Hydrogen H_2 for defossilisation in energy and industry uses: present and future

Learning objectives

- Overview of H_2 uses, now and in future
  - possible for all energy sectors, and heavy industry
- Key is:
  - renewable electricity => electrolysis (‘Power-to-Gas’)
  - massive scaling & deployment needed
- Thermodynamics and efficiency of electrolysis
  - various technologies (water (H^+ / OH^-), steam)
  - heat integration
- Storage technologies and distribution paths of H_2

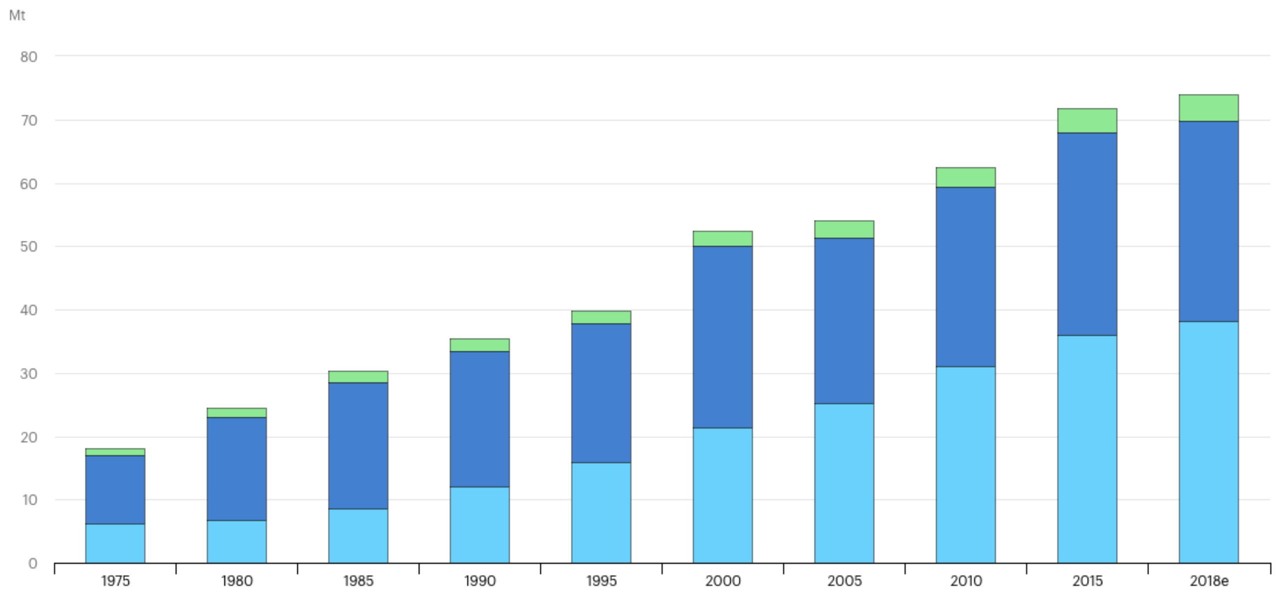
Grey, blue, green H_2

- **Grey H_2** : made from fossil sources
- **Blue H_2** : made from fossil sources but including carbon capture
- **Green H_2** : made from renewable sources (mainly electrolysis from hydro, wind, PV)

Annual H_2 production

- ≈75 Mt/yr ≈ 830 10^9 m^3 /yr ≈ 10 EJ (2800 TWh) = 2% of world energy
  - 49% from natural gas
  - 29% from oil
  - 18% from coal
  - 4% from electrolysis

96% from fossil sources



Global demand for pure hydrogen, 1975-2018

- By comparison: natural gas 4000 10^9 m^3 /yr = 140 EJ (24% of world energy – 580 EJ)

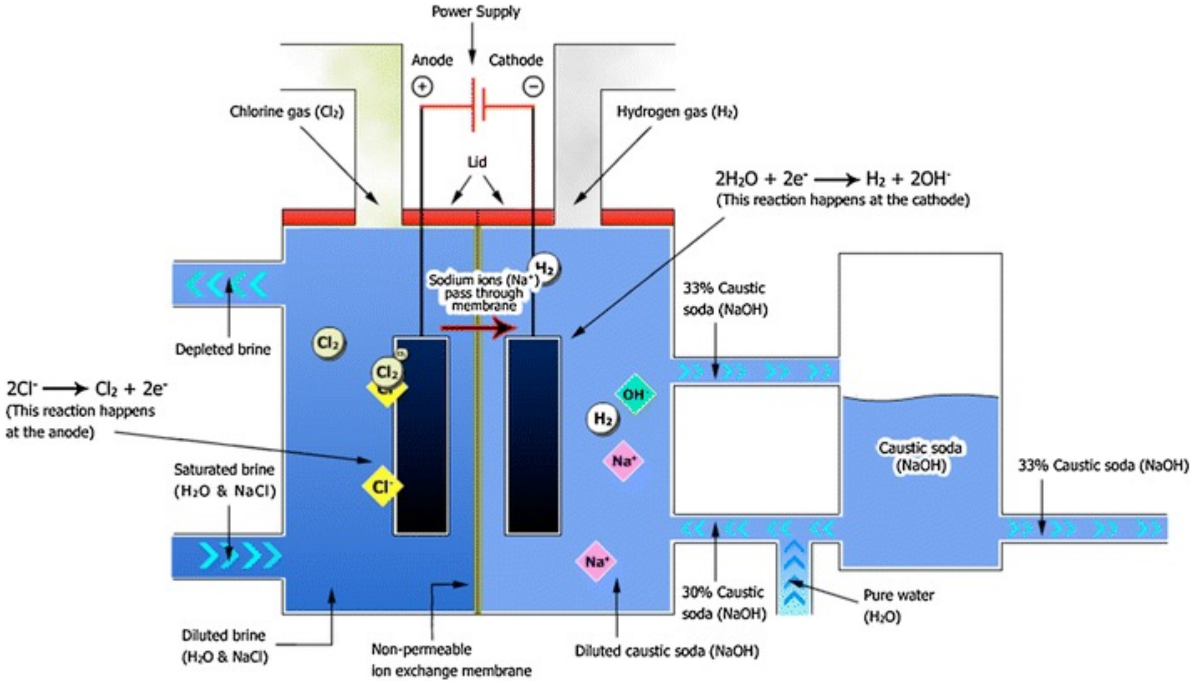
Electrolytic H_2 : e.g. chlor-alkali-industry

- Production 2017: 58 Mton Cl_2 (650 plants)
- Elec. consumption: 2.1 – 3.4 kWhe / kg Cl_2
- (take average of 2.5 kWhe / kg Cl_2) => 150 TWhe

  ≈ **30 GWe** worldwide
- ≈ 0.6% of world electricity (25 PWh)
- this co-produces 1.6 Mt H_2 = 54 TWh H_2, accounting for >½ of all electrolytic H_2

Chlor-alkali process (1888)

$2NaCl + 2H_2O \Rightarrow 2NaOH + Cl_2 + H_2$



https://www.eurochlor.org/

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

H_2 is now mainly made from fossil fuels

Process	Reaction	ΔH (kJ/mol)	T (°C)	P (bar)	Efficiency (% HHV)
Steam reforming	$CH_4 + H_2O \rightarrow \mathbf{3\ H_2} + CO$	+206	500-700	1-30	85
Partial oxidation	$CH_4 + 1/2O_2 \rightarrow 2\ H_2 + CO$	-36	700 (**C**POX) >1000 (POX)	1-150	60-75
Autothermal reforming	$CH_4 + xH_2O + yO_2 \rightarrow H_2,CO$	0	700-900	1-50	70-80
Pyrolysis	$CH_4 \rightarrow 2\ H_2 + C$	+75	600-900	1-10	50
Gasification	$C(H_xO_y) + H_2O \rightarrow H_2 + CO$	+132	1100	50-70	60
Shift reaction	$CO + H_2O \rightarrow H_2 + CO_2$	-41	HTS 350 LTS 200	1-30	-

Thermal reforming

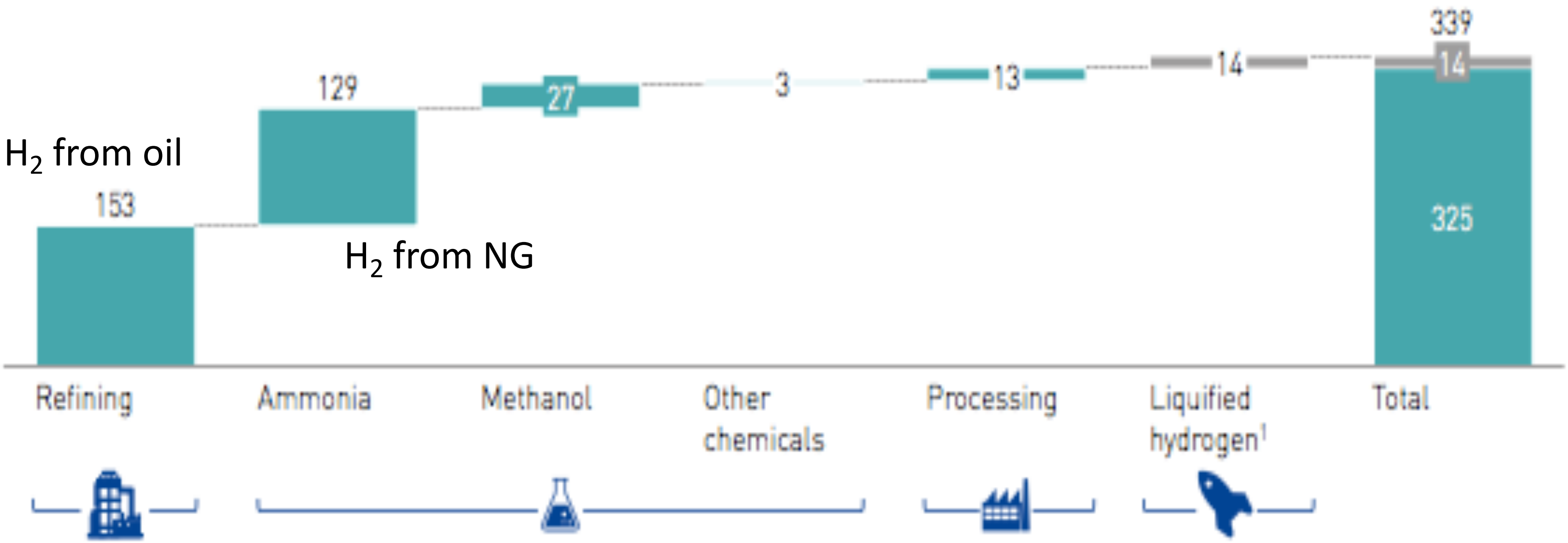
linde-le.de

Linde, Texas, STR, HT-shift, PSA
NG, 110000 m^3/h, 99.99% pure H_2

- Steam reforming (STR):
  - ☺ 100 m^3/h to 140’000 m^3/h plants
  - ☺ catalyst lifetime (Ni) > 10 yrs
  - ☺ very well known and established
  - ☺ highest H_2 yield, lowest operation temperature
  - ☹ endothermal, sluggish, large scale
  - ☺ 80-90% efficiency, 10’000 h^{-1} GHSV (ratio gas flow : reactor volume)
- Partial oxidation (POX):
  - 😐 in reality a substoichiometric combustion reaction followed by STR
  - ☺ simple, fast, compact
  - ☹ low H_2 yield, high T, difficult T-control, risk of carbon deposits
  - ☹ 70-75% efficiency, 80’000 h^{-1} GHSV
- Autothermal reforming (ATR):
  - ☺ intermediate behaviour between STR and POX
  - 😐 75-85% efficiency, 25’000 h^{-1} GHSV

Current uses of H_2 (EU)

Total hydrogen use in the EU, in TWh



H_2 from oil

H_2 from NG

Refining
- Hydro-cracking
- Hydro-treating (e.g., fuel desulfurization)
- Biorefinery

Ammonia
- Production of ammonia (for urea and other fertilizers)

Methanol
- Production of methanol and derivatives

Other chemicals
- Other chemicals (e.g., polymers, polyurethanes, fatty acids)

Processing
- Heat treating of steel
- Welding of metals
- Forming and blanketing gas
- Glass production

