Power-to-X
Electrolysis and synthetic fuels

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Outline

- Water electrolysis
- Types of electrolyzers
- Synthetic fuels

Learning objectives

- Explain the main **principles** of an electrolyzer
- Outline the characteristics of the most **common types** of electrolyzers (AEC, PEMEC and SOEC)
- Explain the function of the **components in a stack**
- Explain the shape of a **polarization curve**
- Calculate the **voltage efficiency** and the heat evolved at a given cell voltage
- Calculate the total **current, voltage and electrical powe**r of an electrolyzer stack if given dimensions (electrode area add number of cells) and working point (cell voltage and current density)
- Explain the **concept of power-to-X**
- Explain the main **synthesis paths to synthetic fuels** from hydrogen (Sabatier, Fischer-Tropsch, Methanol and Haber-Bosch)
- Explain the advantages and disadvantages **of powering vehicles with hydrogen** instead of batteries
- Explain the advantages and disadvantages of **converting hydrogen into carbon based synthetic fuels**
- Explain **CCS** and **CCU**
- Discuss the **challenges with carbon capture** (CCS and CCU)

Renewable and finite reserves

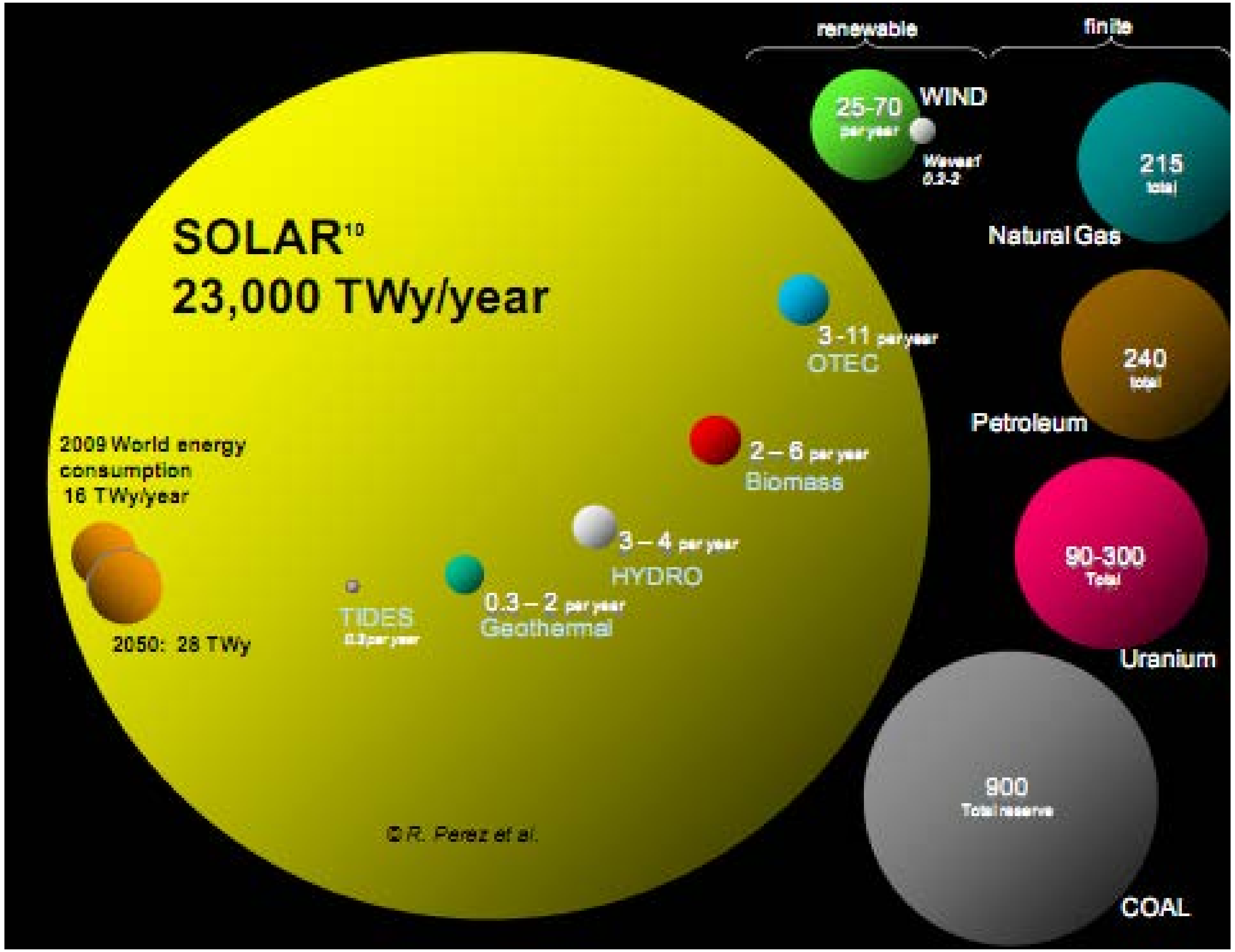
Total recoverable reserves for the finite resources.

(TWy).

Yearly potential for renewables.

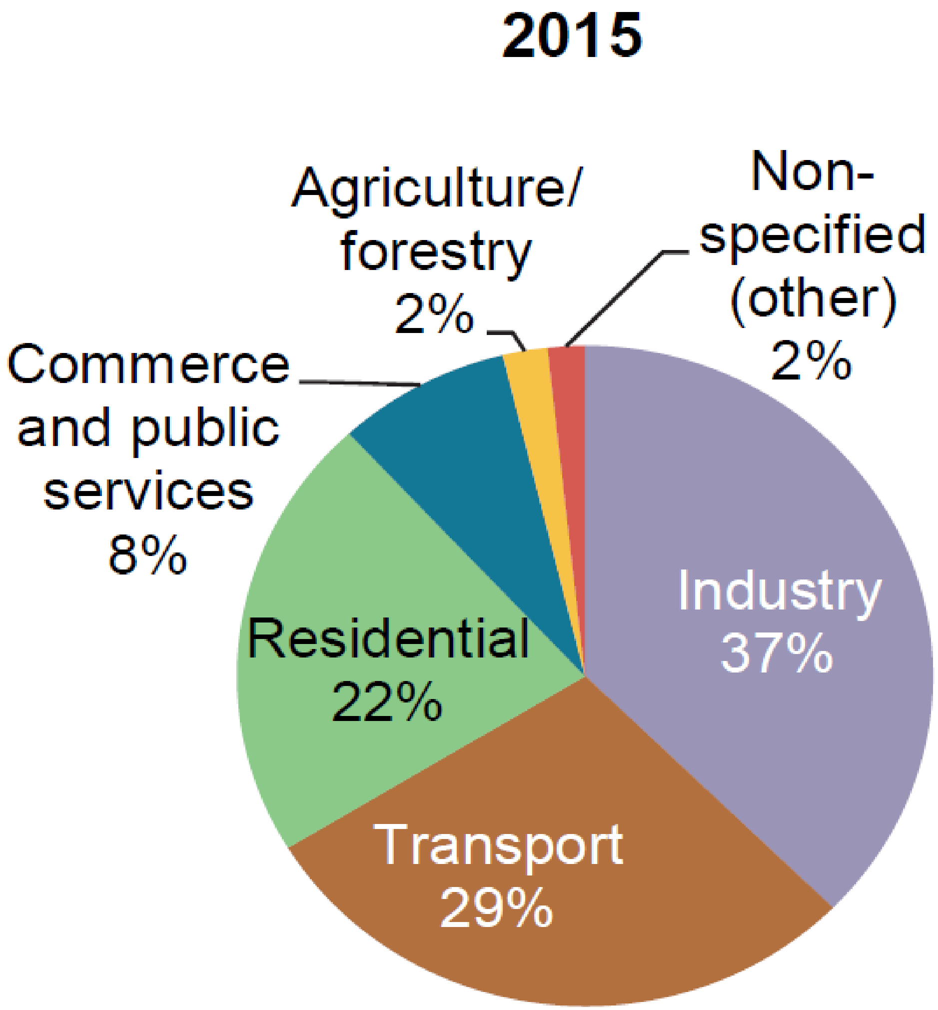
(TWy/y = TW)

Global energy consumption 2016: 17.6 TWy



Source: Perez & Perez, 2009 + update 2015 IEA-SHCP-Newsletter Vol. 62, Nov. 2015 – draft

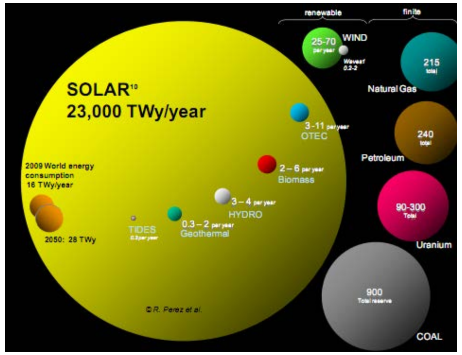
Global energy consumption by sector



9 384 Mtoe

IEA, World Energy Balances 2017

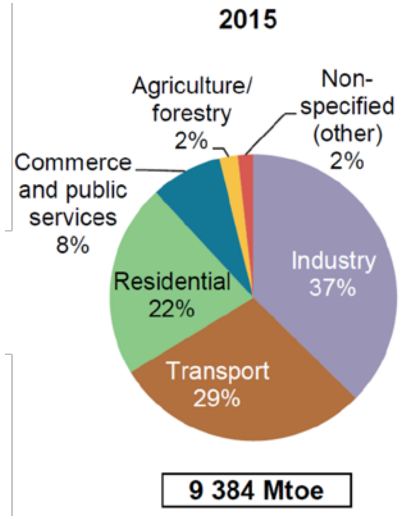
The transport problem



Transport needs

29 % of the 18 TW

= 5.2 TW



IEA, World Energy Balances 2017

Source	TW	Fluctuating	Electrical	Thermal	Chemical
Solar	23,000	Yes	X		
Wind	25 - 70	Yes	X		
OTEC*	3 - 11	No	X		
Biomass**	2 - 6	No			X
Hydro	3 - 4	No	X		
Geothermal	0.3 - 2	No	X	X	
Waves	0.2 - 2	Yes	X		

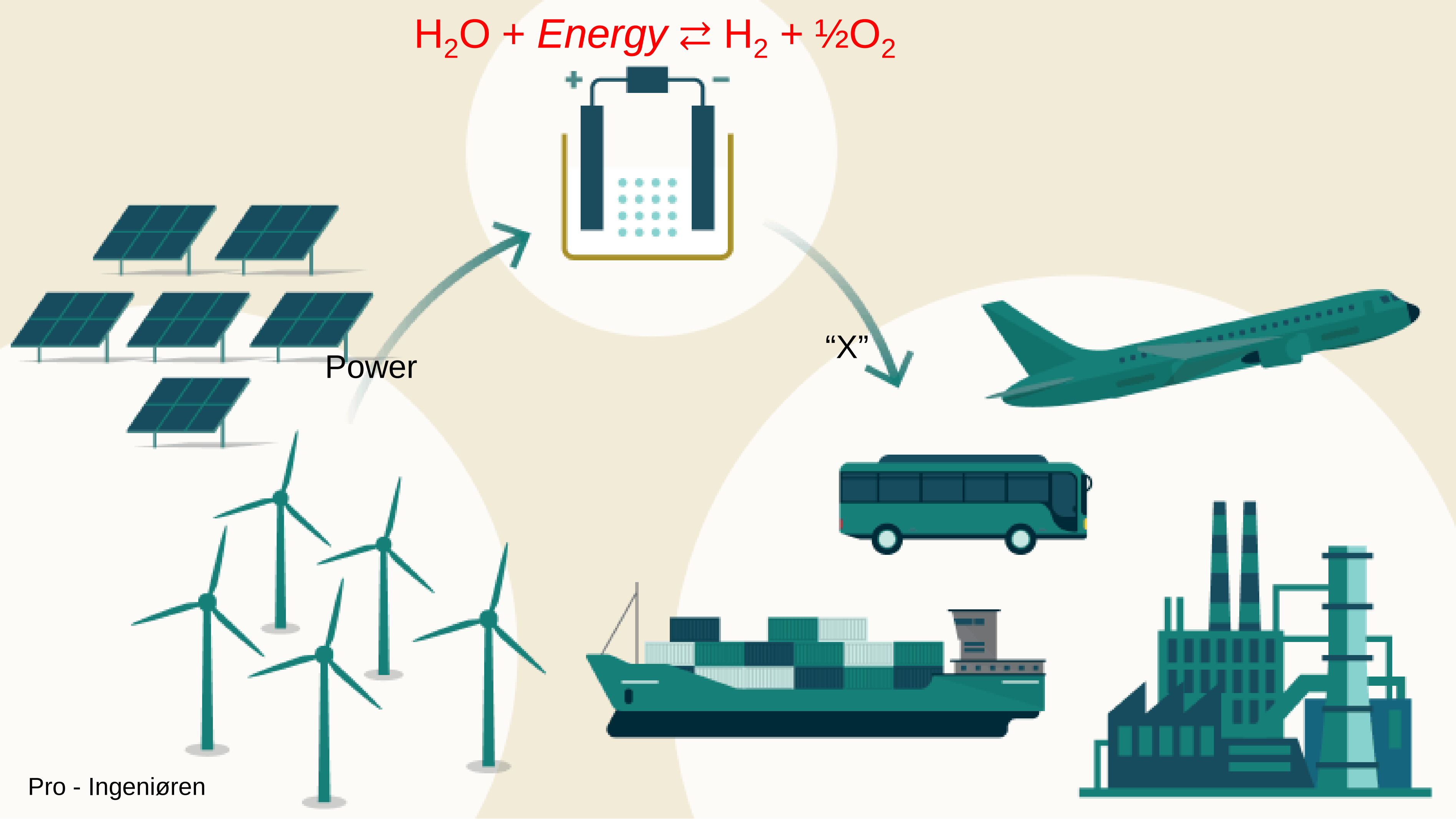
** OTEC = Ocean thermal energy conversion*

*** Some biomass will be used for chemicals – return as waste*

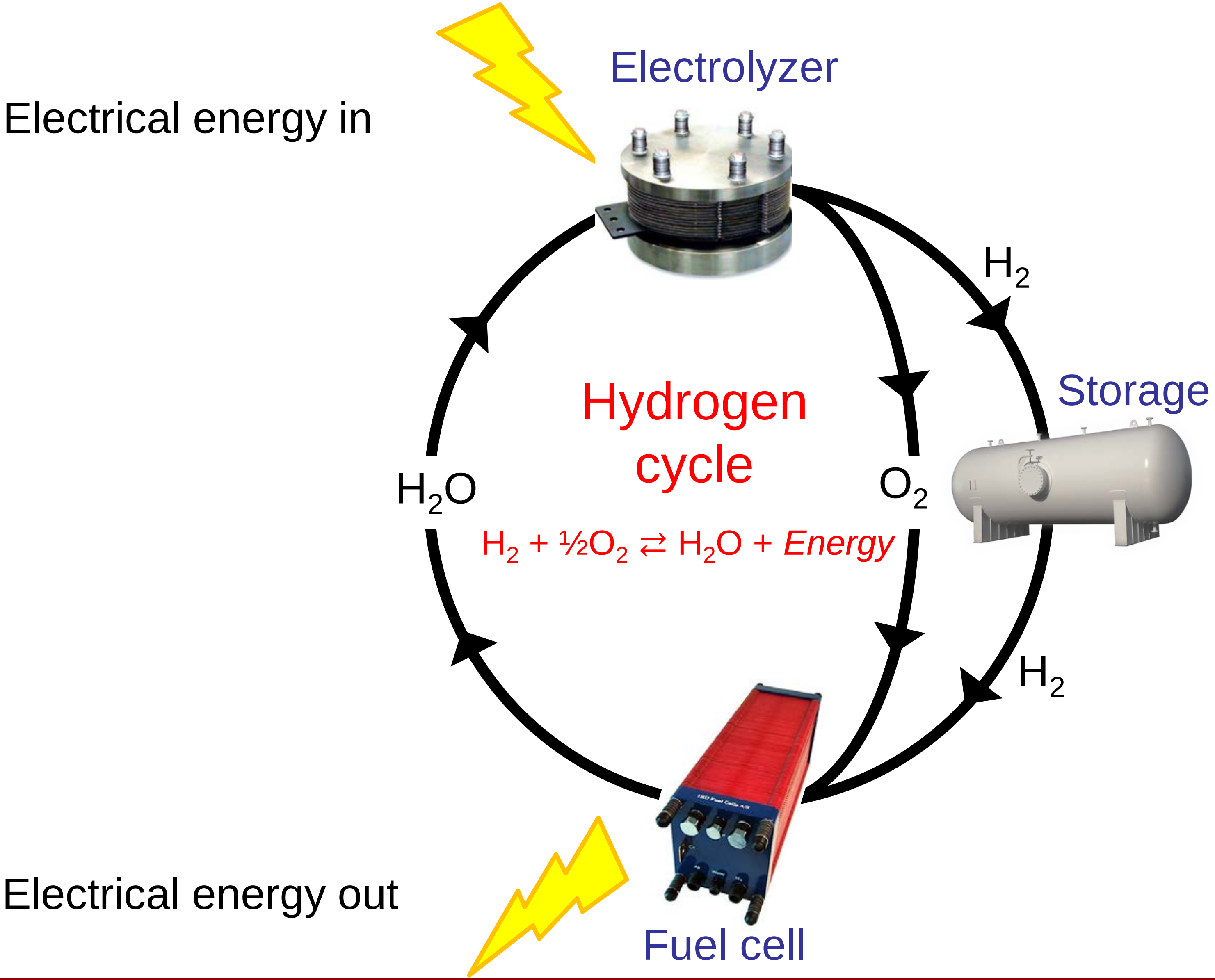
A need for storage and conversion

Power-to-X

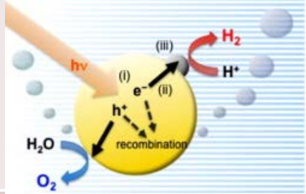
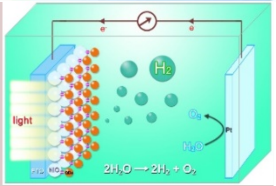
The raw material: water. - abundant, inexpensive, non-toxic



