

Electrochemistry for Materials Technology

ENERGY APPLICATIONS

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gem.epfl.ch

ELECTROLYSIS

H₂ from H₂O electrolysis

- H₂ does not occur naturally on Earth
- It stems mostly (95%) from fossil sources now; this relates to its main current use (which is **chemical, not energetical**)
- **Green H₂** can be made – via electrolysis - mainly from variable renewable electricity (PV, wind) which is driving the energy transition and must be stored
- H₂ offers all energy uses (1.power, 2.heat, 3.mobility) in addition to being a chemical **feedstock** for heavy industry
- It therefore has huge decarbonisation potential, but must be made on a **massive scale (TW !!)**

Grey, blue, green H₂

- Grey H₂ : made from fossil sources
- Blue H₂ : made from fossil sources but including carbon capture
- Green H₂ : made from renewable sources

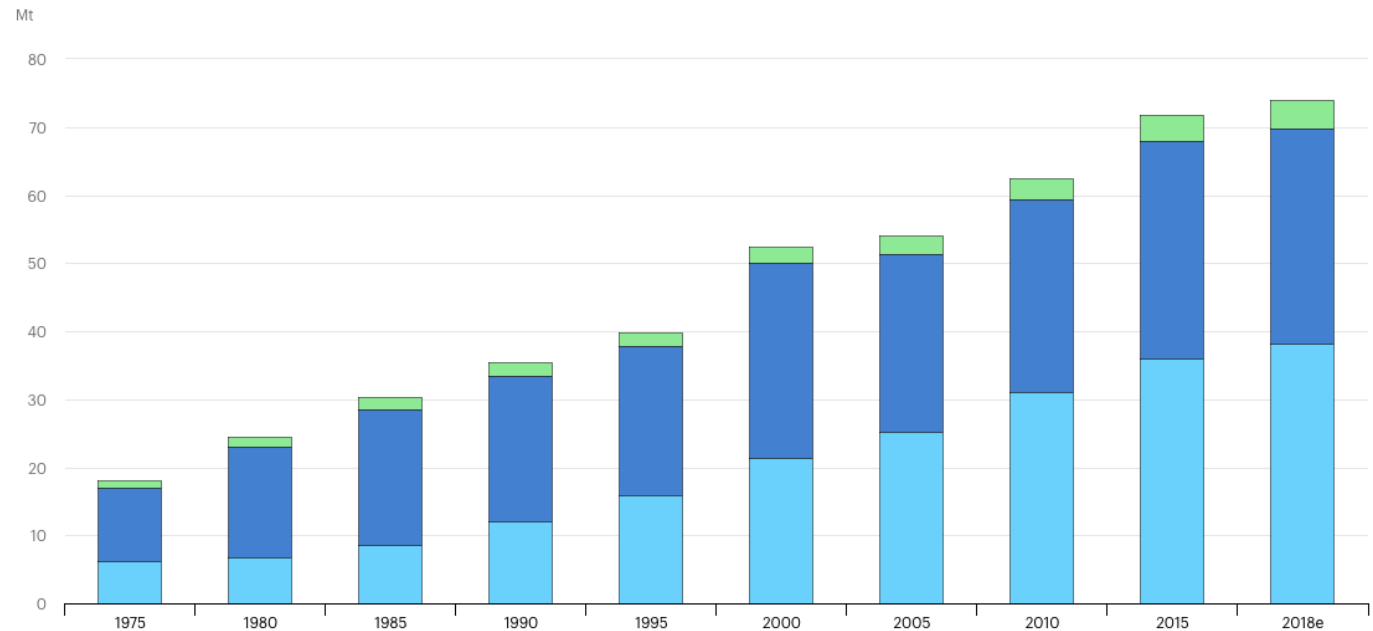
Annual H₂ production

- ~75 Mt/yr \approx 830 10⁹ m³ /yr \approx 9 EJ (2500 TWh) = 1.6% of world energy
 - 49% from natural gas
 - 29% from oil
 - 18% from coal
 - **4% from electrolysis**

} 96% from fossil sources

not green! Global demand for pure hydrogen, 1975-2018

= 3 Mt H₂/yr
 = 33 bio m³/yr
 = 100 TWh H₂ (LHV)
 67% efficiency
 150 TWh electricity
 (0.6% of world electricity)
 ~20 GWe



- by comparison: natural gas 4.10¹² m³ /yr = 140 EJ (24% of world energy – 580EJ)

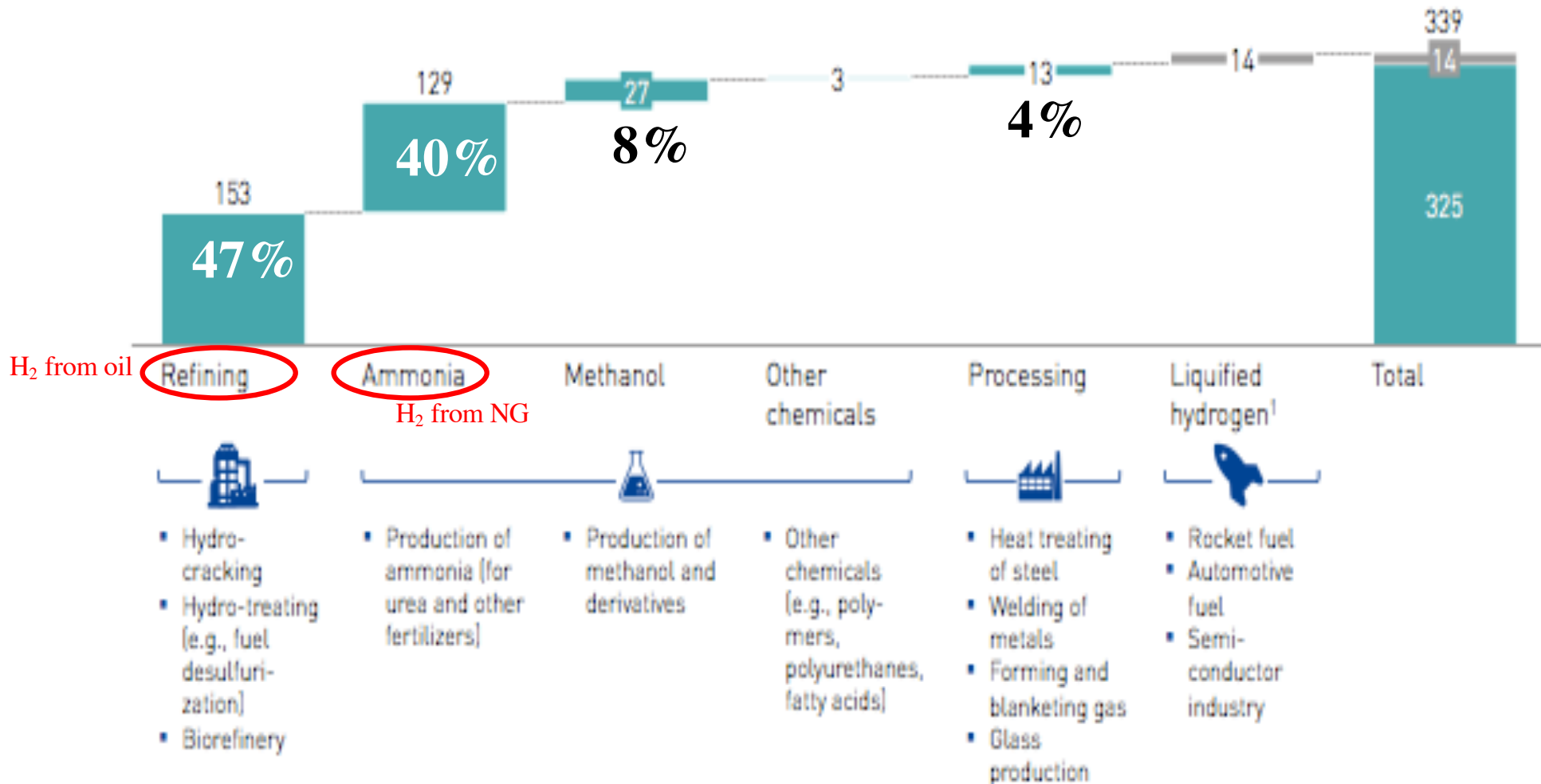
H₂ current uses (EU)



FUEL CELLS AND HYDROGEN
JOINT UNDERTAKING

fch.europa.eu
H2 Roadmap for Europe, January 2019
Exhibit 17 p.40

Total hydrogen use in the EU, in TWh



H₂ current uses (EU)

- Refineries (47%): hydrodesulphurisation (HDS), hydro-cracking
 - Ammonia (NH₃) production (fertiliser) (40%)
 - Methanol (8%) and other chemicals (1%)
 - 'Light' industries (4%): where reducing atmosphere is needed
 - metal treatment
 - semiconductor industry
 - glass making (floating on liquid tin)
 - food (fats hydrogenation)
 - **325 TWh** or 1.2 EJ (**2% of final EU energy**)
- 50 kWe – 2 MWe electrolysers
10 – 500 Nm³/h H₂ flows per unit

Annual H₂ demand per segment



FUEL CELLS AND HYDROGEN
JOINT UNDERTAKING

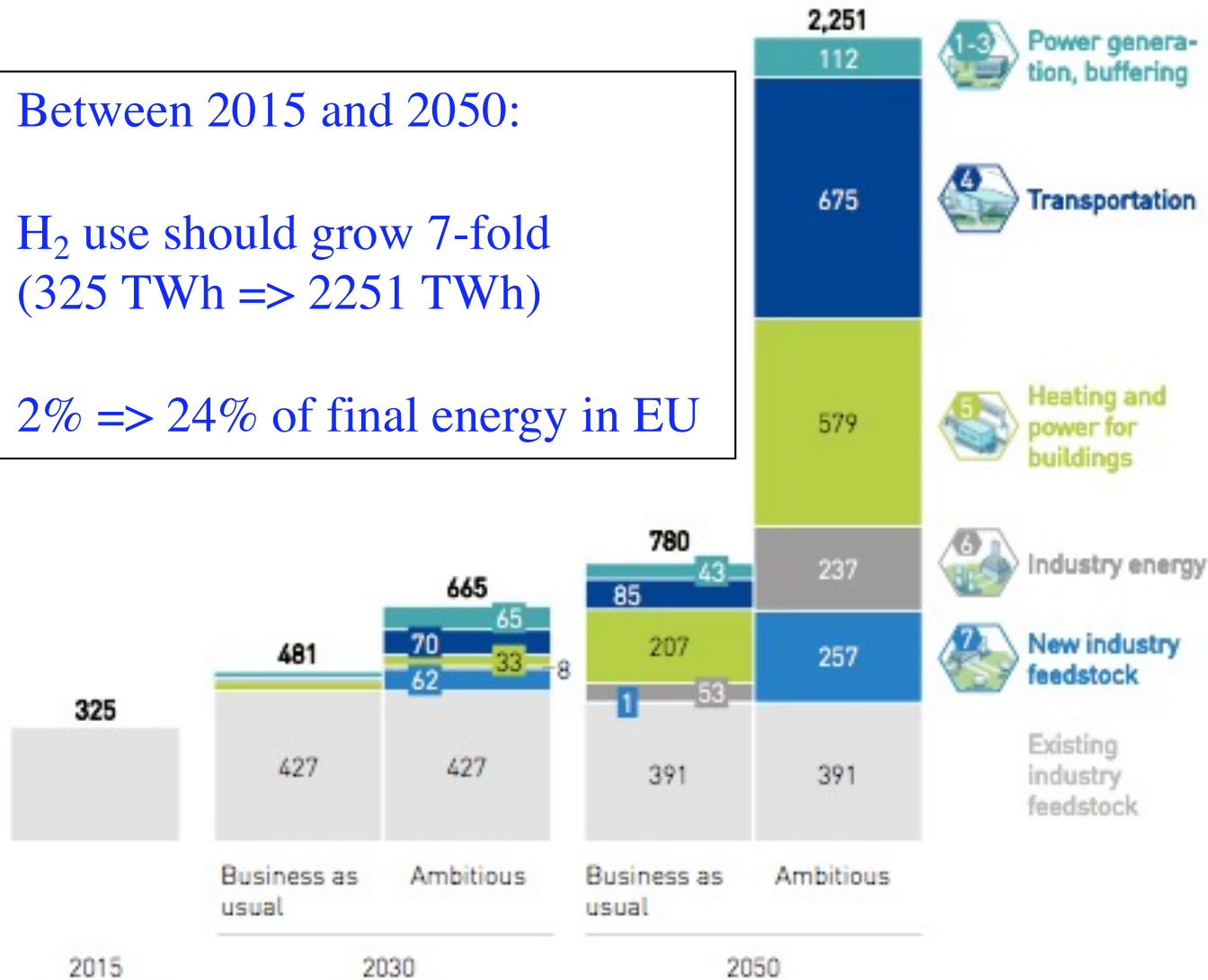
Final energy demand	14,100	11,500		9,300	
Thereof H ₂	2%	4%	6%	8%	24%

fch.europa.eu
H2 Roadmap for Europe
January 2019
Exhibit 2 p.8
Exhibit 22 p 49

Between 2015 and 2050:

H₂ use should grow 7-fold
(325 TWh => 2251 TWh)

2% => 24% of final energy in EU

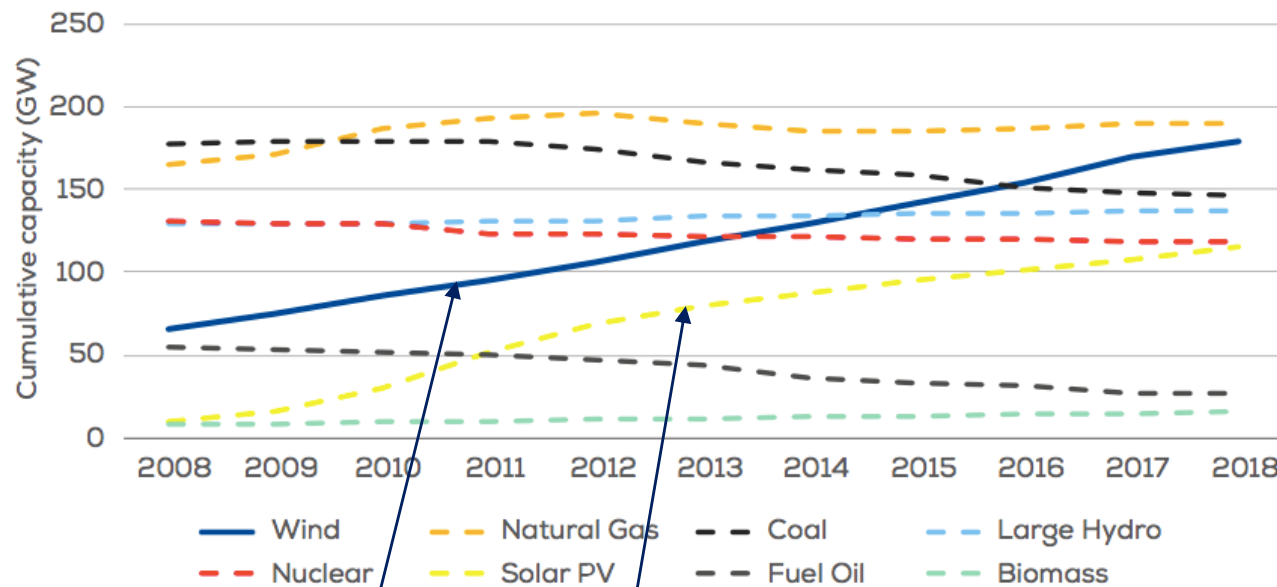


Water electrolysis

- 5 x more expensive than fossil fuel steam reforming for H₂ production (only 4% of world H₂ production is by electrolysis)
- for electricity storage (H₂ economy)
- ...and mobility (FCEV: electric fuel cell cars)
- target: improve the electrolysis efficiency (V_{in})
 - power efficiency= $(P_{out}/P_{in})=(V_{out}/V_{in}) \cdot (I_{out}/I_{in})$
 - Classical alkaline (liq. OH⁻) 1.8 V
 - Polymer electrolyte (80C) 1.9 V (higher current)
 - Ceramic electrolyte (800C) possible even at 1 V!