Liquified hydrogen[1]
- Rocket fuel
- Automotive fuel
- Semi-conductor industry

FUEL CELLS AND HYDROGEN
JOINT UNDERTAKING

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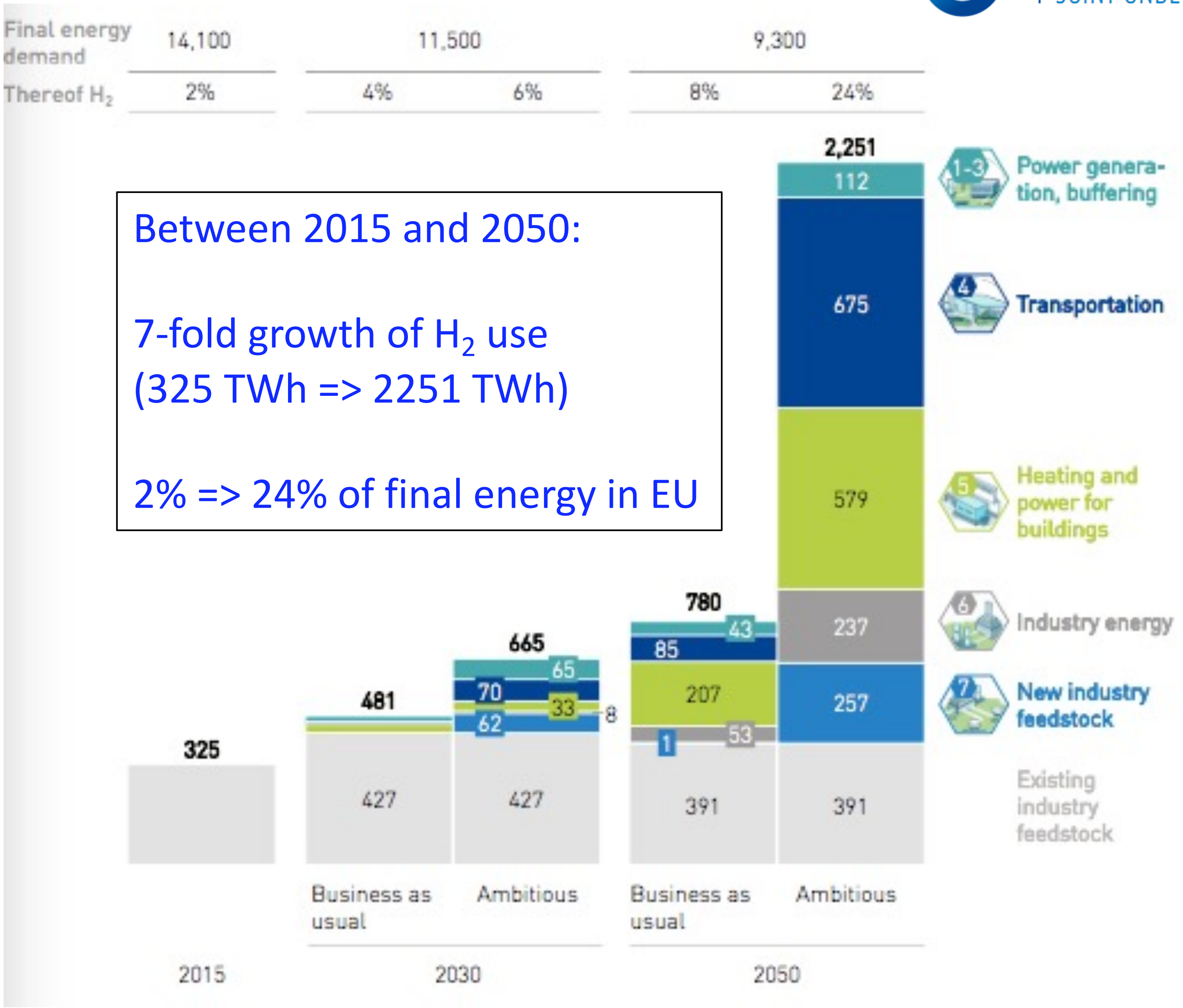
H2 Raodmap for Europe, January 2019
Exhibit 17 p.40

H_2 current uses

- Refineries (47%): hydrodesulphurisation (HDS), hydro-cracking
- Ammonia (NH_3) production (fertiliser) (40%)
- Methanol (8%) and other chemicals (1%)
- ‘Light’ industries (4%): where reducing atmosphere is needed
  - metal treatment
  - semiconductor industry
  - glass making (glass floating on liquid tin baths)
  - food (fats hydrogenation)
- 325 TWh or 1.2 EJ (2% of final EU energy)

Future uses and impact of H_2

Annual H_2 demand per segment



Between 2015 and 2050:

7-fold growth of H_2 use
(325 TWh => 2251 TWh)

2% => 24% of final energy in EU

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H2 Raodmap for Europe
January 2019
Exhibit 2 p.8
Exhibit 22 p 49

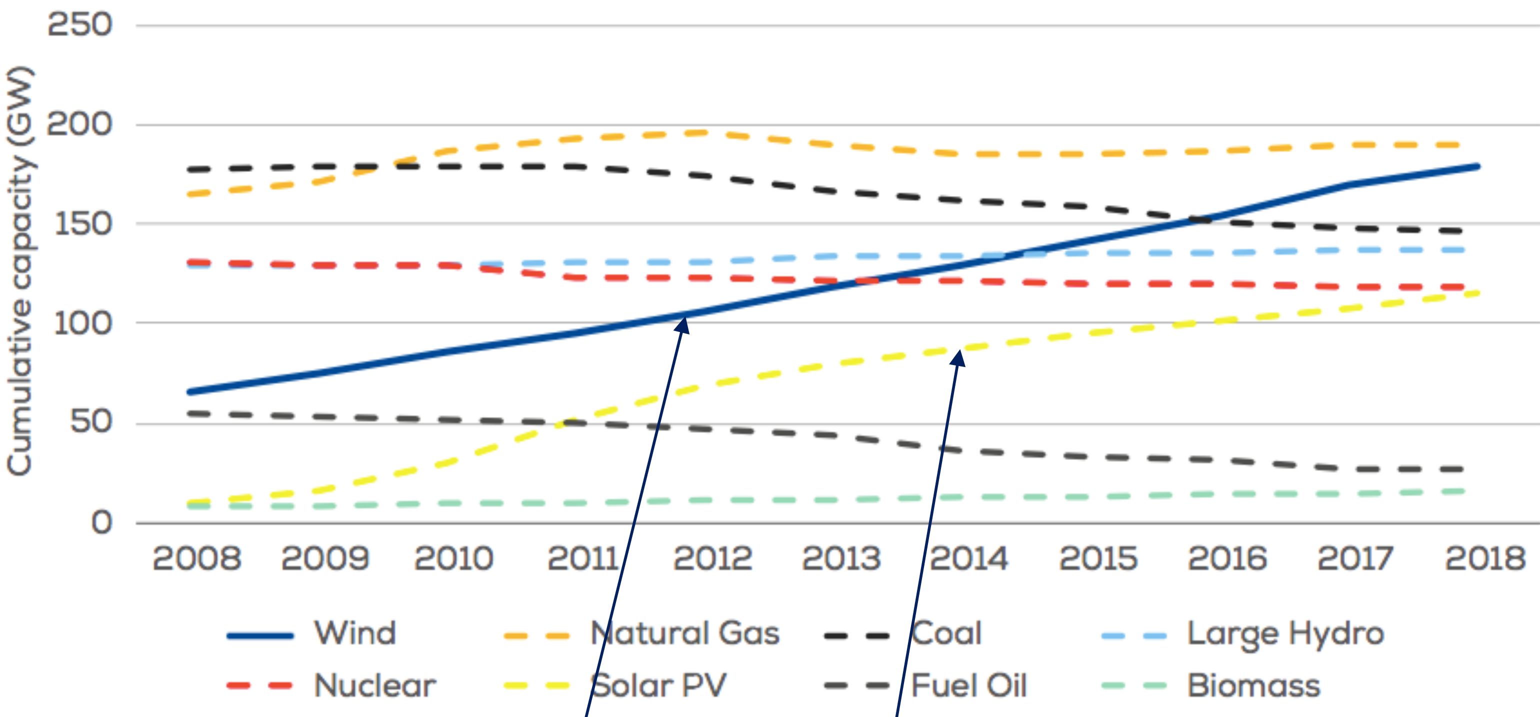
Future H_2 uses

- Mobility : fuel cell vehicles
- Residential heating : natural gas network admixing, and/or H_2 pipelines
- Industry:
  - – industry heating: replacing coal, natural gas
  - – industry feedstock:
    - refineries
    - ammonia, methanol, other industries
    - steel making
  - – light industries

Where will this H_2 come from?

FIGURE 1

Total power generation capacity in the European Union 2008-2018



Source: WindEurope

2018 (EU) :

Wind: 179 GWe
362 TWhe (14%)
26.7 b€ inv. (2018)

Solar: 126 GWe
120 TWhe (4.6%)

Solar worldwide:
+102 GWe in 2018
Total 509 GWe
(2.2% of electricity)

From growth in Wind + Solar PV ⇨ **STORAGE by ELECTROLYSIS**

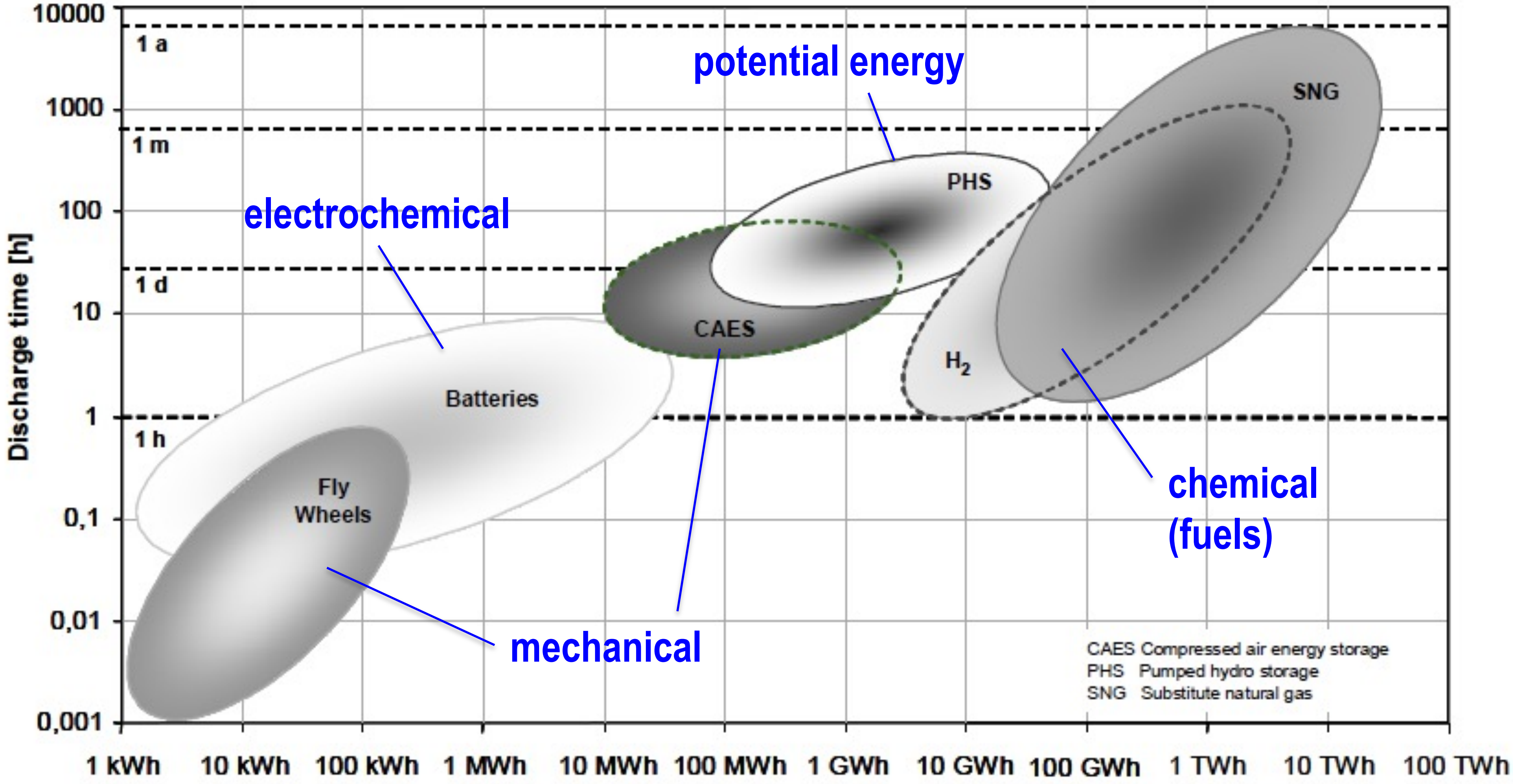
Electricity Storage as Power-to-Gas

- the electrical grid has little storage capacity
- seasonal electricity demand varies significantly
- the difference (summer-winter) is exacerbated when replacing base-load (nuclear) with renewables like PV and hydro (summer-excess, winter-deficit)

→long term storage is required

  - as fuel, by electrolysis (H_2, CH_4, …)