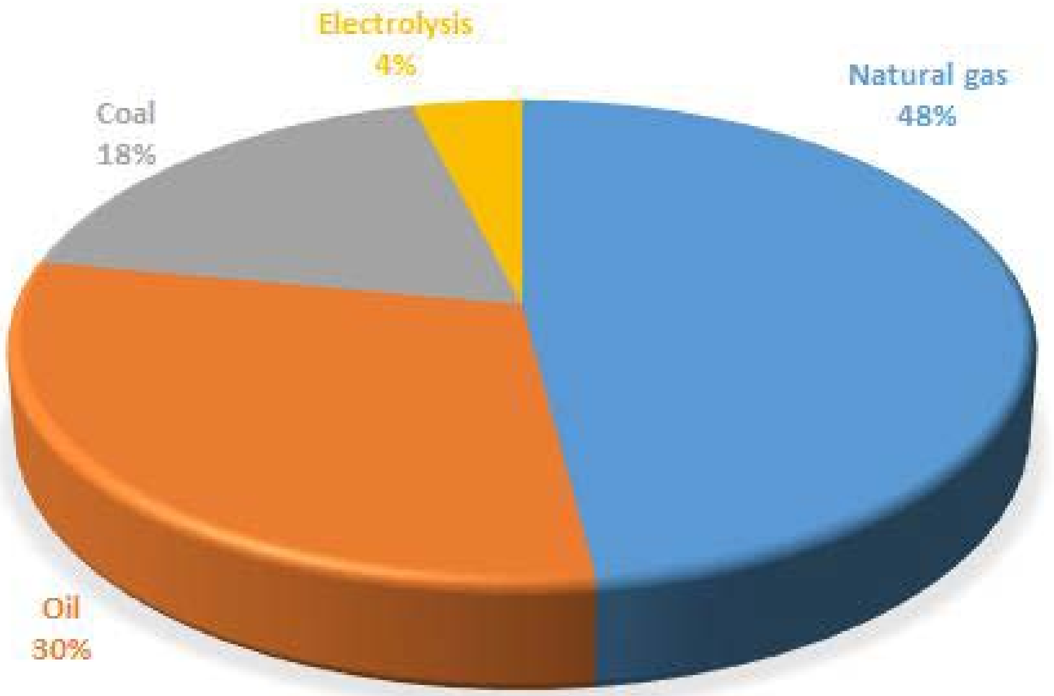
The hydrogen cycle



Hydrogen production

Class	Principle	Share
Chemical	Reforming of carbonaceous fuels. (+cracking of ammonia) 	Completely dominating (~96%)
Electrochemical	Electrolysis 	Commercial, but very limited (~4%)
Thermochemical	Combined thermal/chemical 	Experimental
Photochemical	Purely light driven 	Experimental
Photo-electrochemical	Combined photo- and electrochemical 	Experimental
Microbial	Anaerobe digestion 	Experimental

Electrolysis vs reforming



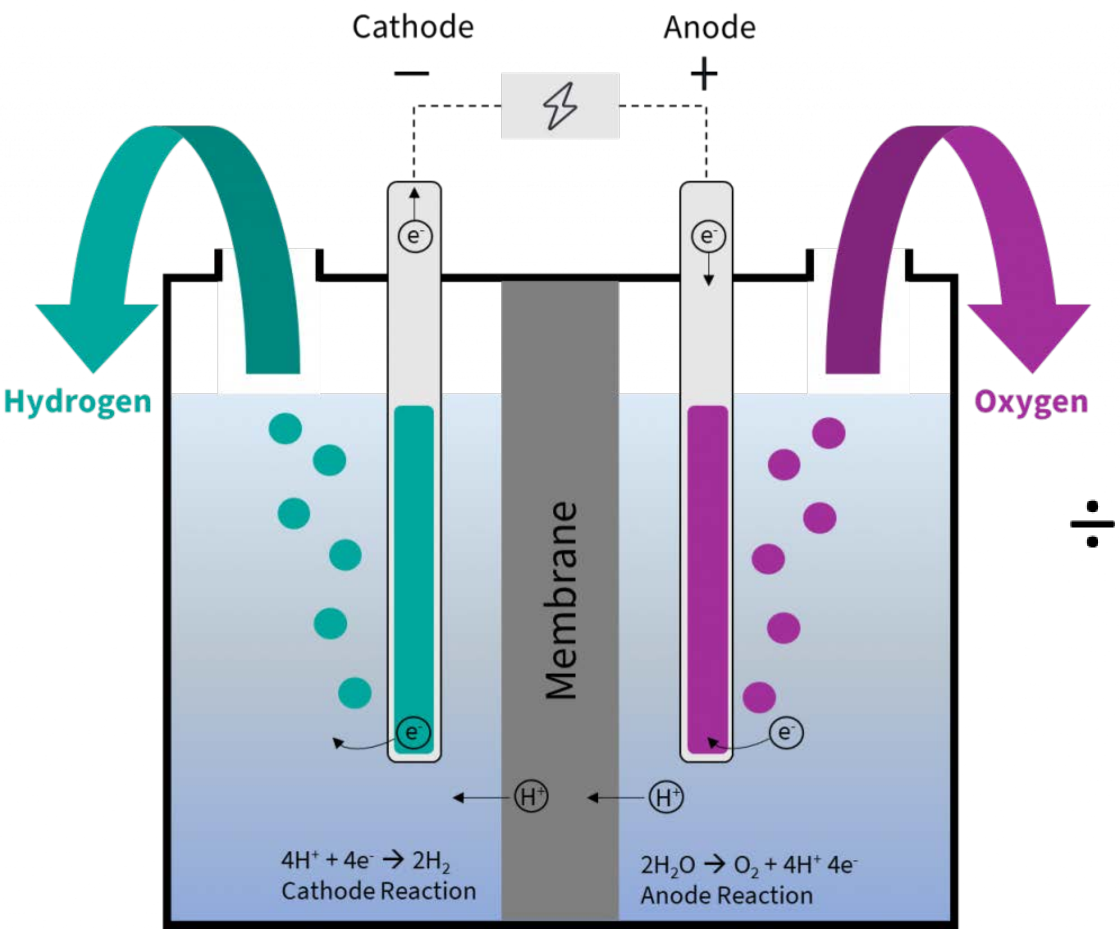
ResearchAndMarkets.com

Note: 4 % hydrogen is always quoted. It may vary.

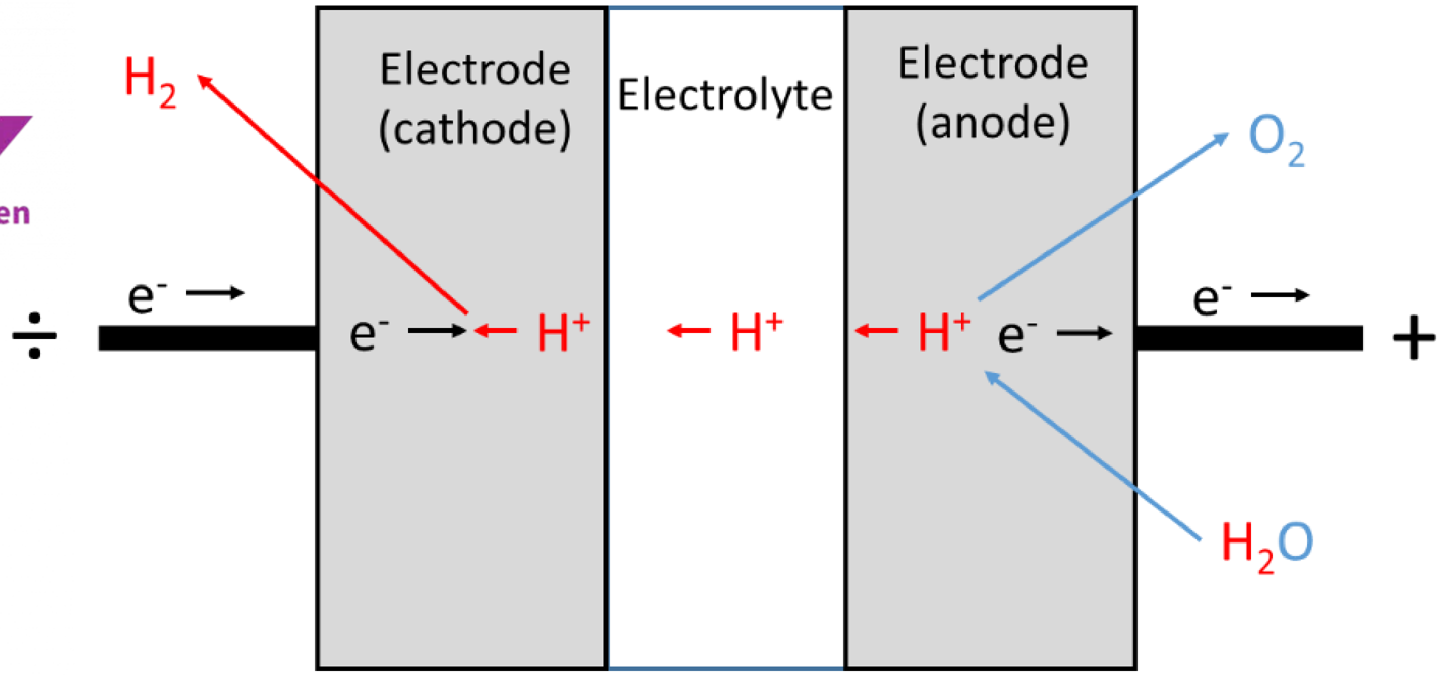
It is mostly a by-product from the chlor-alkali process making Chlorine and sodium hydroxide.

Water electrolysis

Electrolysis

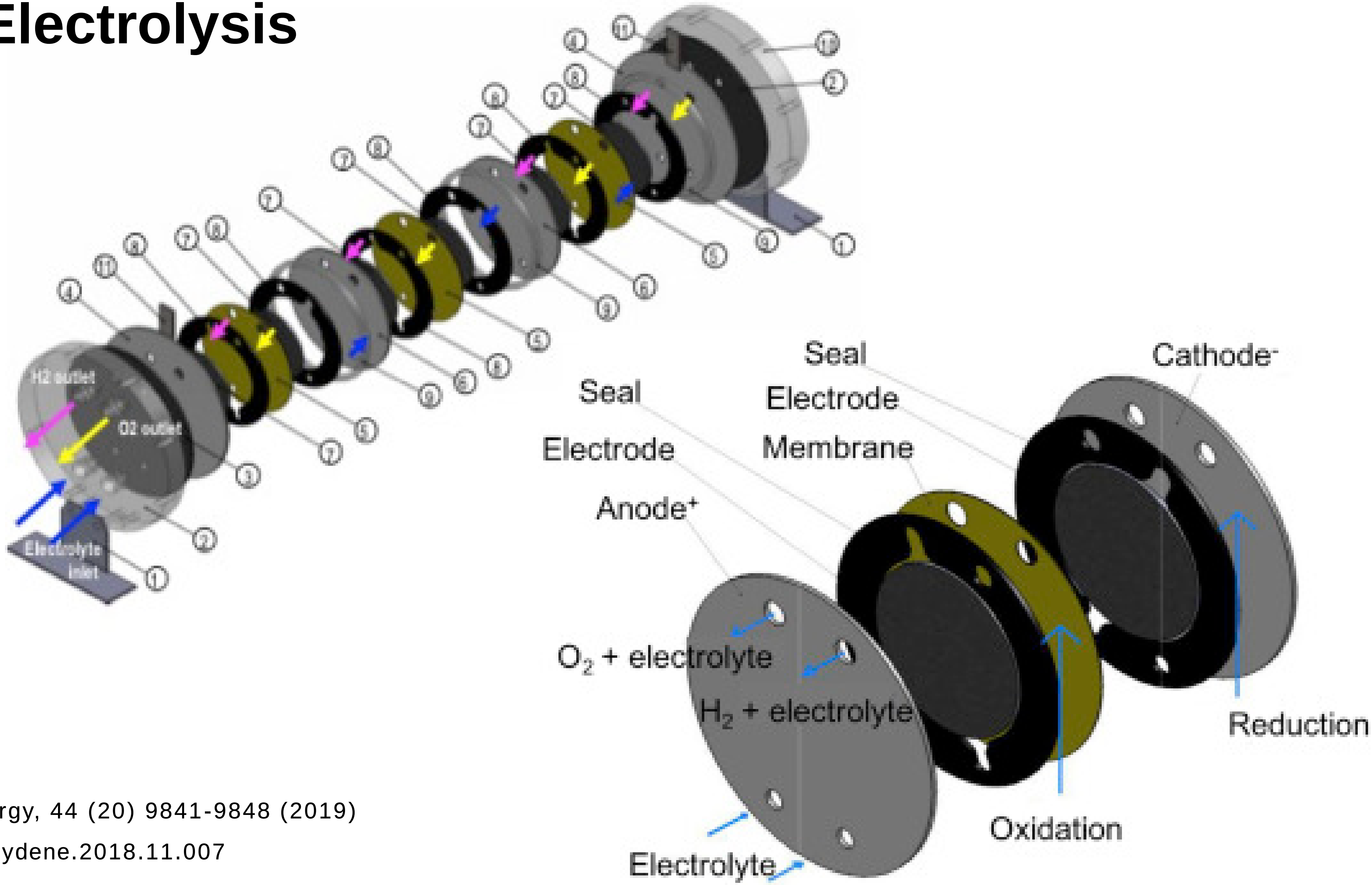


$$2H_2O \rightarrow 2H_2 + O_2$$



Example: system with acidic electrolyte

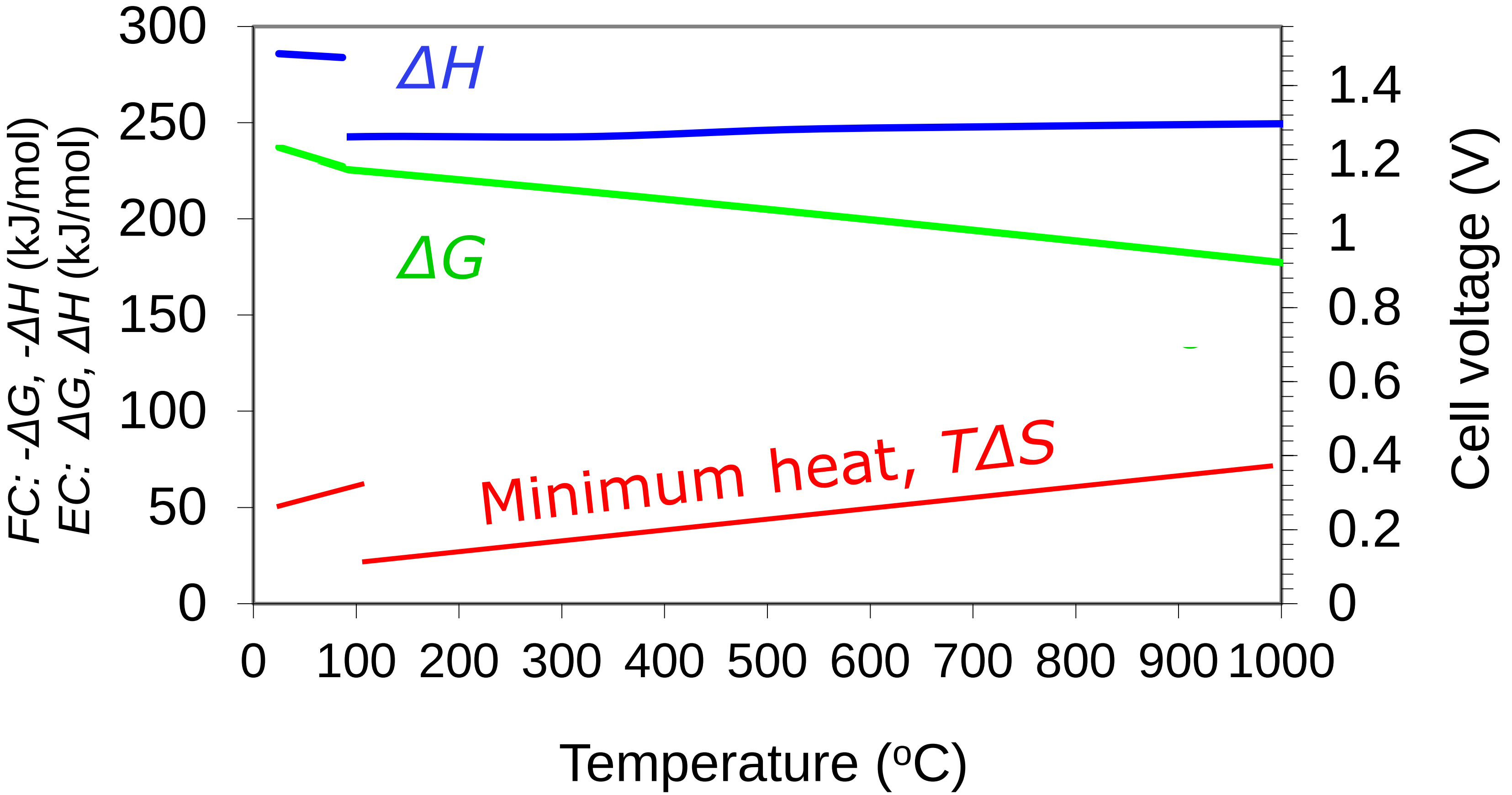
Electrolysis



Int. J. Hydrogen Energy, 44 (20) 9841-9848 (2019)
doi.org/10.1016/j.ijhydene.2018.11.007

The available/necessary energy (H_2)

$H_2 + ½O_2 \rightleftarrows H_2O$



Source: JANAF

https://janaf.nist.gov/

$$\Delta G_r = \Delta H_r - T\Delta S_r$$

The maximum electrical efficiency

ΔG_r is maximum work related to a fuel

ΔH_r is total energy related to a fuel

Maximum fuel cell efficiency:

$$\eta_{FC} = \frac{\Delta G^o(T)}{\Delta H^o}$$

Maximum electrolyzer efficiency:

$$\eta_{EC} = \frac{\Delta H^o}{\Delta G^o(T)}$$

$$\left(\eta = \frac{What\ \ you\ \ get}{What\ \ you\ \ pay} \right)$$

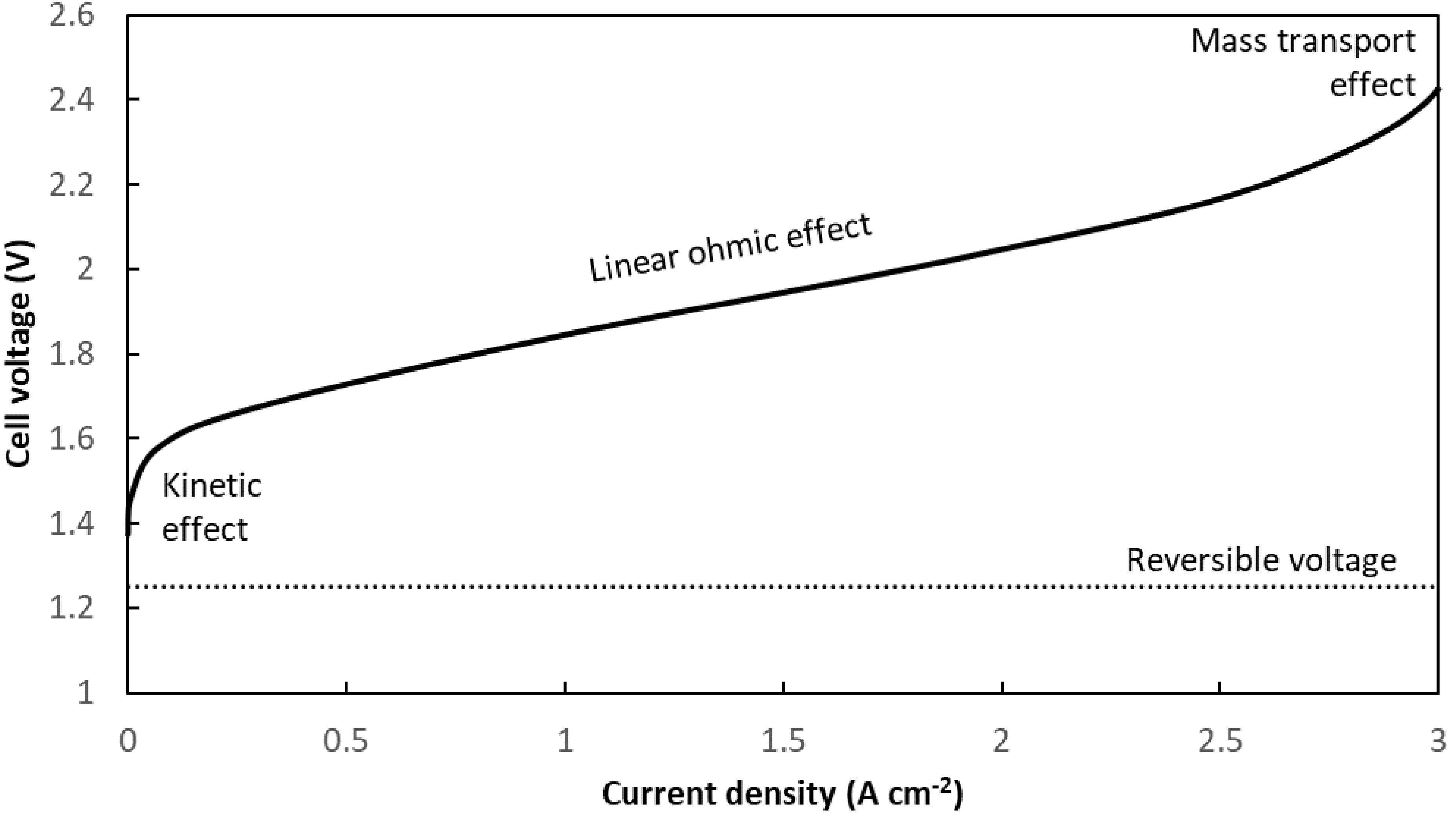
The available/necessary energy

25°C, 1 bar	Fuel cell ($\rightarrow$)	Electrolyzer ($\leftarrow$)
	$H_2(g) + ½O_2(g) \leftrightarrow H_2O(l)$	
ΔH (higher heating value)	-285.8 kJ/mol	285.8 kJ/mol
ΔG	-237.1 kJ/mol	237.1 kJ/mol
η_{max}	$\Delta G/\Delta H$ = 83%	$\Delta H/\Delta G$ = 121%
	$H_2(g) + ½O_2(g) \leftrightarrow H_2O(g)$	
ΔH (lower heating value)	-241.8 kJ/mol	241.8 kJ/mol
ΔG	-228.6 kJ/mol	228.6 kJ/mol
η_{max}	$\Delta G/\Delta H$ = 95%	$\Delta H/\Delta G$ = 106%