Electricity sources

FIGURE 1
Total power generation capacity in the European Union 2008-2018



2020 :

+14.7 GW in 2020
+105 GW in 2021-2025

Wind: EU 220 GWe
458 TWh (15% of Europe's electricity)
World : 732 GWe

Solar Europe: 137 GWe
150 TWh (5% of Europe's electricity)
+16.5 GWe in 2020

Solar worldtotal:
710 GWe
+140 GWe in 2020

Hydro (world) : 1212 GWe

Source: WindEurope

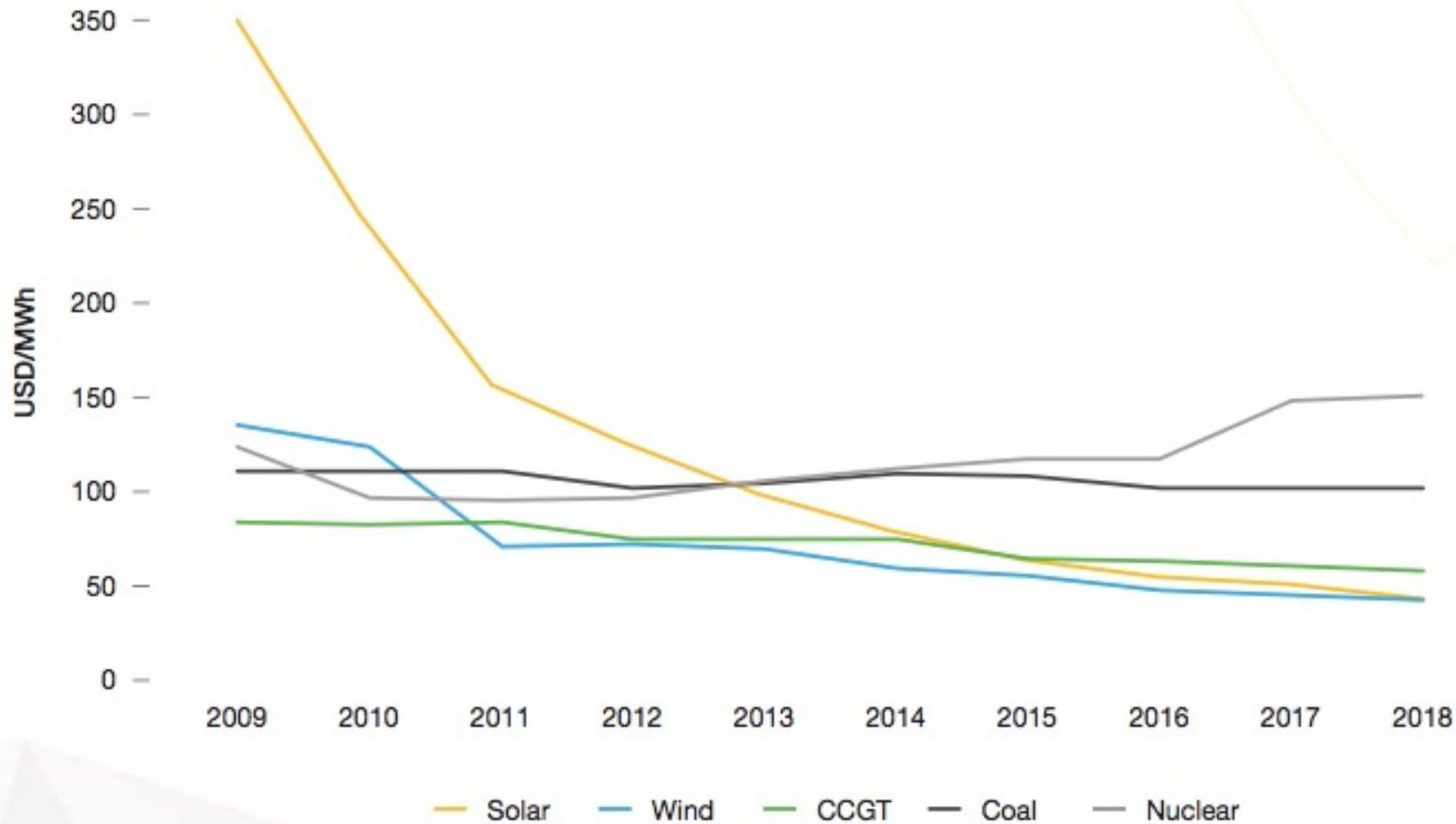
growth in Wind + Solar PV



STORAGE by ELECTROLYSIS

Solar PV and wind is the cheapest electricity

FIGURE 3 SOLAR ELECTRICITY GENERATION COST IN COMPARISON WITH OTHER POWER SOURCES 2009-2018

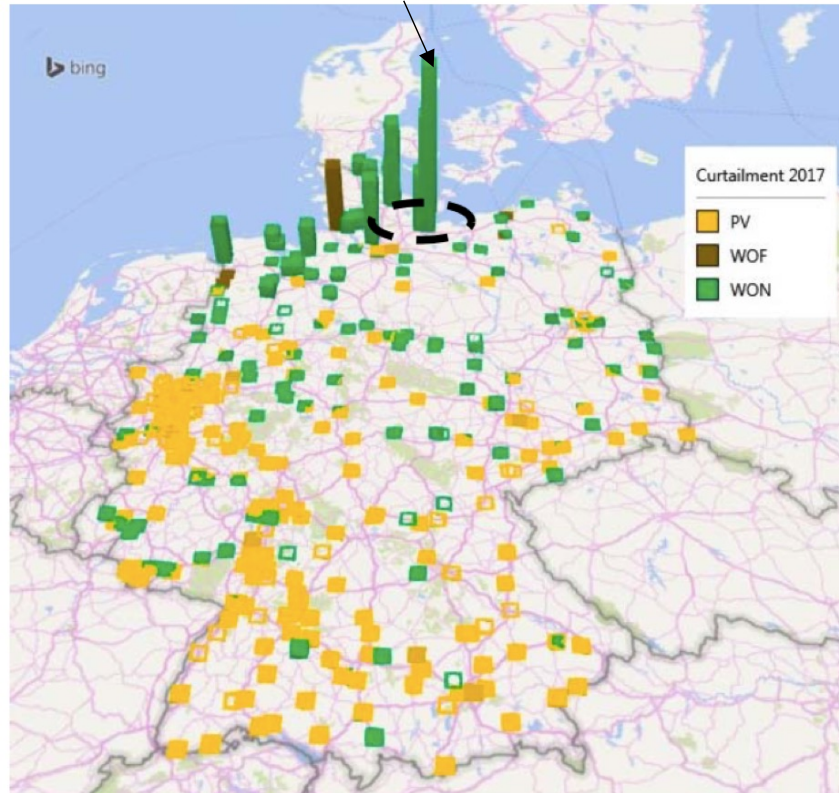


Source: Lazard (2018). All prices in 2019 USD.

© SOLARPOWER EUROPE 2019

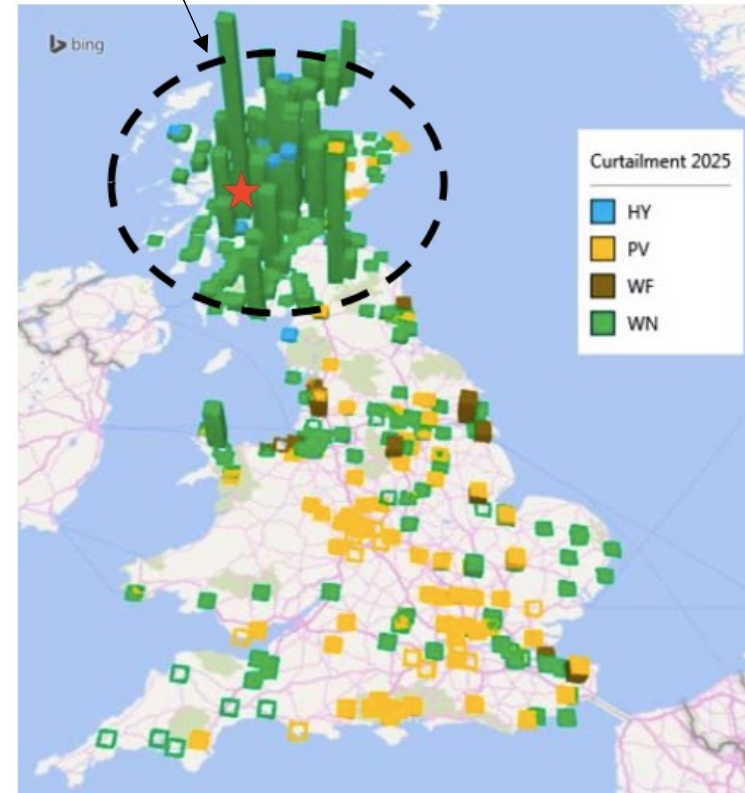
Excess electricity production

Max: 427 GWhe



Germany 2017

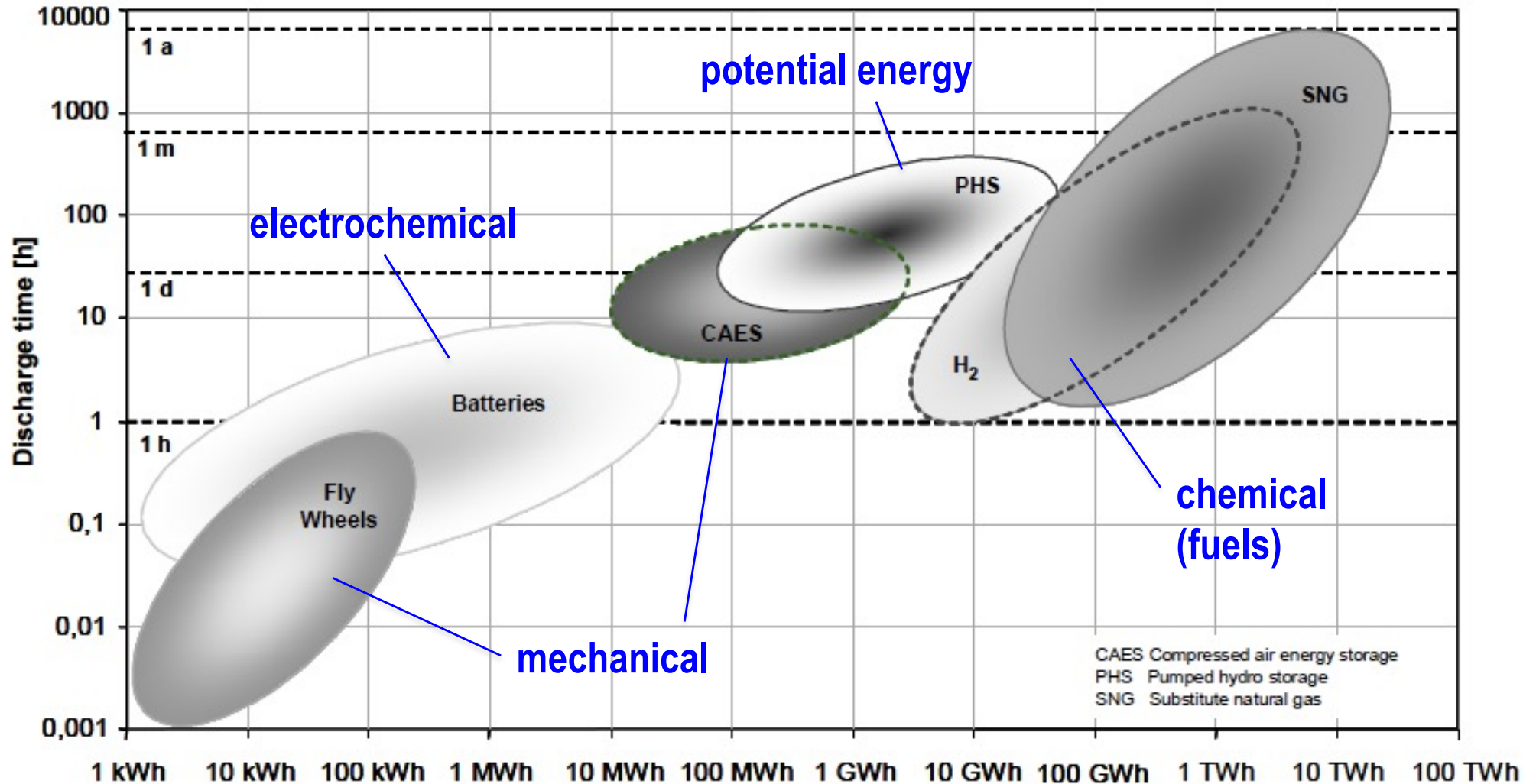
Max: 117 GWhe



UK 2025

*(2017-June) STUDY ON EARLY BUSINESS CASES FOR H₂ IN ENERGY STORAGE AND MORE BROADLY POWER TO H₂ APPLICATIONS
Prepared for Fuel Cells & Hydrogen Joint Undertaking by Tractebel and Hincio*

Electricity storage schemes

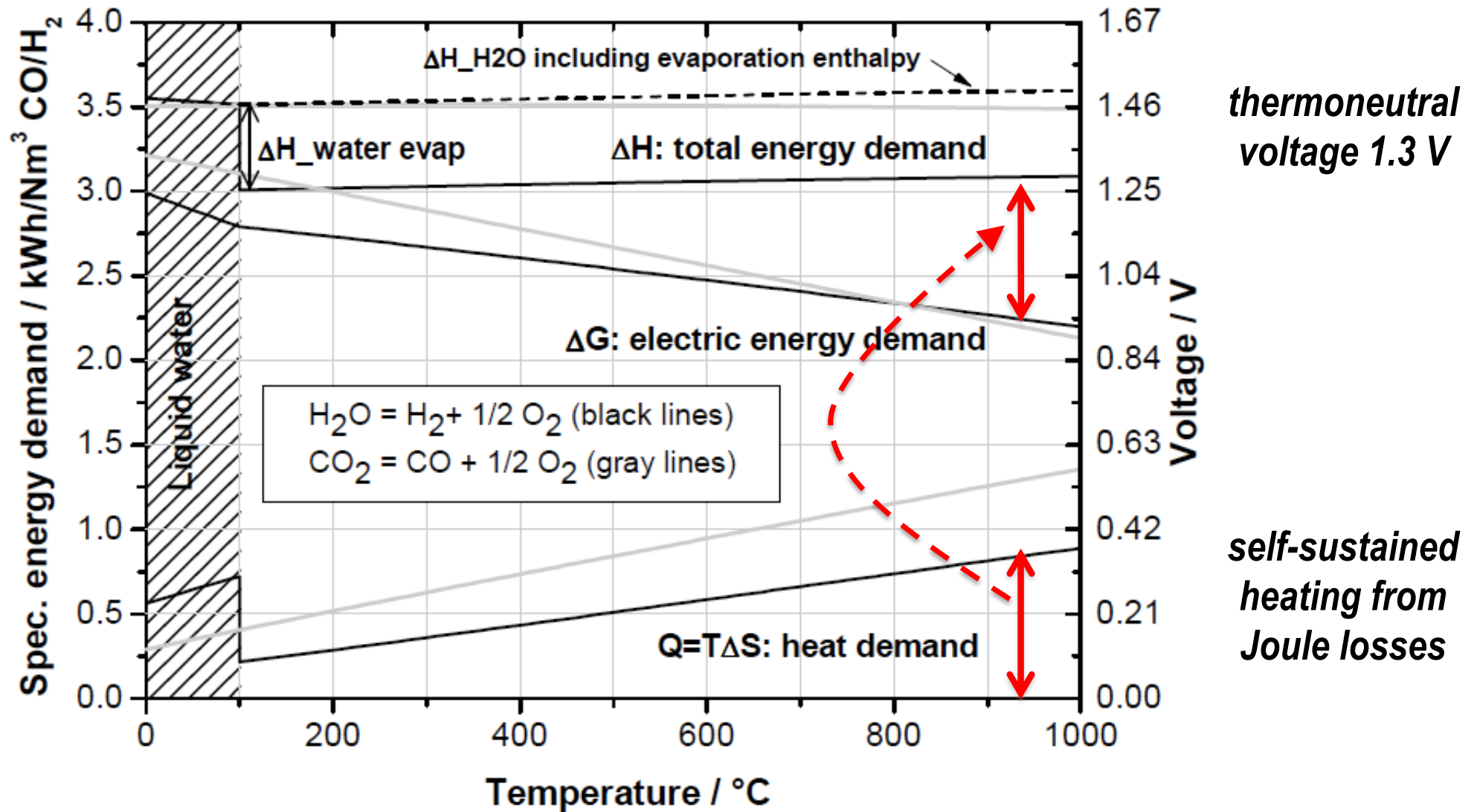


Storing Renewable Energy in the Natural Gas Grid, Methane via Power-to-Gas (P2G): A Renewable Fuel for Mobility
 M. Specht, U. Zuberbühler, F. Baumgart, B. Feigl, V. Frick, B. Stürmer, M. Sterner, G. Waldstein, ZSW-Ulm

→ converting electricity to fuel gives the largest capacities

Thermodynamics

at 700C, electrical input is reduced by 1/3 compared to liquid water electrolysis



Q. Fu, ROLE OF ELECTROLYSIS IN REGENERATIVE SYNGAS AND SYN FUEL PRODUCTION, in Syngas: Production, Applications and Environmental Impact, Editor: A. Indarto and J. Palgunadi, 2011 Nova Science Publishers, Inc.