Storage schemes overview



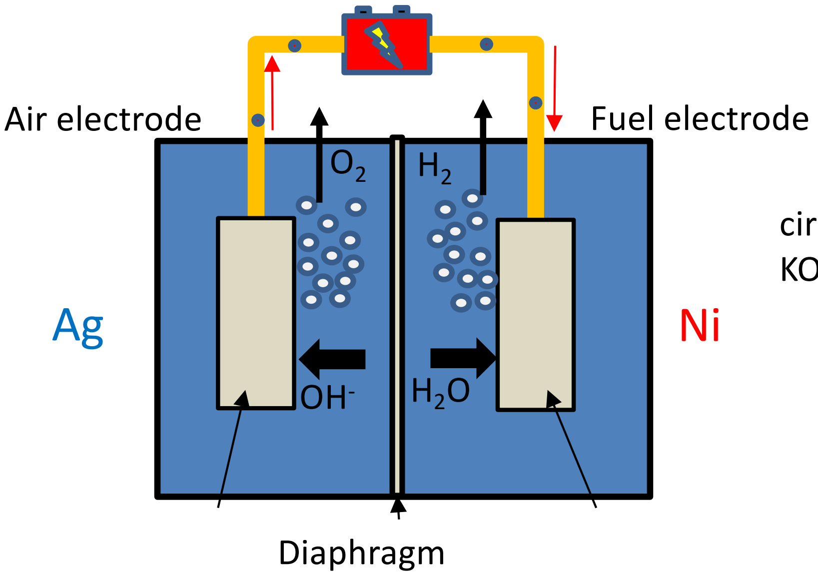
Storing Renewable Energy in the Natural Gas Grid, Methane via Power-to-Gas (P2G): A Renewable Fuel for Mobility
M. Specht, U. Zuberbühler, F. Baumgart, B. Feigl, V. Frick, B. Stürmer, M. Sterner, G. Waldstein, ZSW-Ulm

→ converting electricity to fuel gives the largest capacities

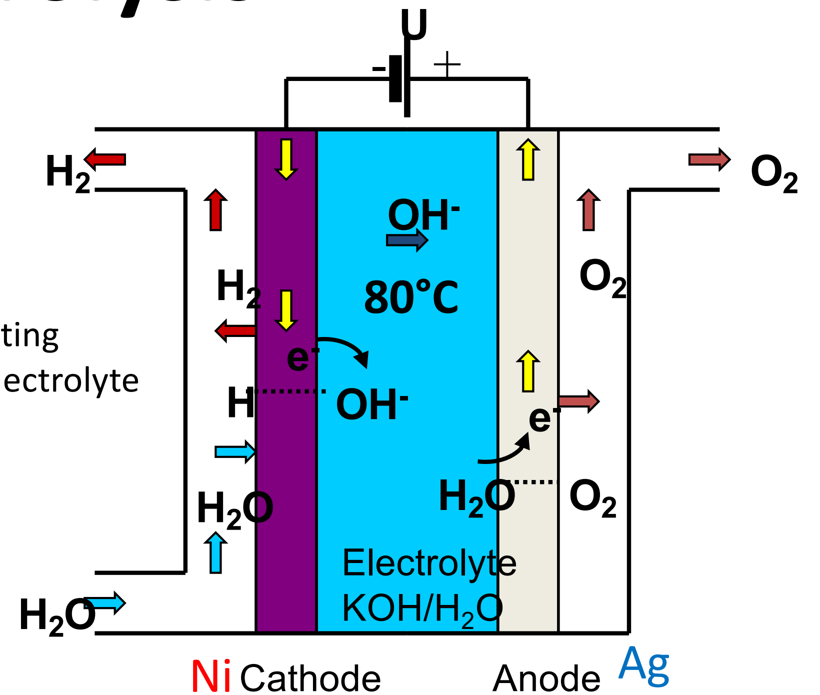
Electrolyser Technologies

• AEL : alkaline water	80°C
• PEMEL : proton exchange membrane (water)	80°C
• AEMEL : anionic exchange membrane	60°C
• SOE : solid oxide ceramic (steam)	700°C
• PCCEL : proton conducting ceramic (steam)	500°C

1. Alkaline electrolysis



circulating
KOH electrolyte



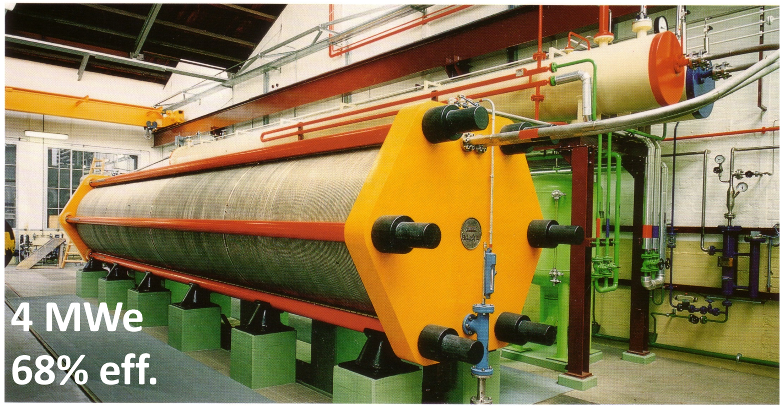
Ni Cathode

$2H_2O + 2e^- \rightarrow 2OH^- + H_2$

Anode Ag

$2OH^- \rightarrow ½O_2 + 2e^- + H_2O$

1– 30 bar



Monthey (VS)

Advantages :

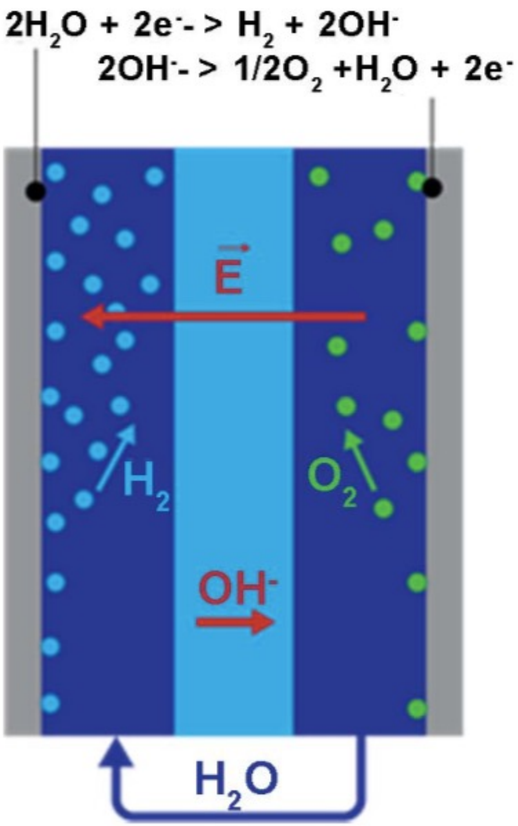
- Mature technology
- Large capacity (1400 Nm^3/h)
- Low cost
- Long life

Limitations:

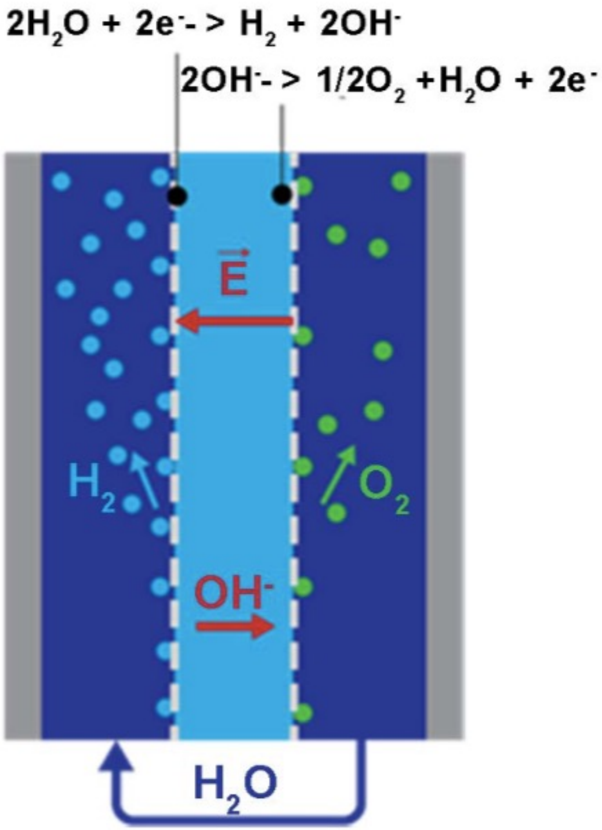
- Low current density
- Limited load range
- Limited dynamics
- Gas crossover at higher p

slide adapted from T.Macherel, Prof A. Züttel, EPFL

Electrolyte Resistance and Gas Bubbles



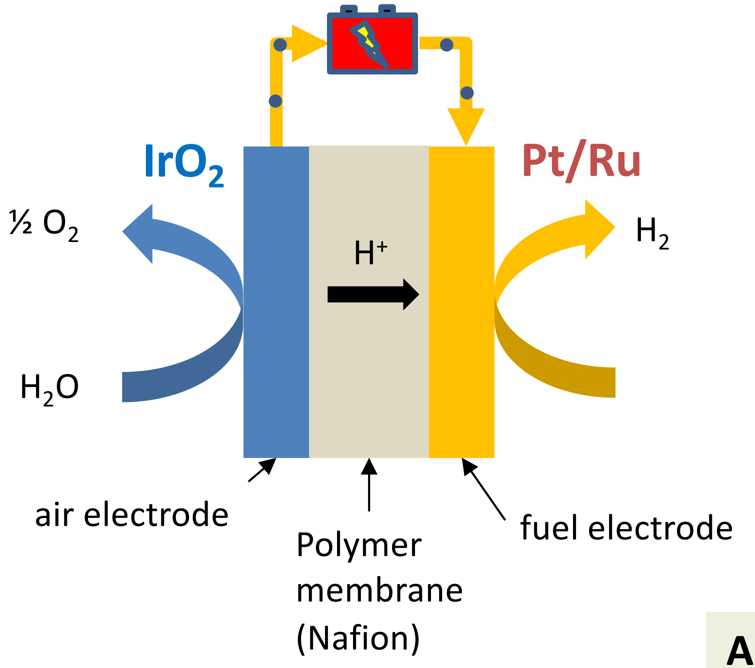
alkaline electrolyzer



zero-gap alkaline electrolyzer

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

2. Polymer electrolyte membrane electrolysis



At air electrode (anode) :

$$H_2O_{(l)} \rightarrow \frac{1}{2}O_{2(g)} + 2H^+ + 2e^-$$

At fuel electrode (cathode) :

$$2H^+ + 2e^- \rightarrow H_{2(g)}$$

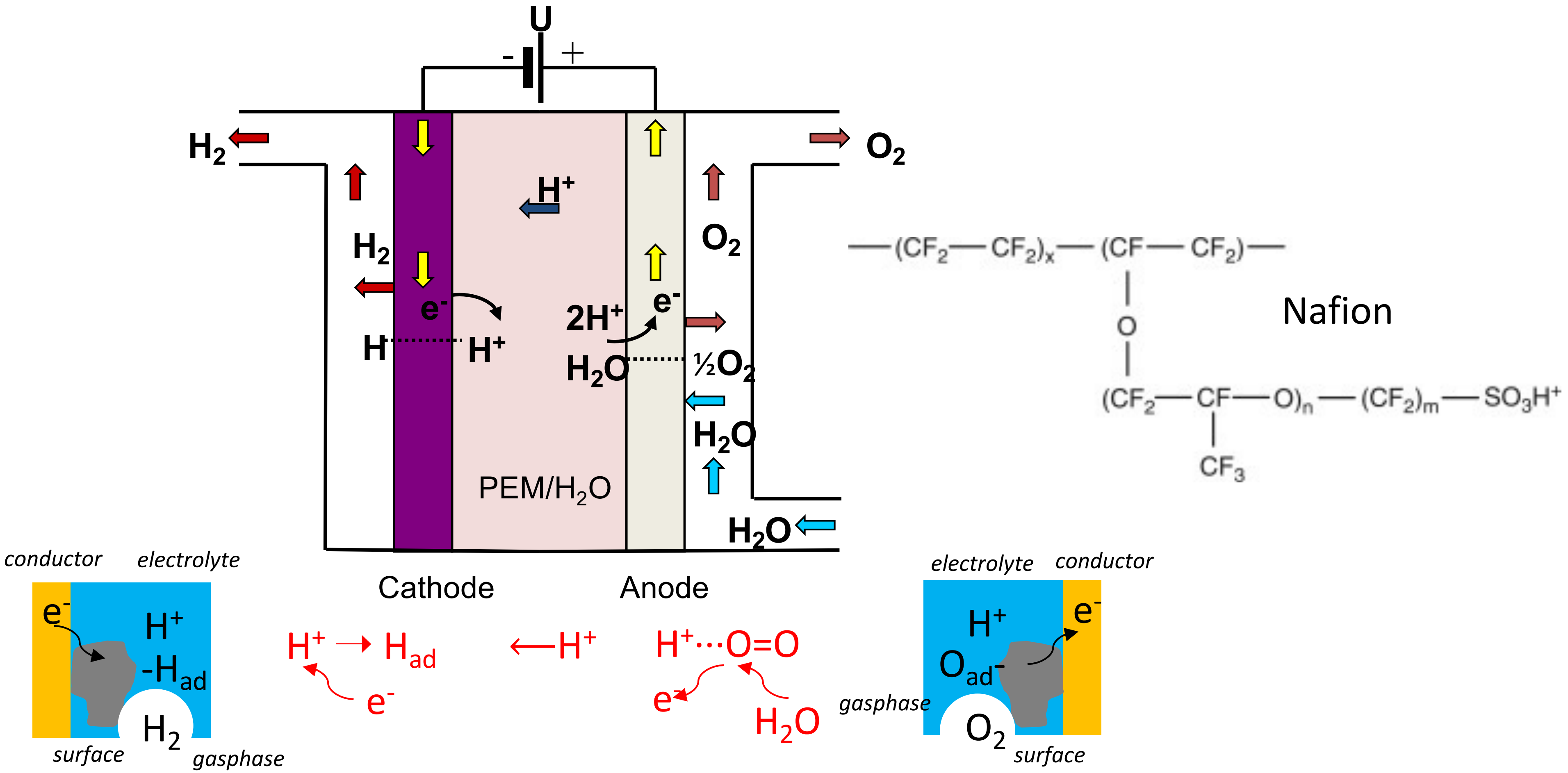
Advantages :
- High current density
- Wide load range
- Fast dynamics