$$\left(\eta = \frac{\text{What you get}}{\text{What you pay}} \right)$$

The polarization curve

$H_2(g) + ½O_2(g) \rightleftarrows H_2O(l)$



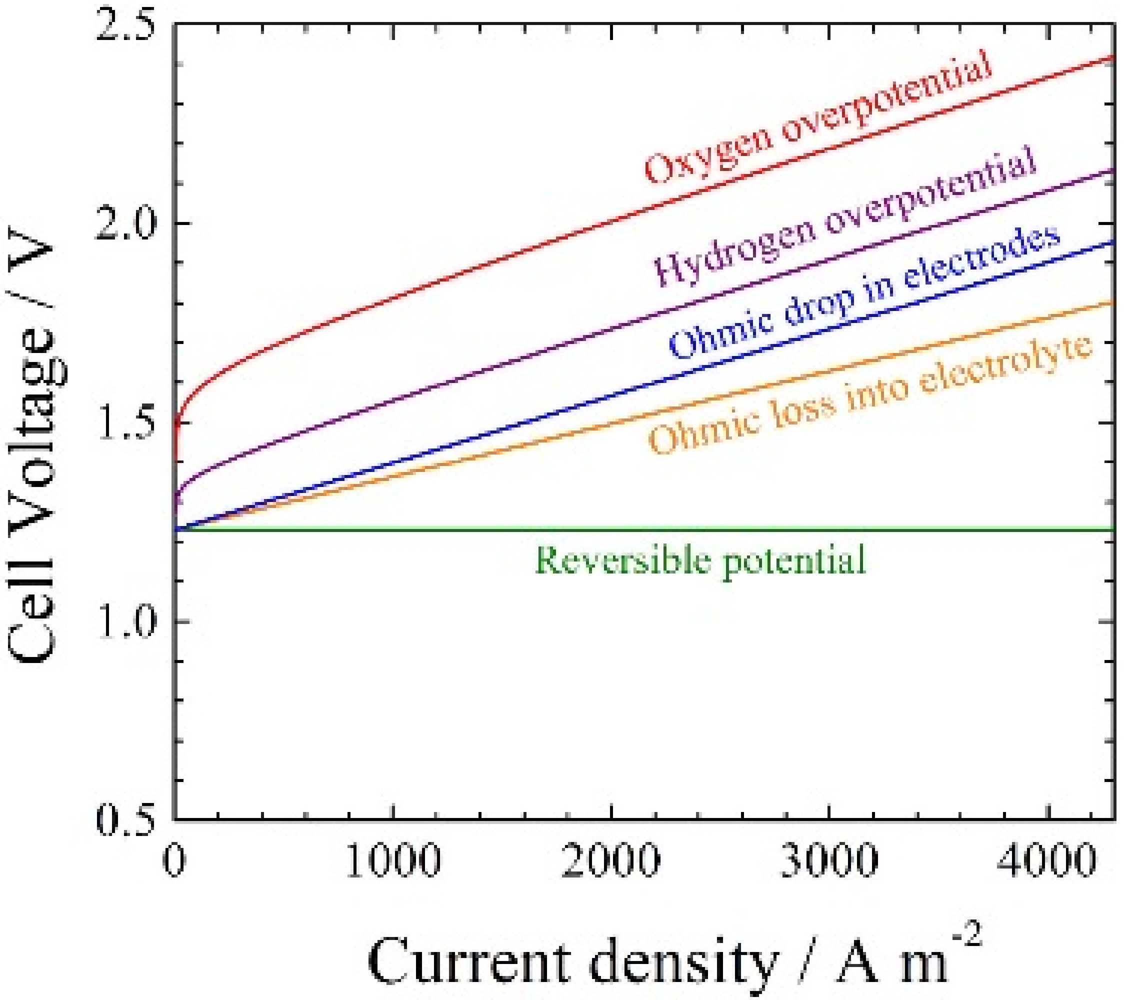
$$E = \frac{\text{Energy}}{\text{charge}}$$

$$E_{\text{rev}} = \frac{\Delta G(T)}{nF}$$

F: faradays constant

n: No. of electrons

Schematic overview of losses in electrolyzers



The thermo-neutral voltage

$$H_2O(l) \rightarrow H_2(g) + \tfrac{1}{2}O_2(g)$$

$$E_{tn} = \frac{\Delta H}{nF} = 1.48V\,(HHV, liquid\ water)$$

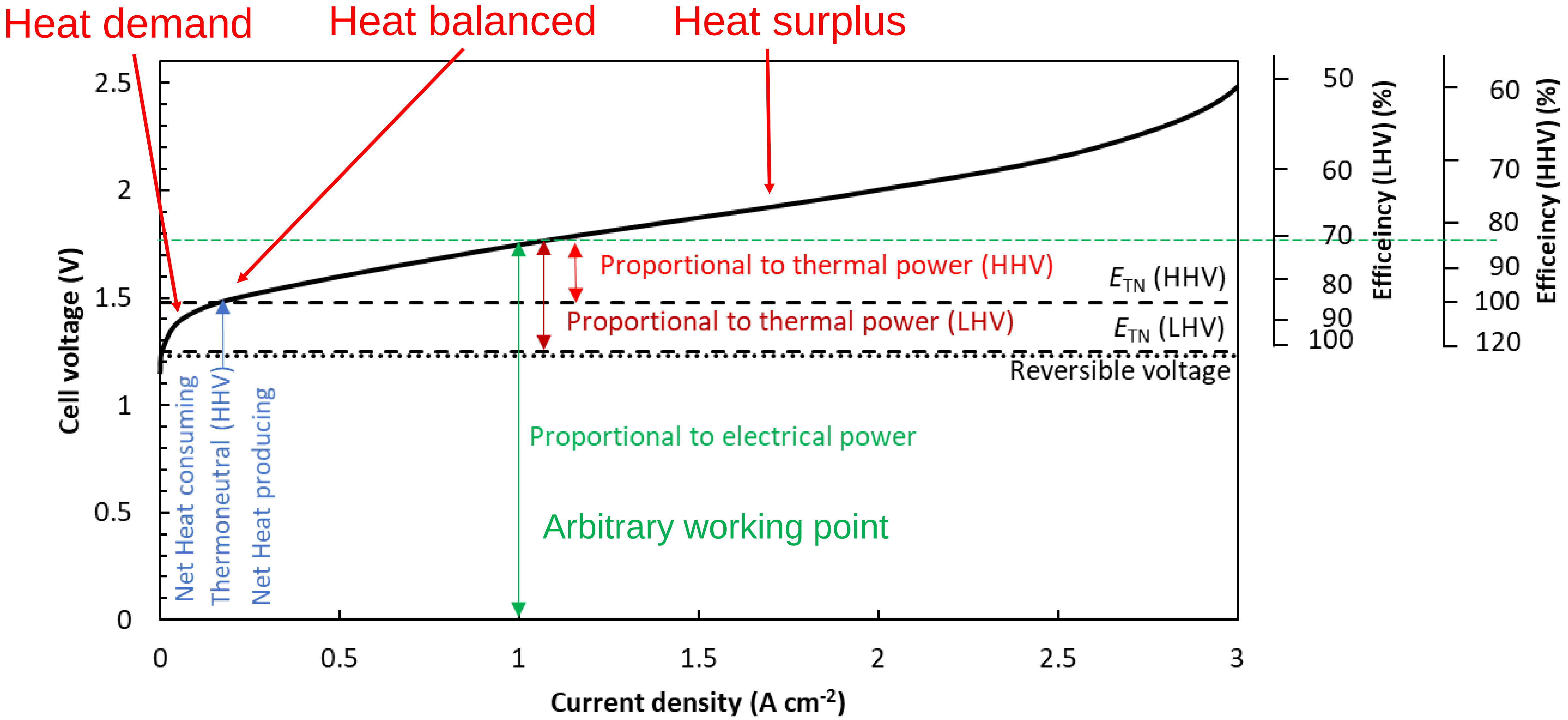
Endothermic (heat consuming)

$$H_2O(g) \rightarrow H_2(g) + \tfrac{1}{2}O_2(g)$$

$$E_{tn} = \frac{\Delta H}{nF} = 1.25V\,(LHV, water\ vapour)$$

At E_{TN} the energy in excess of ΔG produces heat (loss?), which is used (no loss)

The polarization curve



Minimum energy demand

Reference points for commercial electrolyzers

	HHV	LHV	Unit
Enthalpy of reaction	285.8	241.8	$kJ\ mol^{-1}$
Minimum energy demand	39.38	33.32	$kWh\ kg^{-1}$
Minimum energy demand	3.54	3.00	$kWh\ Nm^{-3}$

Nm^{-3}: Normal cubic meter at 1 atm and 0 °C

Example: A system consuming 5 $kW\ Nm^{-3}$

$$\eta_{sys} = \frac{3.54}{5.00} = 71\ \%\ (\text{HHV})$$

Types of electrolyzers

Electrode reactions in electrolyzers

Proton conducting electrolyte

Anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

Cathode: $4H^+ + 4e^- \rightarrow 2H_2$

Total: $2H_2O \rightarrow 2H_2 + O_2$

Oxide ion conducting electrolyte

Anode: $2O^{2-} \rightarrow O_2 + 4e^-$

Cathode: $2H_2O + 4e^- \rightarrow 2H_2 + 2O^{2-}$

Total: $2H_2O \rightarrow 2H_2 + O_2$

Hydroxide ion conducting electrolyte

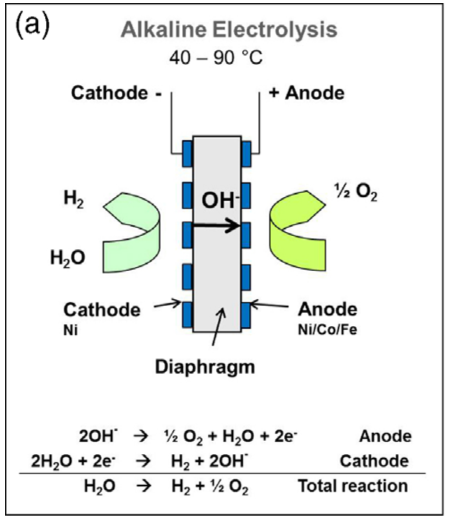
Anode: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

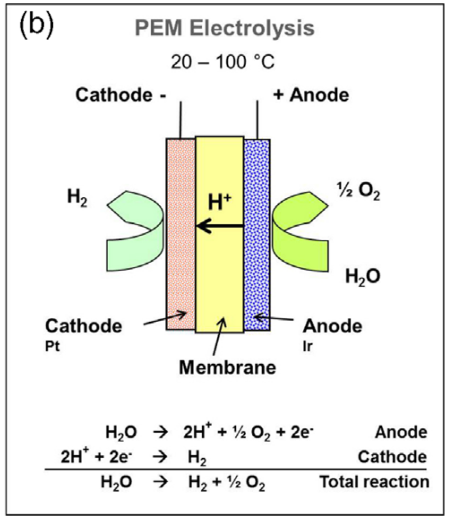
Cathode: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$

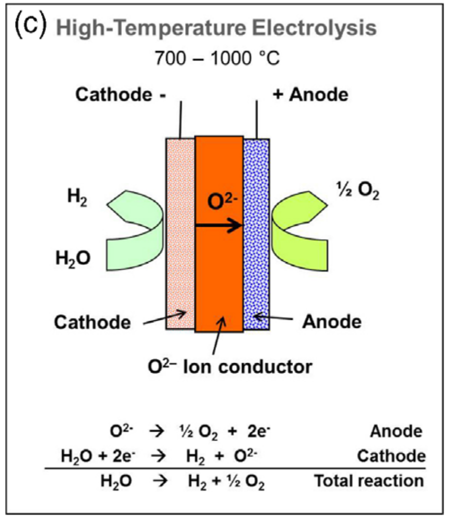
Total: $2H_2O \rightarrow 2H_2 + O_2$

Types of electrolyzer cells

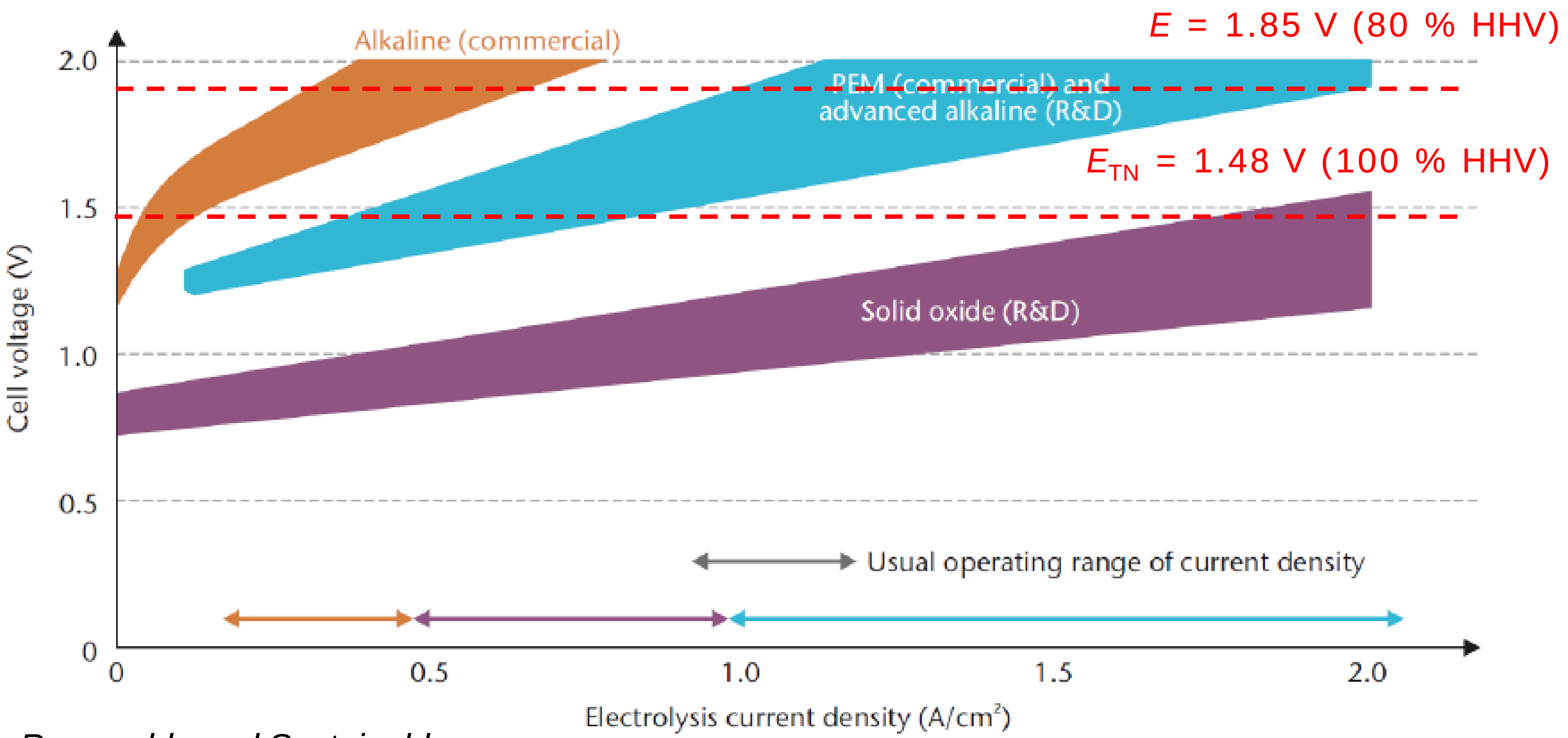
Family	Type	Abrev.	Temperature	Electrolyte (charge carrier)
Low temperature systems	Alkaline electrolyzer	AEC	60-80°C	aq. KOH (OH^-)
	Polymer (PEM) electrolyzer	PEMEC	60- 80°C	Polymer (H^+)
	~~Direct methanol electrolyzer~~	DMEC	60- 80°C	Polymer (H^+)
	~~Phosphoric acid electrolyzer~~	PAEC	200°C	H_3PO_4 (H^+)
High temperature systems	~~Molten carbonate electrolyzer~~	MCEC	650°C	Molten salt (CO_3^{-2})
	Solid oxide electrolyzer	SOEC	700-900°C	Ceramic (O^{2-})







AEC vs PEM vs SOEC (typical and very schematic)



C. Graves et al. *Renewable and Sustainable Energy Reviews* **2011**, *15*, 1–23.

Alkaline electrolyzer (AEC)

- Traditional technology
- Long time commercial
- MW size, 1-35 bar(a)
- Quite inexpensive materials
- Proven technology
- Quite bulky

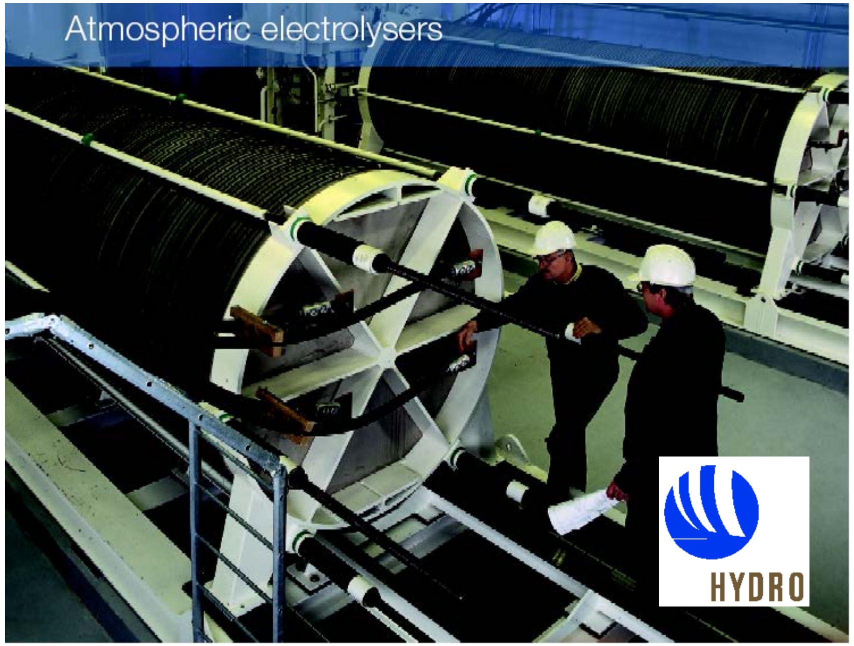
Electrolyte: 25-30 % KOH

Separator:
    Before: asbestos,
    Today: porous diaphragm (Zirfon)

Cathode catalyst (H_2): Ni or Ni compounds

Anode catalyst (O_2): Metal oxides like Ni-Fe oxide

Container and bipolar plates: Ni plated Steel



Diaphragm/membrane for the alkaline electrolyte

Originally: Asbestos.