Thermodynamics

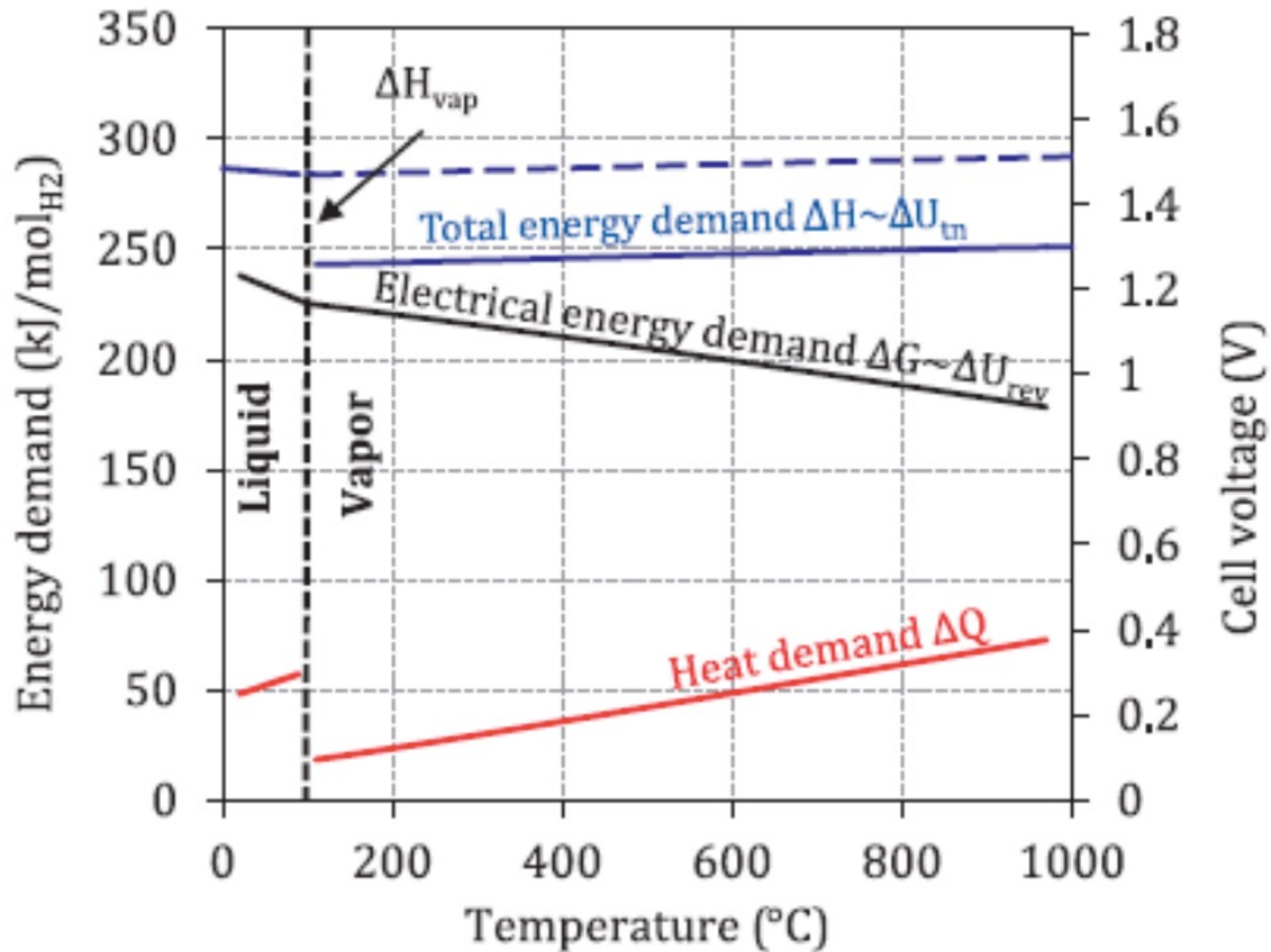
	Reaction	ΔH (kJ/mol)	MJ / Nm ³	kWh / Nm ³
Water	$H_2O(l) \Rightarrow H_2 + \frac{1}{2}O_2$	286	12.77	3.55
Steam	$H_2O(g) \Rightarrow H_2 + \frac{1}{2}O_2$	242	10.80	3.00
	$CO_2 \Rightarrow CO + \frac{1}{2}O_2$	283	12.63	3.51



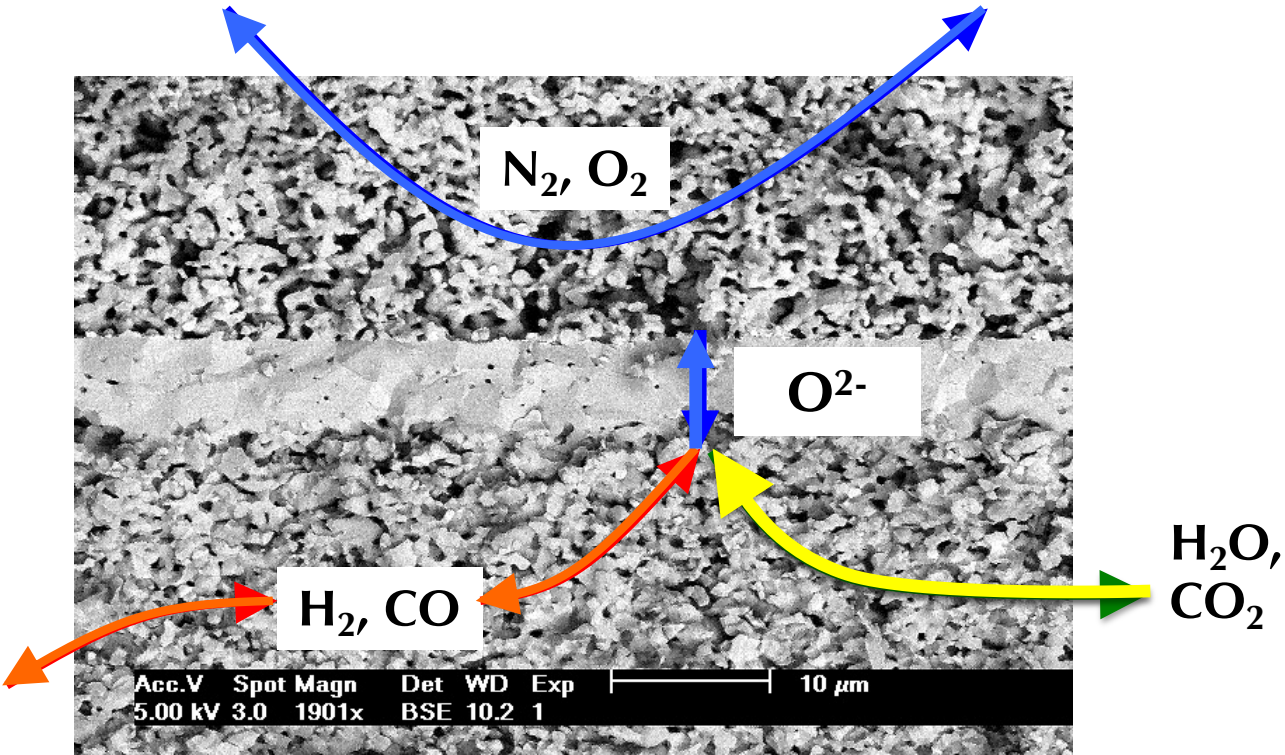
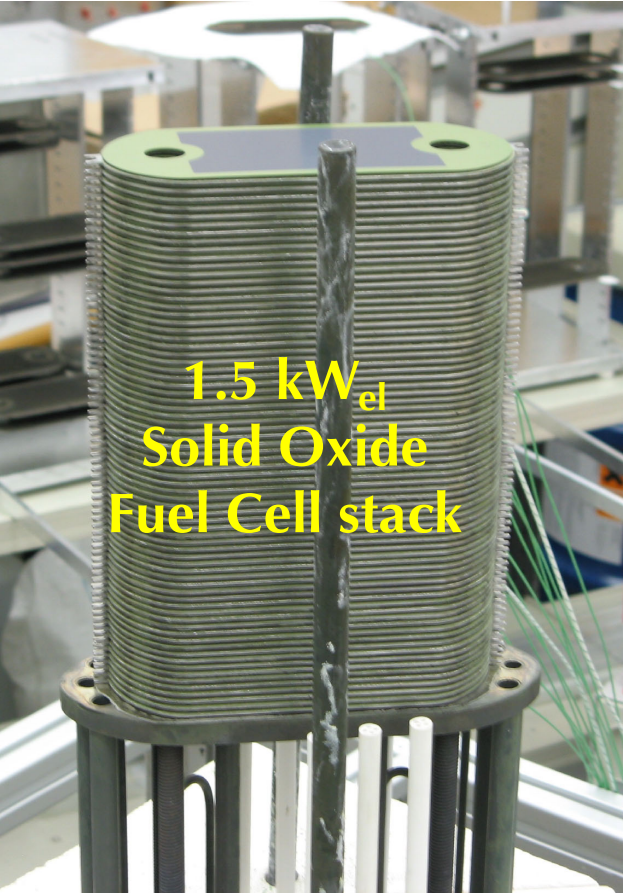
Electrolysis : energy necessary for dissociation



Combustion: energy liberated as heat



Reverse fuel cell = electrolyser



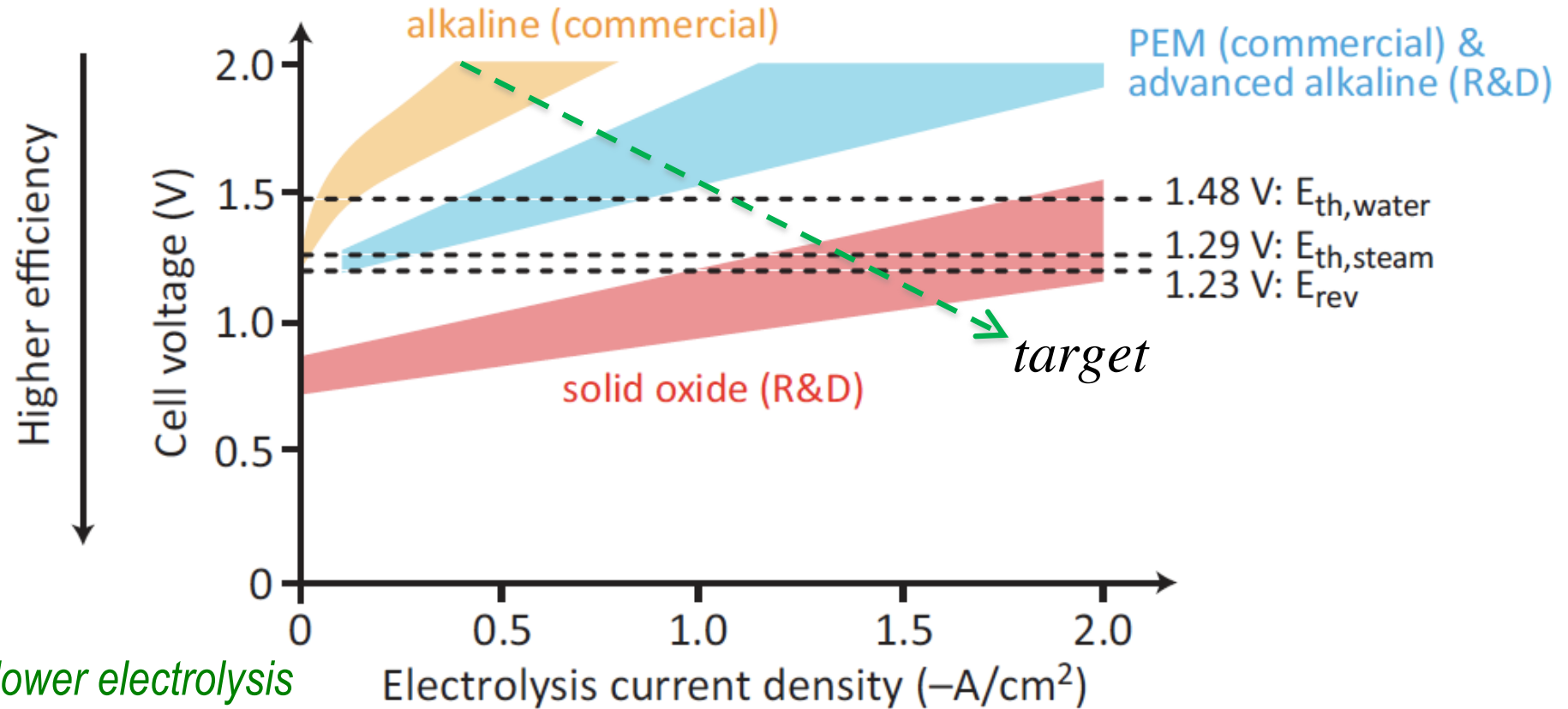
syngas-catalyst

Operating regime :
700-800° C
1 bar (to 5 bar)

MSE-441

FUEL CELL
ELECTROLYSER

Electrolysis technology comparison



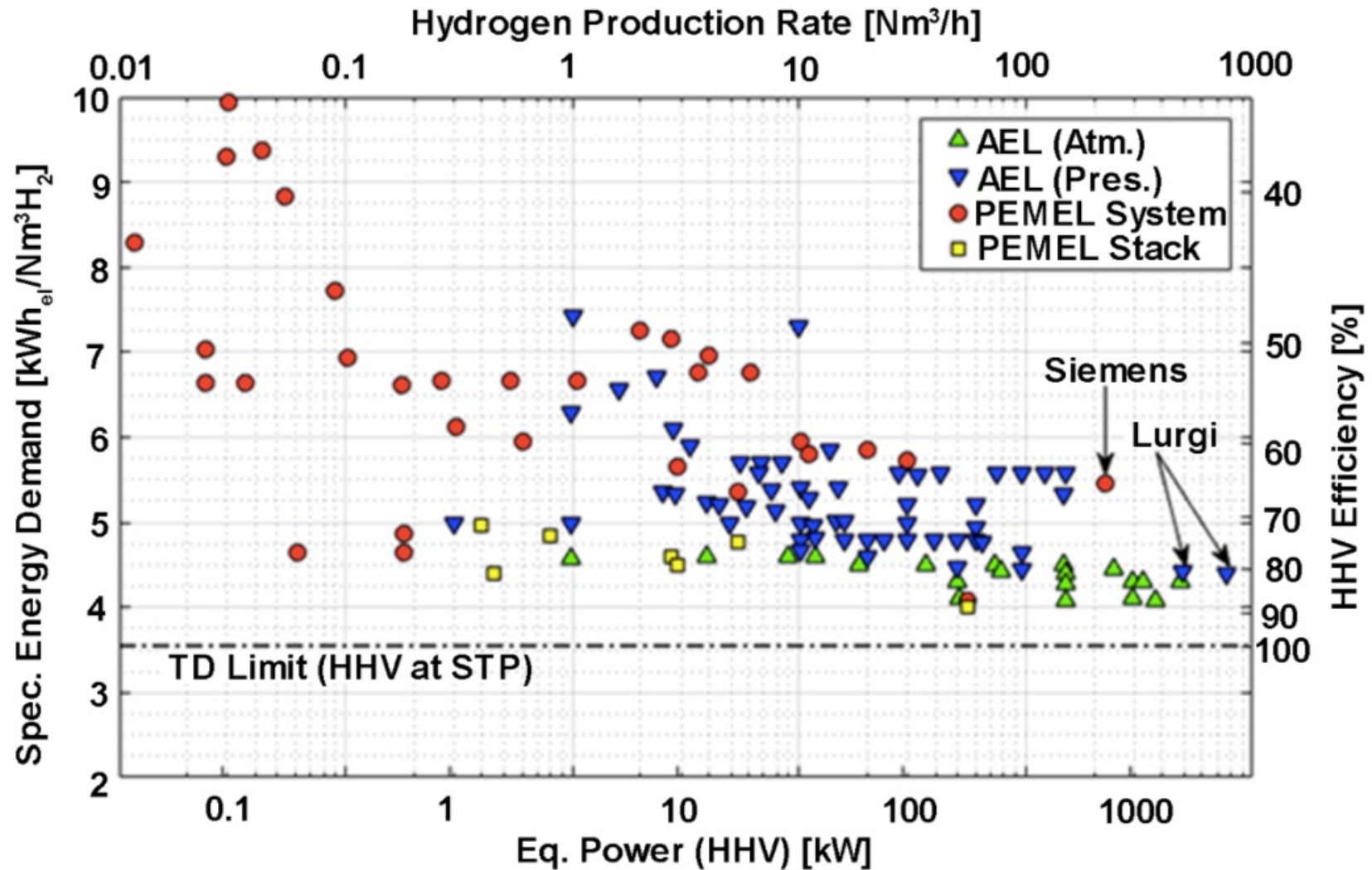
lower electrolysis voltage reduces the parasitic electrical losses

Lower capital cost

higher current density reduces the required catalyst area

Sustainable hydrocarbon fuels by recycling CO₂ and H₂O with renewable or nuclear energy
 Christopher Graves, Sune D. Ebbesen, Mogens Mogensen, Klaus S. Lackner
 Renewable and Sustainable Energy Reviews 15 (2011) 1–23