Limitations:
- scarce and expensive **materials**
(noble metal catalysts; treated Ti interconnect)
- gas crossover

slide from T.Macherel, EPFL

PEM electrolyser

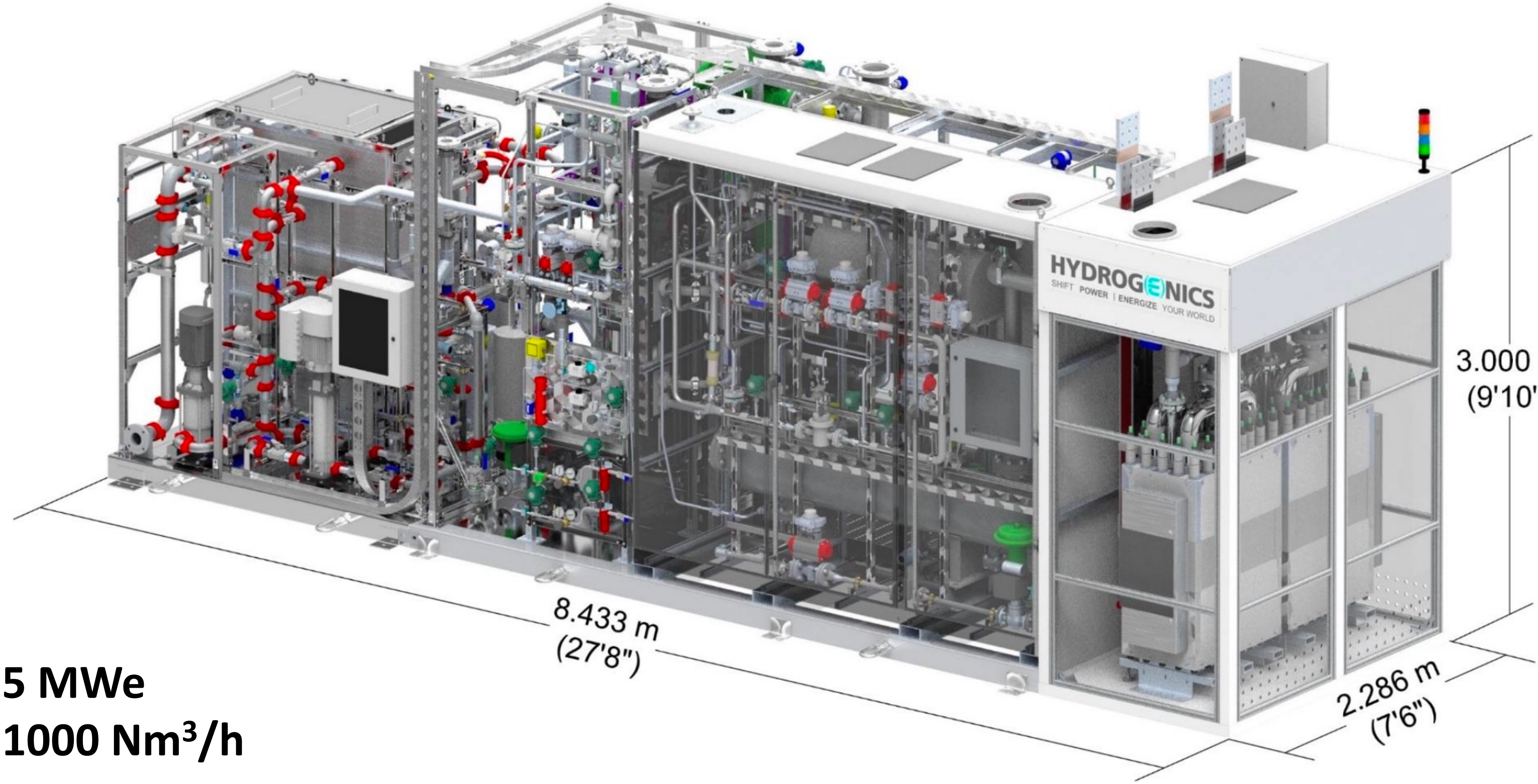
slide from Prof A. Züttel, EPFL



PEMEL started in the 1960s with the development of proton-conducting **acid** polymers, mainly perfluoro sulfonic acid (PFSA) polymer, among which the commercially established **NAFION**.

The sulfonic acid groups in the polymeric structure make the electrolyte **acidity very high** such that **only noble metal catalysts (**Pt, Ru, Ir), are able to sustain this environment. This increases PEMEL cost. For the membrane to be ionically conductive, it must be wet; furthermore, backward penetration of oxygen molecules may occur, which accounts for about 5% electric current consumption.

HYLYZER®-1000 ELECTROLYZER



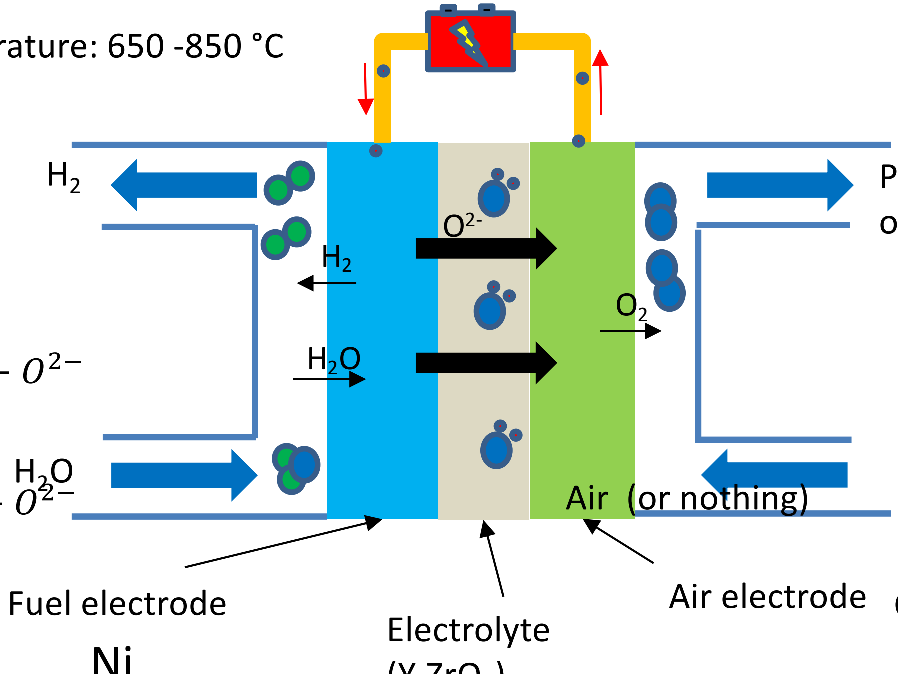
5 MWe
1000 Nm^3/h

Ref.: Denis THOMAS, Cummins – Hydrogenics, “POWER TO HYDROGEN TO POWER SOLUTION PEM Water electrolysis”, e: denis.thomas@cummins.com, FLEXnCONFU Webinar, 3 November 2020

slide from Prof A. Züttel, EPFL

3. Solid oxide electrolysis (steam, CO_2)

Temperature: 650 -850 °C



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

Fuel electrode:

$$CO_2 + 2e^- \rightarrow CO + O^{2-}$$

Air electrode:

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

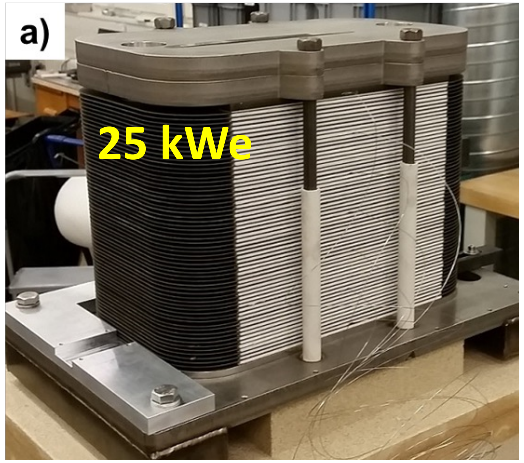
Fuel electrode

Ni

Electrolyte

(Y-ZrO_2)

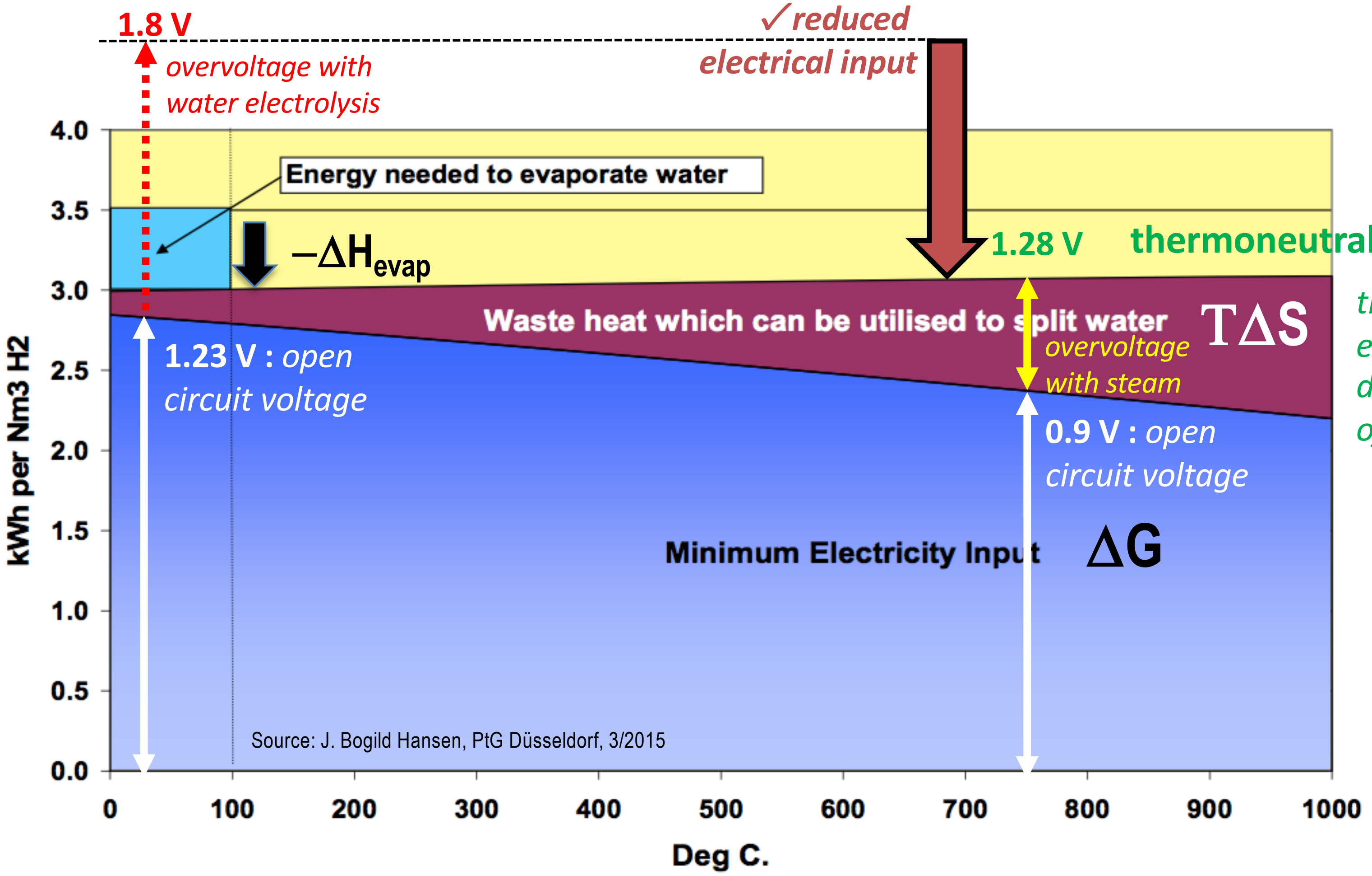
Air electrode oxide, e.g. $LaSrCoFeO_3$



slide from T.Macherel, EPFL

Thermodynamics of H_2O electrolysis

$$\begin{aligned}\Delta H &= \text{total energy}\\ &= \text{electricity} + \text{heat}\\ &= \Delta G + T\Delta S\end{aligned}$$