Very stable but phased out for environmental/health reasons

Alternative mats available

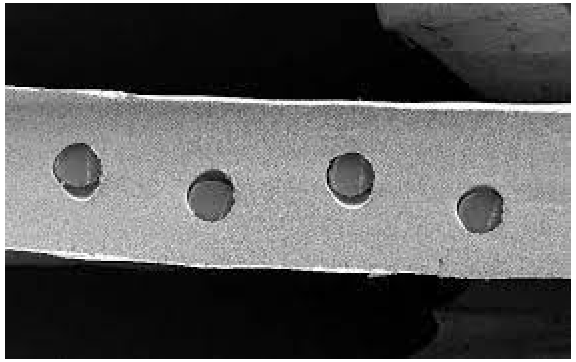
Today: porous composites like Zirfon

A polysulfone based composite made hydrophilic by particles of ZrO_2

The dream: an anion exchange membrane like for PEMEC

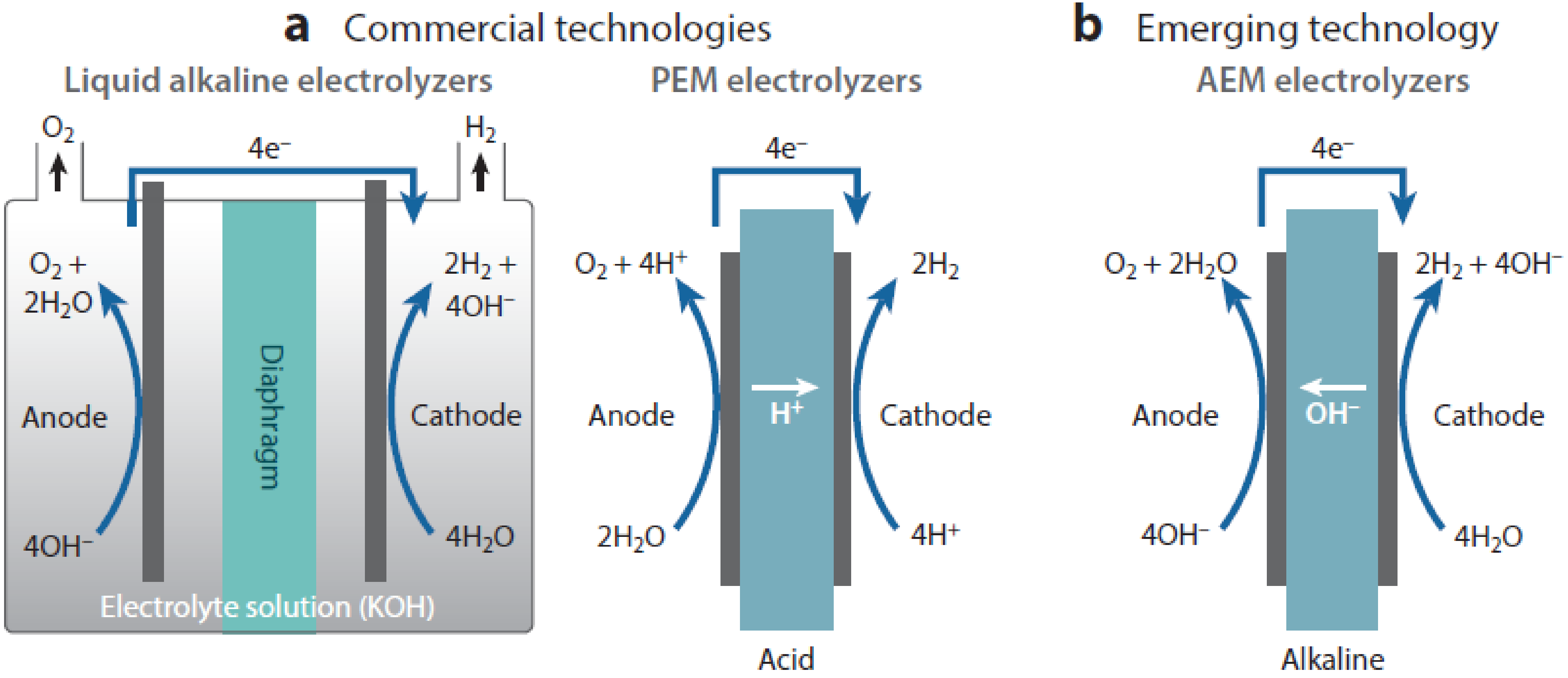
Asbestos substitute
+1 mm

Zirfon Pearl
(Agfa)
500 μm
220 μm



Aemion AEM
(Ionomr)
75 μm

Gap or zero gap



Gap

High internal resistance

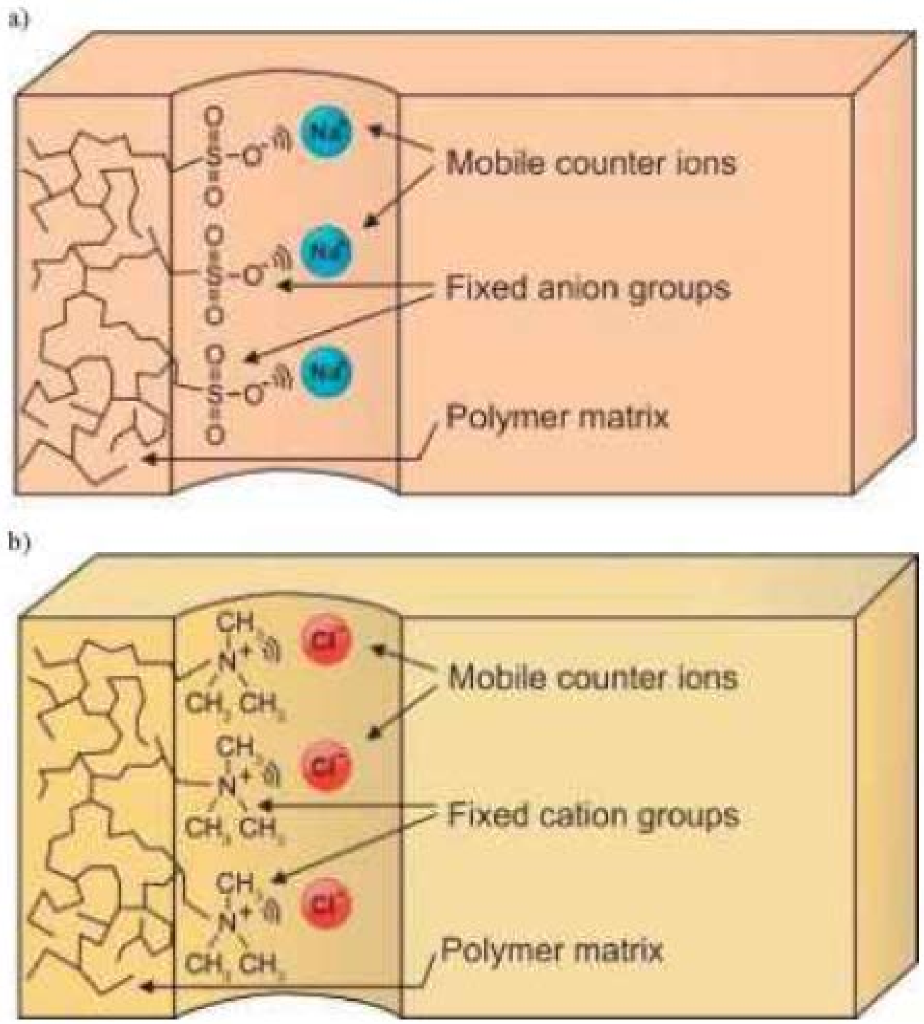
Zero-gap

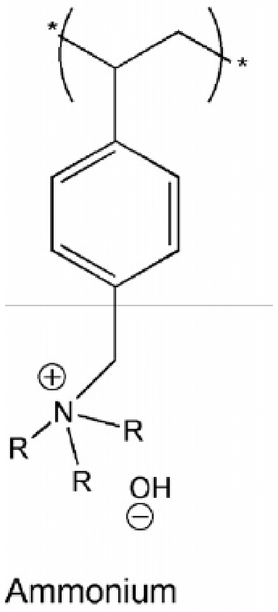
Low internal resistance

Anion-exchange membranes (AEM)

PEM

AEM





Under development

The largest electrolyzers

S-556 unit. 760 $Nm^3/h\ H_2$

INDUSTRIE
HAUTE
TECHNOLOGIE
CLEAN HYDROGEN SOLUTIONS

28 electrolysers Type S-556

21'000 $Nm^3/h\ H_2$ and

10'500 $Nm^3/h\ O_2$

In service since 1973 for Sable Chemical Industries in Zimbabwe

Large scale electrolyzers (Norsk Hydro)

Rjukan, Norway; 1927 – 1970's

Glomfjord, Norway; 1953 – 1991

Used for: Hydrogen → ammonia → fertilizers

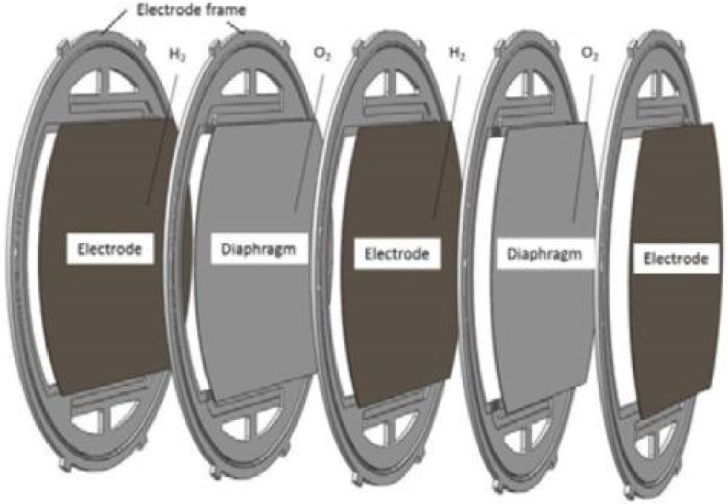
The activity is today with Nel Hydrogen

AEC unit from Green Hydrogen Systems

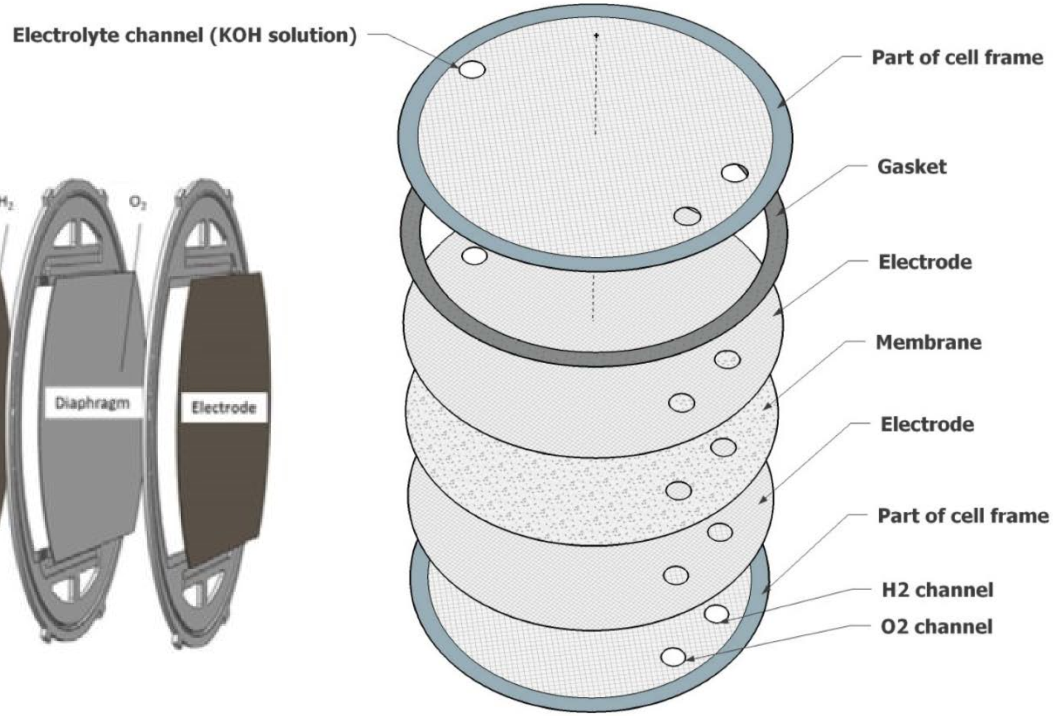
Hyprovide 250 – 450 kW

(1.1 x 1.8 x 2.3 m)

GREEN
HYDROGEN
SYSTEMS



GREEN
HYDROGEN
SYSTEMS



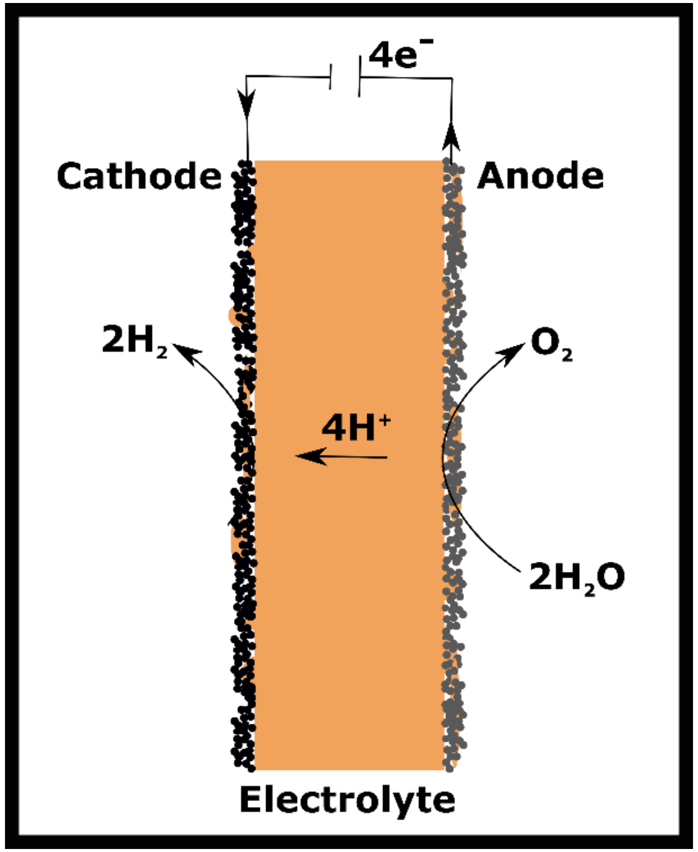
Unknown source

PEM electrolyzers - PEMEC

- Recent technology
- Compact
- Efficient
- Under further development
- Partly commercial
- Medium scale (so far)
- Fast transient response
- Expensive

2 MW stack, Giner

Unknown origin



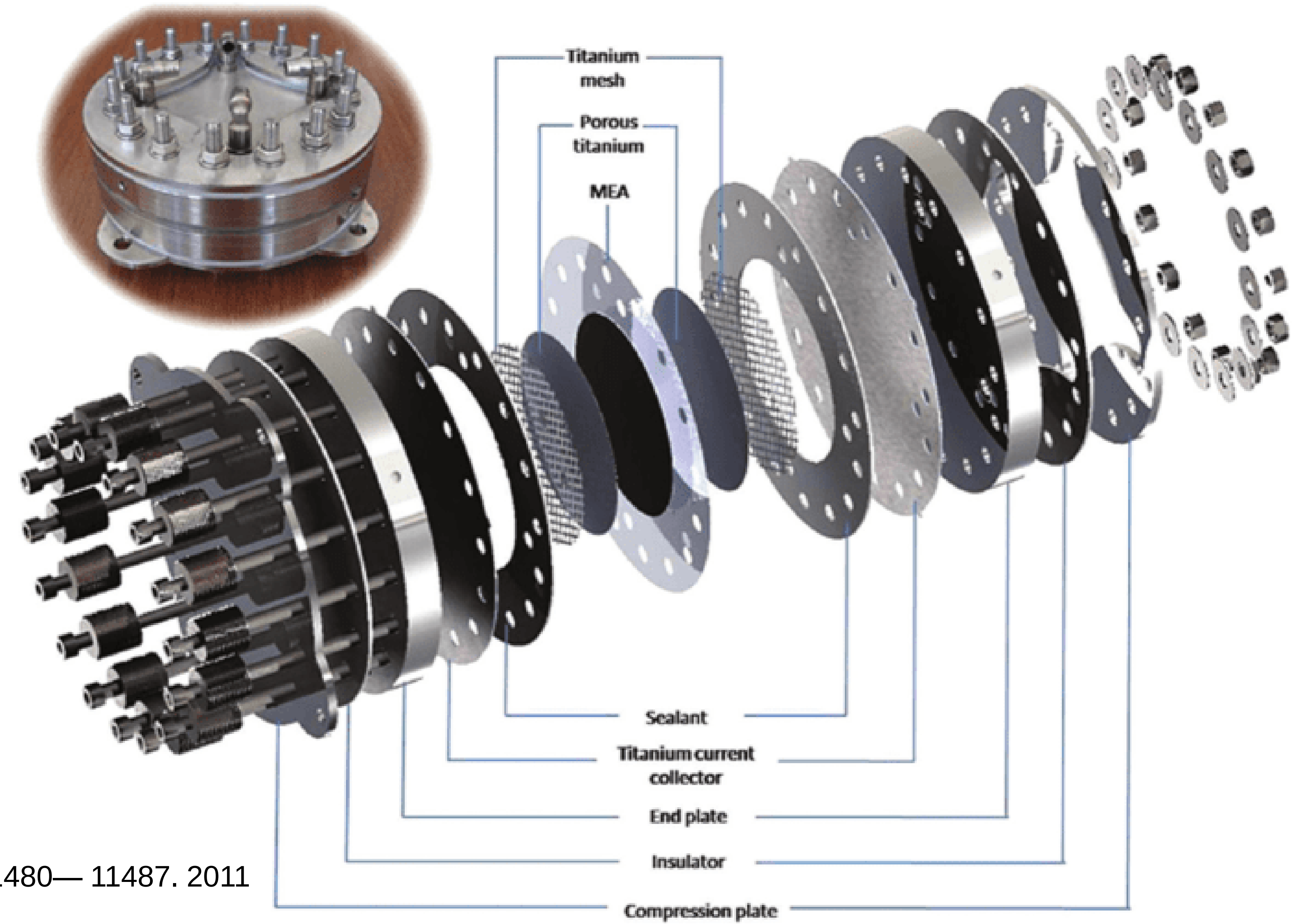
Anode:
Catalyst: IrO_2 or $(Ir, Ru)O_2$
Electrode support:
Noble metal coated porous Ti