Electrolyser efficiencies

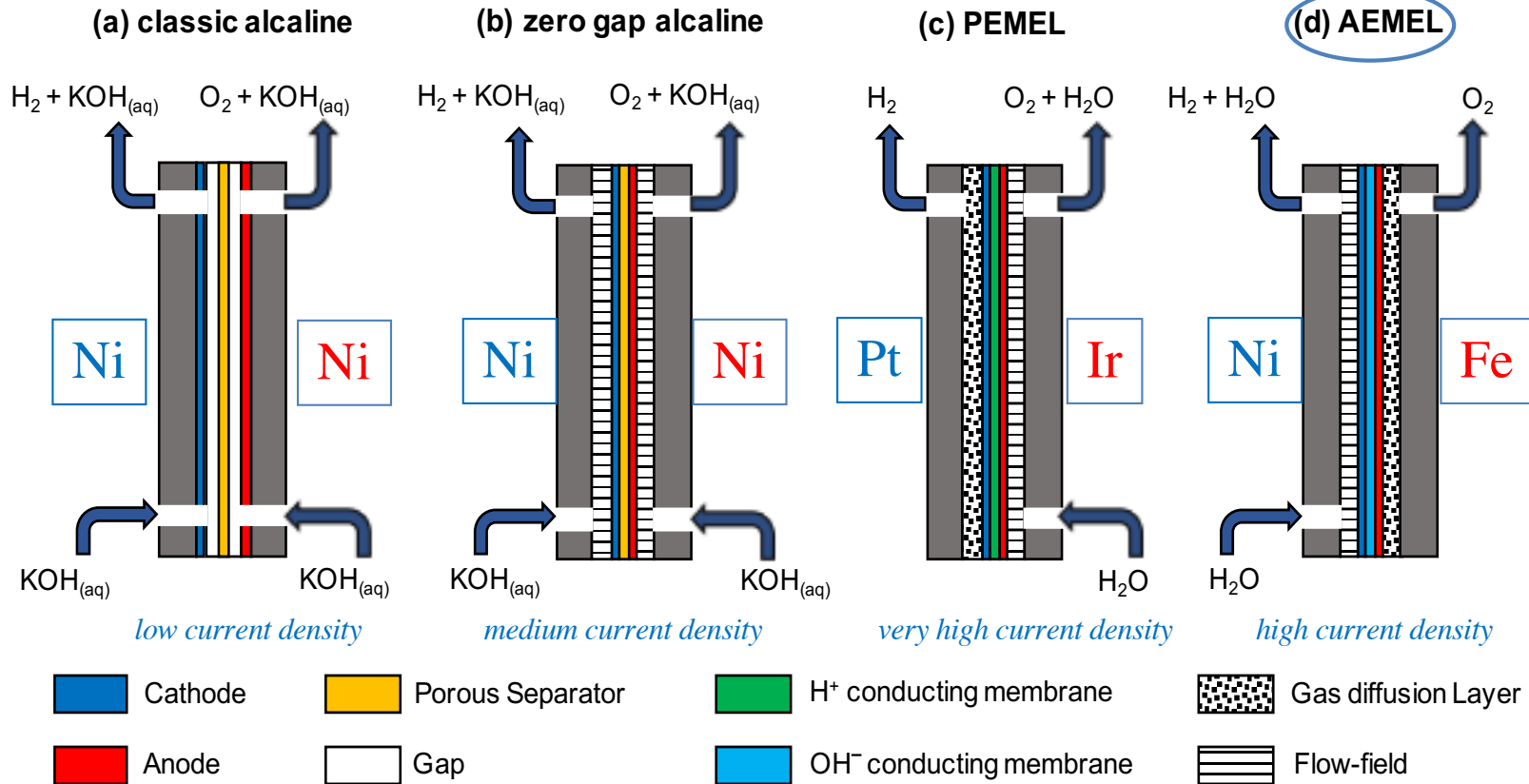


Ref.: Noris Gallandat, Krzysztof Romanowicz, Andreas Züttel, "An Analytical Model for the Electrolyser Performance Derived from Materials Parameters", Journal of Power and Energy Engineering 5 (2017), pp. 34 - 49, <http://www.scirp.org/journal/jpee>, ISSN Online: 2327-5901 ISSN Print: 2327-588X
 slide from Prof A. Züttel, EPFL



***Our industry partner SOLYDERA
reached 98% efficiency on a 75 kWe
steam electrolyzer***

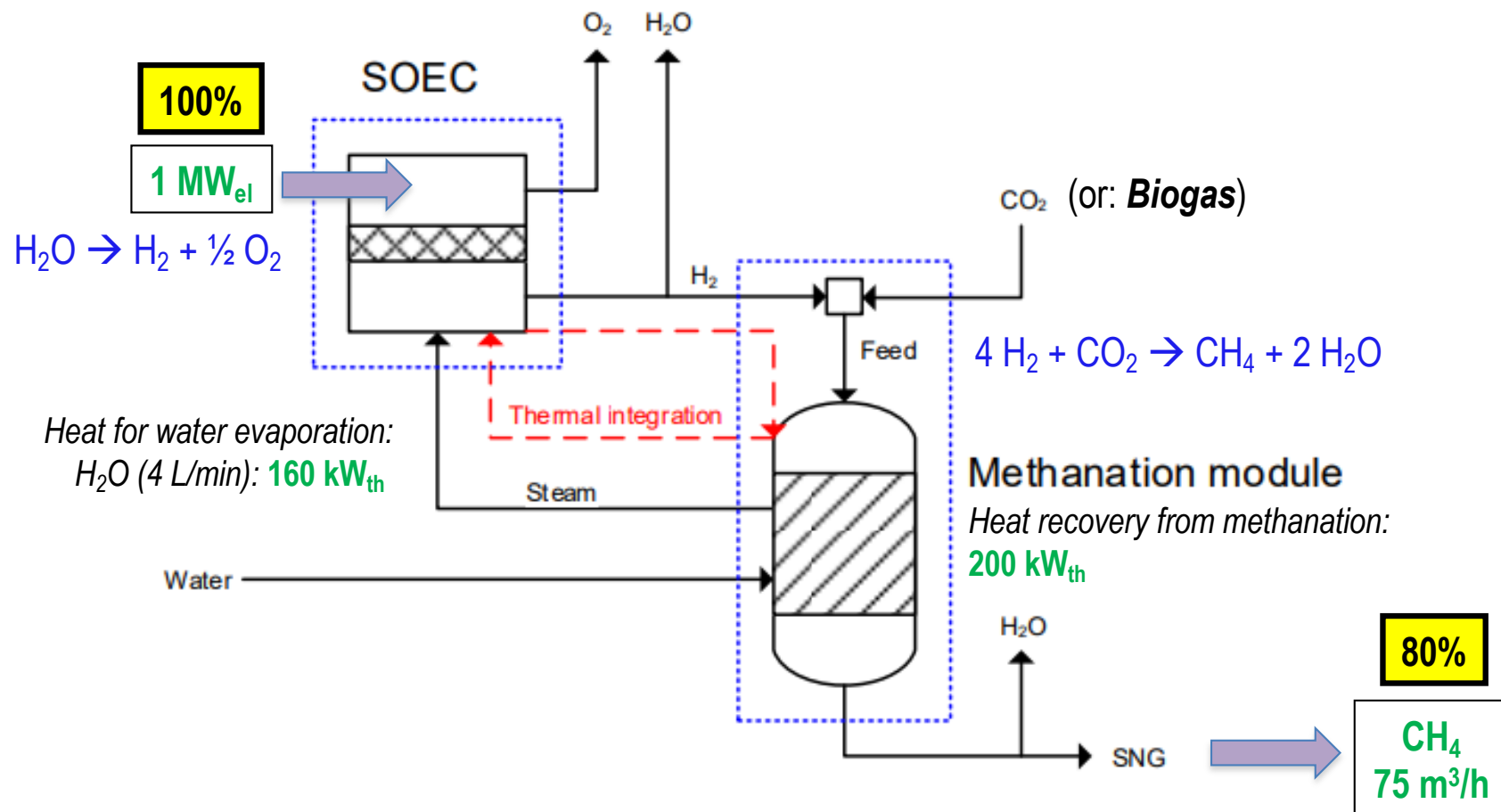
New technology : AEM (anionic exchange membrane electrolysis)



(Figure: Dr Heron Vrabel)

- no critical materials (noble metals Pt, Ir) as catalysts
- alkaline medium (KOH) allows for (Ni-coated) **stainless steel** use (bipolar plates)
(acidic medium (H^+) requires treated/coated (Au, Pt) **titanium** = more expensive)

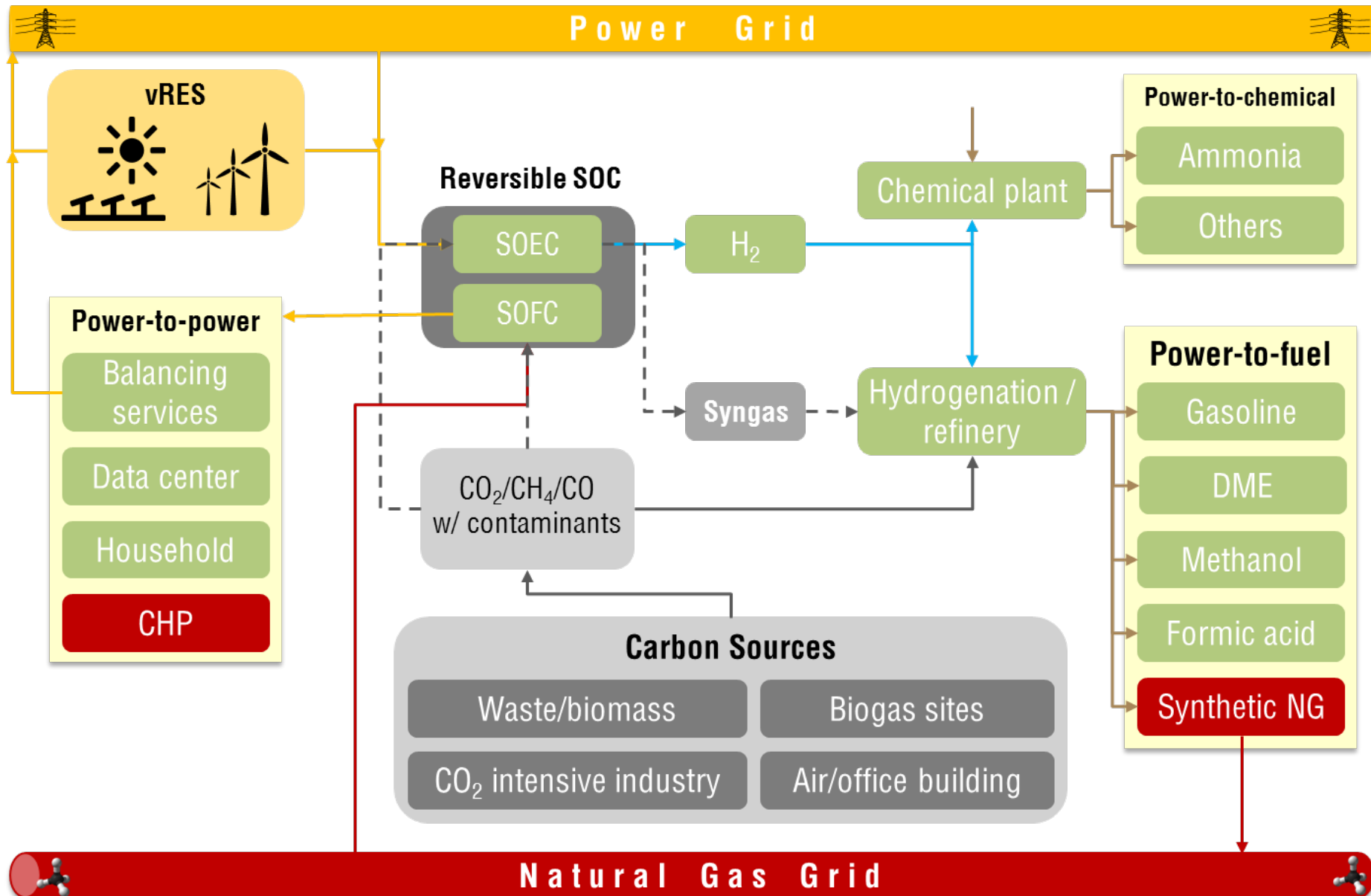
Power-to-Gas (P2G)



Converting H₂ to CH₄ for easy grid injection

Vision: sector coupling

(figure: Dr Ligang Wang)



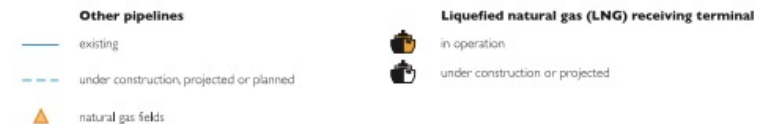
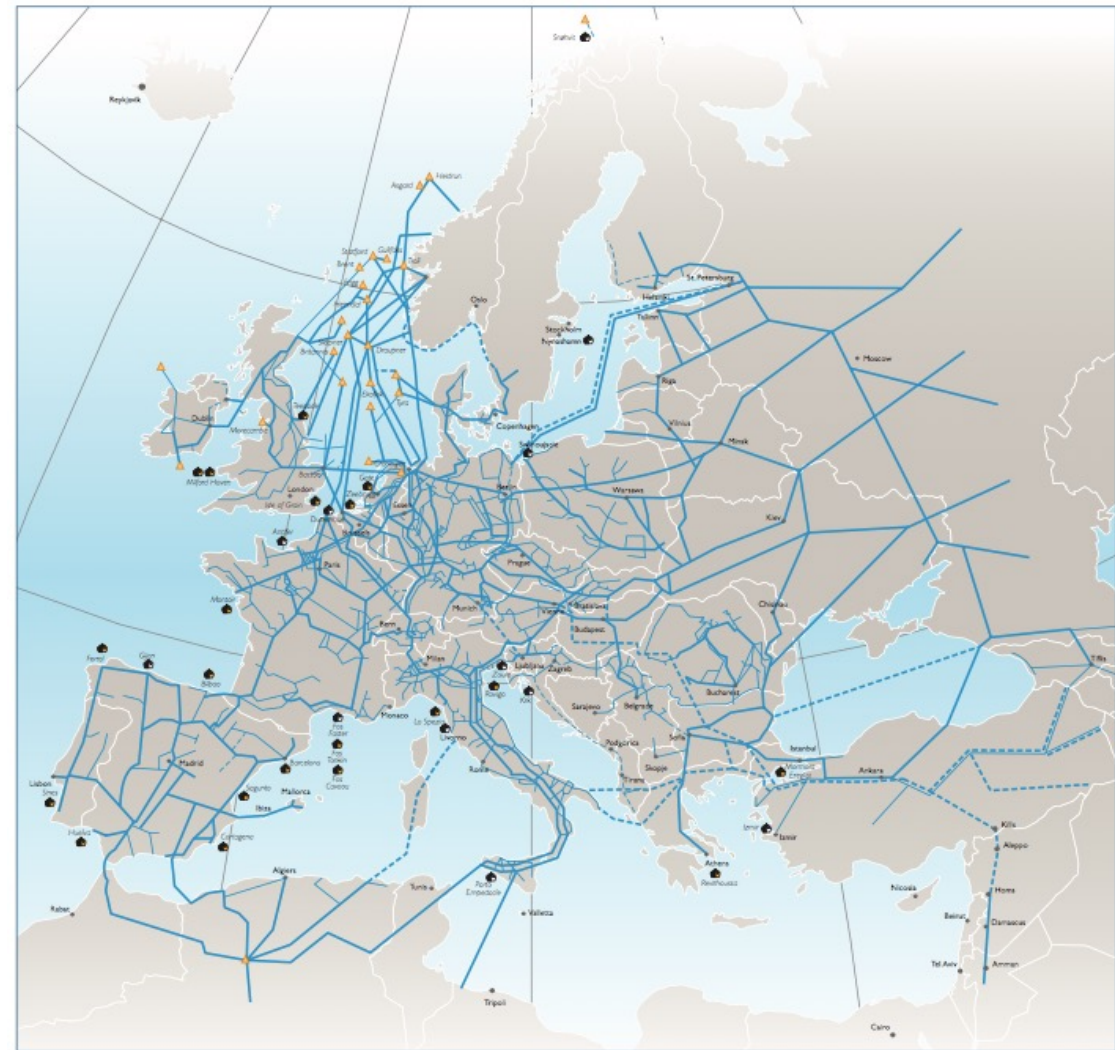
European Gas network

Vested gas pipeline infrastructure.
42% of buildings are heated by NG.
112 million households

Gas consumption: 5375 TWh (19.4 EJ)
(23% of EU energy) = 512 bio m³ NG

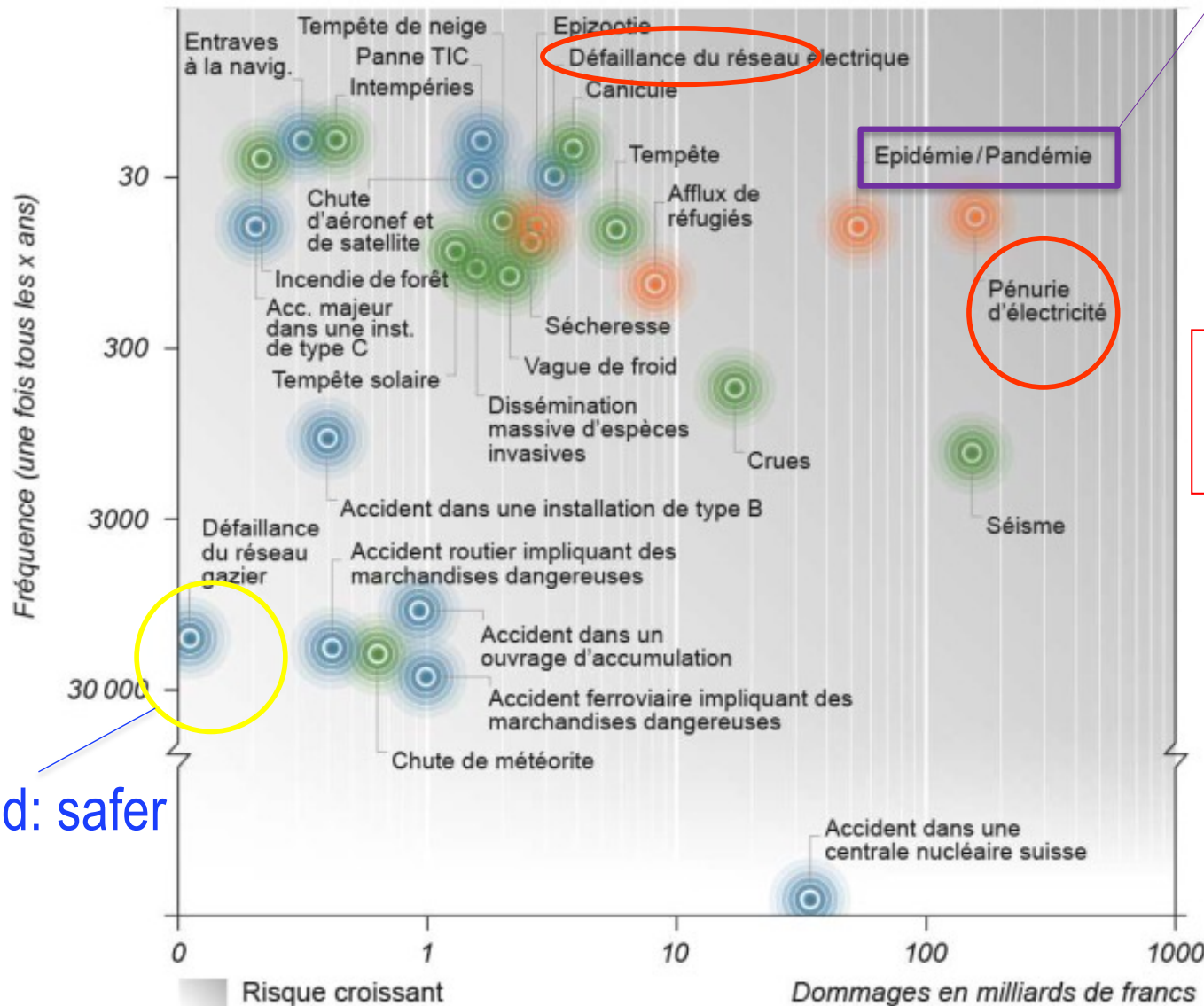
Storage capacity: 1200 TWh
= large reserve for injection of
H₂ (and green methane)