Source: J. Bogild Hansen, PtG Düsseldorf, 3/2015

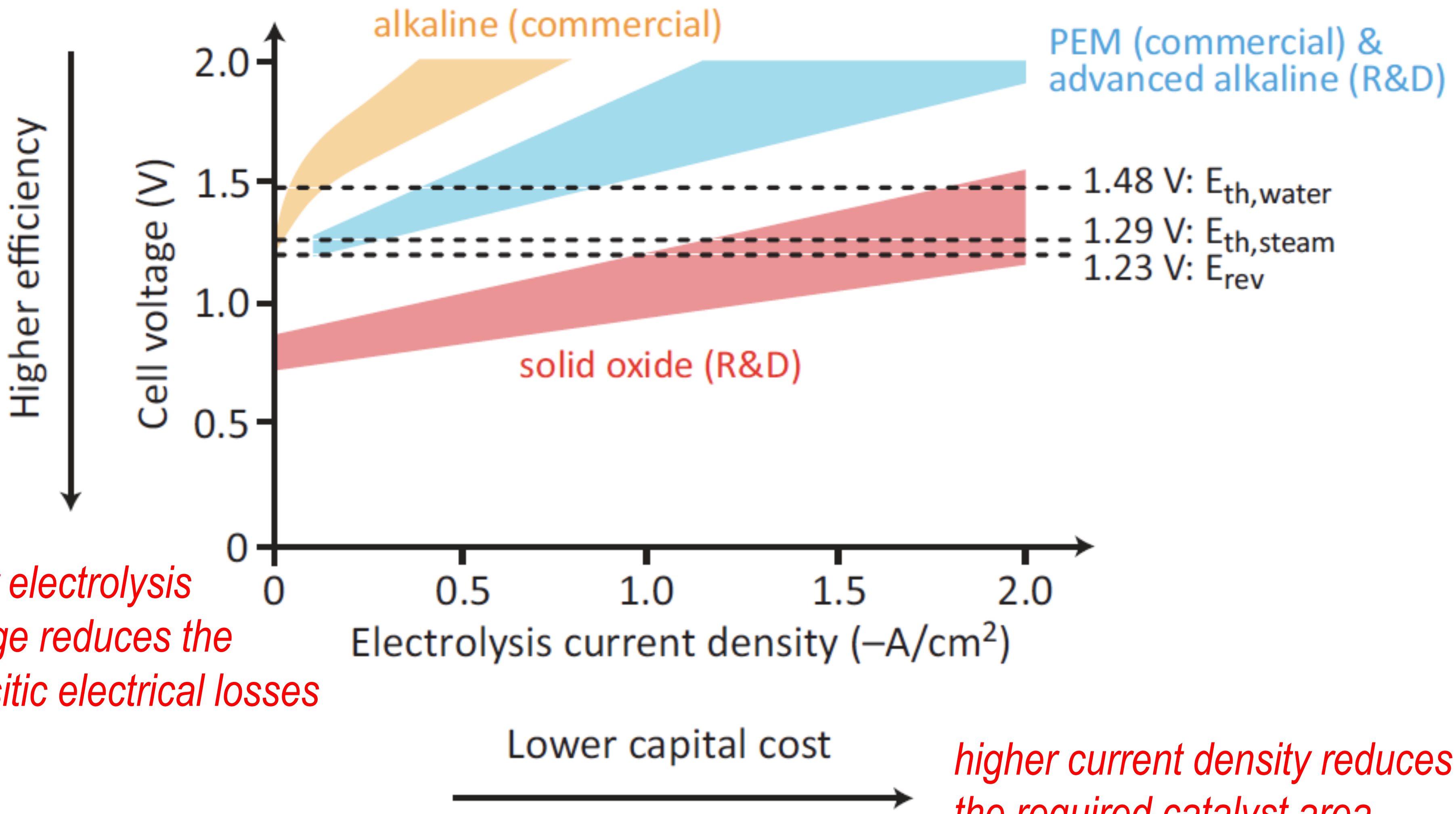
thermoneutral voltage :

the absorbed energy equals the dissociation enthalpy of steam

self-sustained heating from Joule losses

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

Electrolysis technology comparison

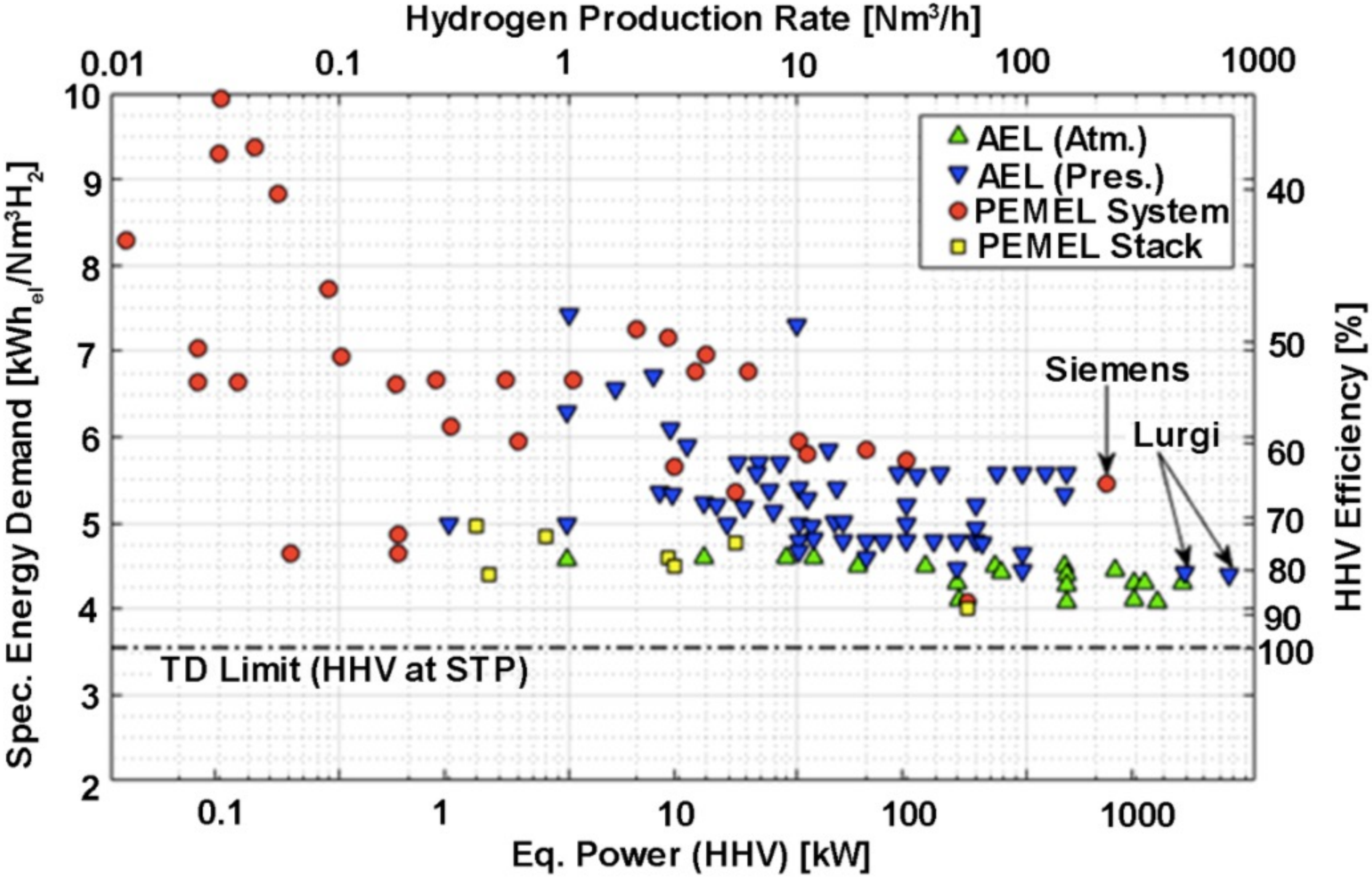


lower electrolysis voltage reduces the parasitic electrical losses

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

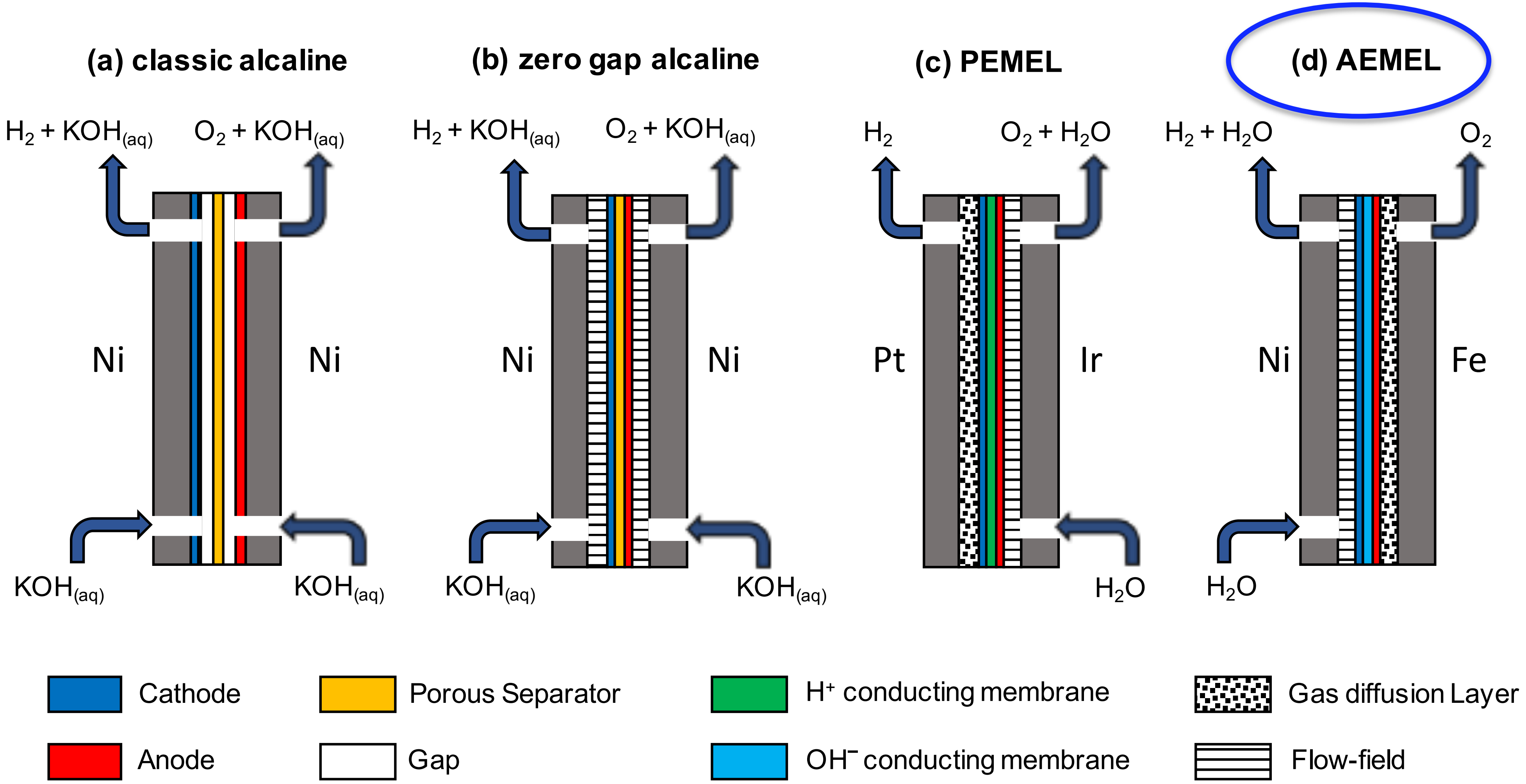
Efficiencies (AEL, PEMEL)