Cathode:
Catalyst: Pt
Electrode support:
Noble metal coated porous Ti or carbon

Electrolyte:
PFSA (Nafion)
(no problems with wetting)

Bipolar plates:
Noble metal coated Ti

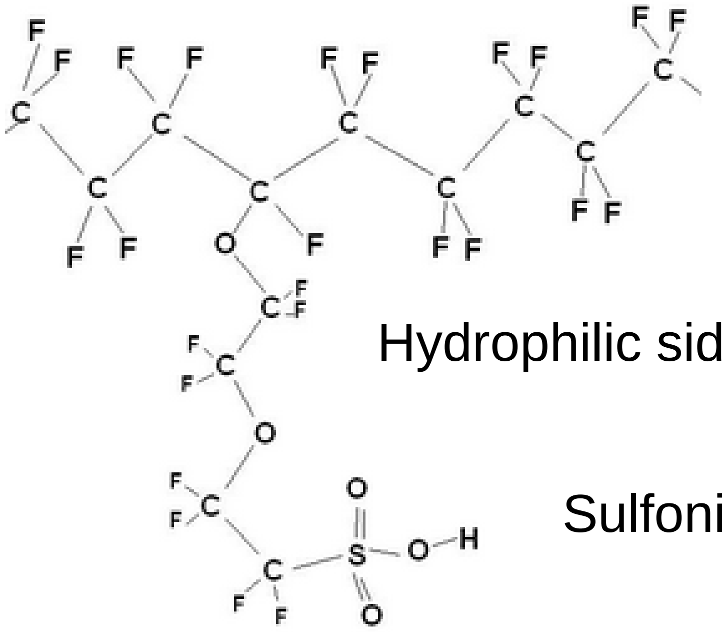
PEMEC



Selamet, O.F. et al., *Int. J. Hydr. Energ.*, 36, 11480— 11487. 2011

https://doi.org/10.1016/j.ijhydene.2011.01.129

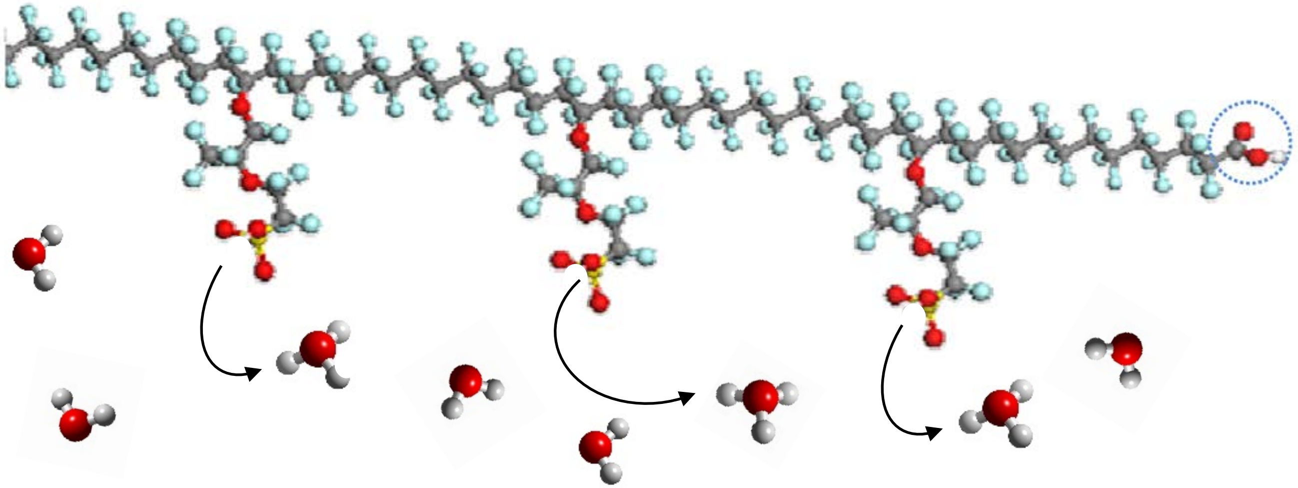
Proton conduction in polymer



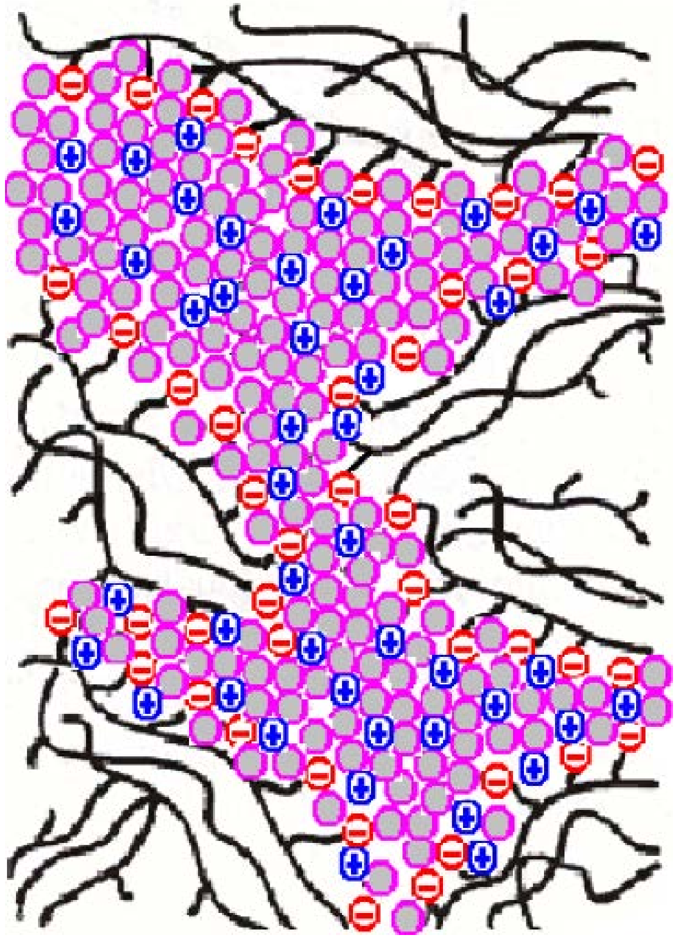
Hydrophobic
backbone

Hydrophilic side chains

Sulfonic acid

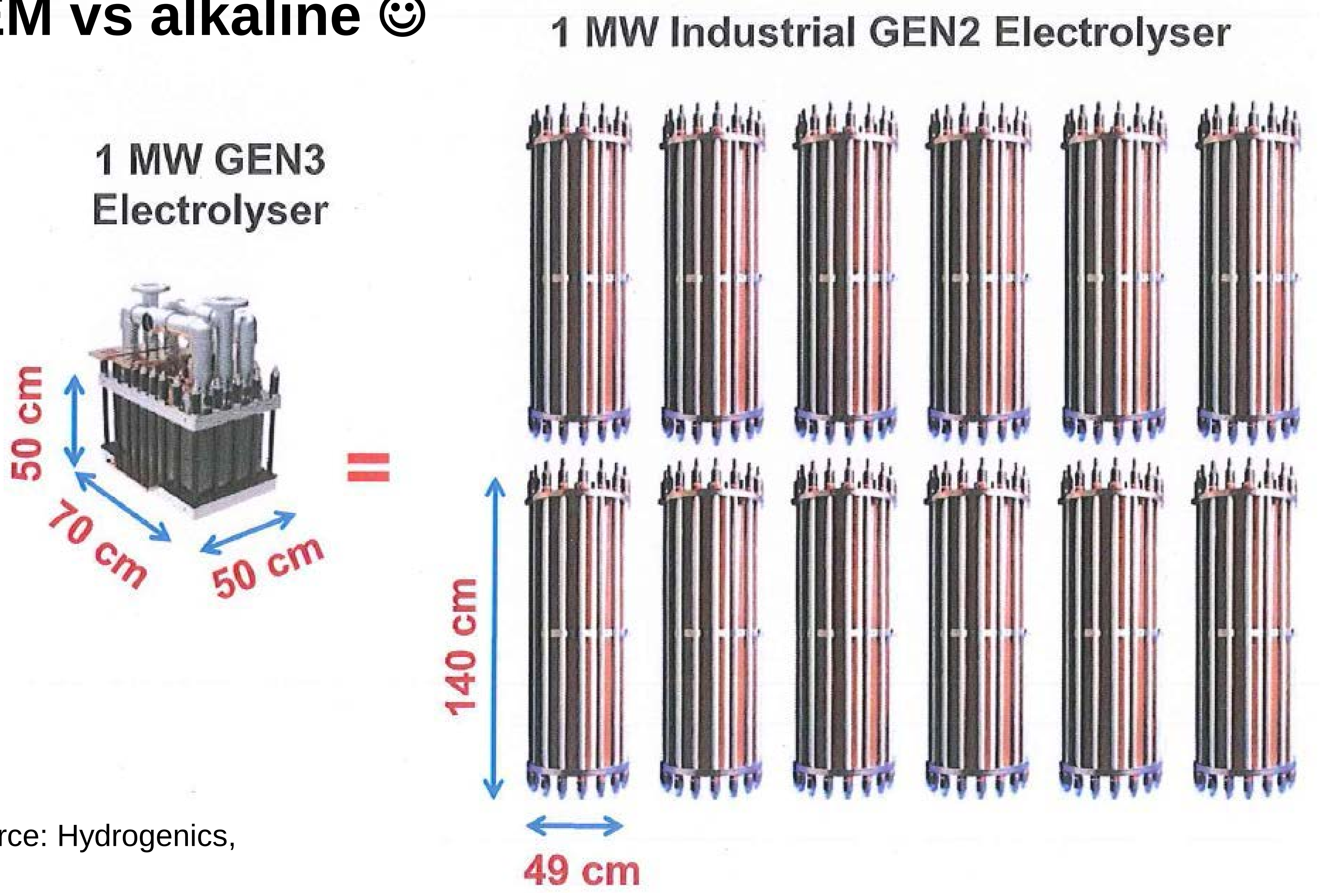


Hydrophobic backbone



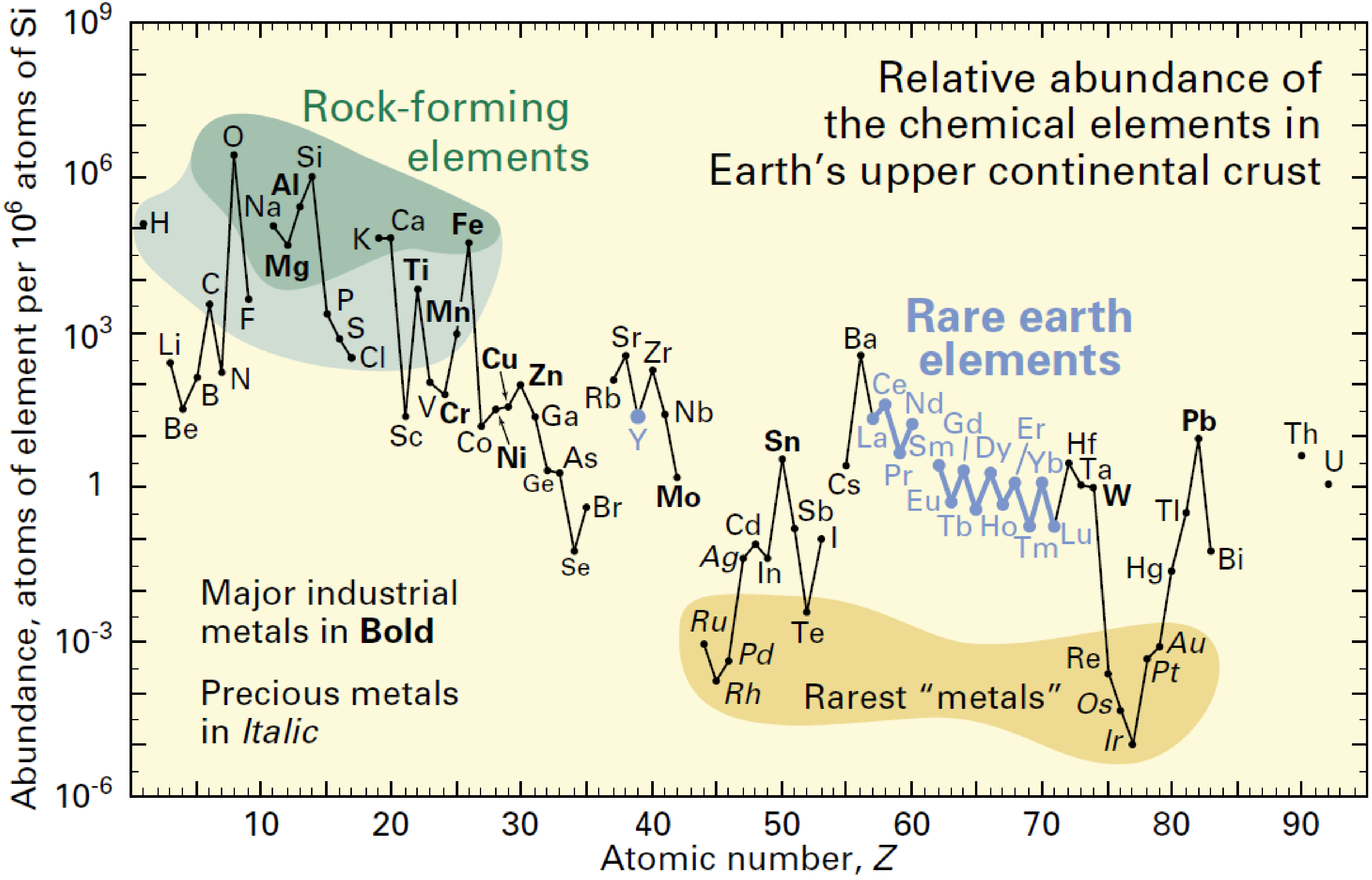
Perfluorosulfonic acid, PFSA

PEM vs alkaline ☺



Source: Hydrogenics,

Elemental abundance

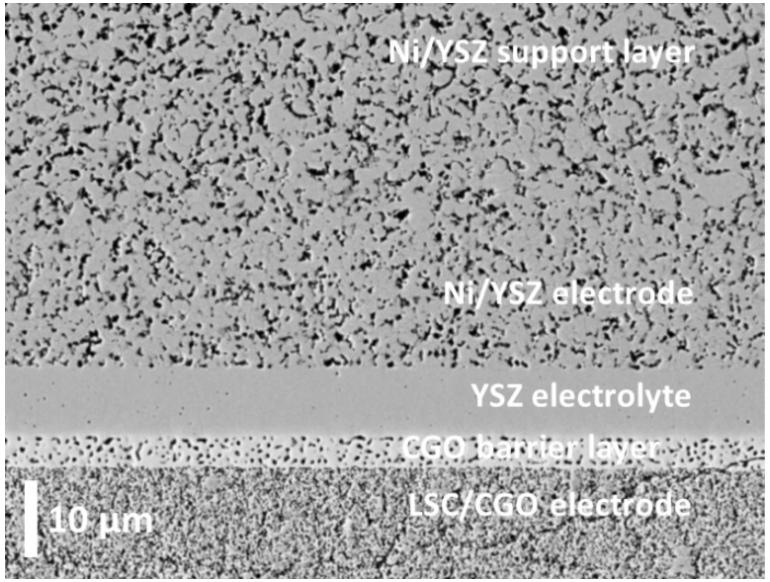


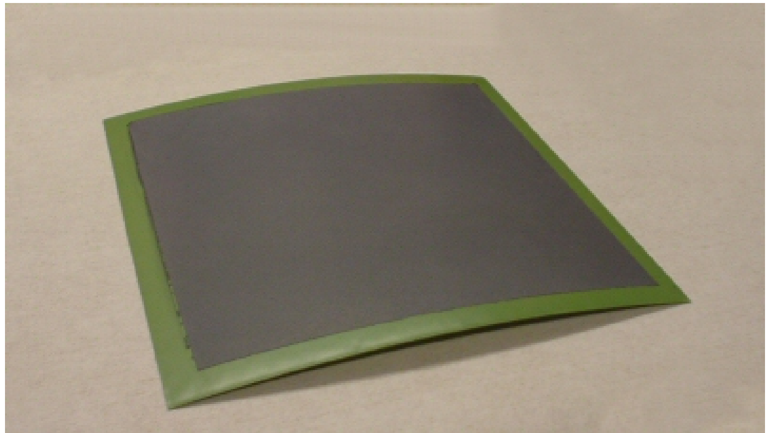
U.S. Geological Survey
Fact Sheet 087-02

Solid oxide electrolyzers - SOEC

- Future technology
- Early development
- Potential for high efficiency
  (Low ΔG and good kinetics)
- Materials like for SOFC
- CO_2 electrolysis
- Not commercial

