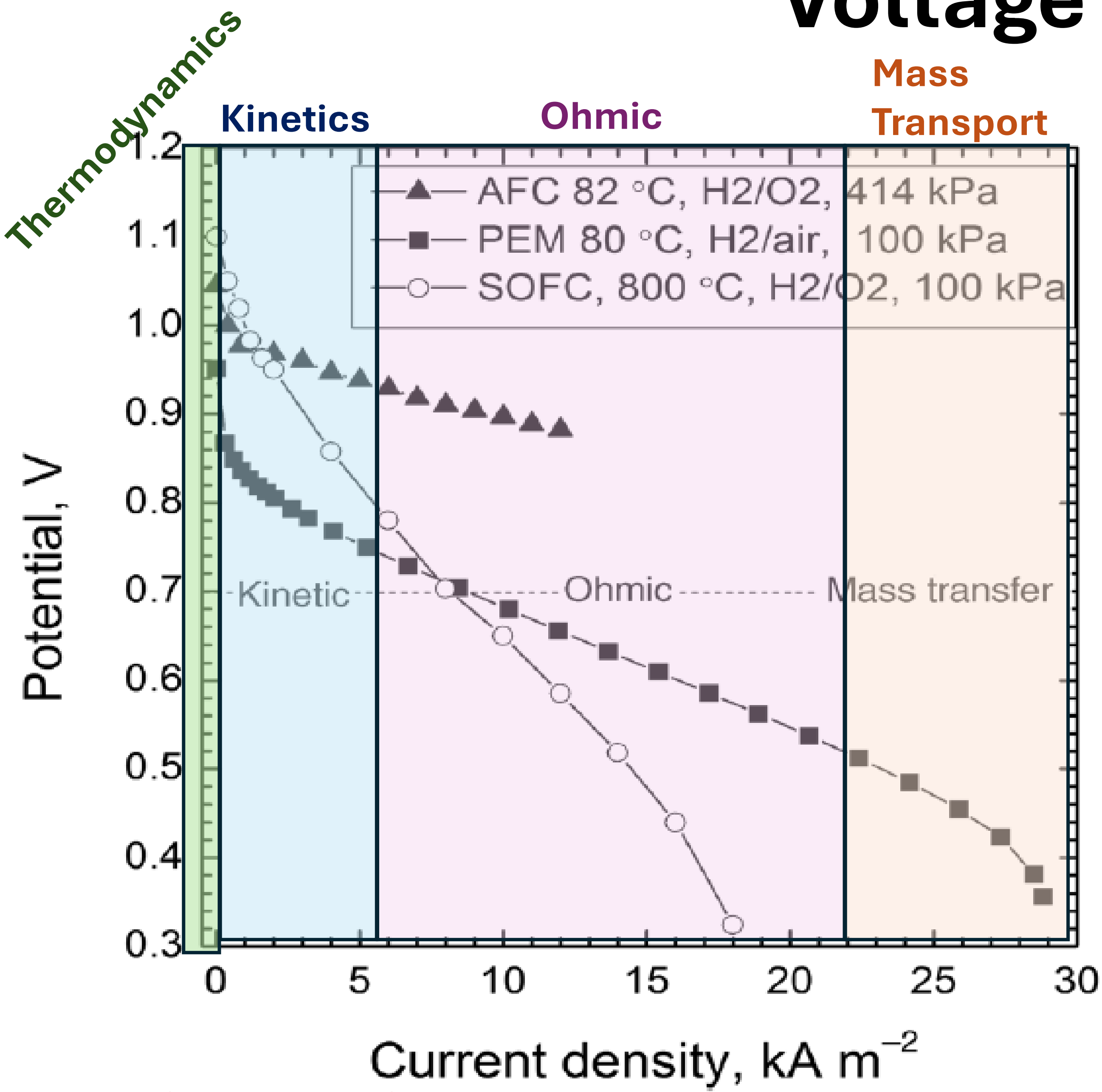


1 kA.m^{-2} = 0.1 A.cm^{-2}

Source: *Electrochemical Engineering, T. F. Fuller and J. N. Harb*

- Dominant at high current densities
- Mass transport of reactants and products from the bulk to the catalyst surface
- Diffusion and Bulk fluid motion (advection)

Voltage losses



$$V = 1.23 - \eta_C - \eta_A - iR_\Omega - \eta_{MT}$$

V – Actual/Measured Cell Potential

E_o – Open Circuit Potential

η_C – Cathodic Over Potential

η_A –Anodic Over Potential

i – Measured Current

R_Ω – Ohmic Resistance

η_{MT} – Mass Transport / Concentration Over Potential

1 kA.m^{-2} = 0.1 A.cm^{-2}

Source: *Electrochemical Engineering, T. F. Fuller and J. N. Harb*

Concept Check

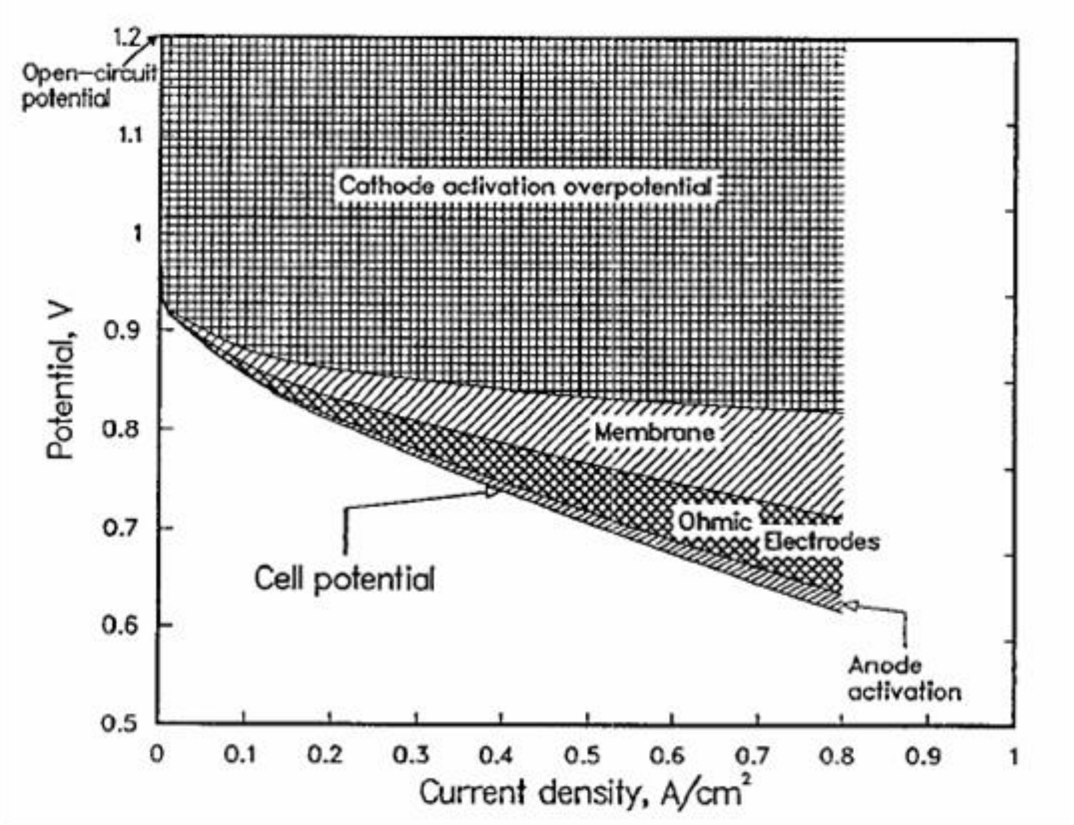
Where is the biggest efficiency loss in a fuel cell?

a) Ohmic resistance due to electron transfer

b) Ohmic resistance due to ion transfer

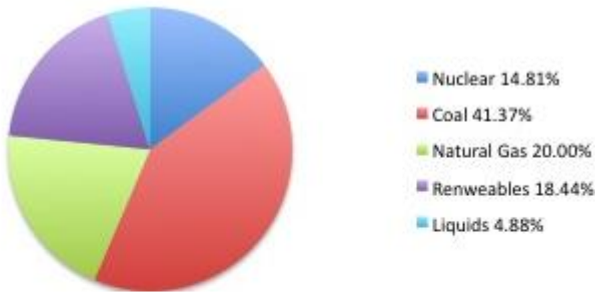
c) Catalytic loss at the anode

d) Catalytic loss at the cathode

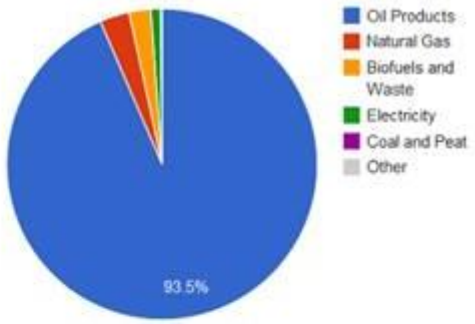


Hydrogen Storage

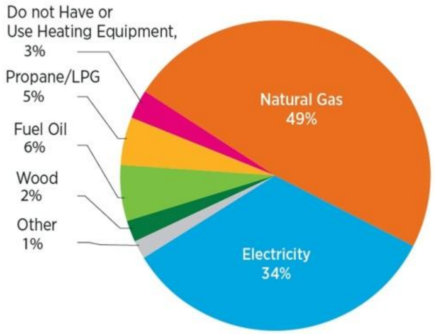
- While H_2 could work for power plants or heating, people always want to use it to compete with oil for the transportation field.