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

4. Recent : AEM
(Anionic Exchange Membrane electrolysis)

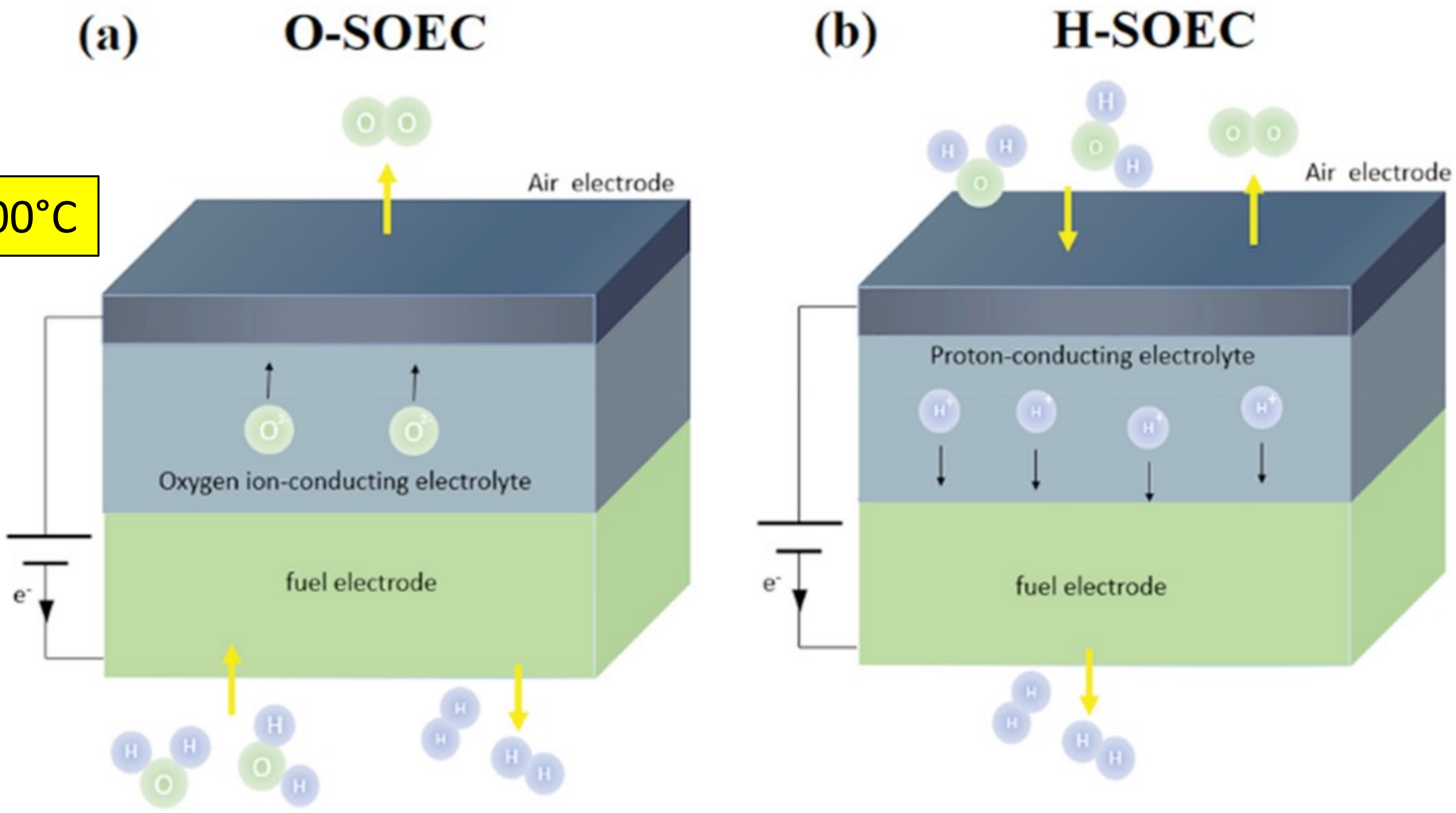


(graph : Dr Heron Vrubel)

AEMEL : combination of PEMEL and classical alcaline

Advantages: no noble metal catalyst, no expensive Ti bipolar plates

5. Recent: proton conducting ceramic electrolyser (PCCEL)



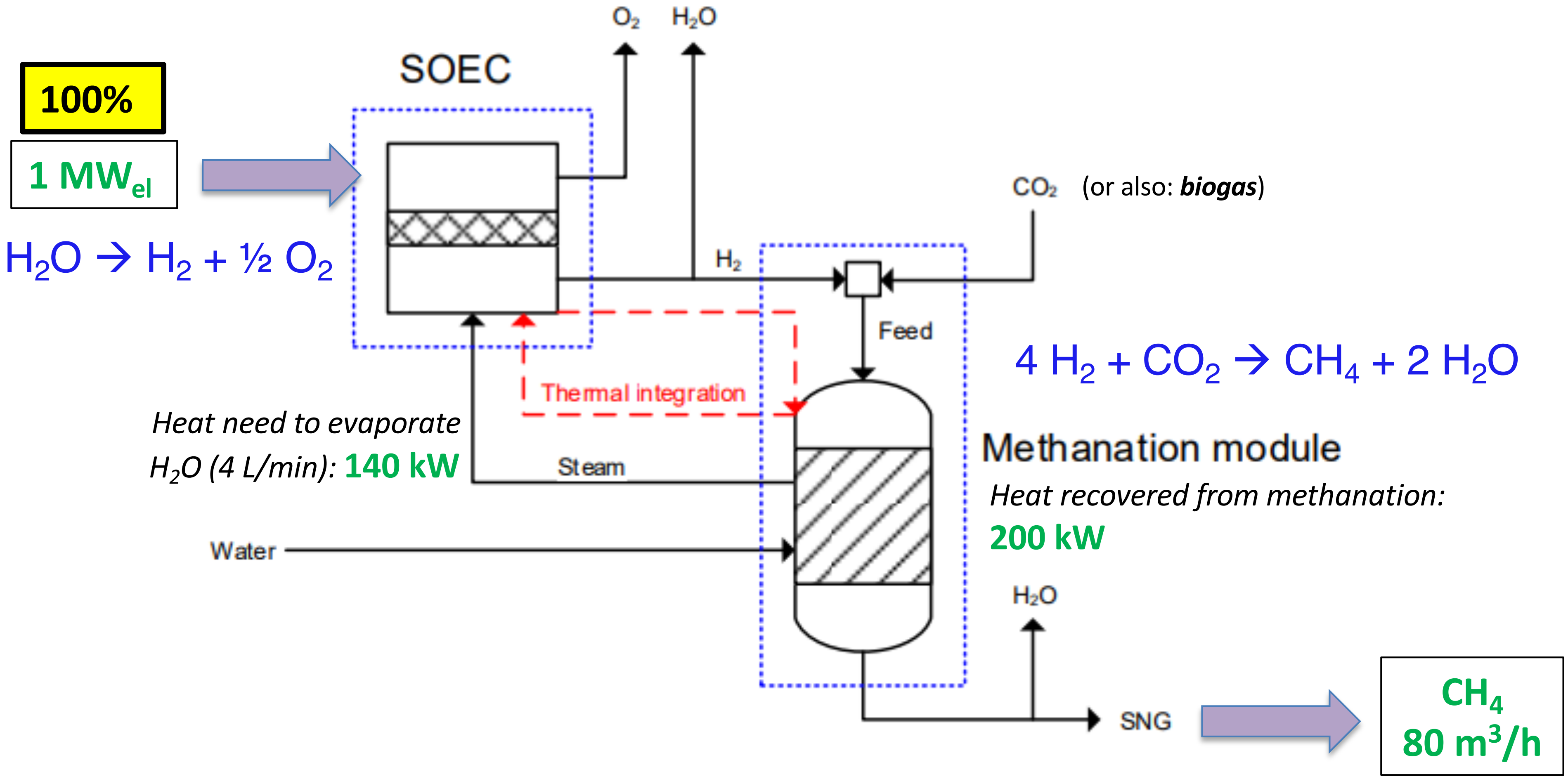
700°C

500°C

Progress Report on Proton Conducting Solid Oxide Electrolysis Cells
Libin Lei, Jihao Zhang, Zhihao Yuan, Jianping Liu, Meng Ni, Fanglin Chen
Advanced Functional Materials Vol 29 Iss 37, 18 July 2019
https://doi.org/10.1002/adfm.201903805

Direct formation of dry H_2 product

SOE (Solid Oxide Electrolysis) based
Power-to-Gas (P2G)



100%

1 MW$_{el}$

$H_2O \rightarrow H_2 + ½ O_2$

(or also: ***biogas***)

$4 H_2 + CO_2 \rightarrow CH_4 + 2 H_2O$

Heat need to evaporate H_2O (4 L/min): **140 kW**

Heat recovered from methanation: **200 kW**

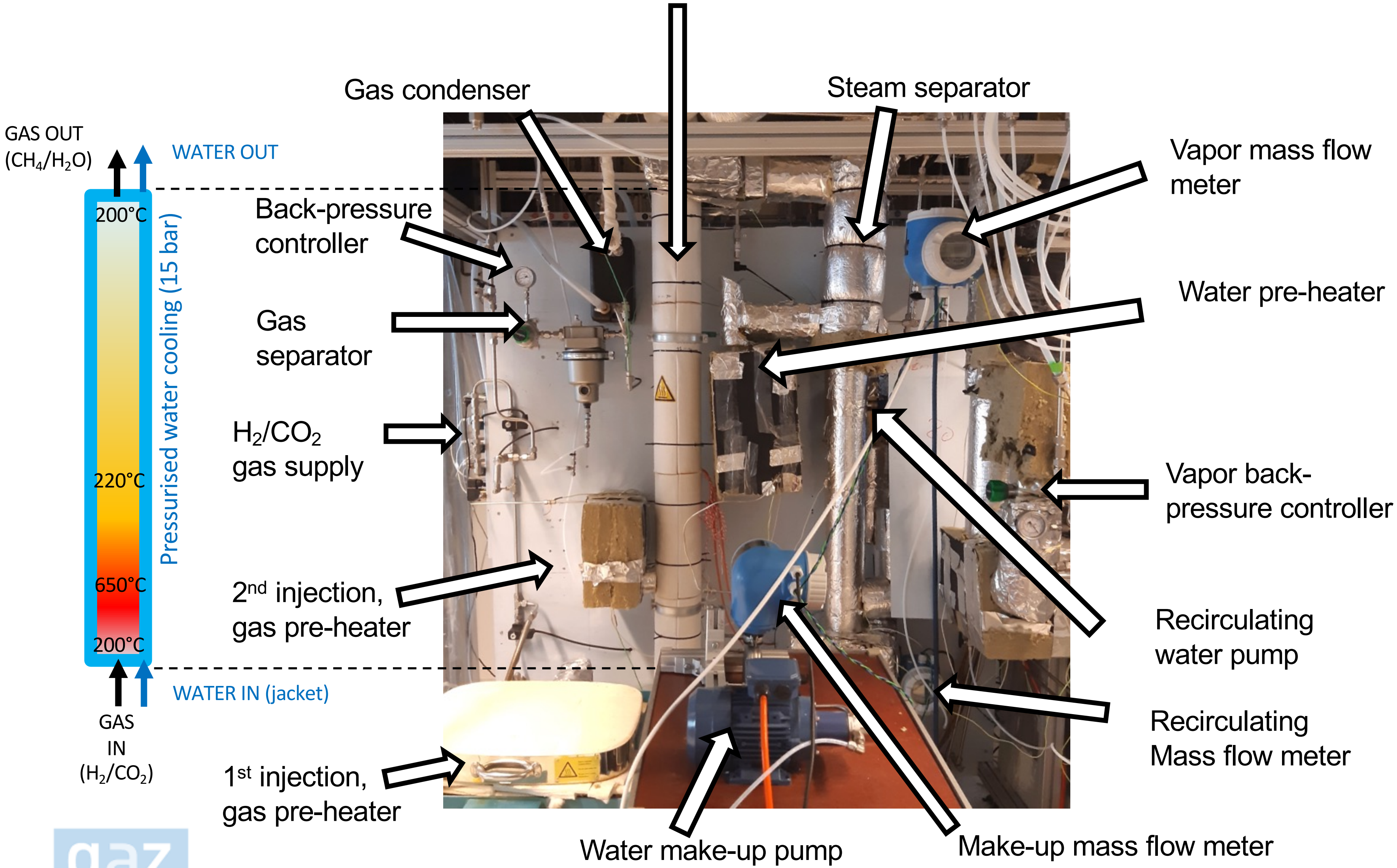
CH_4 80 m^3/h

80%

- ❑ Direct steam generation with the exothermal methanator

Methanation

$4H_2+CO_2 \leftarrow \rightarrow CH_4 + 2H_2O$



GAS OUT (CH_4/H_2O)

WATER OUT

200°C

220°C

650°C

200°C

Pressurised water cooling (15 bar)

WATER IN (jacket)

GAS IN (H_2/CO_2)