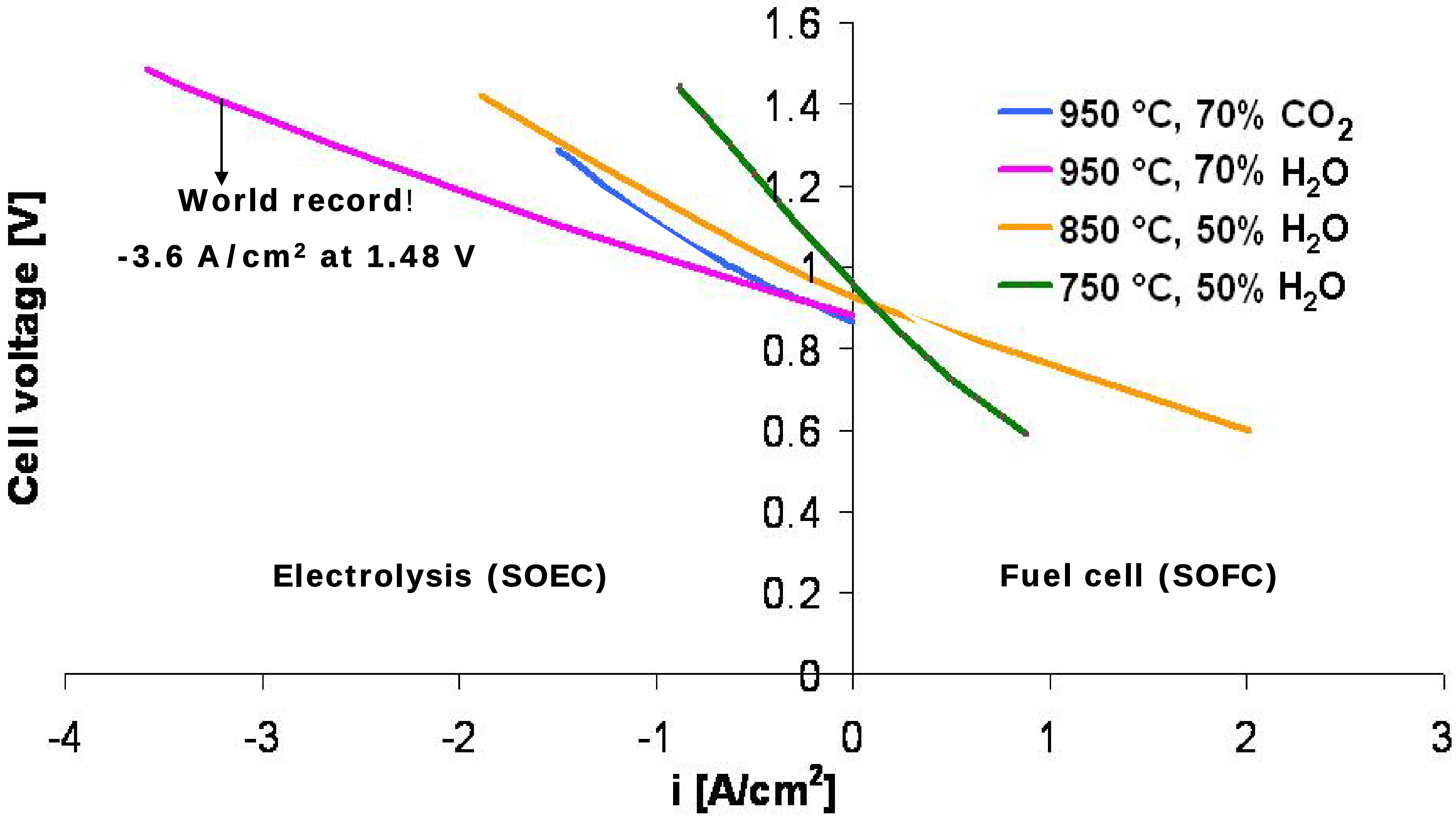
750 - 900 ° C

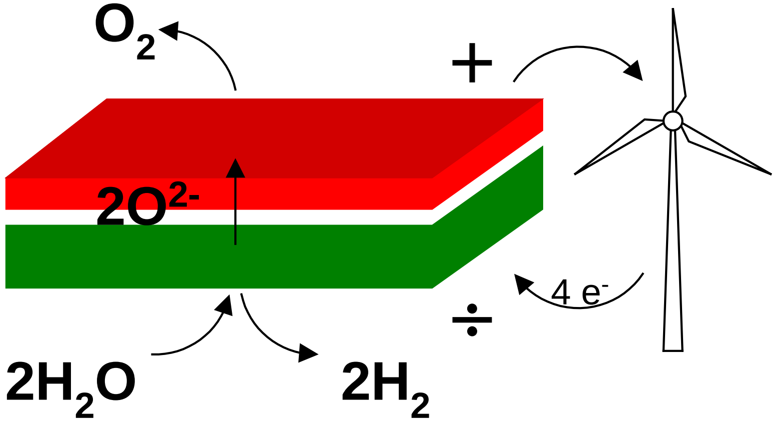




SOFC/SOEC from DTU

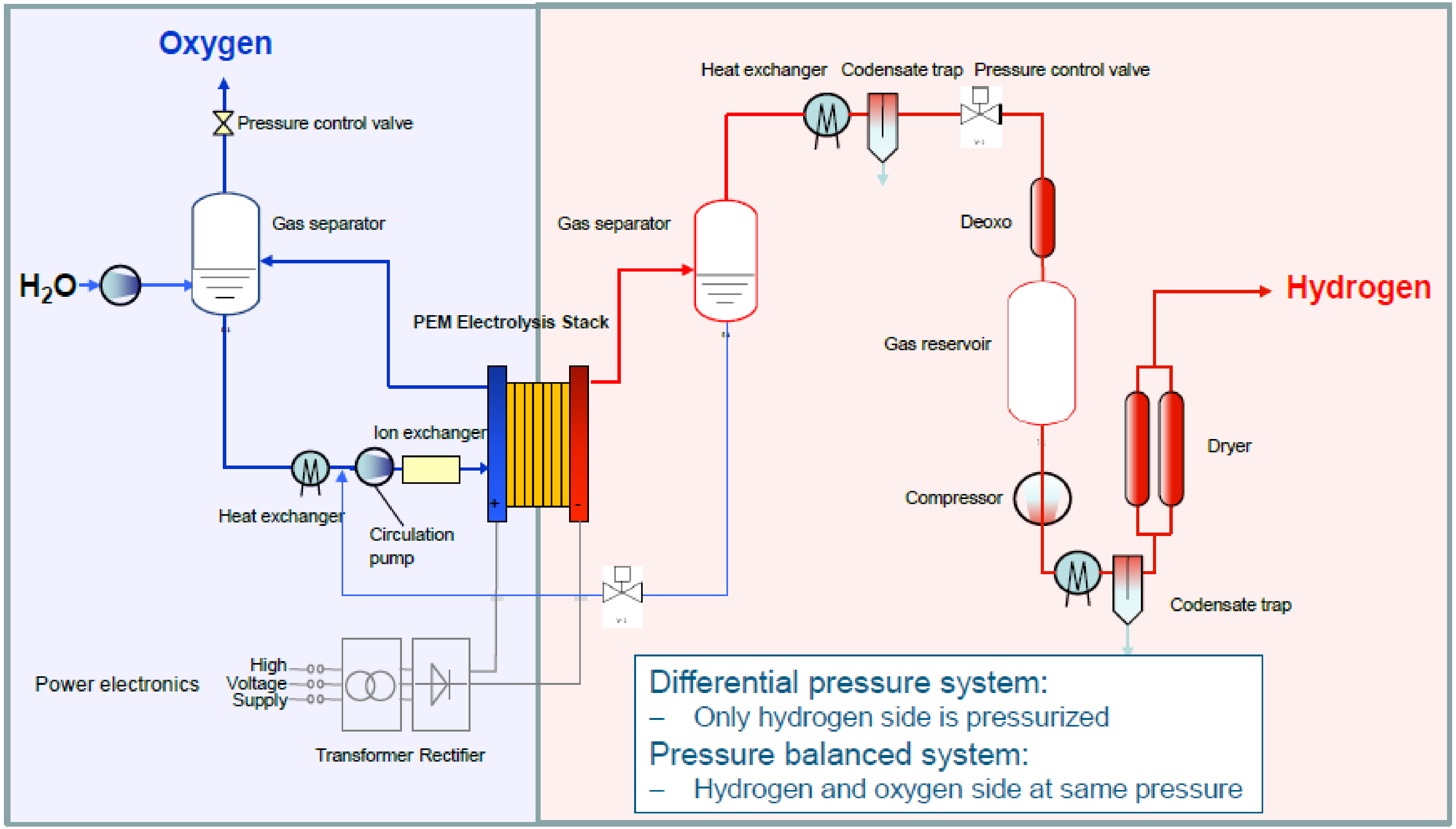
Solid oxide electrolyzer cell (SOEC)





SOFC/SOEC from DTU Energy

A PEMEC system



Differential pressure system:
– Only hydrogen side is pressurized

Pressure balanced system:
– Hydrogen and oxygen side at same pressure

High pressure electrolysis

Isothermal compression work, $w_{compression}$ of *n* mole gas from P_1 to P_2

$$w_{compression} = nRT\ln\frac{P_2}{P_1}$$

Same work for any pressure decade

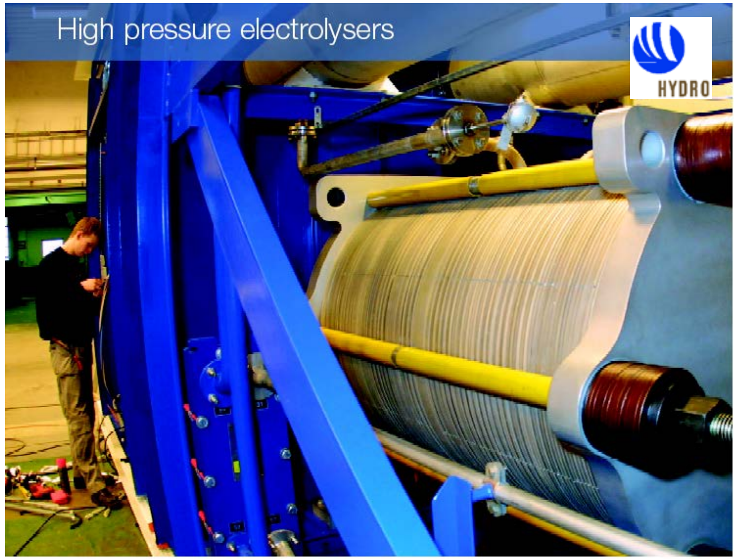
1-10 bar or 10-100 bar

(*for a perfect gas only*)

PEMEC,
40 bar (Giner)

PEMEC, 80 bar (ITM)

AEC units, 30 bar (Hydro/Nel)



Summary on the three electrolyzers

AEC:

Traditional version:

- Well-proven
- Robust
- Bulky
- No strategic materials
- Fully commercial.

New generations on the way which are expected to resemble PEMEC

PEMEC:

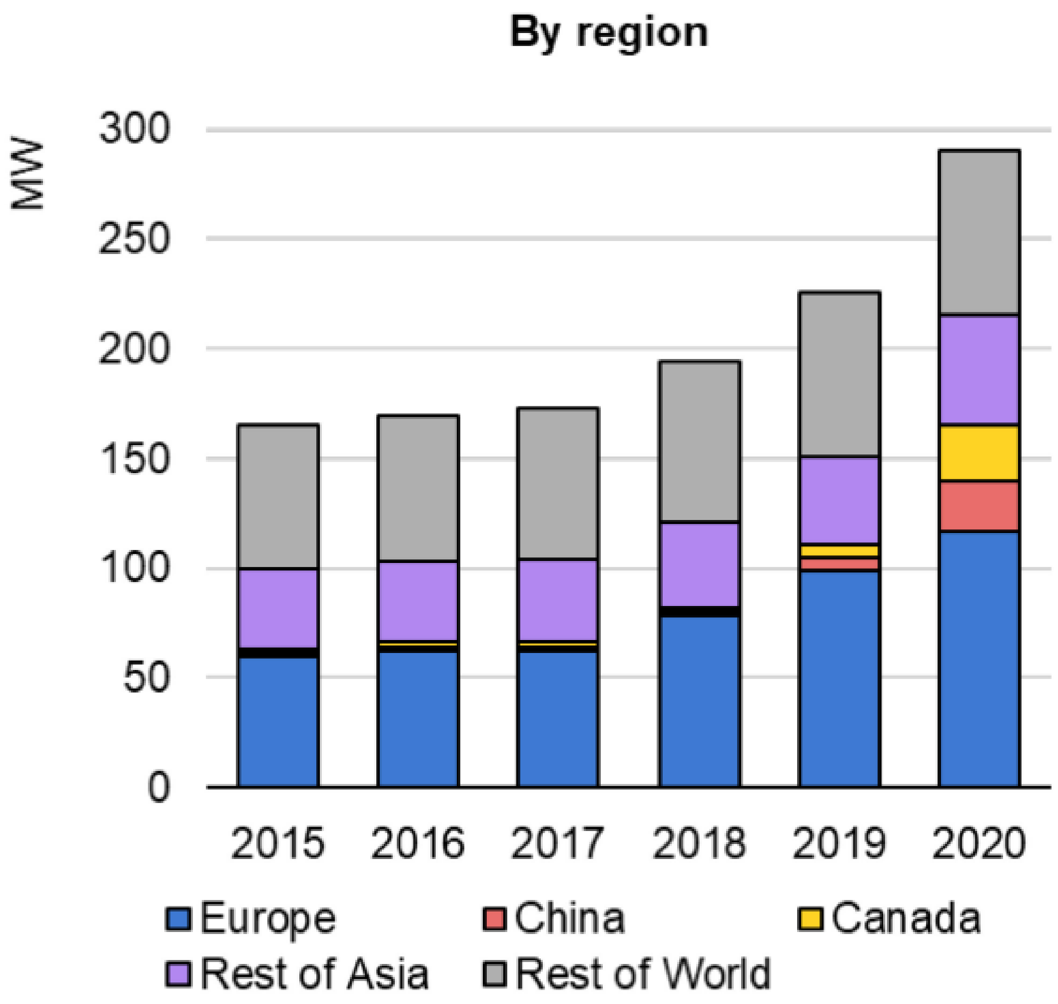
- Compact
- Pure water
- High rate (several A cm^{-2})
- Costly
- Limited scaling due to iridium.
- Fully commercial.

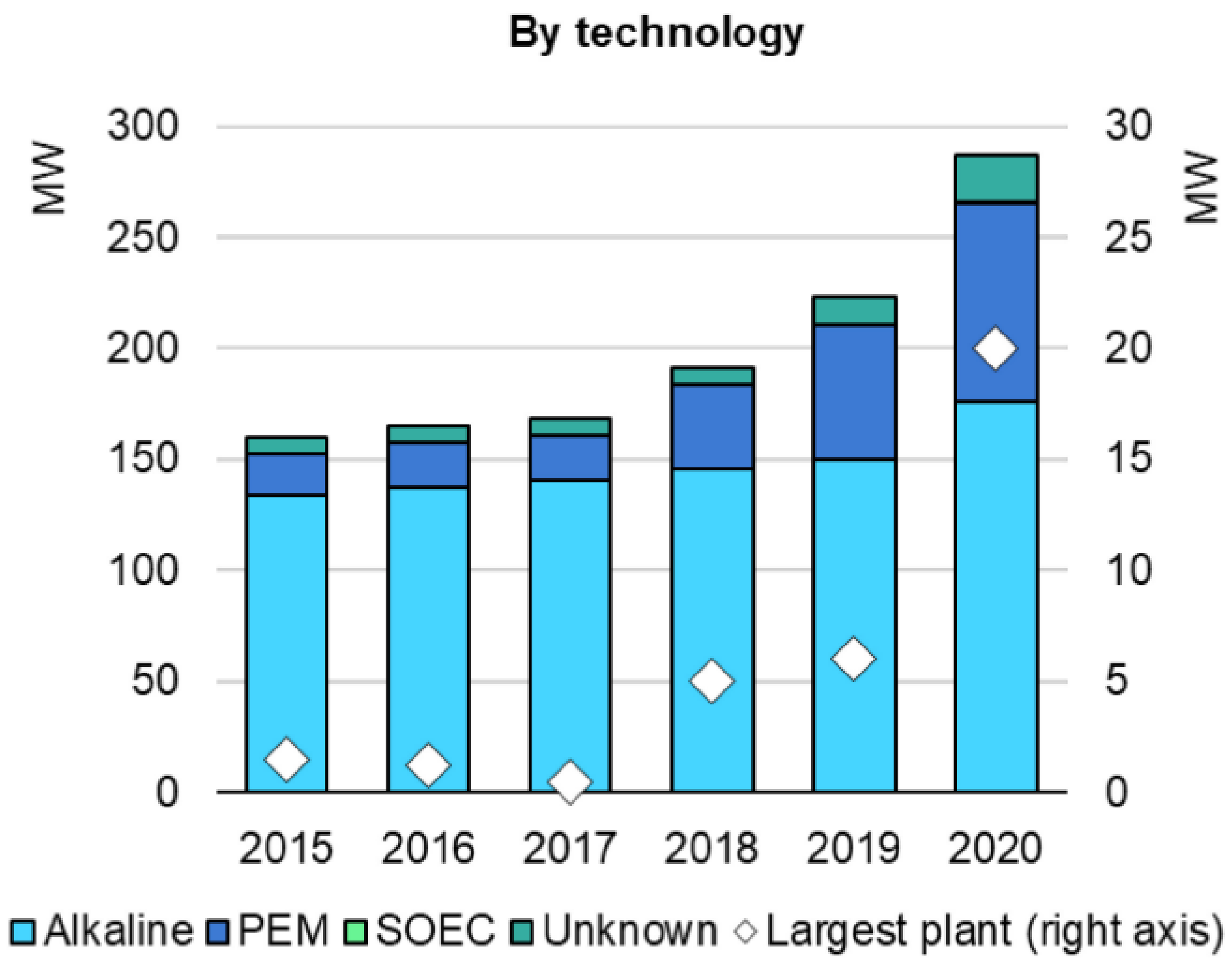
SOEC:

- High conversion efficiency (thermoneutral or better)
- No strategic materials.
- Possible dual mode (EC/FC)
- Not fully commercial yet.
- Scaling up pending.