Electrical Power



Transportation

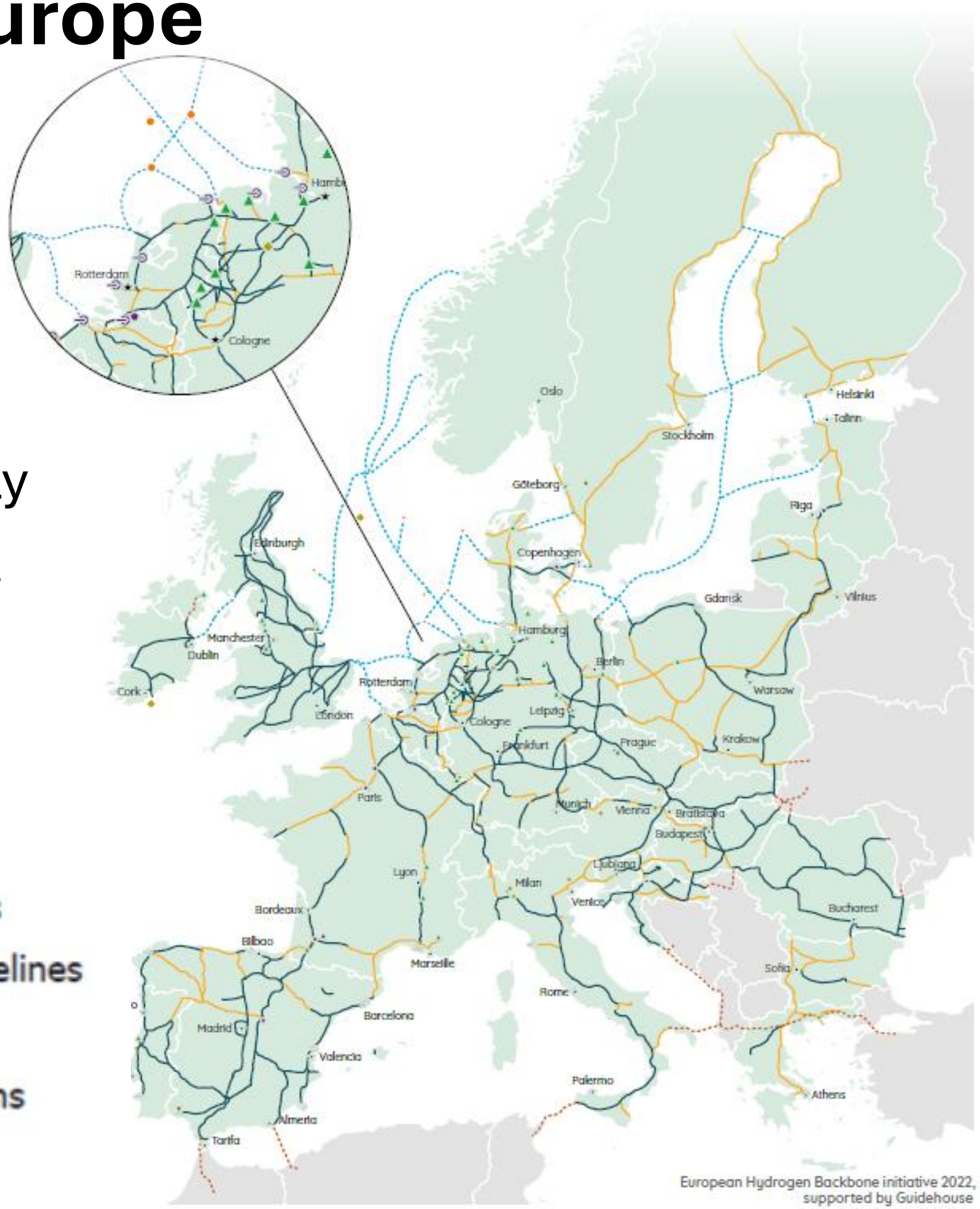


Heating

- While salt caverns have already been used to store H_2 for stationary applications, storage for automotive and mobile applications need to be compact.

H_2 pipelines in Europe

- Denmark wants to supply 10-25% of Germany's H_2 needs (as of 2021)



European Hydrogen Backbone initiative 2022, supported by Guidehouse

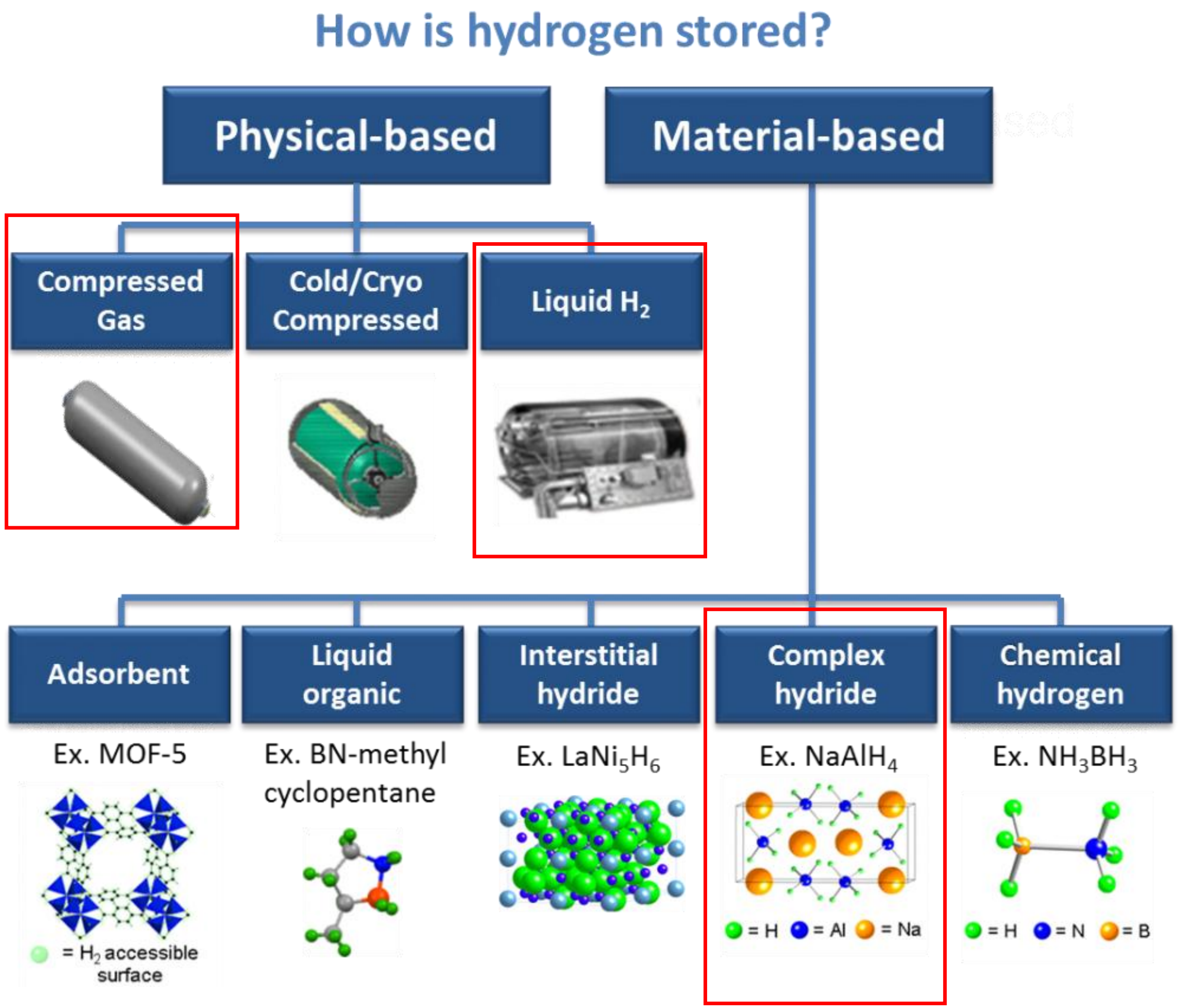
▬ Newly constructed H2 pipelines

▬ Repurposing of natural gas pipelines

▣ Compressor Station

△ Hydrogen storage in salt caverns

Methods for H_2 storage



How is hydrogen stored?

- Physical-based
  - Compressed Gas
  - Cold/Cryo Compressed
  - Liquid H_2
- Material-based
  - Adsorbent: Ex. MOF-5
  - Liquid organic: Ex. BN-methyl cyclopentane
  - Interstitial hydride: Ex. $LaNi_5H_6$
  - Complex hydride: Ex. $NaAlH_4$
  - Chemical hydrogen: Ex. NH_3BH_3

Compressed Gas

- Compressed gas is the most popular option.
- Compression is typically 700 atm, 5.4 wt.%.
- Compressor efficiency is between 75-90%.
- Obviously, compression leads to safety concerns.