Gas condenser

Steam separator

Vapor mass flow meter

Back-pressure controller

Water pre-heater

Gas separator

H_2/CO_2 gas supply

Vapor back-pressure controller

2nd injection, gas pre-heater

Recirculating water pump

Recirculating Mass flow meter

1st injection, gas pre-heater

Water make-up pump

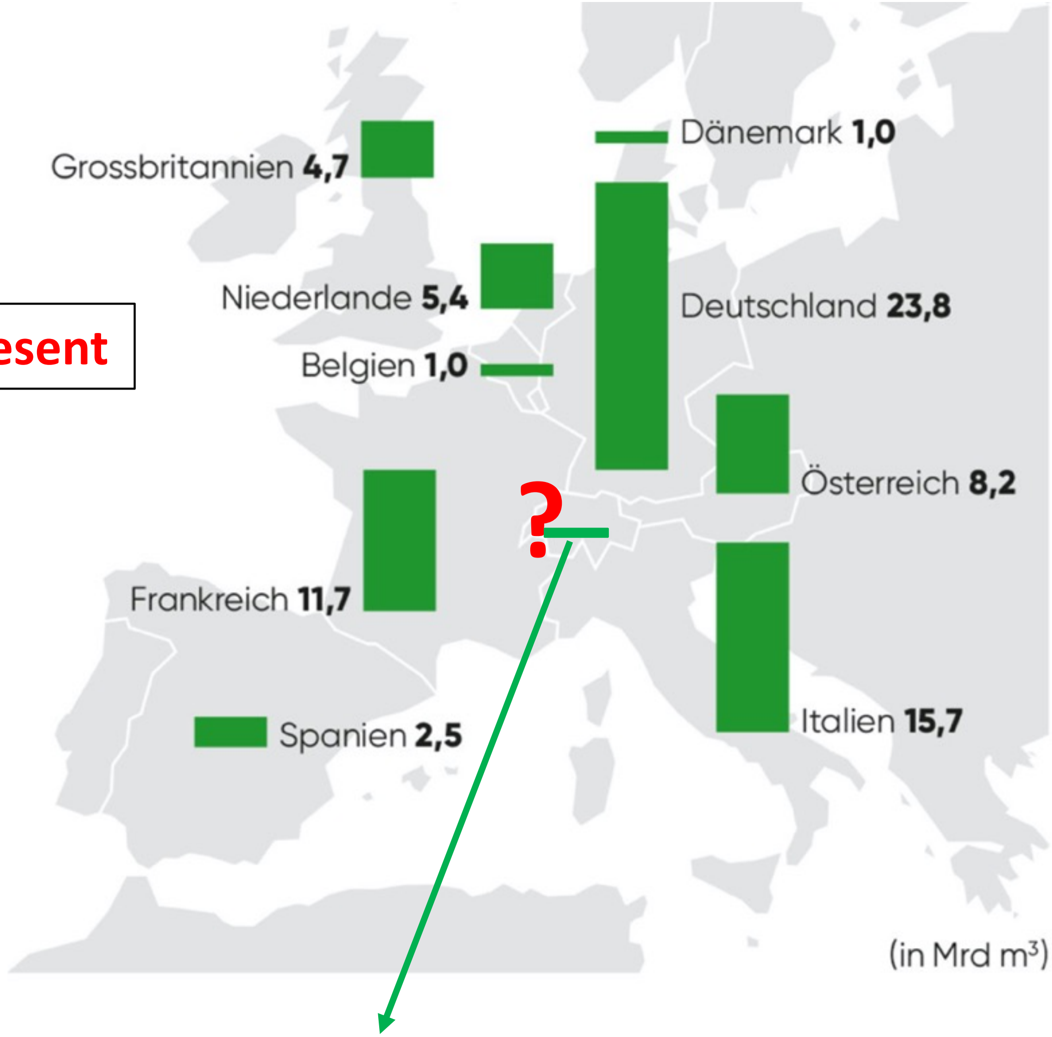
Make-up mass flow meter

- Direct steam generation with the exothermal methanator

Seasonal gas storage in Switzerland?

https://gazenergie.ch/de/wissen/detail/knowledge-topic/7-erdgas-speicher/

no NG storage at present



with 1 bio m^3 gas (=10 TWh), the Swiss winter electricity gap would be covered (=a deficit of ~1 TWhe / month).

Application example: oil refinery

https://refhyne.eu/

Rheinland refinery (Shell) (D)

Consumption: **180’000 t H_2** / yr (from fossils)

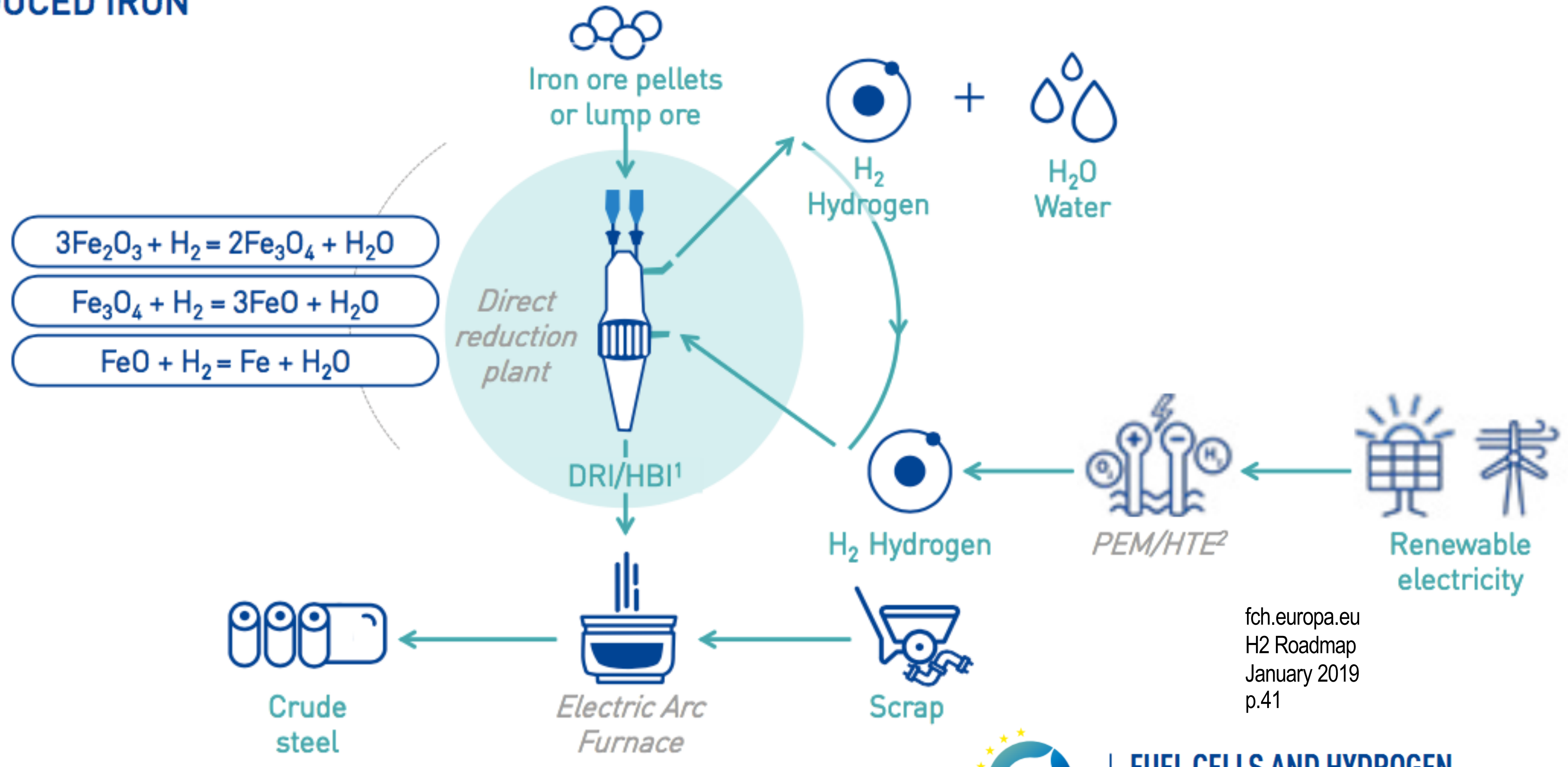
10 MWe PEM-electrolyser:
=> supplies **1300 t H_2** / yr (<1% !!)

REFHYNE
CLEAN REFINERY HYDROGEN FOR EUROPE
2018-2022

FCH | FUEL CELLS AND HYDROGEN JOINT UNDERTAKING 10 M€

H_2 for steel making : DRI

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



$$3Fe_2O_3 + H_2 = 2Fe_3O_4 + H_2O$$

$$Fe_3O_4 + H_2 = 3FeO + H_2O$$

$$FeO + H_2 = Fe + H_2O$$

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H2 Roadmap
January 2019
p.41

FUEL CELLS AND HYDROGEN
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[1] Direct reduced iron/hot briquetted iron

[2] Polymer electrolyte membrane electrolysis/high temperature electrolysis

Briefest summary on electricity storage

- By far the most used today : pumped hydro storage (**PHS**)
  - 93% of world total (173 GWe)
  - minimal installation size of **5 MWe** (for economics)

- Smaller scale and short term : **batteries**
  - 5% of world total (9 GWe), dominated by Li-ion batteries (90%)
  - maximal discharge time = **1 day**
  - adapted for residential PV (**1-20 kWe**)

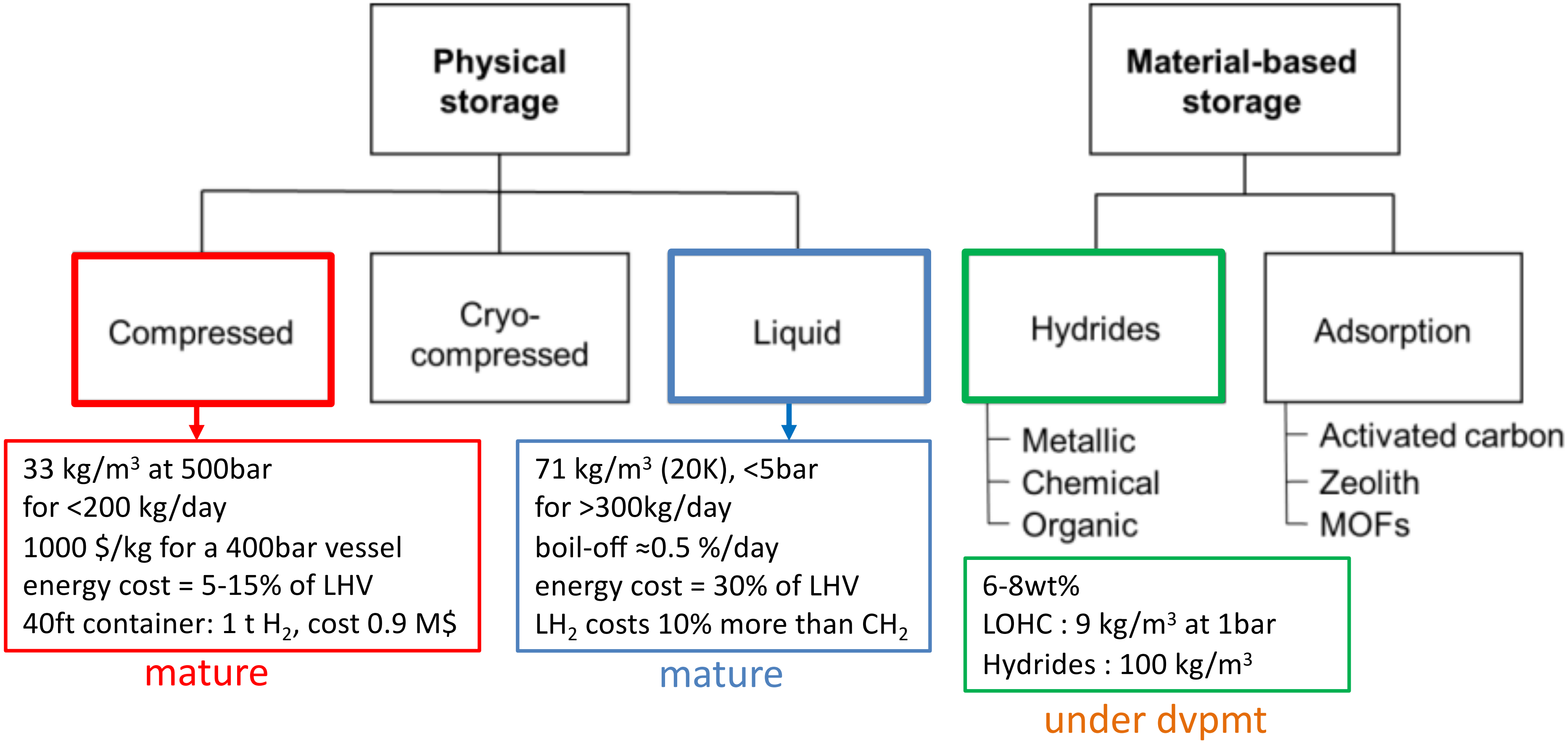
- Middle segment between PHS and batteries is ideally captured by **P2G**
  - from few **10 kWe to few MWe**
  - energy size and power size are uncoupled => long term storage
  - for storage > 1 day, P2G is economical today already

H_2 storage : the key problem

- as compressed H_2 gas (=> 1000 bar)
- as liquid H_2 (1 bar)
  - optional: further cryo-compression of liquid H_2
- as physically adsorbed H_2-layer on high surface area materials
  - sorption increases at low T
- as H in hydride materials
  - solid solution ---- > hydride H (interstitial H, up to intermetallic compound)
  - complex hydrides (e.g. $NaBH_4$)
- as H in other chemical compound
  - LHOC (liquid hydrogen organic carrier)
  - Formic acid ($H_2 + CO_2 \rightarrow HCOOH$)
  - NH_3

H_2 storage overview

(figure: Leonardo Gant)