10 vol% H₂ admixing:
= 51 bio m³ H₂ = **169 TWh** (608 PJ)
>40 GWe



Risks in Switzerland

Risk report (June 2015): catastrophes and situations of urgency



electrical grid:
vulnerable

Cost of an
extended black-out:
2-4 billion Fr / day

gas grid: safer

Electrolyser sizes (100 kWe - 10 MWe)

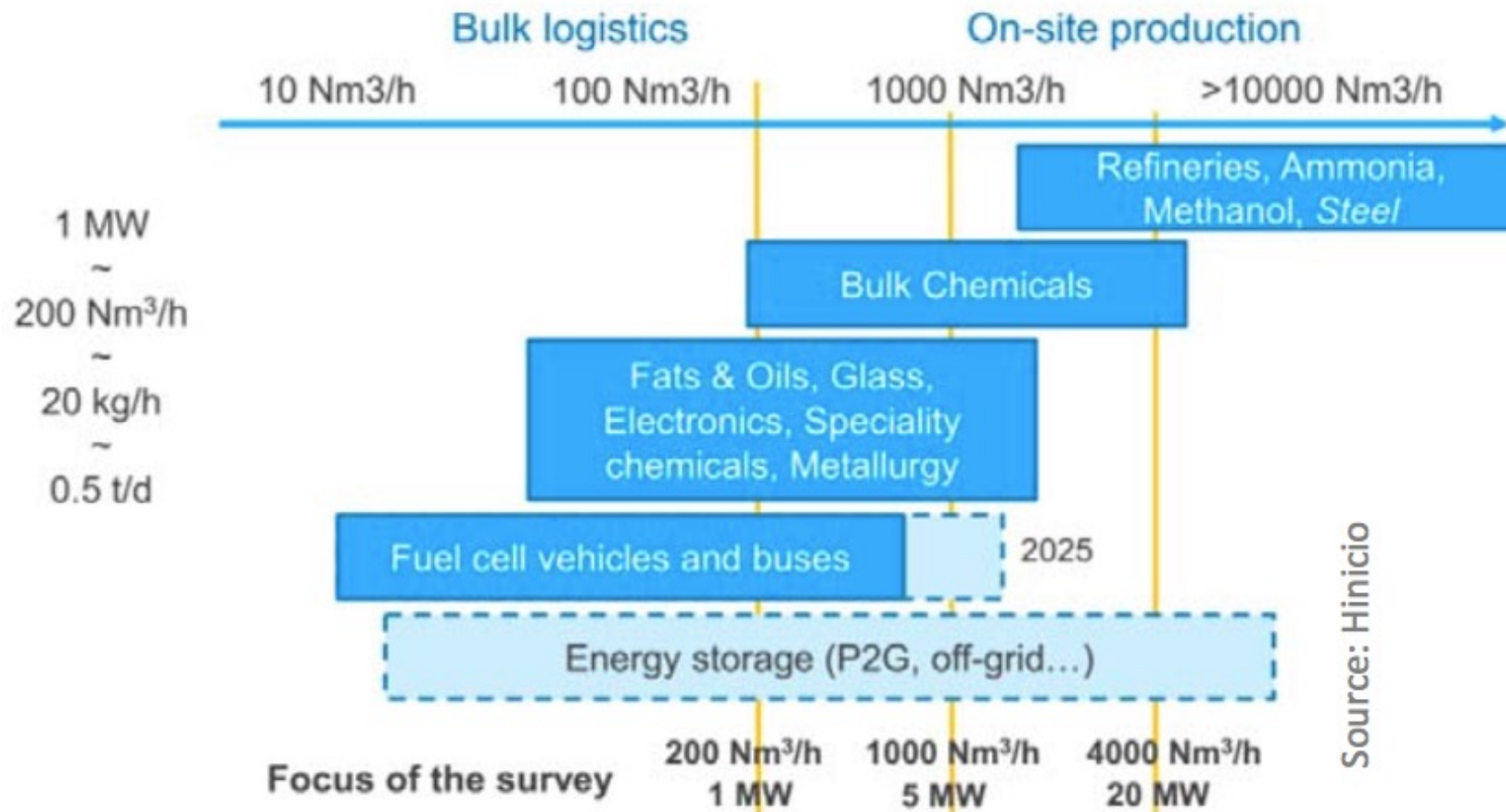


Figure 108: Selection of electrolyser size



FUEL CELLS AND HYDROGEN
JOINT UNDERTAKING

fch.europa.eu

June 2017

STUDY ON EARLY BUSINESS CASES FOR H2
IN ENERGY STORAGE AND POWER TO H2 APPLICATIONS

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Largest electrolysers to date:

- 08.02.2021, **20 MWe** PEMEL :

<https://www.airliquide.com/fr/magazine/transition-energetique/inauguration-du-plus-grand-electrolyseur-pem-au-monde>

- 18.01.2021, **88 MWe** Alkaline EL :

<https://www.thyssenkrupp.com/en/newsroom/press-releases/pressdetailpage/first-green-hydrogen-project-becomes-reality--thyssenkrupp-to-install-88-megawatt-water-electrolysis-plant-for-hydro-quebec-in-canada-93778>

Example: oil refinery

<https://refhyne.eu/>

Rheinland (Shell) (D)

Consumption: **180'000 t H₂** / yr
(fossil)

10 MWe PEM electrolyser:
=> supplies **1300 t H₂** / yr (<1% !!)

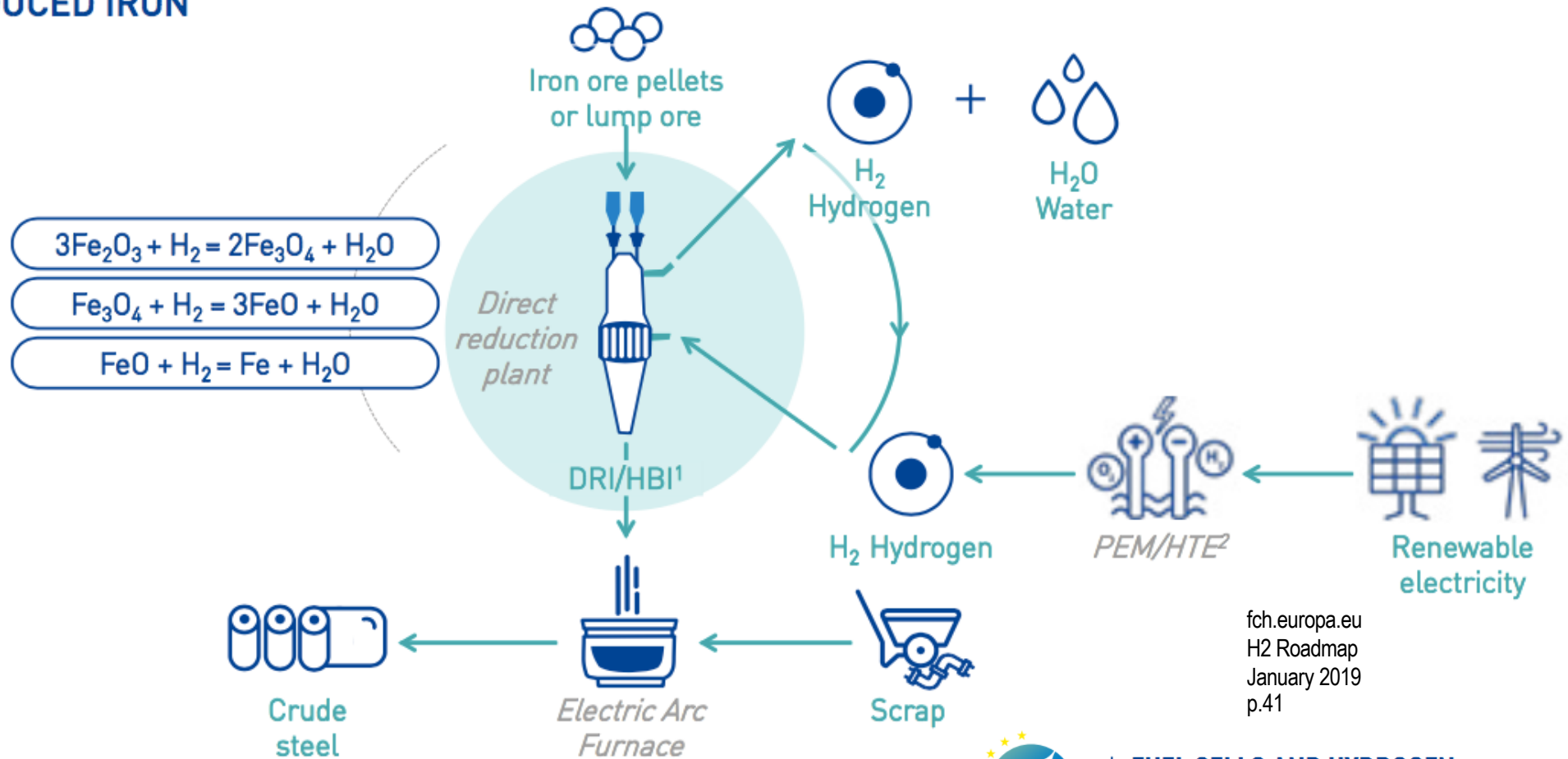
 **REFHYNE** 2018-2022
CLEAN REFINERY HYDROGEN FOR EUROPE

 **FUEL CELLS AND HYDROGEN** 10 M€
JOINT UNDERTAKING



H₂ for steel making : DRI

EXHIBIT 18: DEEPLY DECARBONIZED STEELMAKING THROUGH HYDROGEN-BASED DIRECT REDUCED IRON



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H2 Roadmap
January 2019
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FUEL CELLS AND HYDROGEN
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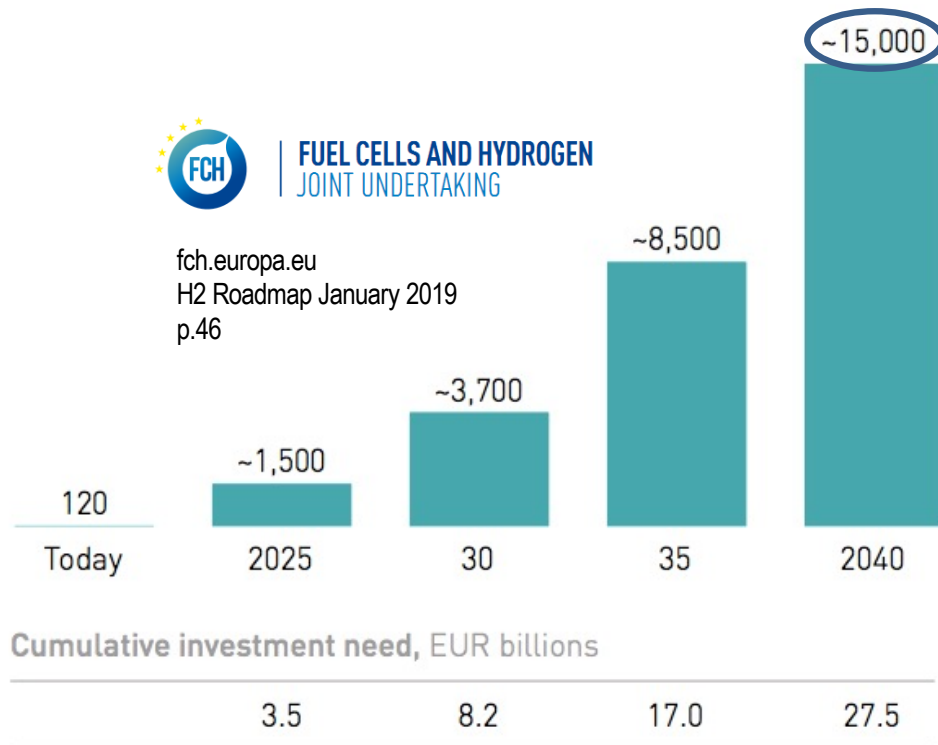
1 Direct reduced iron/hot briquetted iron
2 Polymer electrolyte membrane electrolysis/high temperature electrolysis

Mobility: H₂ refueling stations (HRS)

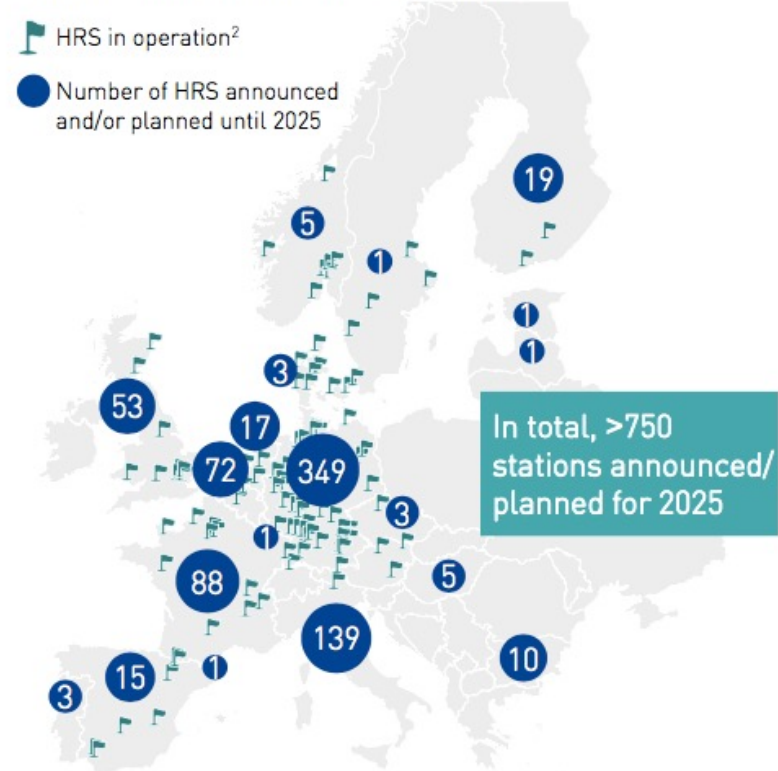
EXHIBIT 21: FUTURE HRS REQUIREMENT

Required large HRS¹, number

AMBITIOUS SCENARIO



Current and planned HRS in Europe



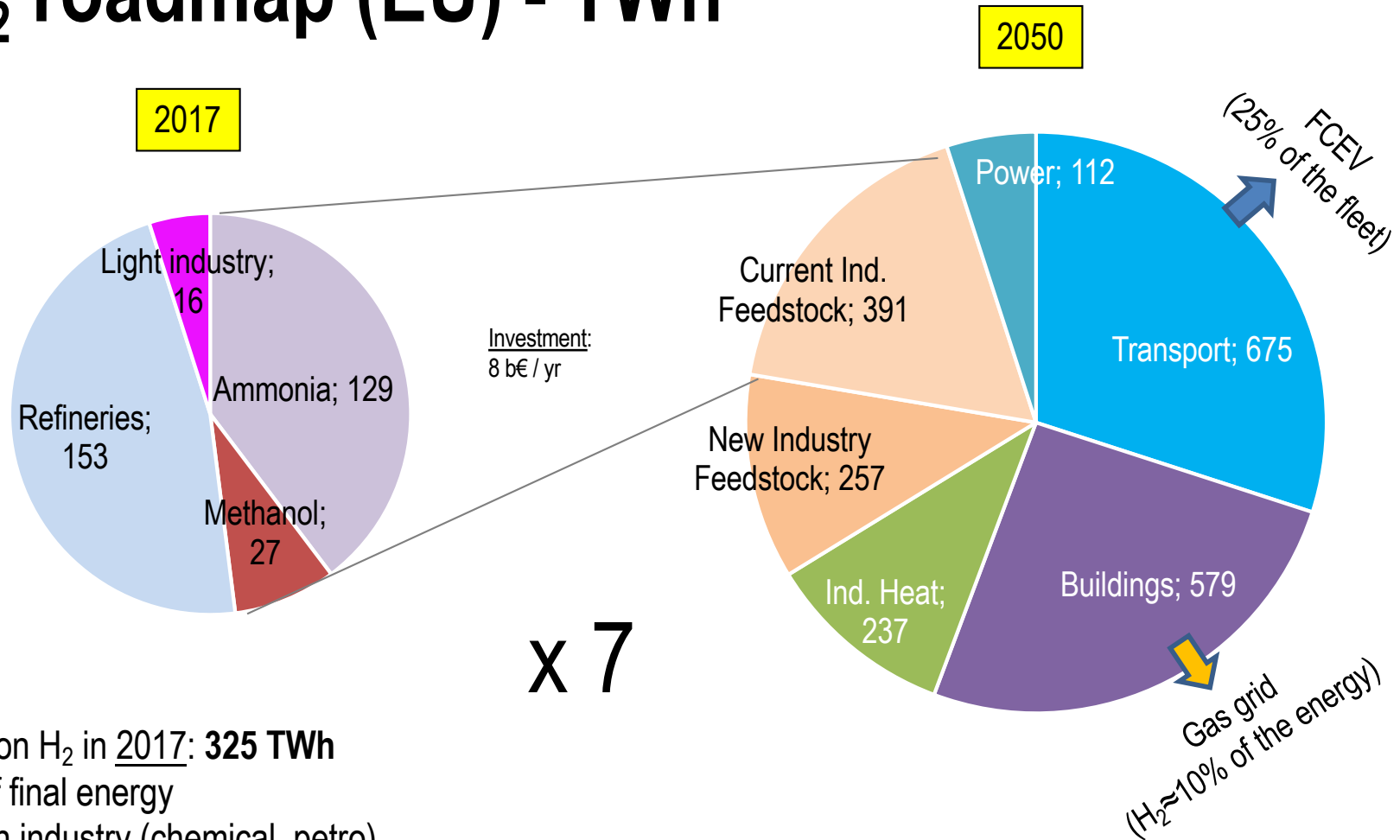
¹ Equivalents of medium HRS (1,000kg daily capacity); utilization relative to steady-state