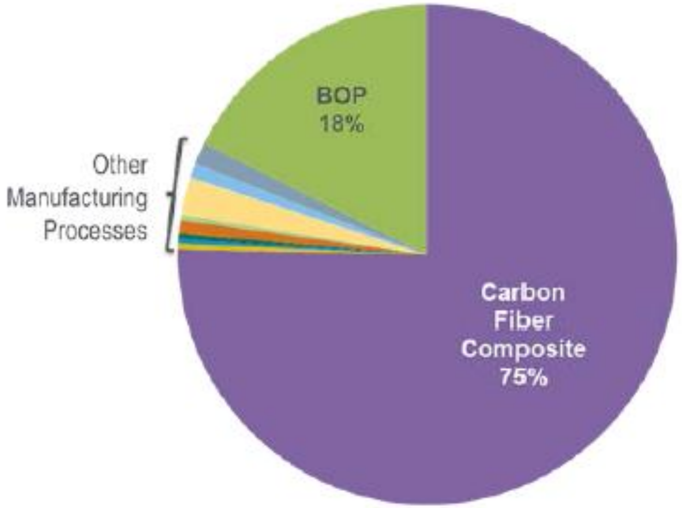


Figure 3.3.1 Systems Analysis sub-program cost analysis of a 700-bar Type IV hydrogen storage system shows >75% of cost is in the filament wound carbon fiber composite layer.

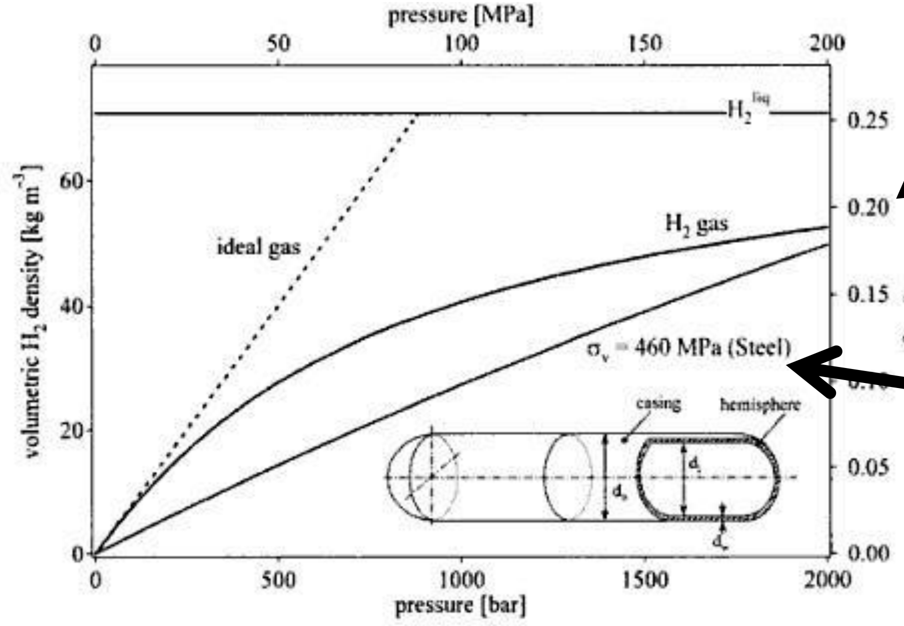
Compressed Gas

$$PV = nRT \Rightarrow P = \frac{n}{V}RT \Rightarrow P = \rho RT$$

- What assumptions do we make about the ideal gas law?

Compressed Gas

- The graph below show H_2's deviation from ideal gas conditions.
- The higher the pressure, the thicker the container walls need to be.
- Hydrogen embrittlement



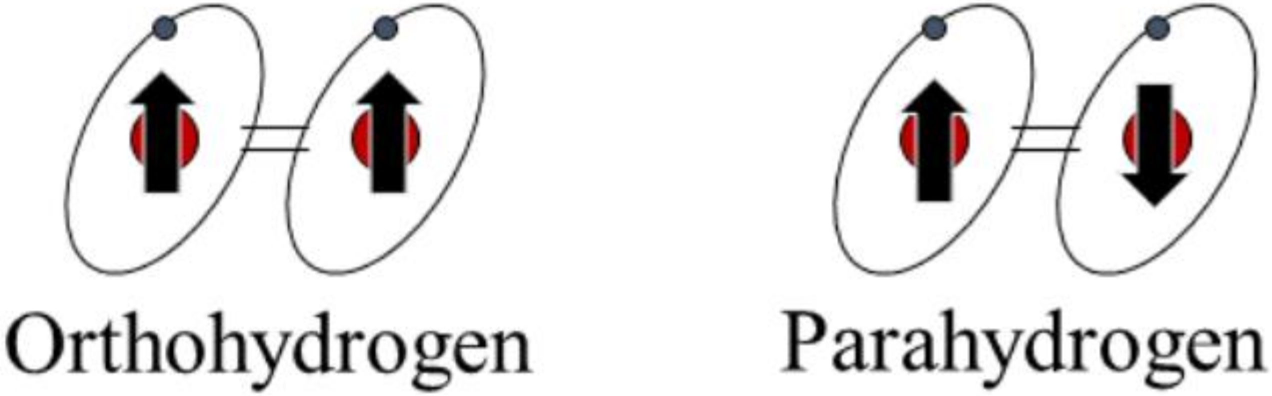
- Ratio of steel wall thickness to diameter needed to prevent the container from cracking.
- 0.5 is all steel, no container.

The best steel has a tensile strength of 1100 MPa

Figure from here

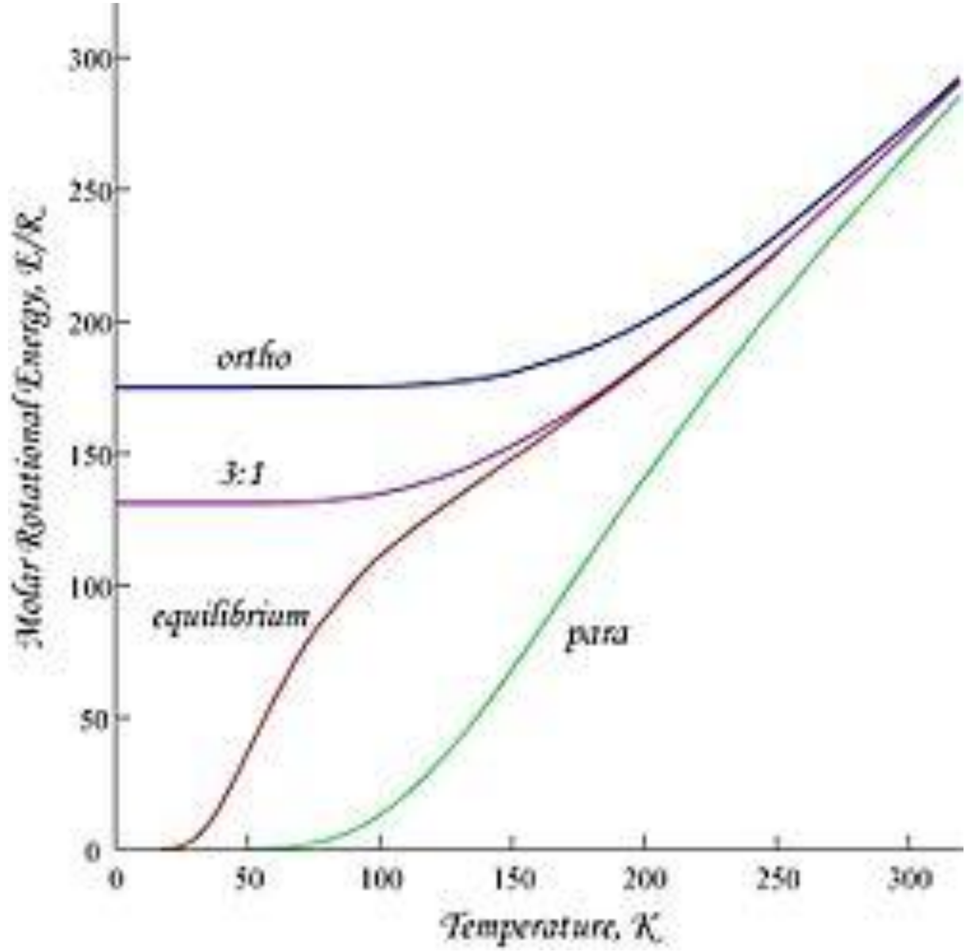
Liquid H_2

- H_2 liquefies at -252 °C.
- At room temperature we have 75% ortho-H_2 and 25% para H_2.
- However liquid H_2 is 99% para-H_2.
- Heat of conversion from ortho to para = 527 KJ/Kg (exothermic)
- Heat of vaporization = 449 KJ/Kg
- Entropy effects decrease the theoretical efficiency of this process.