Electrolysis - IEA, Global Hydrogen Review 2021

Global installed electrolysis capacity by region and technology, 2015-2020





A tremendous need for electrolysis

EU Hydrogen strategy 2020	
2020-2024	6 GW of electrolysis, 1 million tonnes of hydrogen
2025-2030	40 GW of electrolysis, 10 million tonnes of hydrogen
2030-2050	13-14 % of total energy mix - hydrogen

Repower EU 2022	
2030	10 million tonnes of hydrogen internally produced + 10 Mt imported hydrogen. 90-100 GW_{LHV} Electrolysis, 140 GW electricity rated (utilization 43 %, eff. 70%)

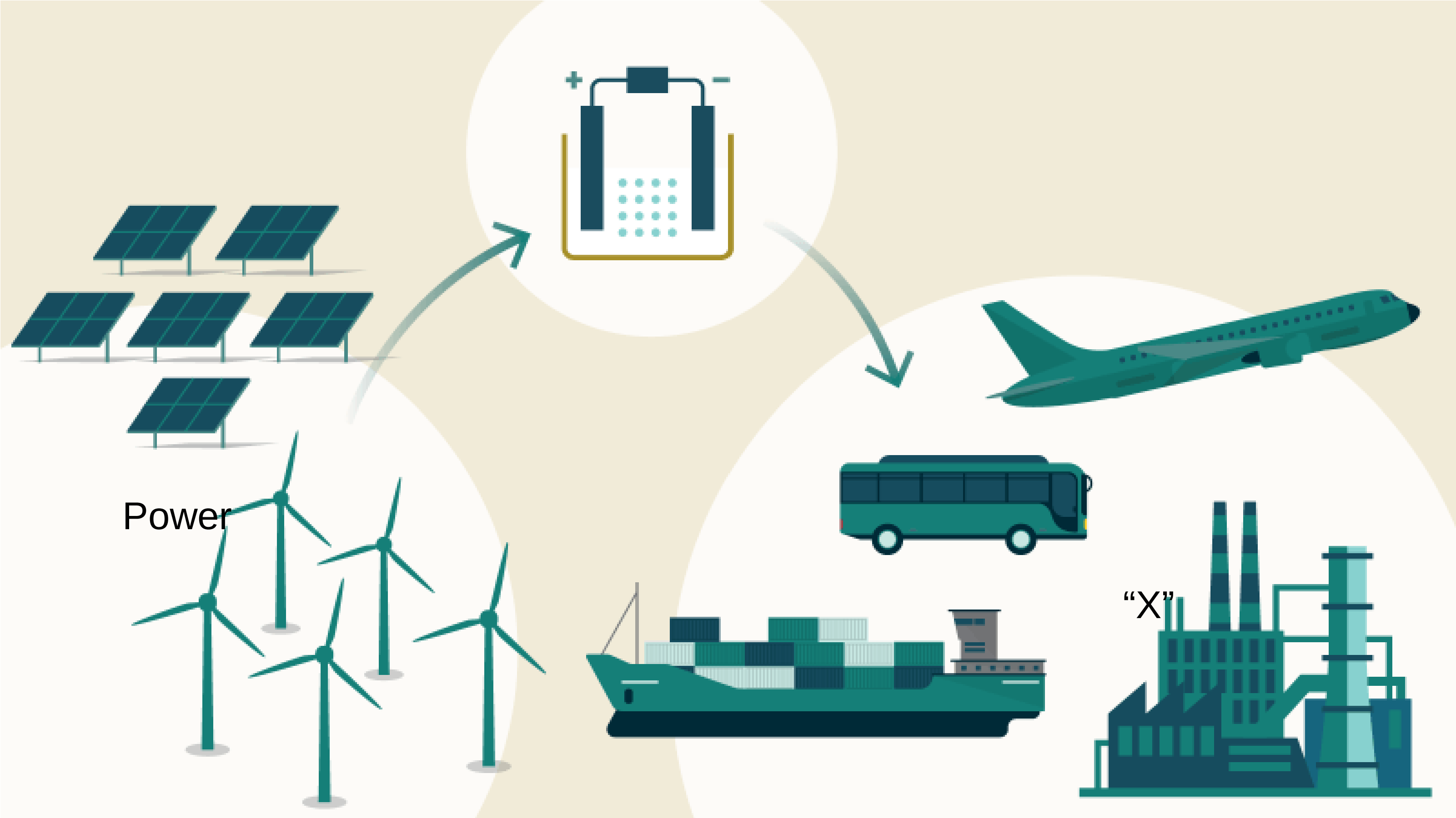
BloombergNEF's New Energy Outlook (NEO)	
2030	Green Scenario: 1.9 TW of electrolyzers to kick-start the hydrogen sector.
2050	Red (nuclear) Scenario 3.572 TW of nuclear capacity to power electrolyzers

- Total world average energy flow: 18 TW
- Several GW of electrolyzer projects in the European pipeline
- European production capacity for electrolyzers is currently in the order of 2 GW per year (*currently: 1.75 GW_{LHV} or 2.5 GW_{LHV} electricity rated*)*

*Joint Declaration. European Electrolyser Summit, Brussels 5 May 2022, Hydrogen Europe.

Power-to-X
(PtX)

Power-to-X



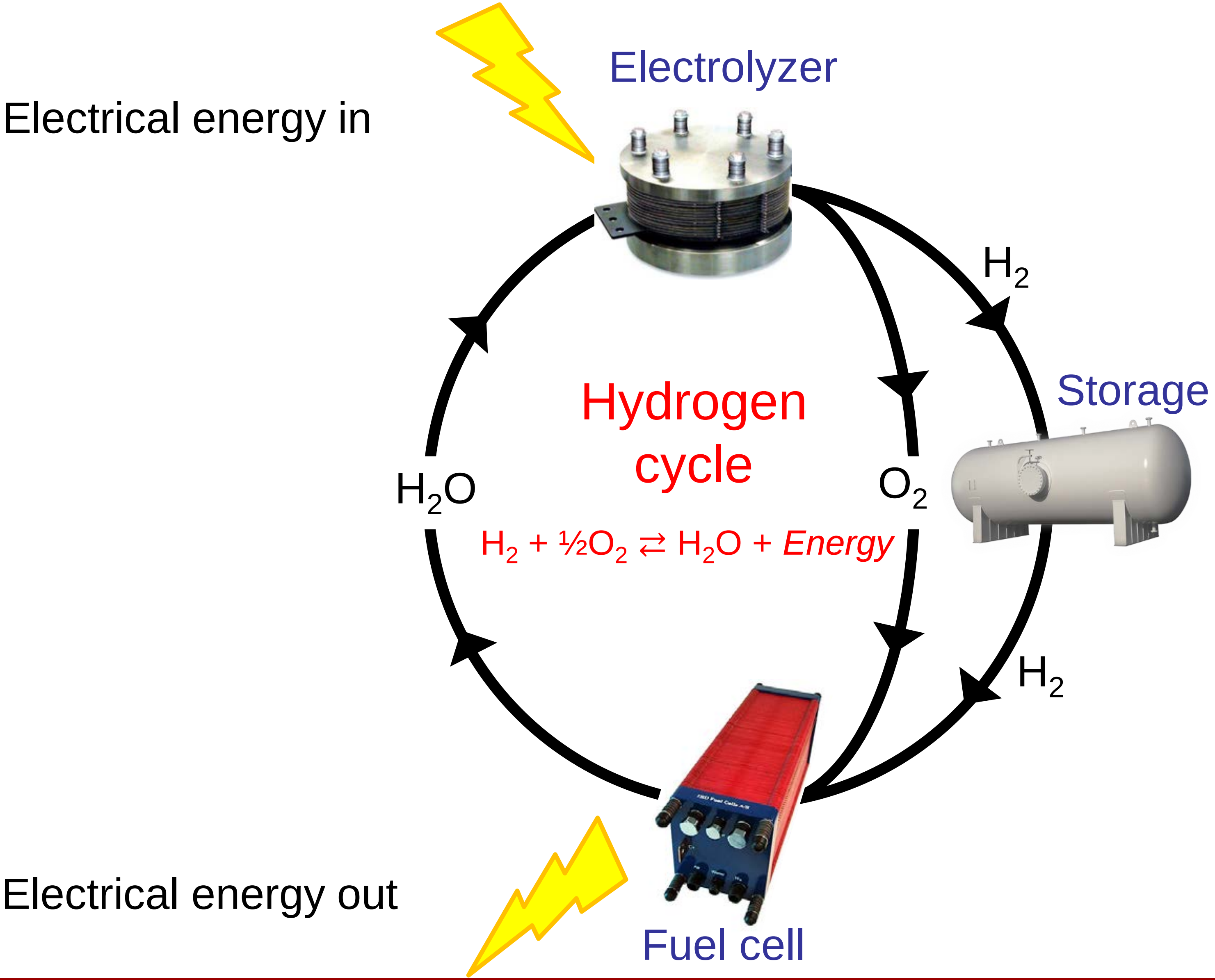
Pro - Ingeniøren

Power-to-gas
Power-to-liquid
Power-to-fuel
Power-to-chemicals
Power-to-whatever …

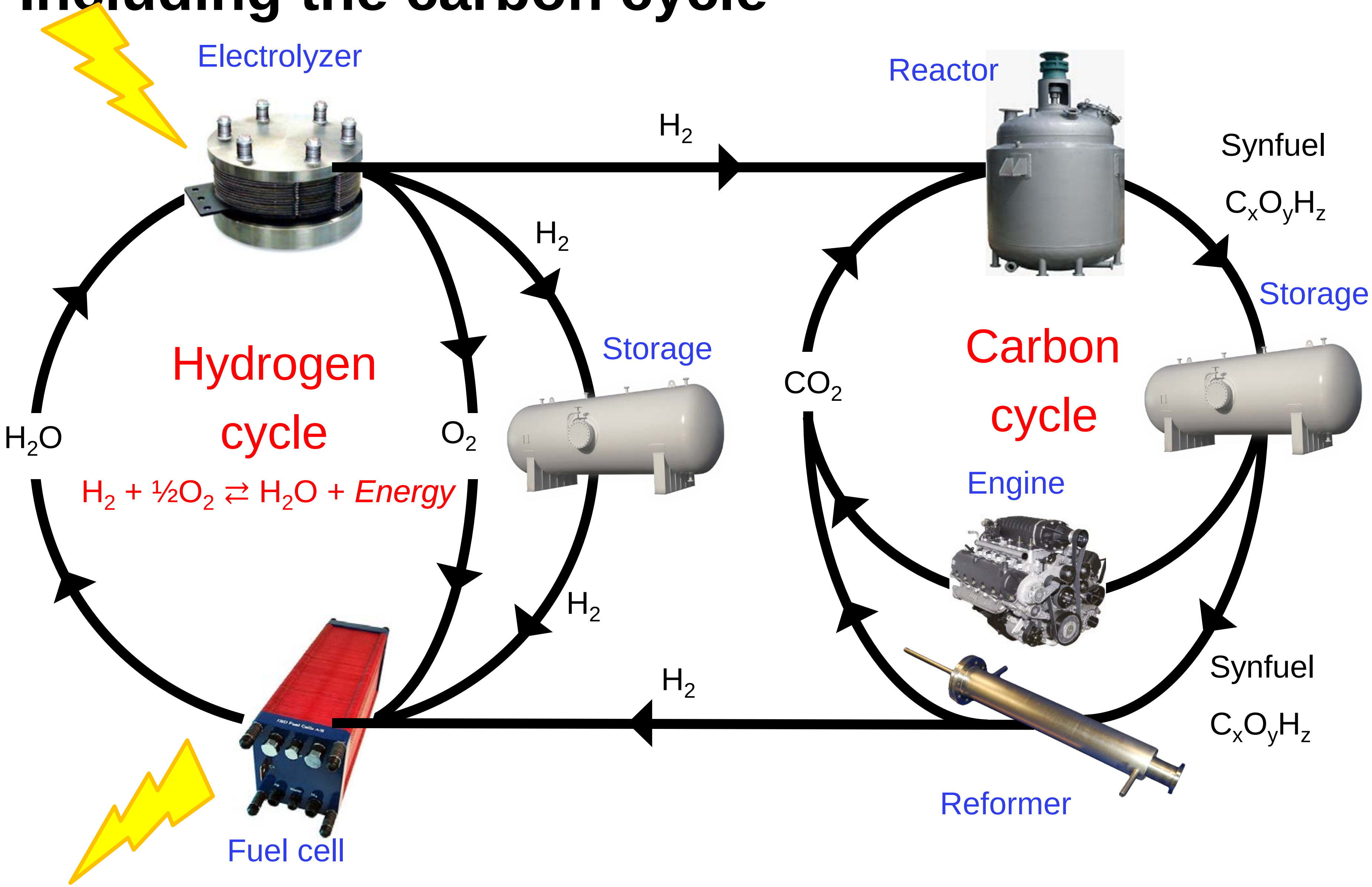
X =

- Hydrogen for
  - Transport
  - Storage
  - Industry
- Carbonaceous fuels for
  - Heavy transport
  - Storage
  - Industry
- Chemicals for industry
- Ammonia for
  - Fertilizers
  - Fuel

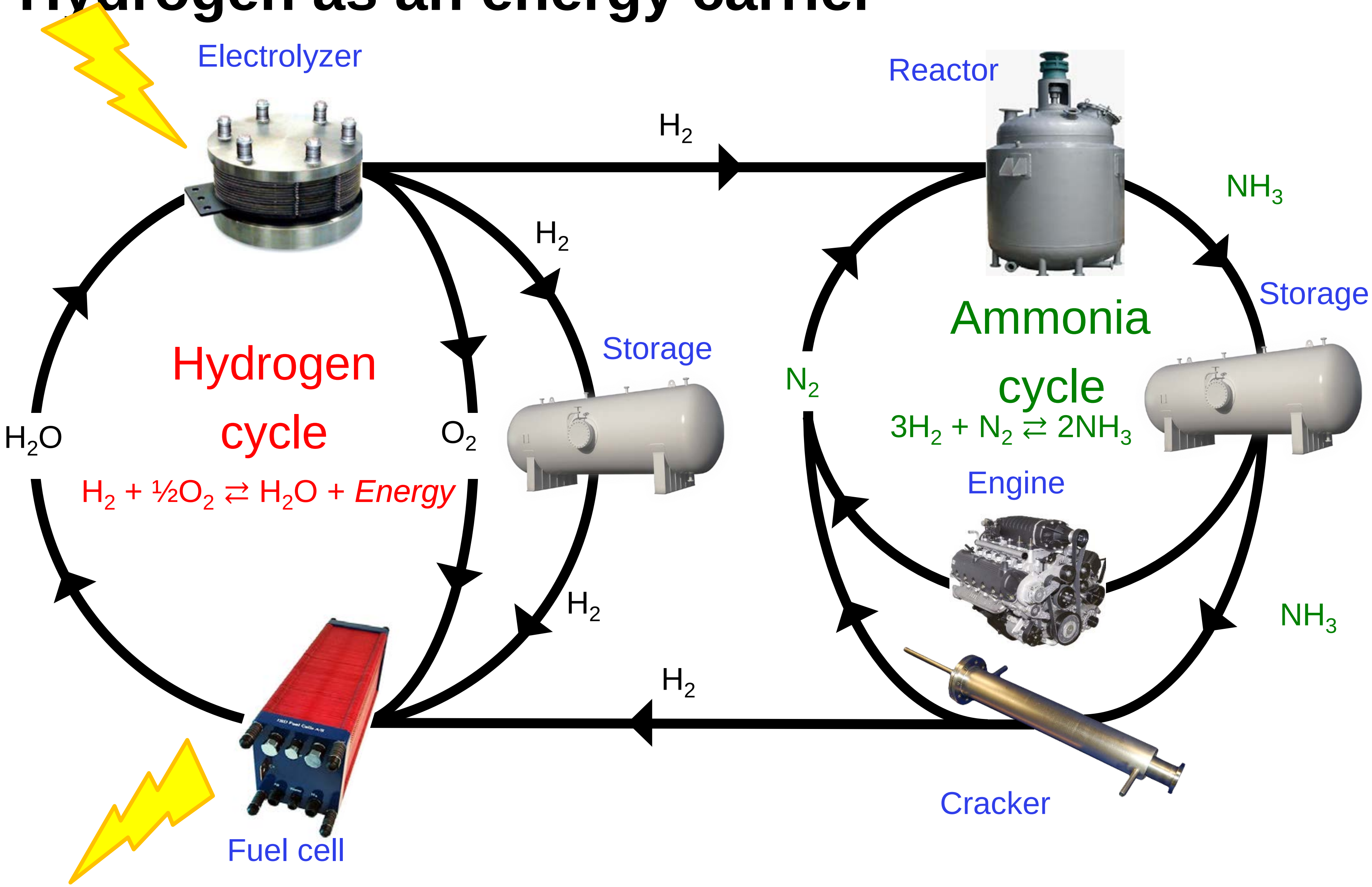
The hydrogen cycle



Including the carbon cycle



Hydrogen as an energy carrier



Synthetic fuels - hydrocarbons

The Sabatier process

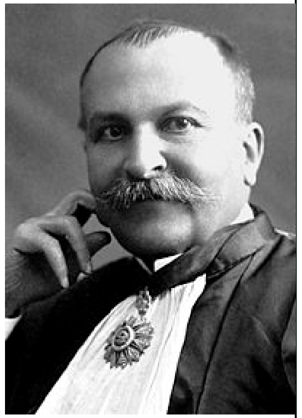
Synthesis of methane from hydrogen and carbon dioxide

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta H = -165.0 \text{ kJ/mol}$$

300-400 ºC with a nickel catalyst

Uses:

- Production of "*synthetic natural gas*"
- Upgrading of biogas by conversion of CO_2 to more methane.



The Sabatier process was discovered by the French chemist *Paul Sabatier* in the 1910s

The Fischer–Tropsch process

Synthesis of liquid hydrocarbons from hydrogen and carbon monoxide

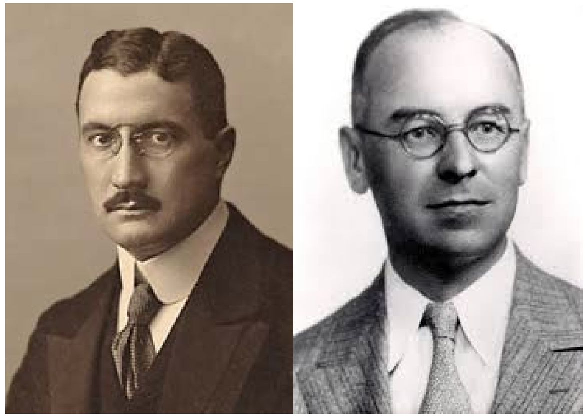
Carbon monoxide is formed from carbon dioxide by the *reverse water gas shift* reaction:

$$CO_2 + H_2O \rightarrow {\color{red}CO} + H_2 \qquad \Delta H = +41 \text{ kJ mol}^{-2}$$

Hydrocarbons by the Fischer–Tropsch process:

$$(2n + 1)\, H_2 + n\, CO \rightarrow {\color{red}C_nH_{2n+2}} + n\, H_2O \qquad \Delta H << 0$$

Developed by *Franz Fischer* and *Hans Tropsch* in 1925
Used in Germany during World War II and in South Africa during the embargo in the apartheid days



Methanol

Methanol synthesis from syngas ($CO + H_2$ and some CO_2) or just $CO_2 + H_2$ at 200-300 ºC and 50–100 bar

1) $CO + 2H_2 \rightleftarrows CH_3OH$ $\Delta H_r = -89$ kJ mol^{-1}

2) $CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O$ $\Delta H_r = -48$ kJ mol^{-1}

3) $CO + H_2O \rightleftarrows CO_2 + H_2$ $\Delta H_r = -41$ kJ mol^{-1}

Catalyst: $Cu/ZnO/Al_2O_3$ (same as in a methanol reformer)

Cu is the catalyst, but both ZnO and the carrier Al_2O_3 promotes the catalyst

Ammonia, the Haber–Bosch process

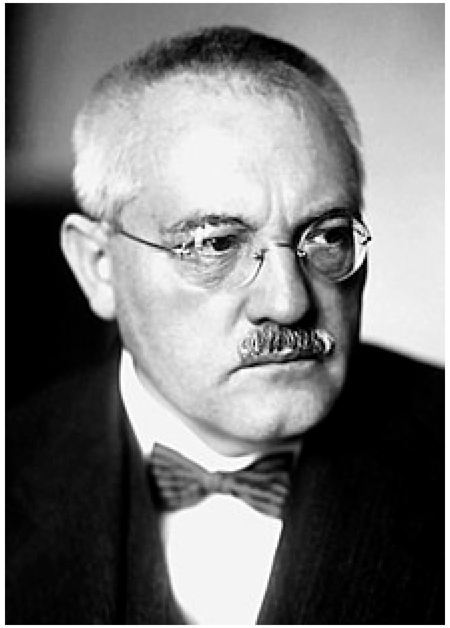
The Haber-Bosch process is still the state-of-art process for ammonia synthesis