² Indicative position

1000 kg H₂/day/HRS

=> x 15'000 HRS = 15 Mt H₂/day = 5.5 Gt H₂/yr = 198 TWh (712 PJ), >50 GWe

H₂ roadmap (EU) - TWh



Production H₂ in 2017: **325 TWh**

- 2% of final energy
- only in industry (chemical, petro)
- H₂ from fossil sources

(electrolysis would need **55 GWe** equivalence*)

2050: **2250 TWh**

- 24% of final energy
- multiple uses in all sectors

(equivalent electrolysis* : **385 GWe**)

*100% load, 67% LHV efficiency electricity → H₂
>1100 GWe or **1.1 TWe** for electrolyser load of 3000h/yr

385 GWe in electrolysis: is this feasible? (3400 TWhe/yr)

13% of world electricity

- existing (EU): ≈ 2 GWe
- 66.7% LHV efficiency = **1.88V** electrolysis voltage (100% = 1.23 V)
- suppose: **1A/cm²** current density
=> 1.88 W/cm² absorbed electrical power density
- for 385 GWe we then need $385 \cdot 10^9 \text{ W} / 1.88 \text{ Wcm}^{-2} = 205 \cdot 10^9 \text{ cm}^2 = 20.5 \text{ km}^2$ membrane surface ; 0.6 km³ water consumption
- *Swiss Lake of Murten : 22.8 km²; 0.6 km³ volume*
- membrane of 50 μm thick, polymer density ≈ 1 => $20 \cdot 10^6 \text{ m}^2 \times 50 \cdot 10^{-6} \text{ m} = 1000 \text{ m}^3 =$ **1000 tons** of polymer
- compare this to the annual plastics production of **330 Mtonnes** / yr
- for >1TWe installed capacity, quantities increase by factor >3
- in terms of electrolyte material, the quantity needed is thus extremely low



GWe/yr deployment needed

Figure 32. Estimated necessary electrolyser manufacturing capacity (GW/year) to meet different installed capacity targets by 2050.

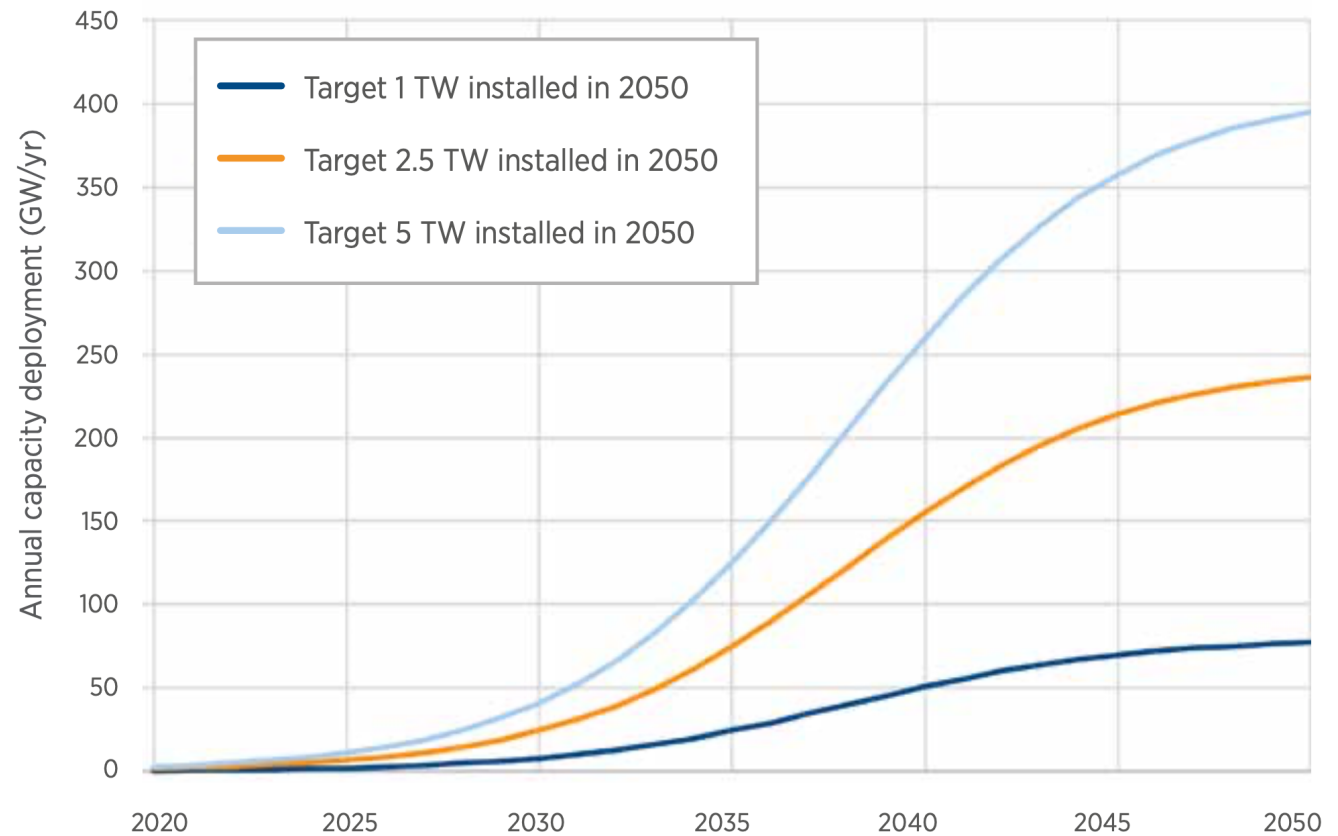
IRENA (2020), *Green Hydrogen Cost Reduction: Scaling up Electrolysers to Meet the 1.50C Climate Goal*, International Renewable Energy Agency. p.85

EU targets:

6 GWe – 2024

40 GWe – 2030

Important economies of scale above 1 GWe/yr production



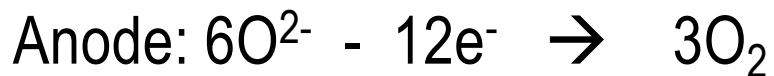
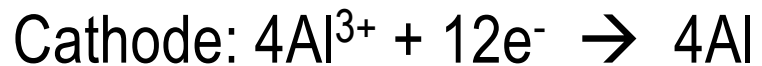
Electrochemistry in industrial production

- For some important products, the only fabrication method is electrochemical (**Cl₂, NaOH, metal extraction,...**)
- Advantages of electrochemical methods:
 - high product selectivity (choice of catalyst and potential (V))
 - easy control of i , V ; usually we use *normal* p and T (no excessive conditions)
 - high efficiency (energy cost = $\Delta G_r + \sum \eta$ = Gibbs free energy + the overpotentials)
- Disadvantages :
 - higher electricity cost vs. the cost of heat/fuels
 - hardware cost
- General rules :
 - choose low overpotential η for the desired reaction
 - ...and high overpotential η for the secondary (side) reactions
 - use cheap catalysts (Fe, Ni, C, Pb,...)

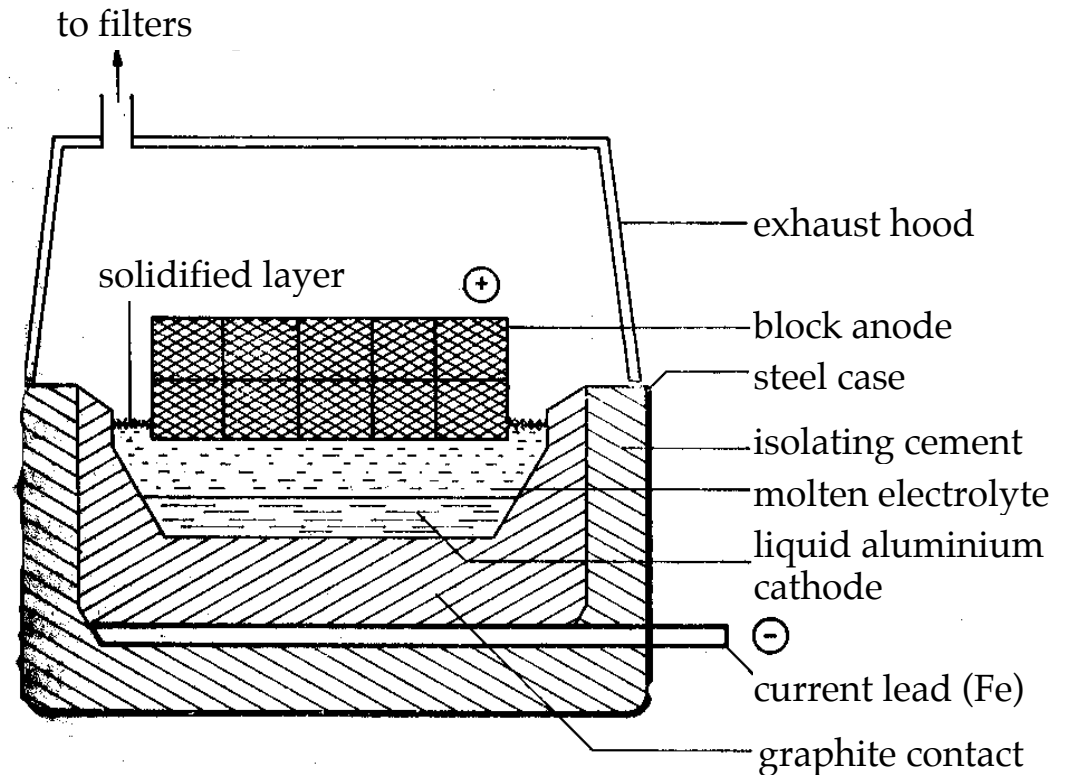
Metal extraction

- Zn (for batteries)
- Cu, Ni, Co, ... (purity)
- ...

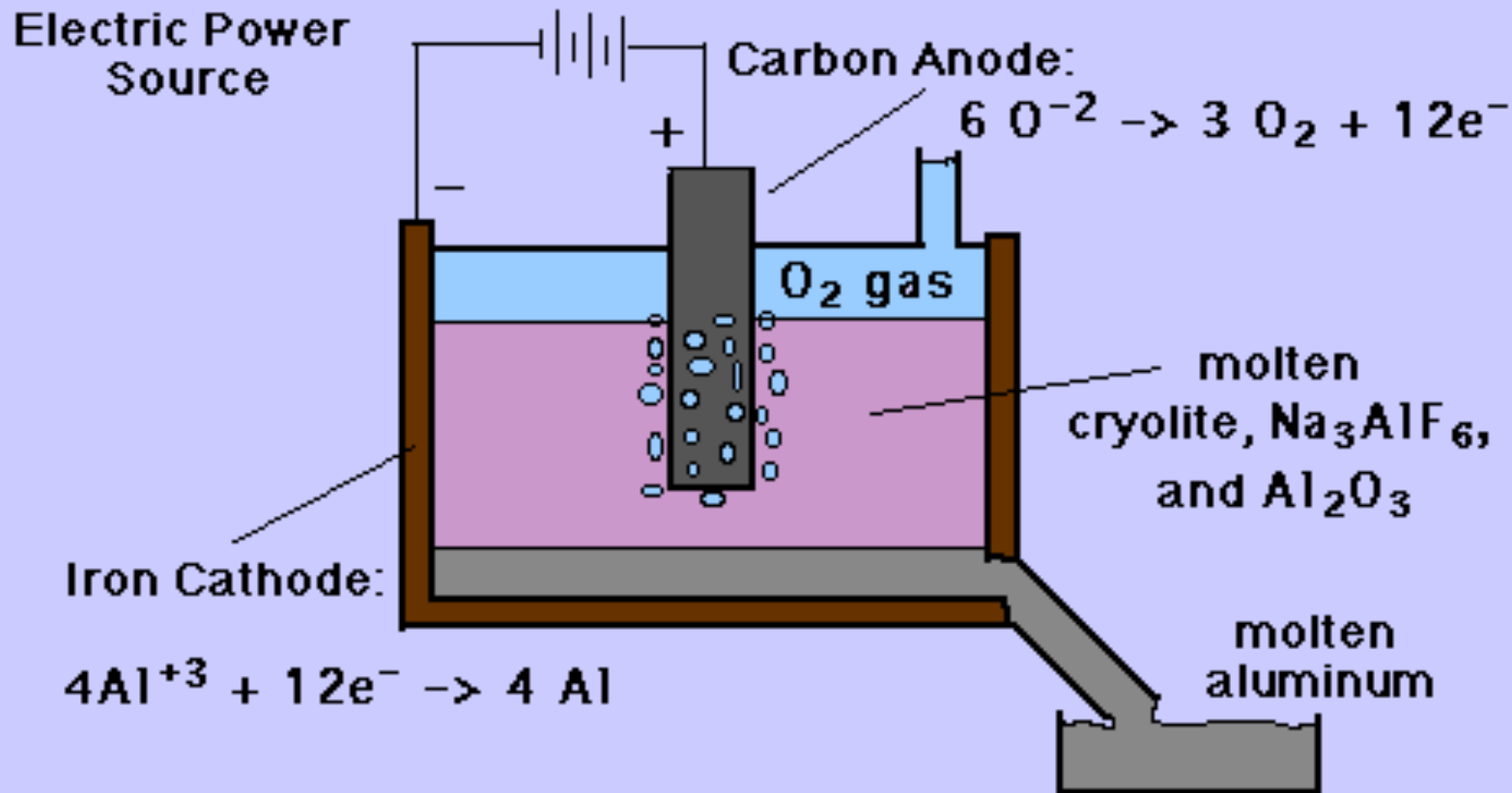
Al_2O_3 dissolves into the cryolite molten electrolyte, to Al^{3+} and O^{2-}



Special case: Aluminium
= from a molten salt
at very high temperature



Electrolysis of Aluminum



Bauxite ore is purified to Al_2O_3 , which is mixed with cryolite, a mixture of NaF and AlF_3 , which melts at 1000 C.