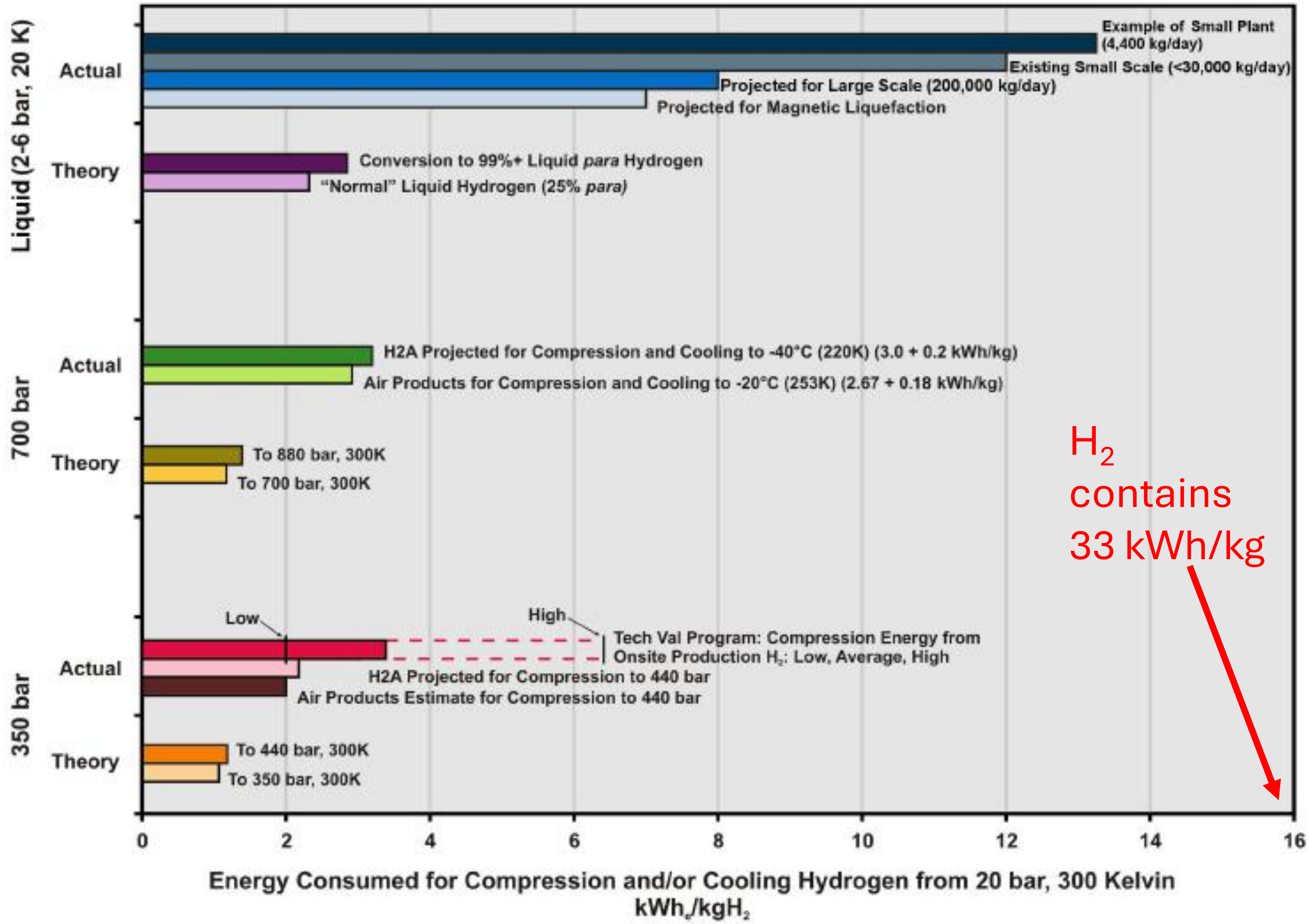
Liquid H_2

- The ortho-H_2 is a triplet state that has 3 degenerate states.
- The para-H_2 is a singlet state with no degeneracy.
- Due to symmetric effects, the ortho-H_2 has higher rotational energy at low temperatures.
- Uncatalyzed ortho to para transition is slow, but gives off a lot of energy.
- If ortho-H_2 is liquefied it will convert to para-H_2, and the heat of conversion will boil it again.



Energy needed

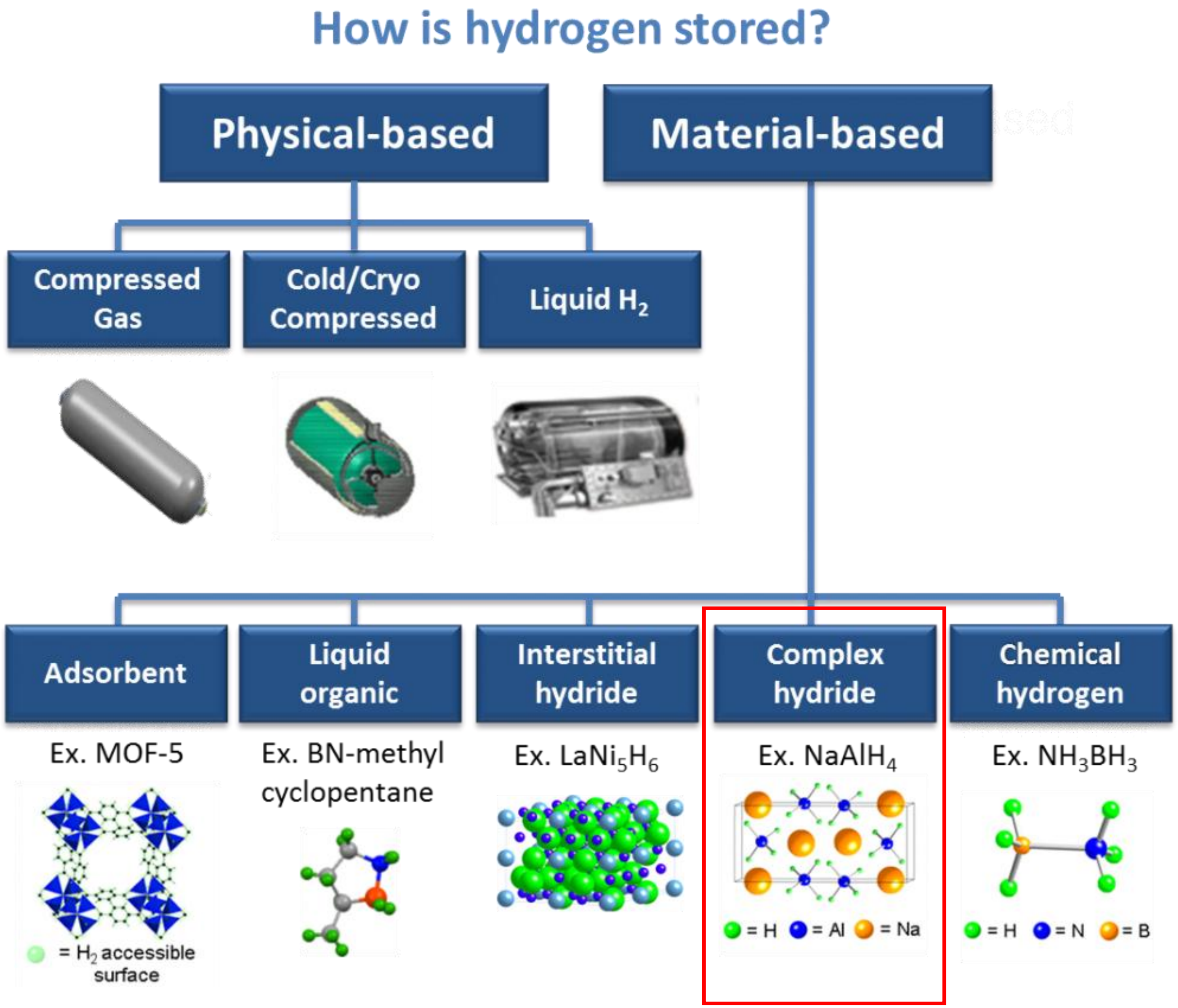
Figure 1: Energy Required for Vehicle Storage of Hydrogen in Different Thermodynamic States



H_2 contains 33 kWh/kg

This means **up to 1/3 of the hydrogen's usable energy is consumed** just to liquefy it

Methods for H_2 storage



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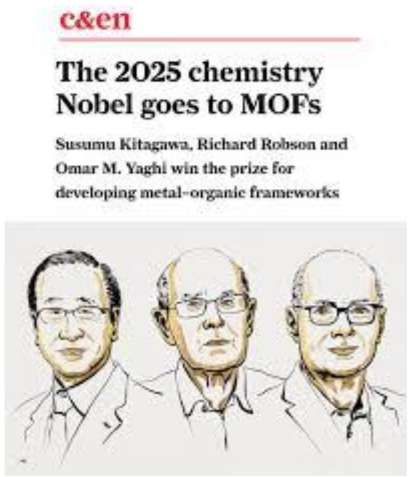
  - Chemical hydrogen: Ex. NH_3BH_3