33 kg/m³ at 500bar
for <200 kg/day
1000 $/kg for a 400bar vessel
energy cost = 5-15% of LHV
40ft container: 1 t H_2, cost 0.9 M$

mature

71 kg/m³ (20K), <5bar
for >300kg/day
boil-off ≈0.5 %/day
energy cost = 30% of LHV
LH_2 costs 10% more than CH_2

mature

6-8wt%
LOHC : 9 kg/m³ at 1bar
Hydrides : 100 kg/m³

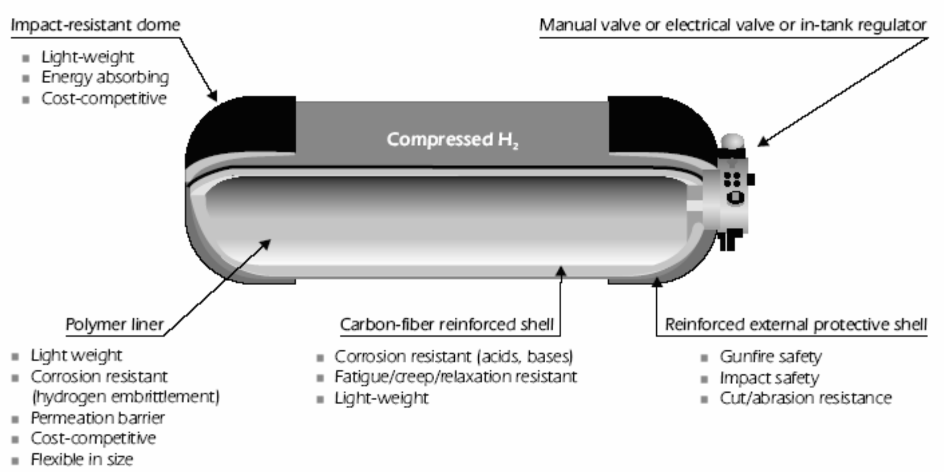
under dvpmt

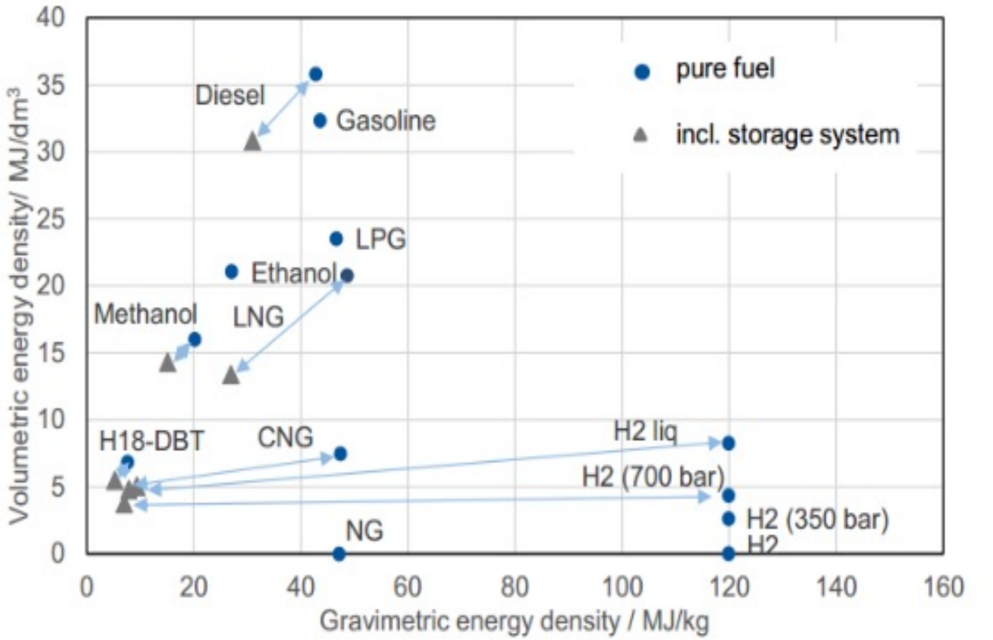
@1 atm

highest gravimetric density:	140	MJ/**kg**	(496.0 moles)
lowest volumetric density:	0.011	MJ/**L**	(1/22.4th of a mole = 0.0446 mole)

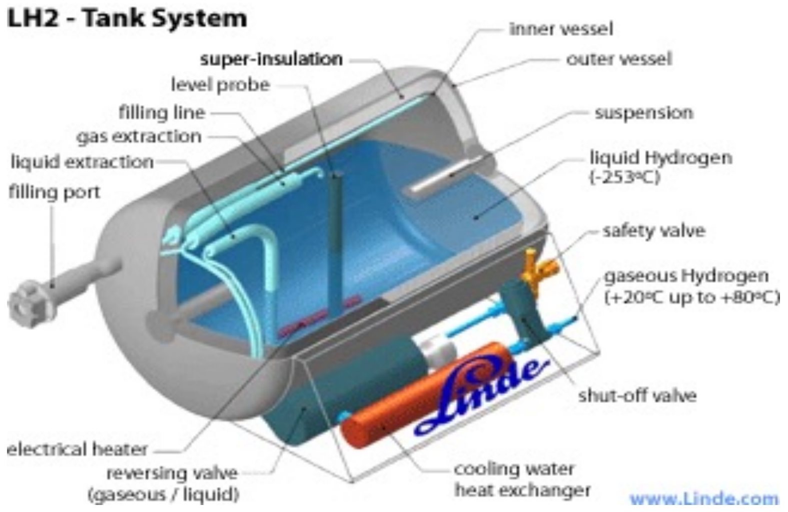
H_2 storage : compressed gas, and liquid

1. CH_2
2. LH_2
3. Pipelines
4. Other methods





loss 0.1 – 3% / day



fuel density (kg^{-1}) alone is high;
not when adding storage medium weigth

(figures: Leonardo Gant)

H_2 compression technologies overview

G. Sdanghi, G. Maranzana, A. Celzard, V. Fierro, "Review of the current technologies and performances of hydrogen compression for stationary and automotive applications", Renewable and Sustainable Energy Reviews 102 (2019), pp. 150 – 170

- Mechanical: **volume flow** for H_2 is confined by a displacement device
  1. reciprocating piston
  2. diaphragm
  3. linear (magnetic)
  4. ionic liquid
- Non-mechanical : specifically designed for H_2 application
  1. cryogenic
  2. electrochemical (**mass flow**)
  3. adsorption (thermal)
  4. metal-hydride (thermal)

In terms of H_2-economy, the cheapest solution today is:
H_2-gas compression + truck-delivery (for small stations); in carbon-/glass fiber storage tanks to reduce weight.
Best values 1-2 wt% @250 bar (steel), 6 wt% @700 bar (composite), and 30 g H_2/L

H_2 compression methods overview

	Piston	Membrane	Screw	Electro-chemical	Metal-hydride	Ionic compressor	Turbo-compressor
Scale Nm^3/h	10 - 115000	1 - 4000	200 - 100000	5 - 280	1 - 12	750	>1000
Max P (bar)	1300	3000	55	950	250	1000	<50
TRL (H_2)	9	9	commercial	7	5-6	8	low
Advant.	availability	availability no contamination	availability low maintenance	no moving parts low OPEX	thermal no contamin. no mov. parts	efficiency no contamination	availability low mainten. high vol. flow
Disadvant.	contamination maintenance	lim. suction maintenance	contamination H2 backflow	low vol. flow R&D	low vol. flow R&D	maintenance	Δp depends on mol weight

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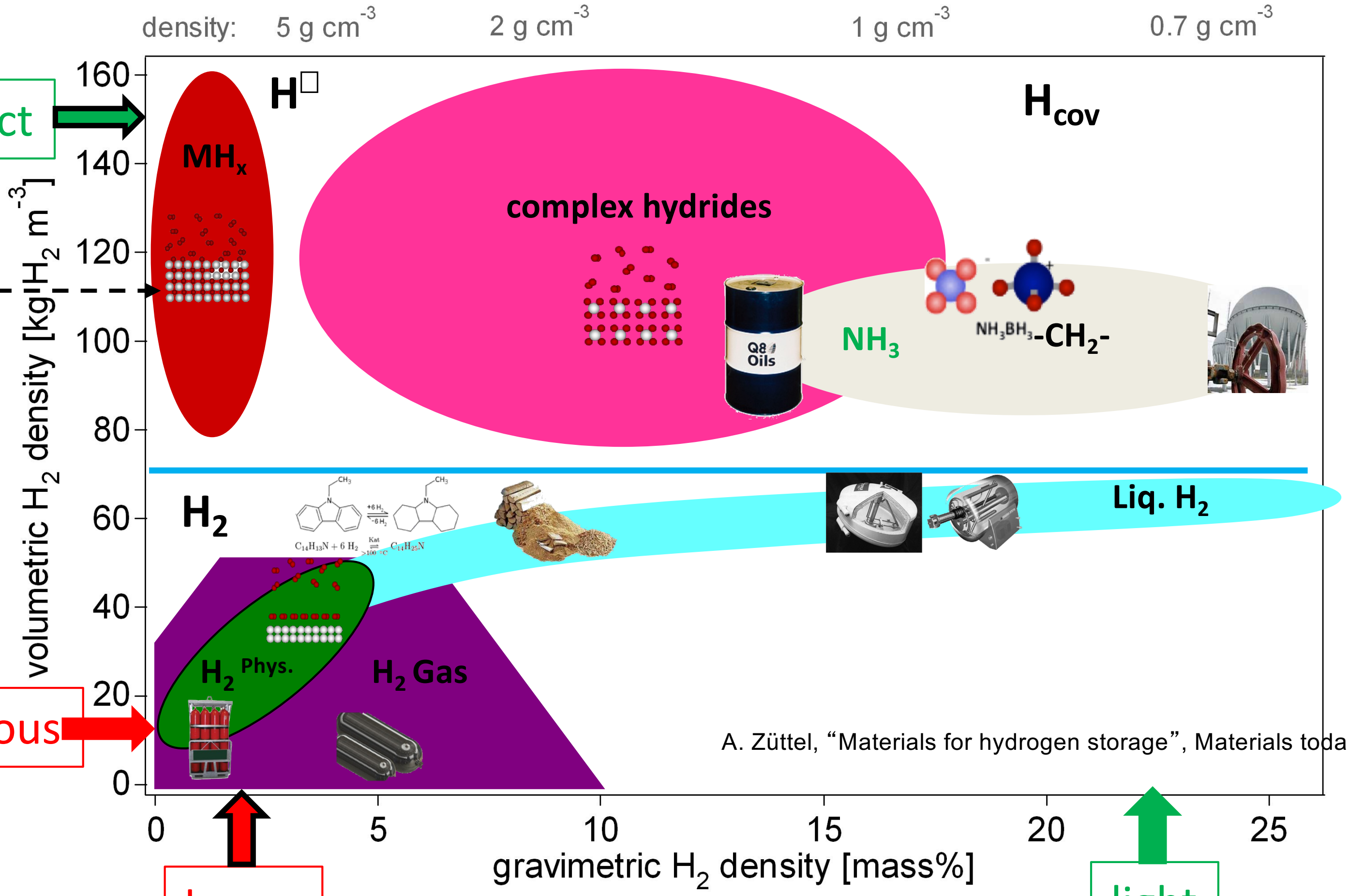
Hydrogen Storage Density comparison

compact

MH:
high volumetric, but
low gravimetric density

voluminous



A. Züttel, “Materials for hydrogen storage”, Materials today, Sept 2003, pp. 18-27

heavy

light

slide from Prof A Züttel, EPFL

Comparison H_2 storage methods

	c-H2(g)	LH2	LOHC	MOFS	M-hydride	Complex hydrides	Salt hydrides
ρ (kg /m³)	50 bar: 4 700 bar: 36	71	57	material-dependent	material-dependent	material-dependent	material-dependent
wt% stored	100	100	6.2	5-9 (cryo) 0.5-1 (amb.)	1.4-2 ($LaNi_5$,AB_2)	5.6 ($NaAlH_4$)	7.7 (MgH_2)
T	20°C	-253°C	150-200C ads 300C desorp.	-176°C ads. Des.:vacuum	0-30°C	70-170C ads. (20-150 bar) 100-200C des. (1bar)	250-300C ads. (10-15 bar) 300-350C des. (1bar)
Storage time	unlimited	limited (boil-off)					
Compression energy as % LHV	6%	22-34%	49% (if no heat avail.)	18% (if no heat avail.)		55% (if no heat avail.)	
Status	commercial	commercial	emerging	R&D		R&D	
Challenge	transport limited (low ρ)	boil-off	purity, stability weight	T_adsorpt P_desorb weight		T ads/des. P_desorb weight	
TRL	9	9	4	3	7	3-4	3-4

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Summary on H_2

- Important intermediate energy vector :
  1. it can store large quantities of renewable electricity (wind, PV, …) via electrolysis technologies
  2. it can be used in all sectors (industry, heating, power, mobility)
- Most hope is invested in (heavy duty) mobility and (heavy) industry, as these are difficult to defossilize
- Different electrolyser technologies will co-exist. The main challenges are:
  1. large scale deployment (TWe capacity will be needed) : high volume low cost manufacturing, materials use, footprint
  2. storage and transport of H_2 (volume, weight)