C. Ophardt c.1997

Aluminium-industry

- Production 2018: 64 Mton Al
- 15 kWhe / kg Al

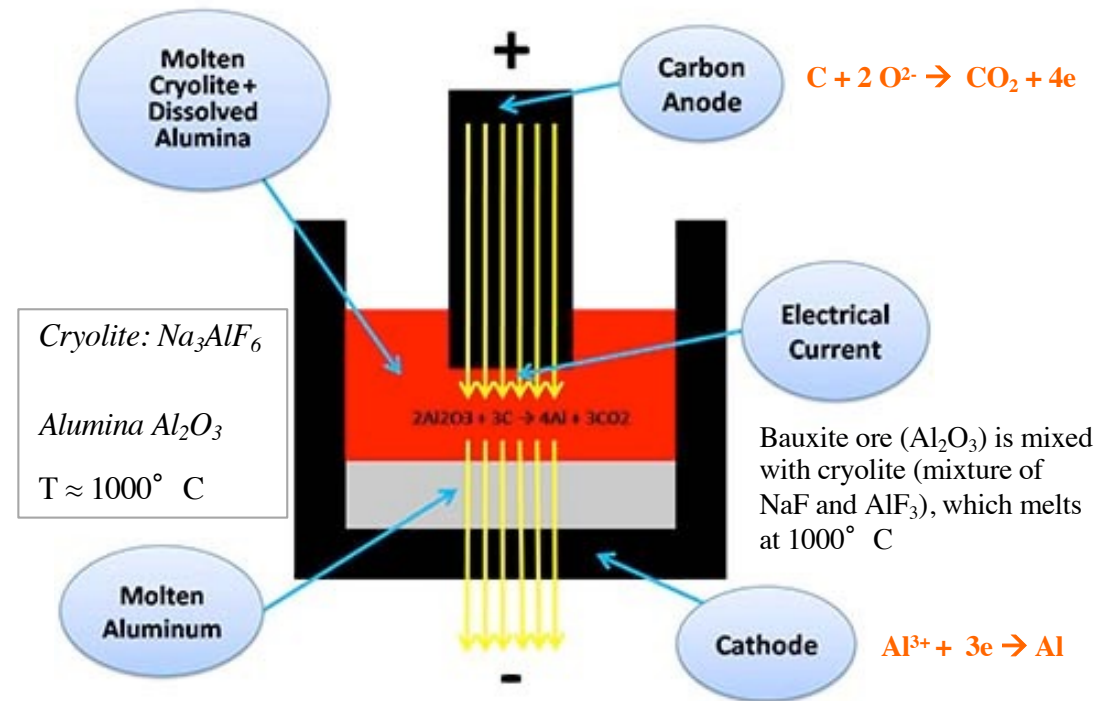
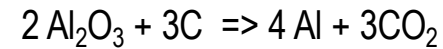
=> **960 TWh**

(≈ 120 GWe)

(≈ 4% of world electricity)

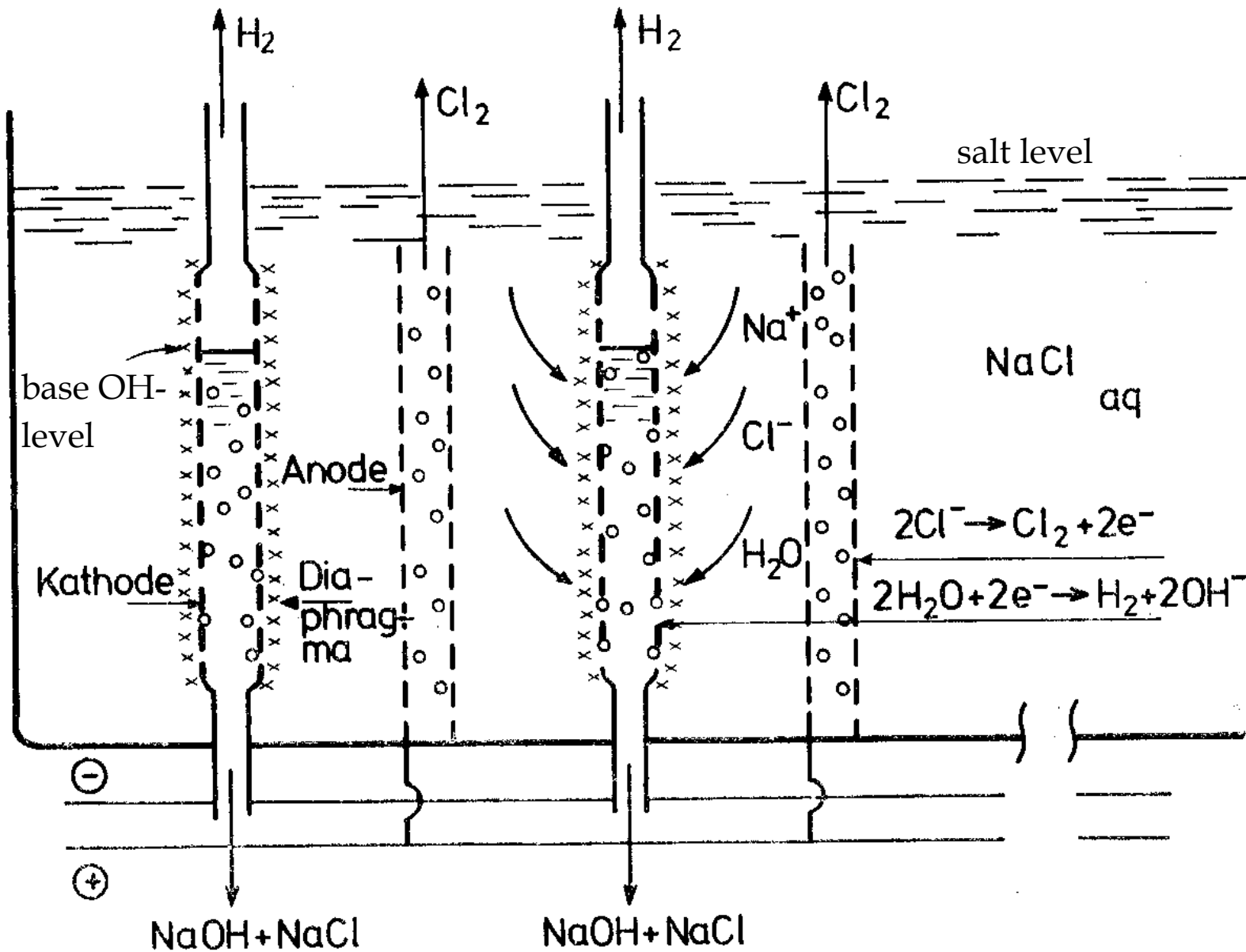
- 272 plants
(~0.5 GWe / plant)

Hall-Héroult Process (1886)



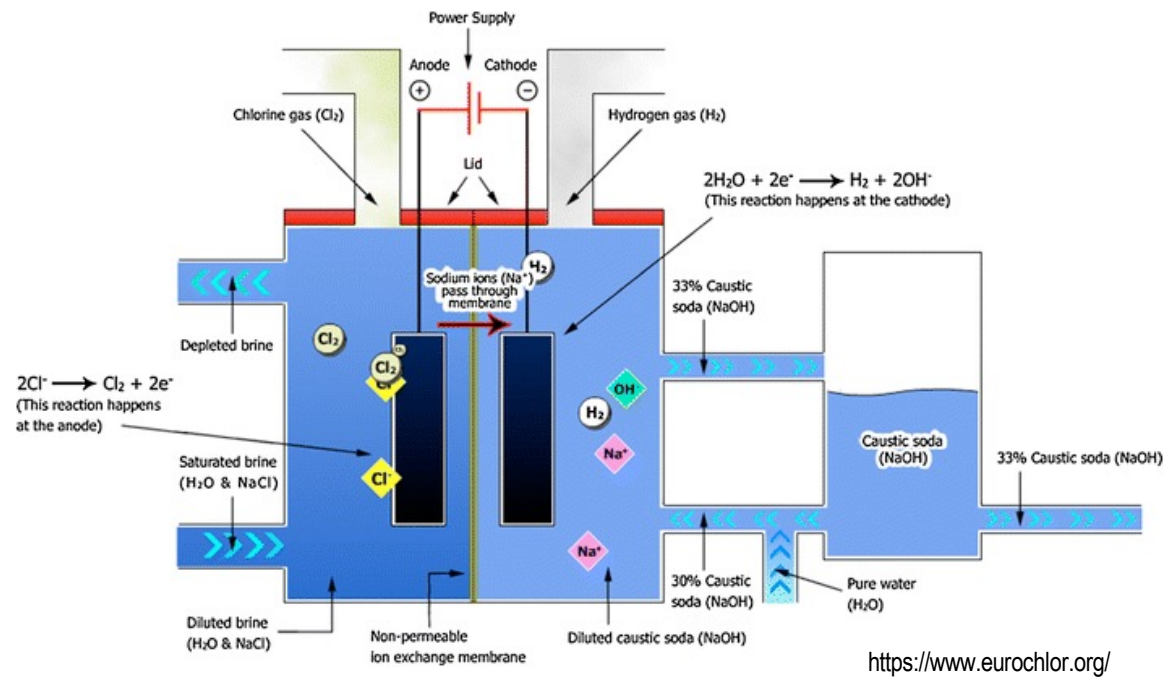
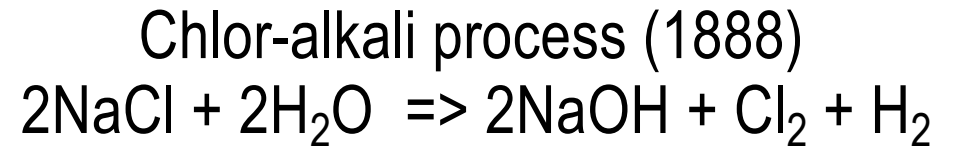
http://www.aluminum-production.com/process_basics.html

Chlorine-alkali synthesis (Cl₂, NaOH)



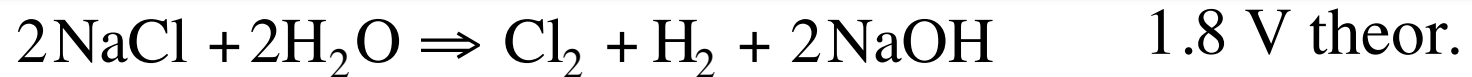
Electrolytic H₂ : example of the chlor-alkali-industry

- Production 2017: 58 Mton Cl₂ (650 plants)
- Elec. consumption: 2.1 – 3.4 kWh / kg Cl₂
- (for 2.5 kWh / kg Cl₂) => **150 TWh** consumed
 ≈ 20 GWe worldwide
 ≈ 0.6% of world electricity
- this co-produces 1.6 Mt H₂ = 54 TWh H₂, accounting for >½ of all electrolytic H₂
- ~30 MWe per plant



Lakshmanan, S. & Murugesan, T. *Clean Techn Environ Policy* (2014) 16: 225. <https://doi.org/10.1007/s10098-013-0630-6>

Chlorine-alkali synthesis

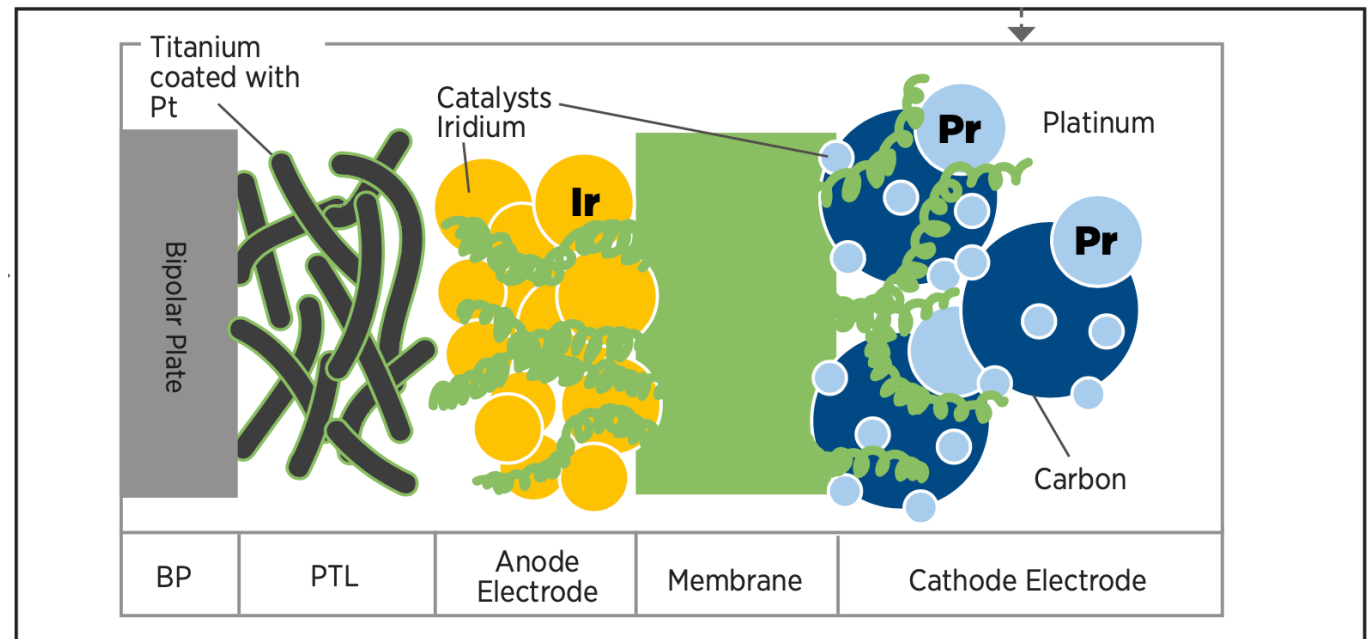


- Graphite : high anodic overpotential η (on purpose!) for O_2 evolution (so as to prevent water electrolysis ($>1.23\text{V}$) !)
- Real electrolysis voltage = 4 V ($E_0 = 1.8 \text{ V}$), $0.25\text{A}/\text{cm}^2$, 40 m^2 , $100'000 \text{ A}$ (400 kW per cell)
- Losses bwt real and theoretical voltage (4 V - 1.8 V) :
 - charge transfer loss $\eta_{a,\text{CT}}$ for Fe/ H_2 (0.2 V)
 - mass transfer overpotential losses $\eta_{a,\text{conc}}$, $\eta_{c,\text{conc}}$
 - ohmic drop in electrolyte (0.4 V; distance between electrodes = 1 cm)
 - Nernst potential displacement by alkaline medium (OH^-) (0.5 V)

Critical materials in PEMEL

IRENA (2020), *Green Hydrogen Cost Reduction: Scaling up Electrolysers to Meet the 1.50C Climate Goal*, International Renewable Energy Agency p.28.

BiP Ti coated with
Pt on anode (O_2) and
Au on cathode (H_2)
represents 50% of stack cost;
noble metal catalysts 10%.



Porous transport layers: 1-5 mg Pt/cm² (2.5 g Pt/kWe)
IrO₂ tends to dissolve : high load of 2-5 mg/cm²

Platinum Group Metals

- Pt (4 ppb), Pd (6 ppb), Rh (1 ppb), Ru (1 ppb), Ir (0.4 ppb)
- Exploitable reserves 71'000 t (proven: 100'000 t; 30'000t Pt; 1'500 t Ir)
- Production: 200 t/yr each for Pt, Pd (a cube of 2 m edge), 500 t/yr all PGM
- >150 years depletion time
- Extremely concentrated in S-Africa (90% of reserves), RUS (8%), who are the main producers. Small producers are CAN, USA, Zambia.
- >50% of use is as automotive exhaust catalysts – compulsory since 1993
 - 1000 t Pt / Pd in 1 billion cars now (1g per car)
 - 40 t / yr is recycled
- Other uses: ammonia, oil additive (for combustion), electronics (hard discs, optical fibres), glasses (liquid crystal), medicine (anti-carcinogenic)

Pt cathode / IrO₂ anode in PEMEL

- Pt example:
 - 2V, 2 A/cm² = 4 W/cm²
 - 0.2 mg Pt/cm² cathode, 1.8 mg/cm² PTL, total 2 mg/cm²
 - => 0.5 g Pt / kWe => 1 kg Pt / 2 MWe
 - suppose 20 t Pt/yr (10% of production) is dedicated to electrolysis
 - => can support 40 GWe / yr
 - Remark: 1 FCEV uses 3g Pt too !
- Ir example:
 - 5 mg/cm² Ir
 - => 1.25 g Ir / kWe => 1 kg / 800 kWe
 - total (!) production of 8 t Ir/yr can support only 6 GWe / yr

Nickel

- Innox steel (=60% of Ni use) – austenitic
 - relatively easy to recycle
 - unreplacable as inox steel
- Special alloys (25% of use)
- Coatings (10% of use)
- **Catalysts**, electronics (5% of use)
- Example AEL (/SOE):
 - $0.5\text{A}/\text{cm}^2$, 2V , $1\text{W}/\text{cm}^2$, $10\text{ mg Ni}/\text{cm}^2$
 - $\Rightarrow 10\text{ mg Ni} / \text{W} \Rightarrow 10\text{ kg} / \text{MWe} \Rightarrow 10\text{ kton} / \text{TWe}$
 - only 0.4% of annual Ni production of 2.7 Mt (=100 kt/yr) would support **1 TWe** deployment