Molecular organic frameworks



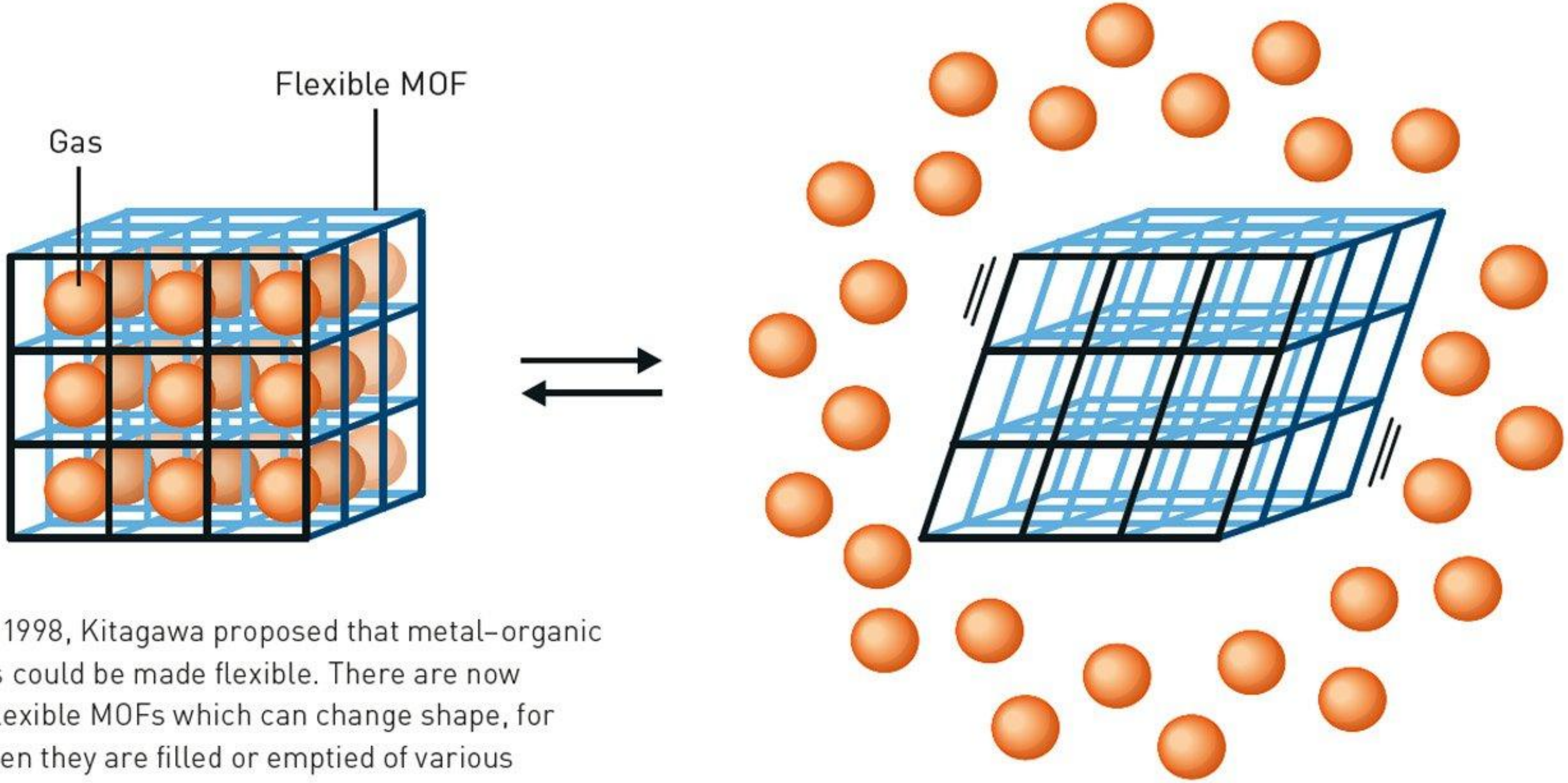
c&en

The 2025 chemistry Nobel goes to MOFs

Susumu Kitagawa, Richard Robson and Omar M. Yaghi win the prize for developing metal-organic frameworks

“for the development of metal–organic frameworks”

Their molecular architecture contains rooms for chemistry



Figu
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Figure 4. In 1998, Kitagawa proposed that metal–organic frameworks could be made flexible. There are now numerous flexible MOFs which can change shape, for example when they are filled or emptied of various substances.

Molecular organic frameworks

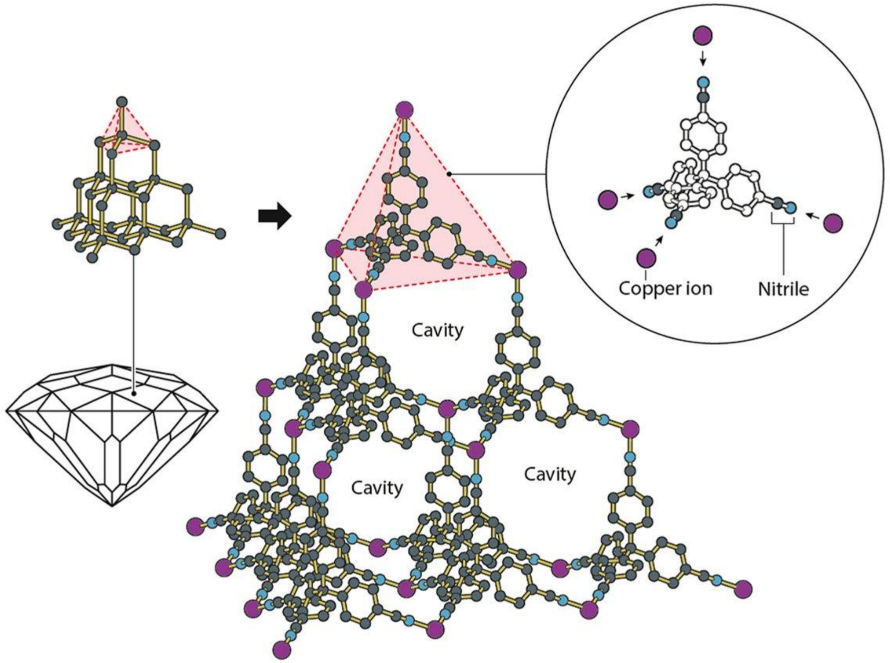


Figure 2. Richard Robson was inspired by the structure of diamond, in which every carbon atom is linked to four others in a pyramid-like shape. Rather than carbon, he used copper ions and a molecule with four arms, each with a nitrile at the end. This is a chemical compound that is attracted to copper ions. When the substances were combined, they formed an ordered and very spacious crystal.

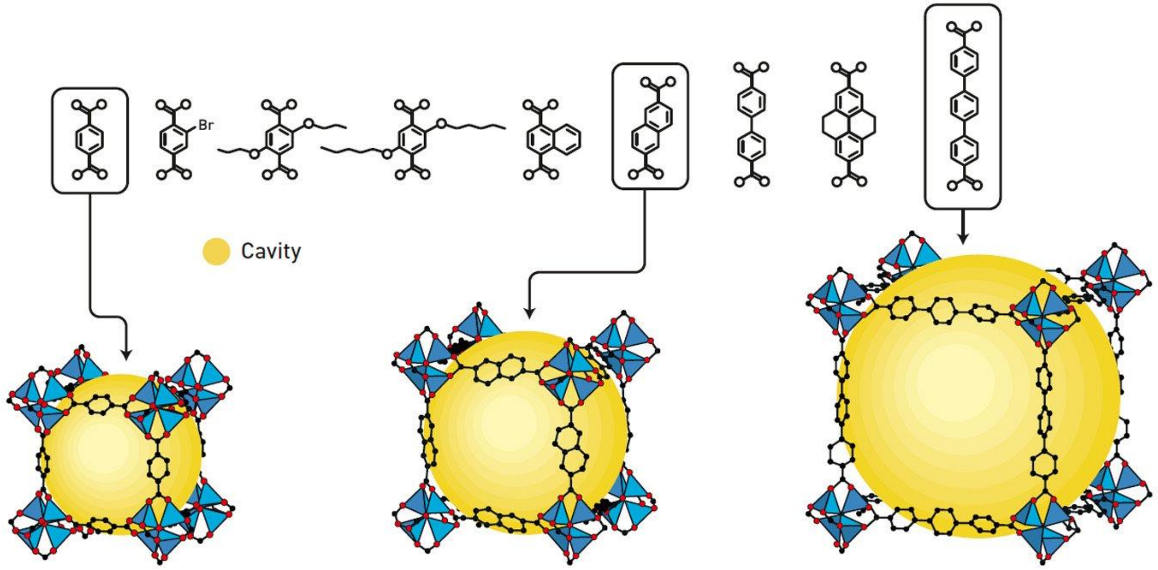
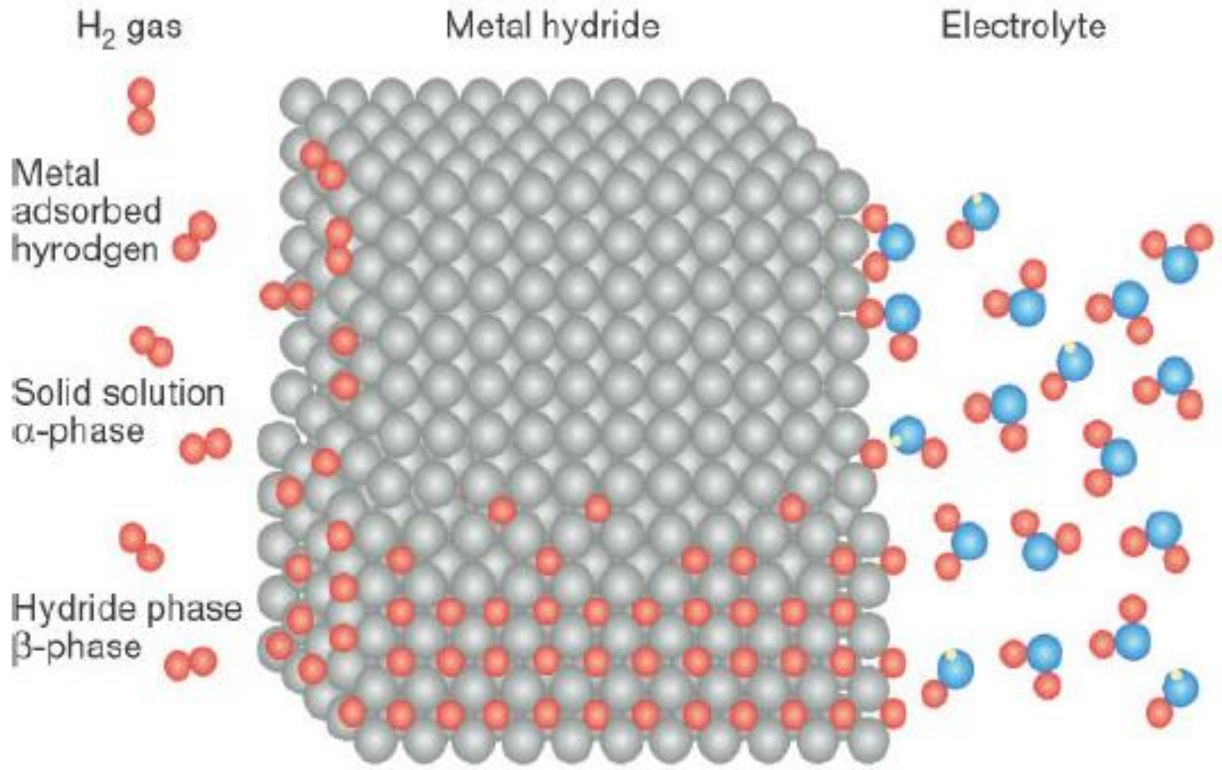


Figure 6. In the early 2000s, Yaghi showed that it is possible to produce entire families of MOF materials. He varied the molecular links, which resulted in materials with different properties. These include 16 variants of MOF-5, with cavities of various sizes.