Nitrogen isolated from air reacts with hydrogen under pressure after

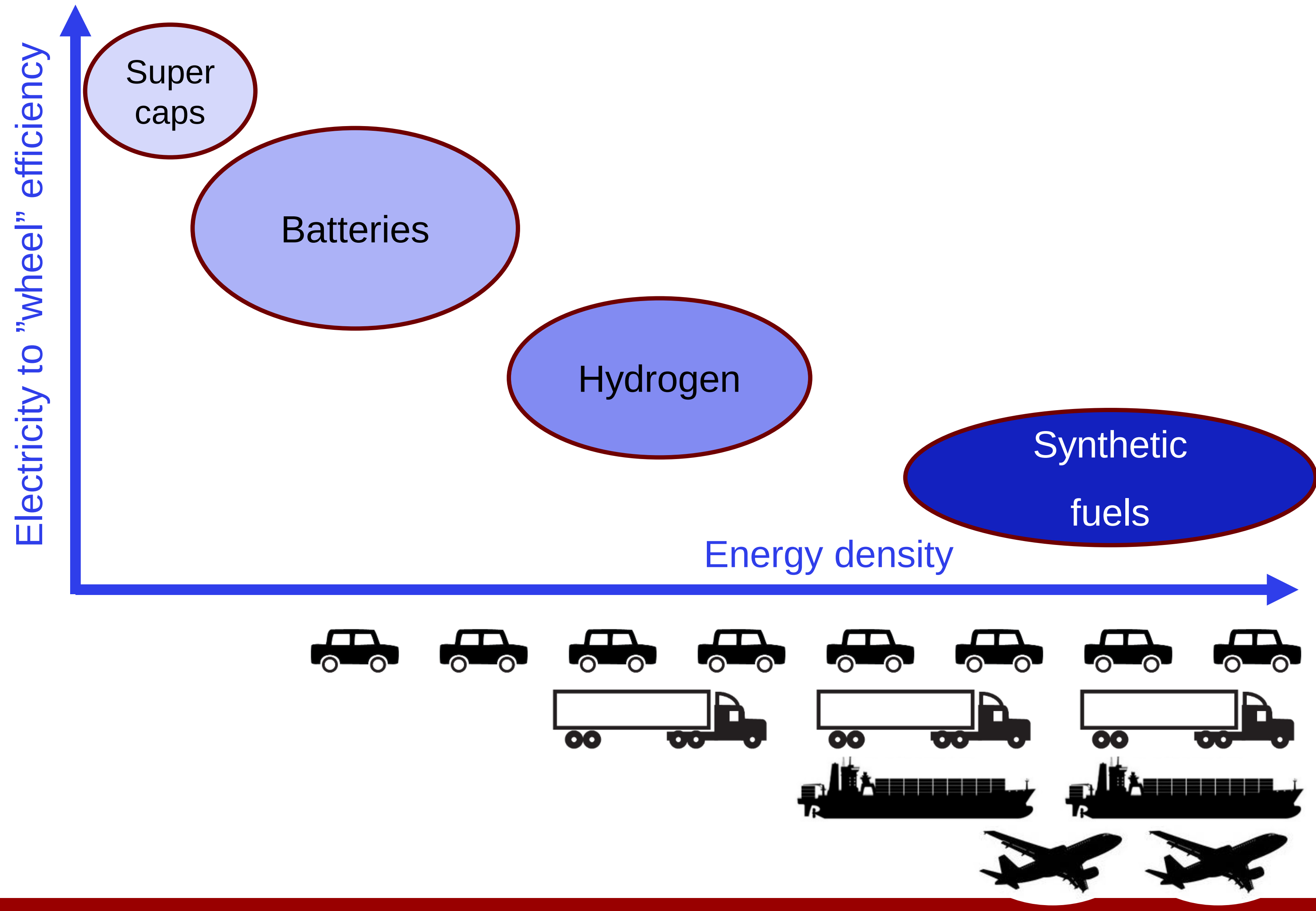
$$N_2 + 3H_2 \rightarrow NH_3 \qquad \Delta H = -91.8 \text{ kJ mol}^{-1}$$

100 – 250 bar and 400 - 500 ºC on an iron based catalyst

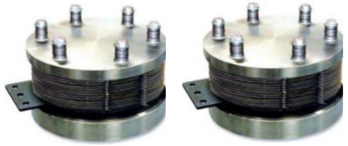
Fritz Haber demonstrated it in 1909 on the lab scale and *Carl Bosch* (BASF) scaled it up 1910.



Efficiency vs. energy density (schematic)



Scaling with power and energy

	Scaling with power	Scaling with energy
Batteries		
Hydrogen		
Synthetic fuels		 (Only storage tank)

Carbon capture CCS and CCU

CCS and CCU (and CCUS)

Carbon capture and storage (CCS)

Concept: collecting CO_2 and storing it somehow/somewhere forever

Motivation: Continued use of fossil fuels without increasing the atmospheric CO_2 concentration. We may even collect and store CO_2 from the atmosphere (negative emissions)

Carbon capture and utilization (CCU)

Concept: collecting CO_2 and using it for synthesizing fuels and chemicals

Motivation: A central part of power-to-X when hydrogen is not practical

Carbon capture, utilization and storage (CCUS)

The term covering both concepts

Ways to capture CO_2

Absorption (*bulk sorption*)

- Amines (pure liquid or solutions)
- Solutions of hydroxides

Adsorption on high surface area materials (*surface sorption*)

- Carbon materials
- Zeolites
- Metal-organic frameworks (MOF)

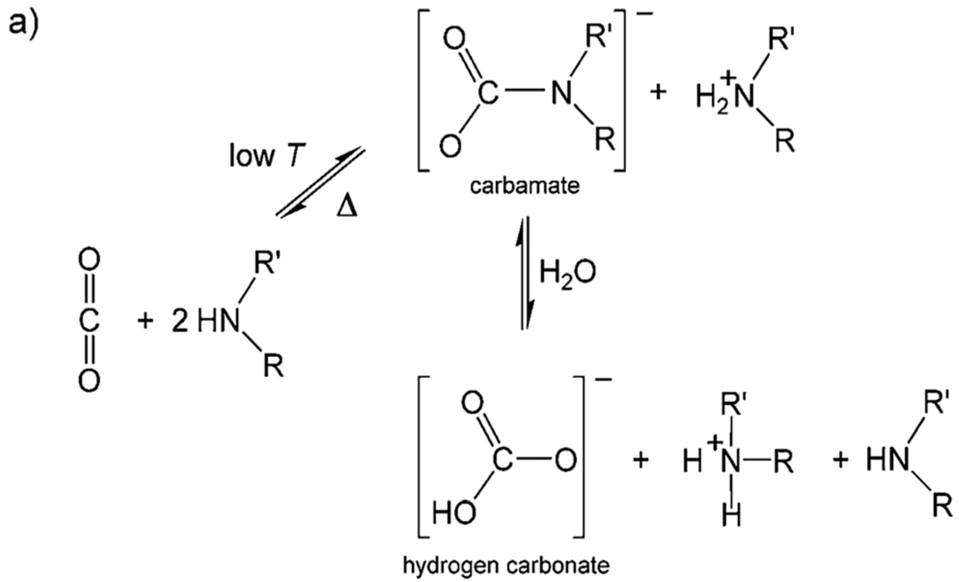
Filtration

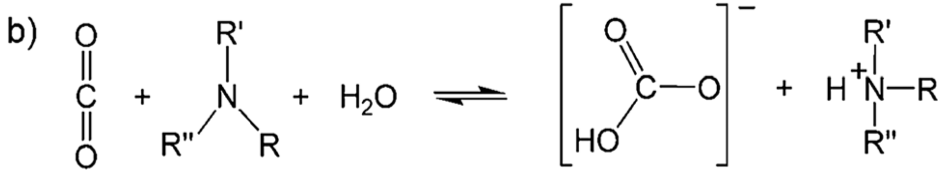
- Selective membranes

Absorption/desorption

Amines (liquids or solutions, state-of-art)

- Monoethanolamine, $NH_2CH_2CH_2OH$ (MEA)
- Diethanolamine, $NH(CH_2CH_2OH)_2$ (DEA)
- Methyldiethanolamine, $CH_3N(C_2H_3OH)_2$ (MDEA)





Desorption at 85-120 ºC

Hydroxides (solutions)

- $Ca(OH)_2$
- NaOH

$$Ca(OH)_2 + CO_2 \rightleftarrows CaCO_3 + H_2O$$

Desorption: reverse of process by heat at around 800 ºC or more

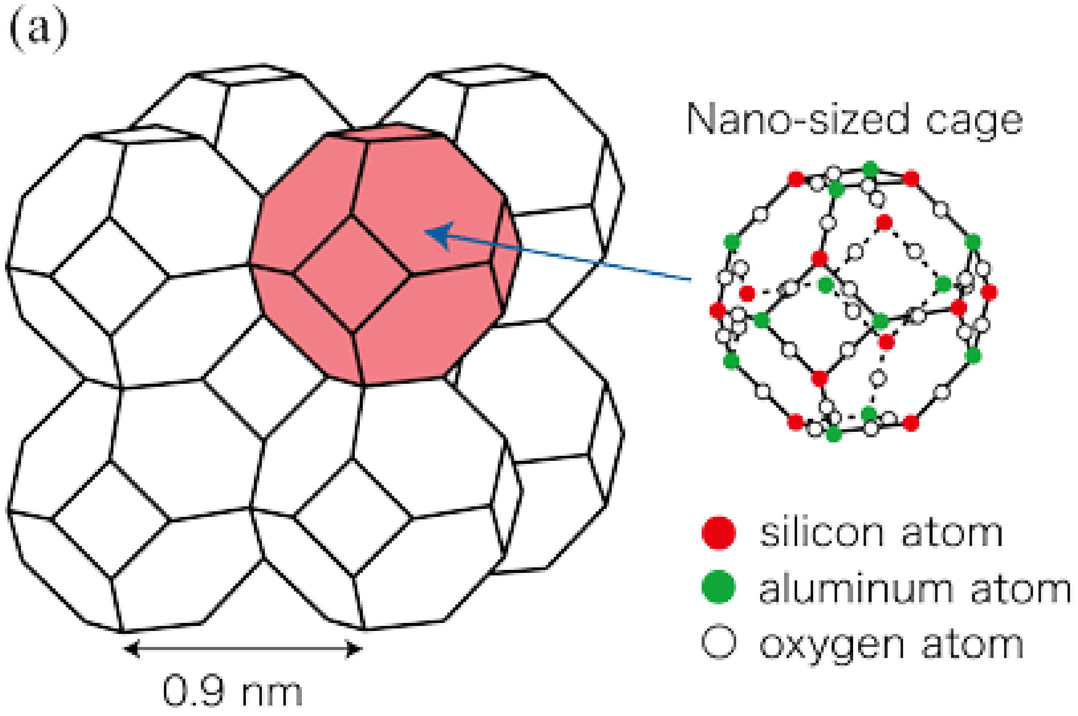
$$CaCO_3 + heat \rightleftarrows CaO + CO_2$$

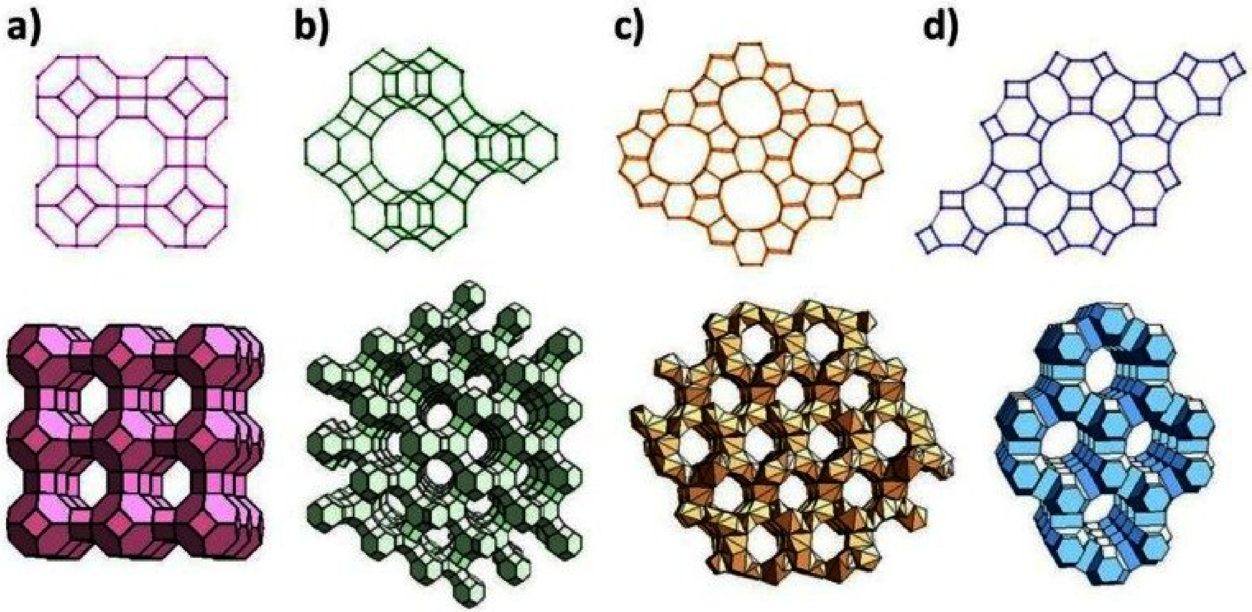
$$CaO + H_2O \rightleftarrows Ca(OH)_2$$

Adsorption/desorption, zeolites

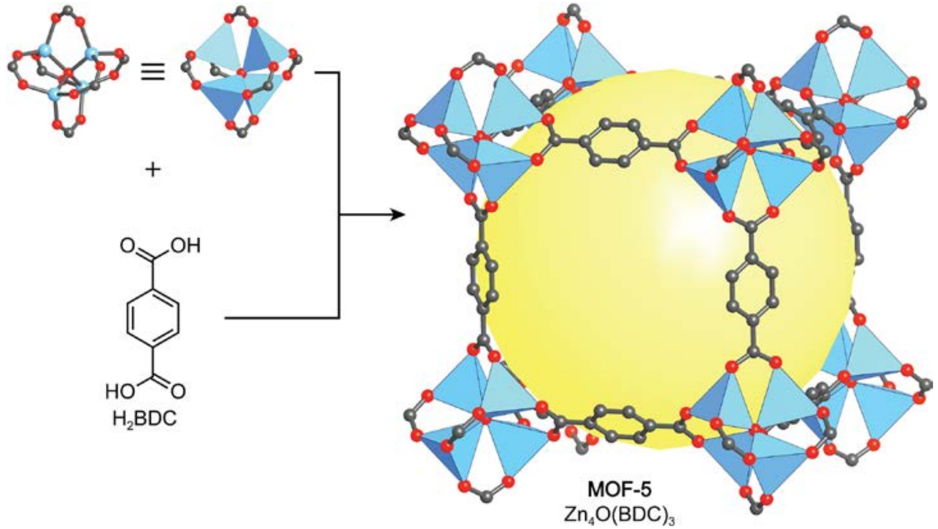
Highly ordered structures of mixed oxides of cations,

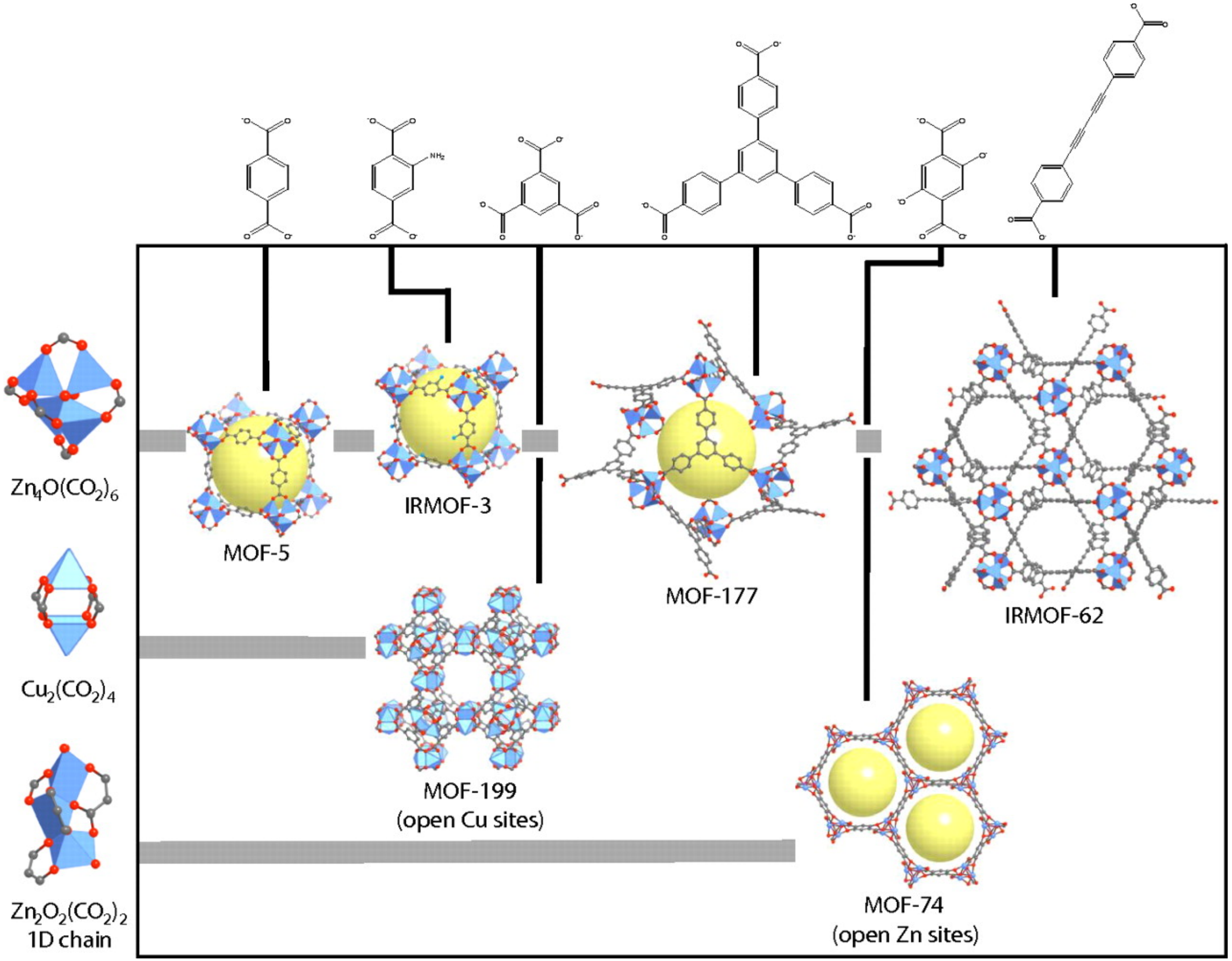
commonly Na^{+}, K^{+}, Ca^{2+}, Mg^{2+} and Si^{4+}.





Adsorption/desorption, MOFs





The optimum material for DAC

- Strong bonding to make capture effective
- Weak bonding to make release energy efficient

- Minimum thermodynamic work for bringing CO_2 from 400 ppm to 1 bar:

$$w_{min} = RTln\,\frac{p_2}{p_1} = RTln\,\frac{1}{400 \cdot 10^{-6}} = 20\text{ kJ mol}^{-1}$$

- The fuel
  - HHV - Methanol: 726 kJ mol^{-1}
  - HHV - Methane: 890 kJ mol^{-1}

Direct air capture (DAC)

climeworks

First commercial CO_2 capturing project in Hinwil, Switzerland in 2017.

900 tons CO_2 each year (for greenhouses)

CarbFix project, Iceland

Deposition of CO_2 as carbonate in minerals

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2$$

DAC by Climeworks

With Audi 2020: 4,000 metric tons of CO2 will be stored as rock underground each year

All for now

Pro - Ingeniøren