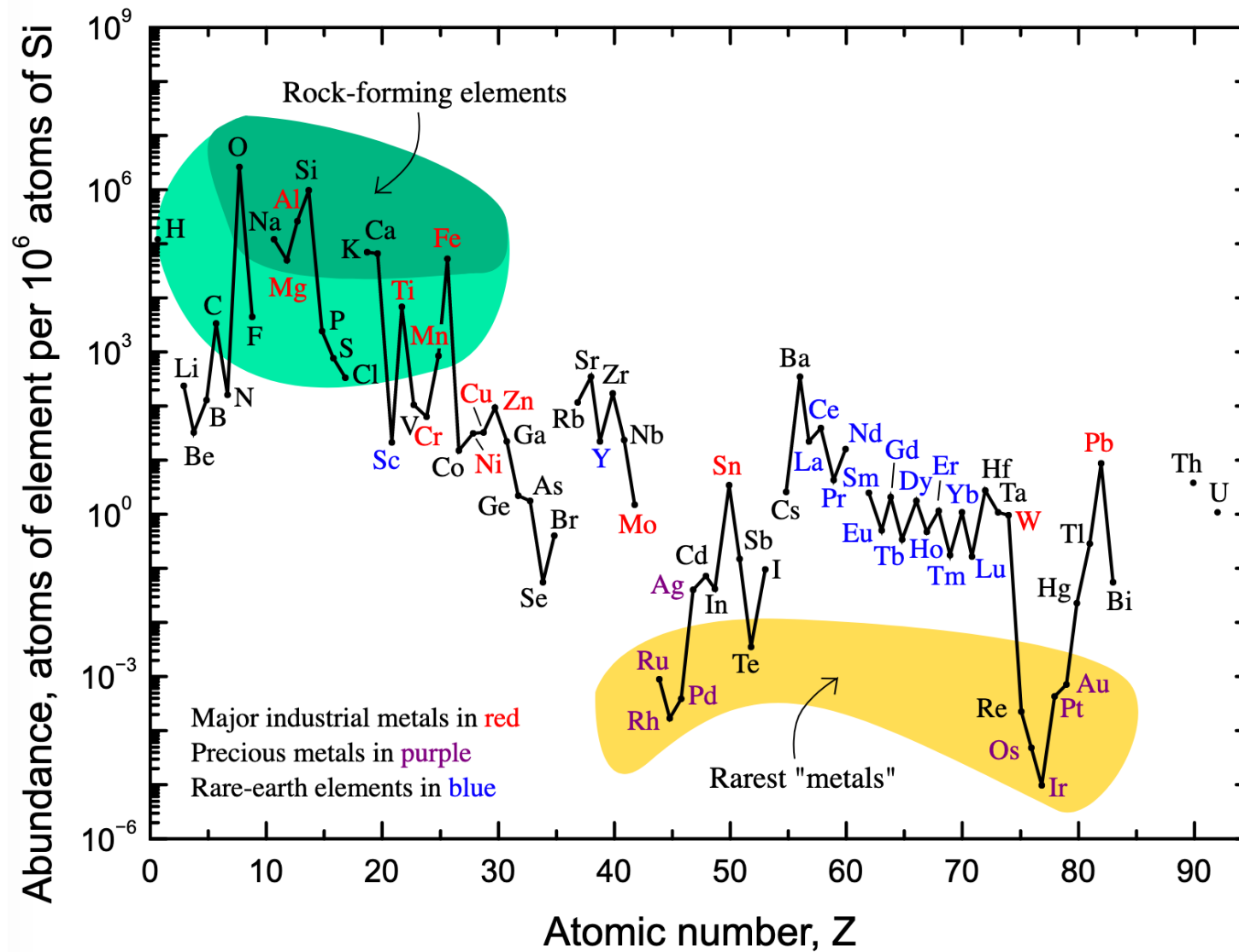
Metal uses today

1. **Fe** by very far the largest : 2500 Mt/yr (= covering Malta* with 1 m of Fe)
2. 'Larger' industrial metals >1 Mt/yr
Al 60 / Cr 44 / Cu 20 / Mn 20 / Zn 13.5 / **Ti 8.5** / Si 6.7 / Pb 5 / **Ni 2.7** Mt/yr
(=covering Malta with 1 mm of Ni)
3. 'Smaller' industrial metals < 1 Mt/yr:
Mg 1 / Sn 0.33 / Mo 0.25 / **Co 0.14** / V 0.11 / W 0.085 / **Li 0.082** / Cd 0.025
(=covering Malty with 50 μm of Co)
4. Precious metals :
Ag 27'000 t, Au 3300 t, **PGM** 500 t (Pt 200 t, Pd 200 t, Rh 22 t, Ir 7 t)
(=covering Malta with 8.5 μm Ag, 0.56 μm Au, 31 nm Pt, 1 nm Ir)

*Malta surface: 316 km²

Densities: Fe 7.87 Ni 8.9 Co 8.9 Ag 10.5 Au 19.3 Pt 21.5 Ir 22.5 t/m³

Relative abundance of elements



Reserves of metals

	Metal	wt% crust	Proven reserves*	Prod. / yr	Depletion time (yrs)	Cost €/kg	Geodistribution – top 3 countries	Energy footprint
abundant	Fe	5%	200'000 Mt	2500 Mt	80 yrs	1	47% (RUS/UKR, AUS, BRA)	0.5 toe/t
	Al	8%	10'000 Mt	60 Mt	200	2	57% (AUS, BRA, CHN, Guinea)	5.6
	Ti	0.4%	1000 Mt	8.5 Mt	120	20	67% (AUS, CHN, BRA, IND)	12
rare	Ni	90 ppm	150 Mt	2.7 Mt	50	20	57% (AUS/NZ, RUS, CAN)	3.6
	Co	40 ppm	15 Mt	140 kt	100	50	58% (RDC, AUS, CAN)	
very rare	Ag	70 ppb	800 kt	27 kt	30	600	44% (Peru, Mex, CHN)	
	Pt	7 ppb	100 kt	200 t	500	24'000	92% (S-Afr, RUS, CAN)	
	Au	4 ppb	100 kt	3300 t	30	48'000	34% (S-Afr, CHN, AUS)	
	Ir	<1 ppb	1.5 kt	8 t	175	140'000	100% (S-Afr, (ZIM, RUS))	

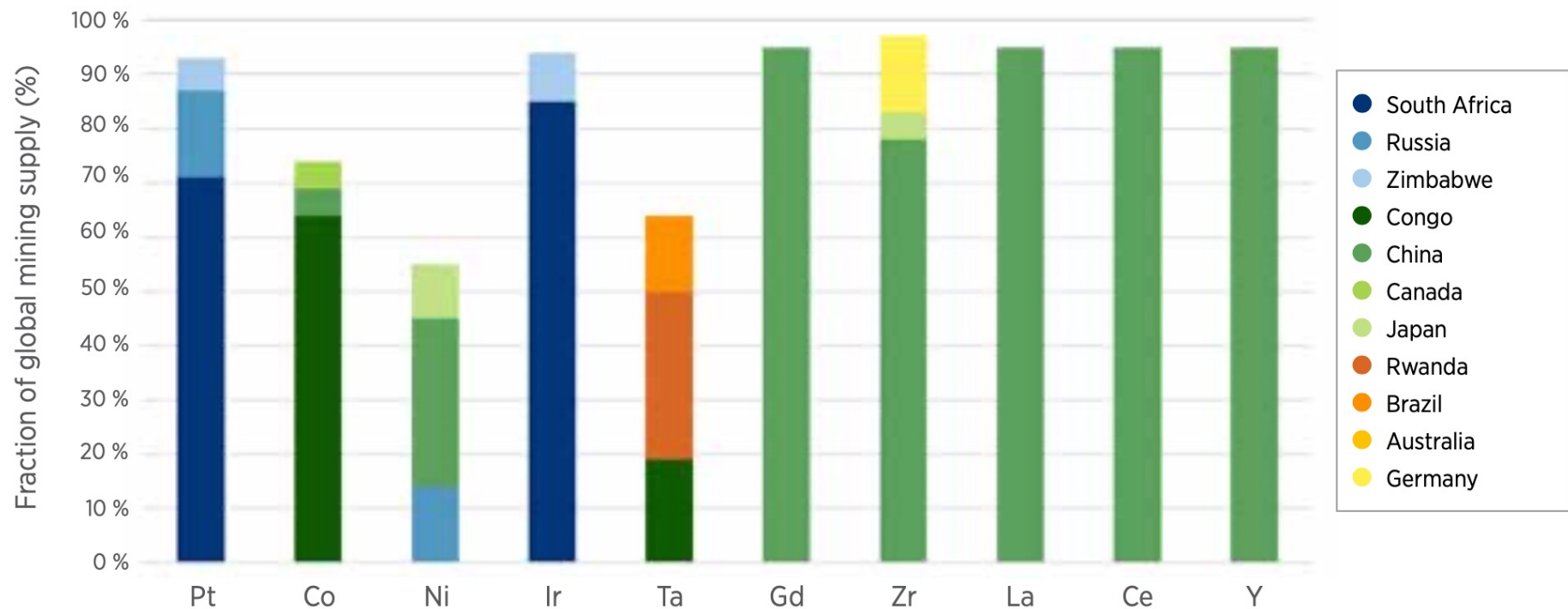
*Currently exploitable reserves \approx ½ proven reserves \approx only 0.01 - 0.1% of natural abundance for the rare elements

Noble metals highly concentrated in 1 country (South-Africa)

Critical materials

IRENA (2020), *Green Hydrogen Cost Reduction: Scaling up Electrolysers to Meet the 1.50C Climate Goal*, International Renewable Energy Agency p.69.

Figure 24. Top producers of critical materials in electrolysers.



Source: European Commission, 2020.

General comments on metal scarcity

- Metal resources are, like fossil resources, **finite**. Extraction cost and energy use increase, as resources get depleted.
- Between 1995-2015, the world metal consumption has doubled.
- **100% recycling is an illusion**, because of the 2nd law of thermodynamics (dispersion; quality loss upon each recycle)
 - examples of dispersive uses: dyes, pigments, catalysts, fertilisers, additives, coatings, galvanisation, solders
- Alloy fine-tuning for the pursuit of hi-tech components, or the high purity requirements of some metals, are **antagonistic with recycling**
 - e.g. >3000 Ni-alloys exist

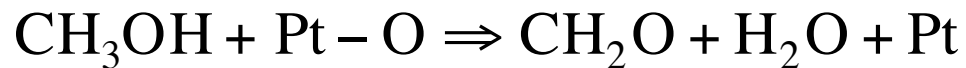
Large scale green H₂ electrolysis deployment

- Several TWe cumulated installed power will be needed
- Demands **massive scaling** and cost reduction
- 1st cost in electrolysis = **electricity** consumption => high efficiency is key
- 2nd cost in electrolysis = **electrolyzer** => can be brought down by:
large scale production, increased lifetime,
more operating hours (3000-4000 h/yr), use of **non-critical** materials
- AEL: should be Pt- and Co-free; only Ni-based
- PEMEL: Pt and Ir use should drop by 10x. Alternatives to coated Ti BiP.
- AEMEL (Ni, Fe based): could be game-changing if durability and performance catch up
- Materials importance: criticality, purity, alloying and ease of recycling

Electro-organic synthesis

- for specific organic reactions: selective oxidation, hydrogenation, halogenation, dimerisation, organometal complexing, ..

- catalyst adsorbates are exploited in the synthesis steps
e.g. selective formaldehyde synthesis

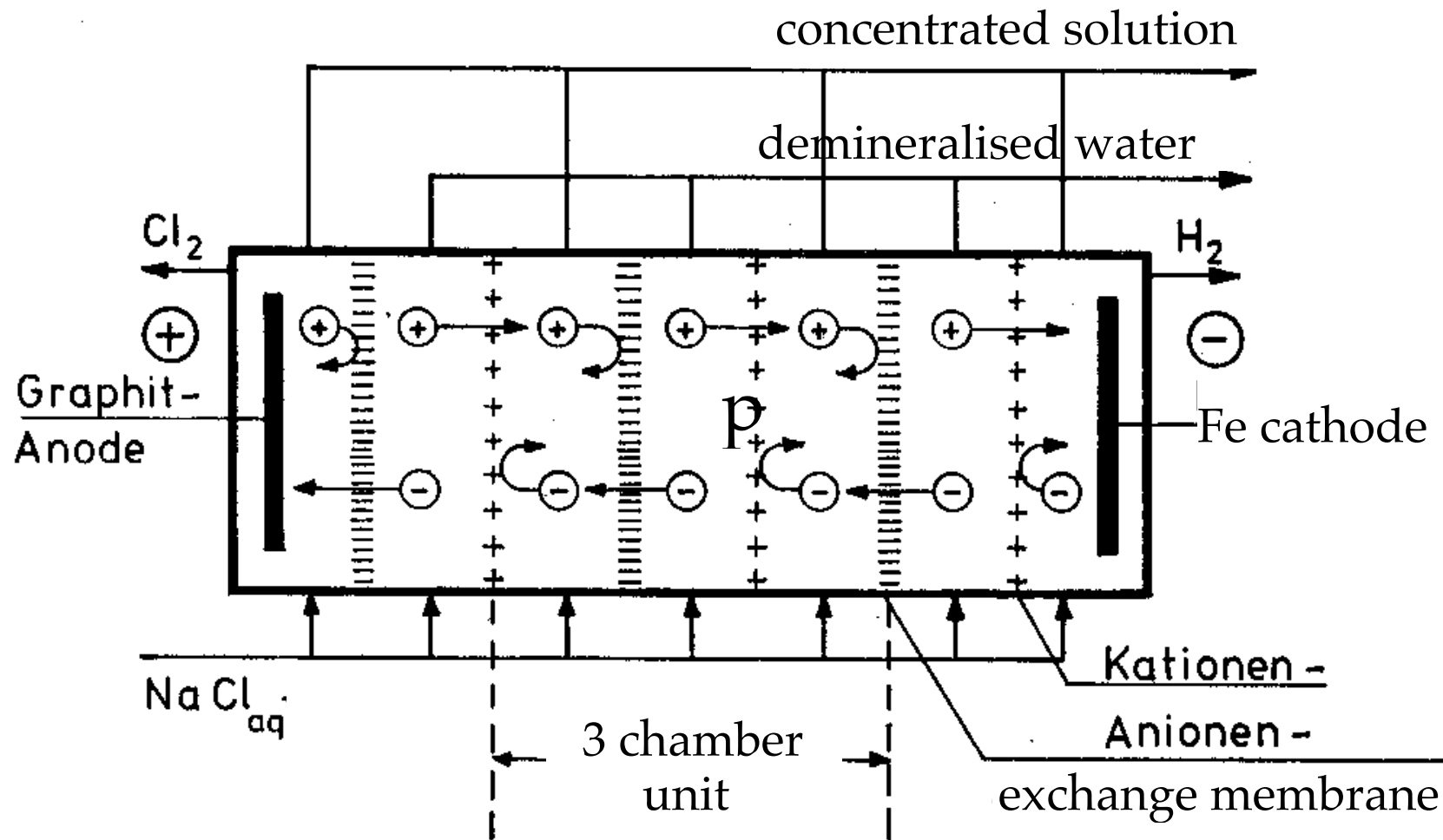


- issue: organic salt-solvent mixtures have low conductivity (=> higher ohmic drops)
- maximisation of area/volume ratio is needed
 - small electrode distances (<100 μm)
 - electrodes with high inner surface (porous, rough)

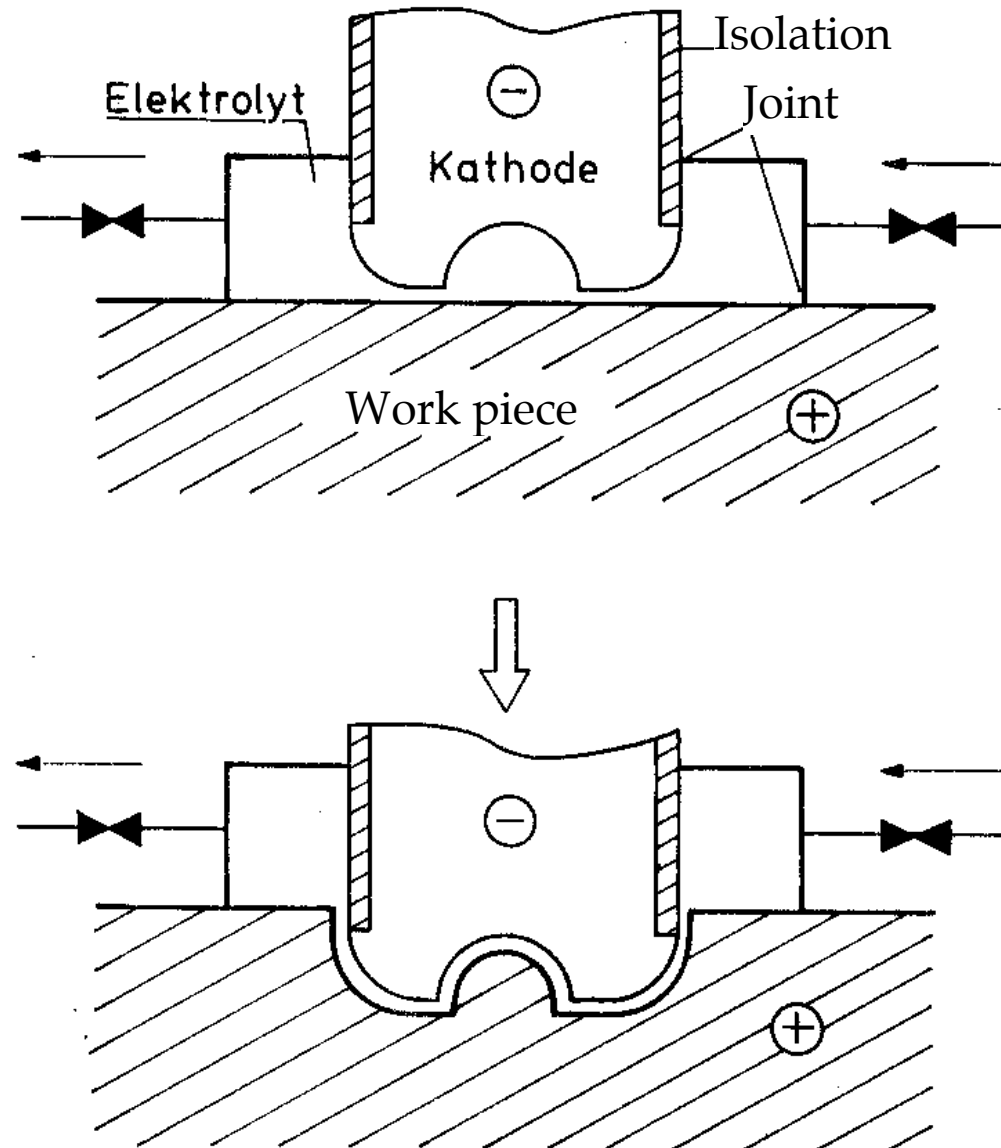
Special electrochemical applications

- Water [purification](#) (ClO^- for disinfection, trace metals)
- Electrophoresis
- Metallurgical powders (for catalyst fabrication)
- Electropolishing, [electromachining](#)
- Galvanoplastics
- Corrosion [protection](#)
- Pollution control sensors (λ -sensor)

Water desalination



Electromachining/polishing



Passivation (corrosion protection)