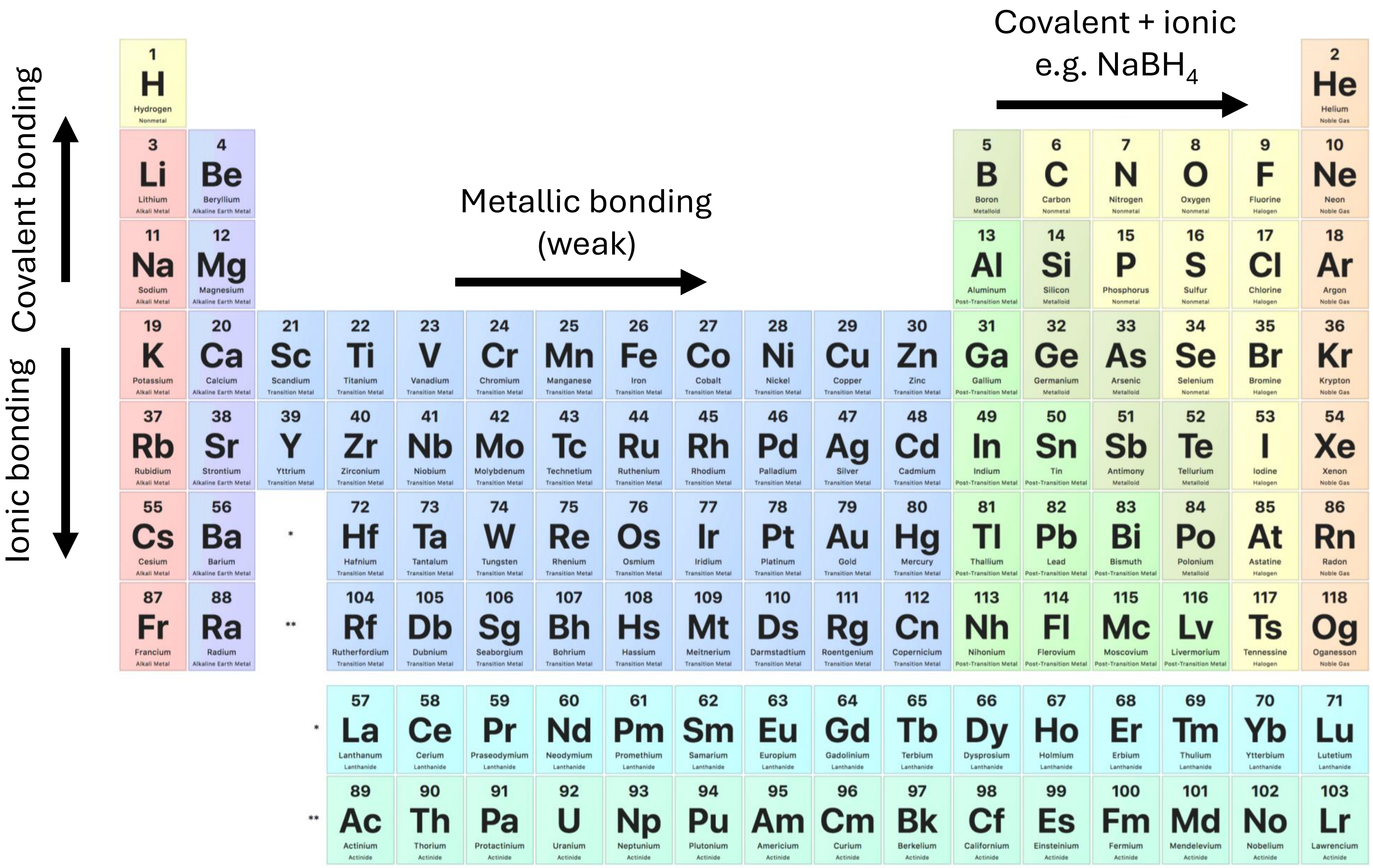
Metal Hydrides

- Small amounts of hydrogen occupies interstitiel sites (α-phase)
- More hydrogen requires the formation of a new phase (β-phase)



Schlapbach & Züttel, Nature **414**, 353 (2001)

Binary Metal Hydrides



Covalent + ionic
e.g. $NaBH_4$

Metallic bonding
(weak)

Covalent bonding

Ionic bonding

1 H Hydrogen Nonmetal																	2 He Helium Noble Gas
3 Li Lithium Alkali Metal	4 Be Beryllium Alkaline Earth Metal											5 B Boron Metalloid	6 C Carbon Nonmetal	7 N Nitrogen Nonmetal	8 O Oxygen Nonmetal	9 F Fluorine Halogen	10 Ne Neon Noble Gas
11 Na Sodium Alkali Metal	12 Mg Magnesium Alkaline Earth Metal											13 Al Aluminum Post-Transition Metal	14 Si Silicon Metalloid	15 P Phosphorus Nonmetal	16 S Sulfur Nonmetal	17 Cl Chlorine Halogen	18 Ar Argon Noble Gas
19 K Potassium Alkali Metal	20 Ca Calcium Alkaline Earth Metal	21 Sc Scandium Transition Metal	22 Ti Titanium Transition Metal	23 V Vanadium Transition Metal	24 Cr Chromium Transition Metal	25 Mn Manganese Transition Metal	26 Fe Iron Transition Metal	27 Co Cobalt Transition Metal	28 Ni Nickel Transition Metal	29 Cu Copper Transition Metal	30 Zn Zinc Transition Metal	31 Ga Gallium Post-Transition Metal	32 Ge Germanium Metalloid	33 As Arsenic Metalloid	34 Se Selenium Nonmetal	35 Br Bromine Halogen	36 Kr Krypton Noble Gas
37 Rb Rubidium Alkali Metal	38 Sr Strontium Alkaline Earth Metal	39 Y Yttrium Transition Metal	40 Zr Zirconium Transition Metal	41 Nb Niobium Transition Metal	42 Mo Molybdenum Transition Metal	43 Tc Technetium Transition Metal	44 Ru Ruthenium Transition Metal	45 Rh Rhodium Transition Metal	46 Pd Palladium Transition Metal	47 Ag Silver Transition Metal	48 Cd Cadmium Transition Metal	49 In Indium Post-Transition Metal	50 Sn Tin Post-Transition Metal	51 Sb Antimony Metalloid	52 Te Tellurium Metalloid	53 I Iodine Halogen	54 Xe Xenon Noble Gas
55 Cs Cesium Alkali Metal	56 Ba Barium Alkaline Earth Metal	*	72 Hf Hafnium Transition Metal	73 Ta Tantalum Transition Metal	74 W Tungsten Transition Metal	75 Re Rhenium Transition Metal	76 Os Osmium Transition Metal	77 Ir Iridium Transition Metal	78 Pt Platinum Transition Metal	79 Au Gold Transition Metal	80 Hg Mercury Transition Metal	81 Tl Thallium Post-Transition Metal	82 Pb Lead Post-Transition Metal	83 Bi Bismuth Post-Transition Metal	84 Po Polonium Metalloid	85 At Astatine Halogen	86 Rn Radon Noble Gas
87 Fr Francium Alkali Metal	88 Ra Radium Alkaline Earth Metal	**	104 Rf Rutherfordium Transition Metal	105 Db Dubnium Transition Metal	106 Sg Seaborgium Transition Metal	107 Bh Bohrium Transition Metal	108 Hs Hassium Transition Metal	109 Mt Meitnerium Transition Metal	110 Ds Darmstadtium Transition Metal	111 Rg Roentgenium Transition Metal	112 Cn Copernicium Transition Metal	113 Nh Nihonium Post-Transition Metal	114 Fl Flerovium Post-Transition Metal	115 Mc Moscovium Post-Transition Metal	116 Lv Livermorium Post-Transition Metal	117 Ts Tennessine Halogen	118 Og Oganesson Noble Gas
		*	57 La Lanthanum Lanthanide	58 Ce Cerium Lanthanide	59 Pr Praseodymium Lanthanide	60 Nd Neodymium Lanthanide	61 Pm Promethium Lanthanide	62 Sm Samarium Lanthanide	63 Eu Europium Lanthanide	64 Gd Gadolinium Lanthanide	65 Tb Terbium Lanthanide	66 Dy Dysprosium Lanthanide	67 Ho Holmium Lanthanide	68 Er Erbium Lanthanide	69 Tm Thulium Lanthanide	70 Yb Ytterbium Lanthanide	71 Lu Lutetium Lanthanide
		**	89 Ac Actinium Actinide	90 Th Thorium Actinide	91 Pa Protactinium Actinide	92 U Uranium Actinide	93 Np Neptunium Actinide	94 Pu Plutonium Actinide	95 Am Americium Actinide	96 Cm Curium Actinide	97 Bk Berkelium Actinide	98 Cf Californium Actinide	99 Es Einsteinium Actinide	100 Fm Fermium Actinide	101 Md Mendelevium Actinide	102 No Nobelium Actinide	103 Lr Lawrencium Actinide

Metal Hydrides

- Stability is determined by Gibbs free energy: $2MH \leftrightarrow 2M + H_2$

- We want a reaction with a low ΔG, so we can fluctuate the temperature to allow for adsorption and desorption of the reaction.

Equilibrium: $\Delta G = RT\ ln\ (K)$ $\qquad ln\ (K) = \frac{\Delta G}{RT}$

Breakdown of ΔG: $\Delta G = \Delta H - T\Delta S$

⬇ Combine 2 above Eqns

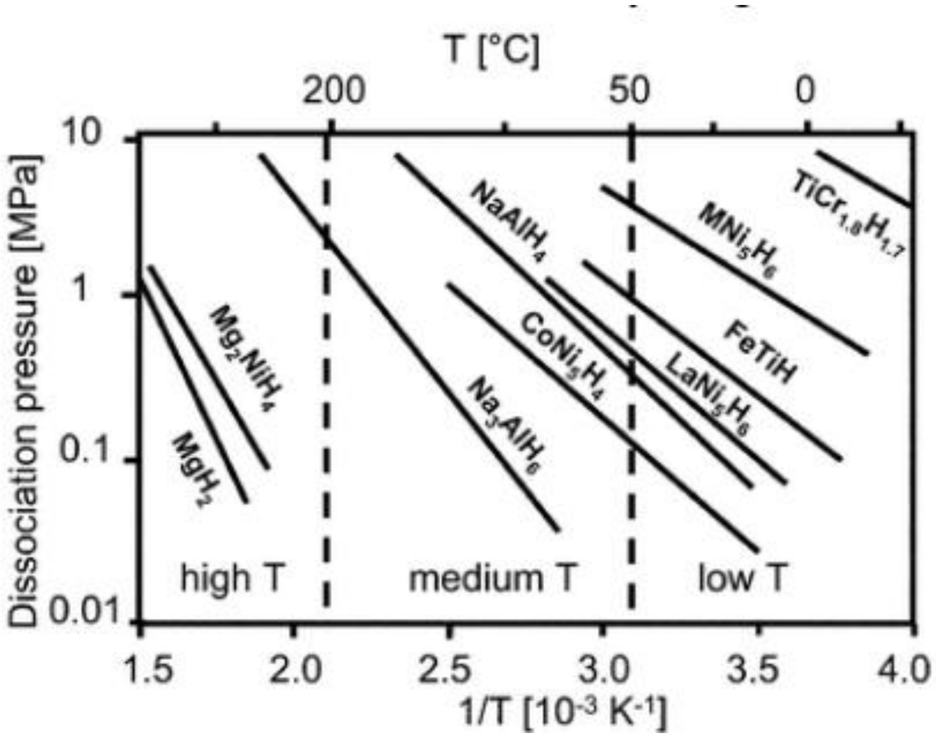
Breakdown of ΔG: $ln\ (K) = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$

$$ln\ \left(\frac{P}{P^0}\right) = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

P^0= equilibrium pressure

Metal Hydrides

- Plot 1/T should tell us the pressure of H_2 being released



Generic metal-hydride reaction

$$2MH \leftrightarrow 2M + H_2$$

M= metal

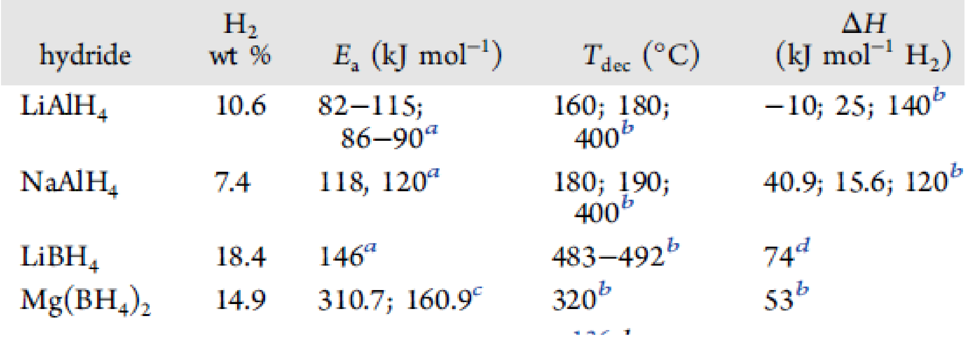
Practical 'good numbers' for metal hydride for H_2 storage

- $\Delta S \approx 120$ J/K/mol H_2
- $\Delta H \approx 30$ kJ/mol H_2

Chem. Rev. 2018, 118, 10775–10839

Metal Hydrides

- In metal hydrides, the mole faction of H_2 is high, whereas the mass fraction of H_2 is quite low.
- Why?
- Below is a list of some of the best H_2 adsorption materials.



hydride	H_2 wt %	E_a (kJ mol^{-1})	T_{dec} (°C)	ΔH (kJ mol^{-1} H_2)
$LiAlH_4$	10.6	82–115; 86–90[a]	160; 180; 400[b]	−10; 25; 140[b]
$NaAlH_4$	7.4	118, 120[a]	180; 190; 400[b]	40.9; 15.6; 120[b]
$LiBH_4$	18.4	146[a]	483–492[b]	74[d]
$Mg(BH_4)_2$	14.9	310.7; 160.9[c]	320[b]	53[b]

Schneemann et al.: Chem. Rev. 2018, 118, 10775−10839

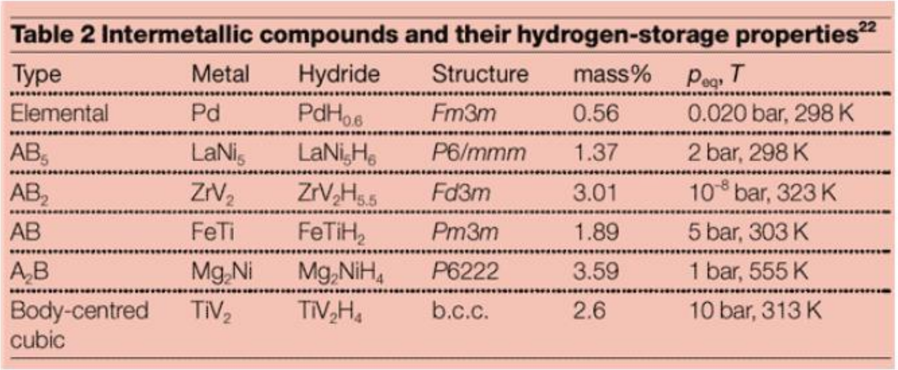
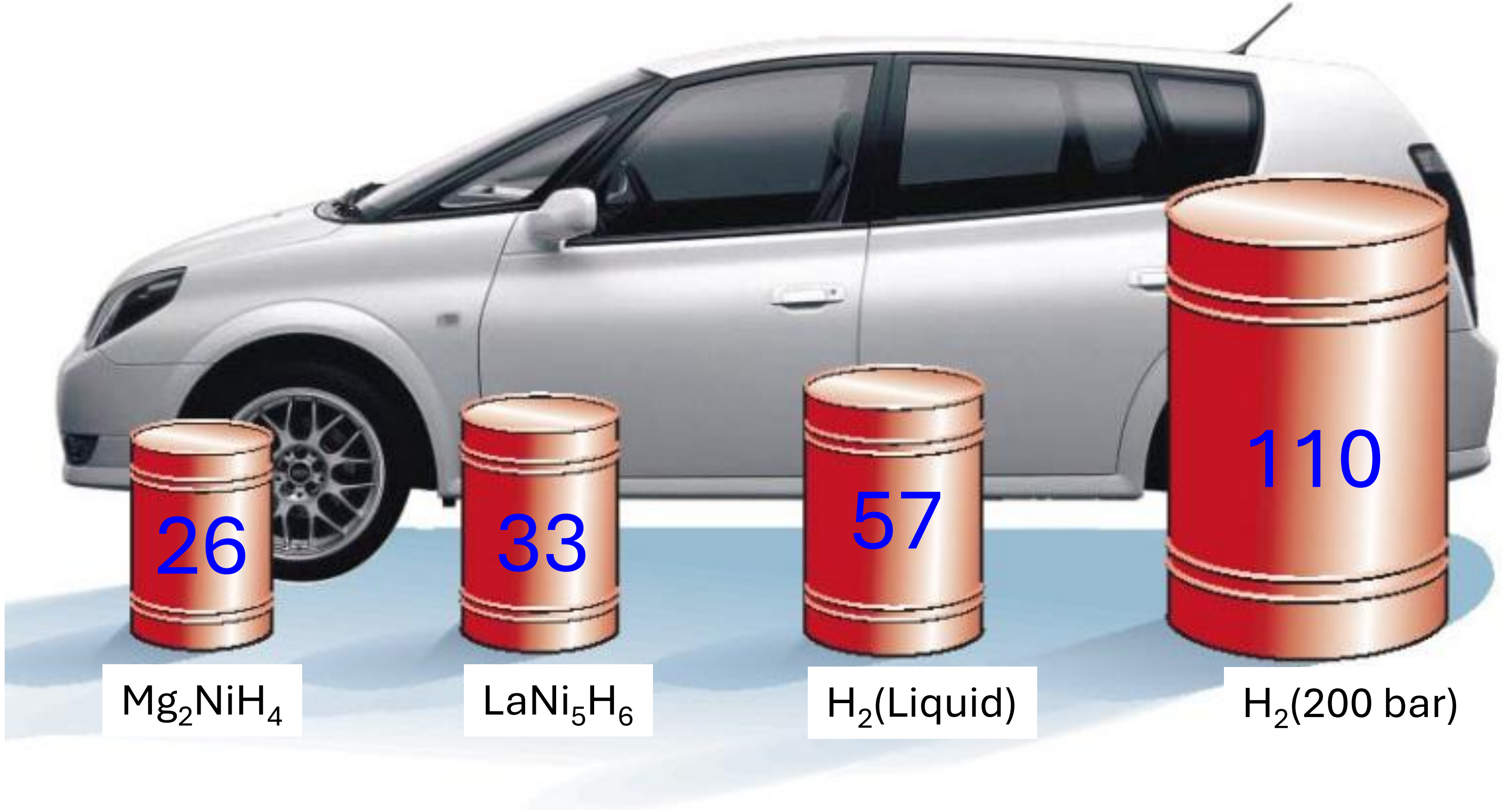


Table 2 Intermetallic compounds and their hydrogen-storage properties[22]

Type	Metal	Hydride	Structure	mass%	p_{eq}, T
Elemental	Pd	$PdH_{0.6}$	*Fm3m*	0.56	0.020 bar, 298 K
AB_5	$LaNi_5$	$LaNi_5H_6$	*P6/mmm*	1.37	2 bar, 298 K
AB_2	ZrV_2	$ZrV_2H_{5.5}$	*Fd3m*	3.01	10^{-8} bar, 323 K
AB	FeTi	$FeTiH_2$	*Pm3m*	1.89	5 bar, 303 K
A_2B	Mg_2Ni	Mg_2NiH_4	*P6222*	3.59	1 bar, 555 K
Body-centred cubic	TiV_2	TiV_2H_4	b.c.c.	2.6	10 bar, 313 K

Schlapbach, L. and Züttel, A., *Hydrogen-Storage Materials for Mobile Applications.* Nature, 2001. **414**(6861): p. 353-358.

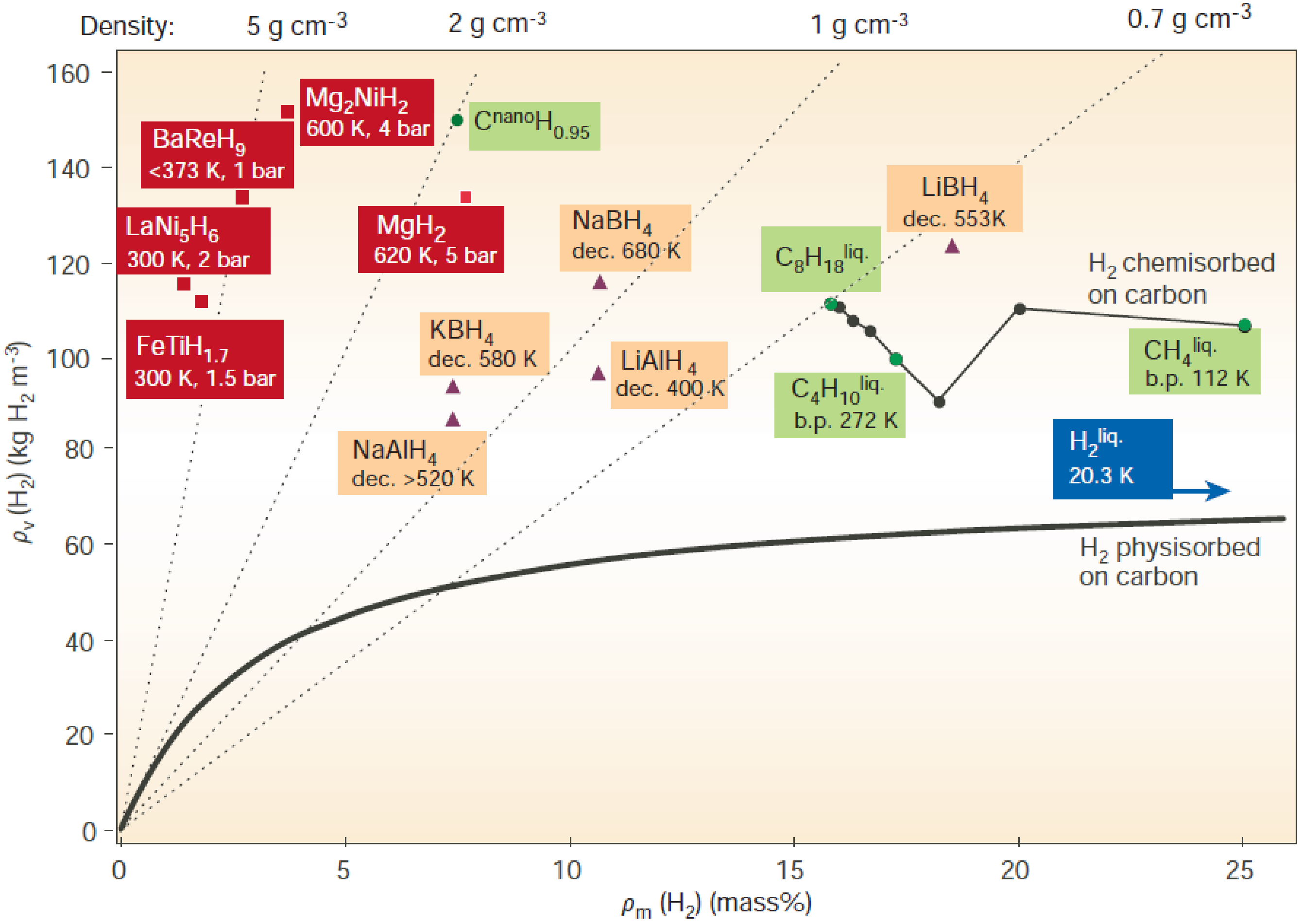
Metal Hydrides



Schlapbach, L. and Züttel, A., *Hydrogen-Storage Materials for Mobile Applications.* Nature, 2001. **414**(6861): p. 353-358.

Metal Hydrides

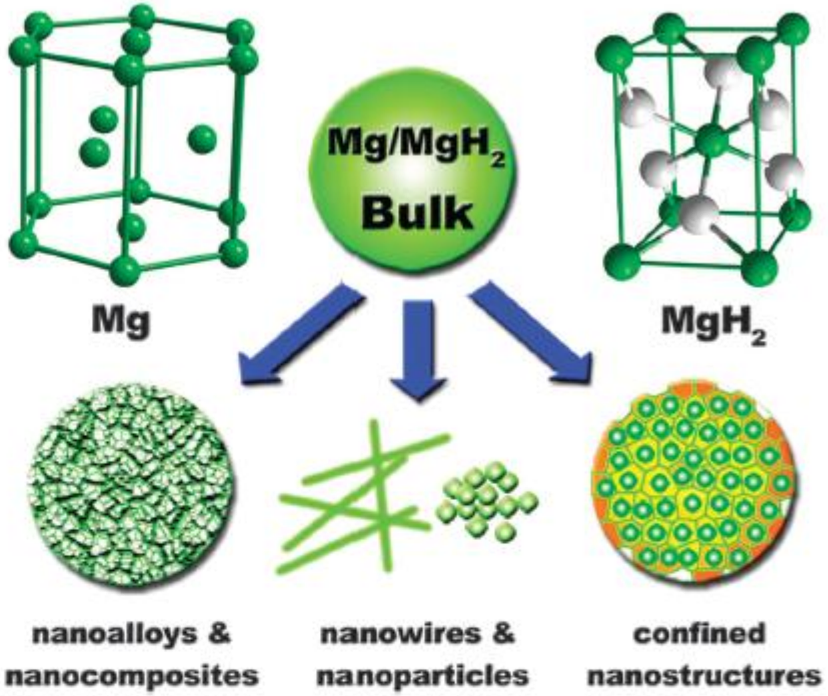
- Comparison of various H_2 storage techniques.



Schlapbach, L. and Züttel, A., *Hydrogen-Storage Materials for Mobile Applications.* Nature, 2001. **414**(6861): p. 353-358.

MgH_2

- High storage capacity (7.6 wt %)
- Cheap and easy to handle
- Challenges- Slow kinetics
  - Particle size
  - Dissociation of hydrogen
- Challenges- too stable (> 250 °C
  - The Mg-H bond is too strong
- Potential solutions
  - Alloying
  - Catalysts



Good review by Cheng et. al, E&ES, 2012

Concept Check

The most thermodynamically favorable state for H_2 in liquid is?

a) The para form

b) The meta form

c) The alpha form

d) The ortho form

Lecture - Learning Objectives

At the end of this lecture, you should be able to:

- Understand the major components in the hydrogen economy and in a PEM fuel cell.
- Understand where the efficiency losses are in fuel cells
- Understand electrocatalysis concerning half reactions and Tafel losses.
- Understand the basic principles behind different H_2 storage techniques.