Storage and Power-to-Gas

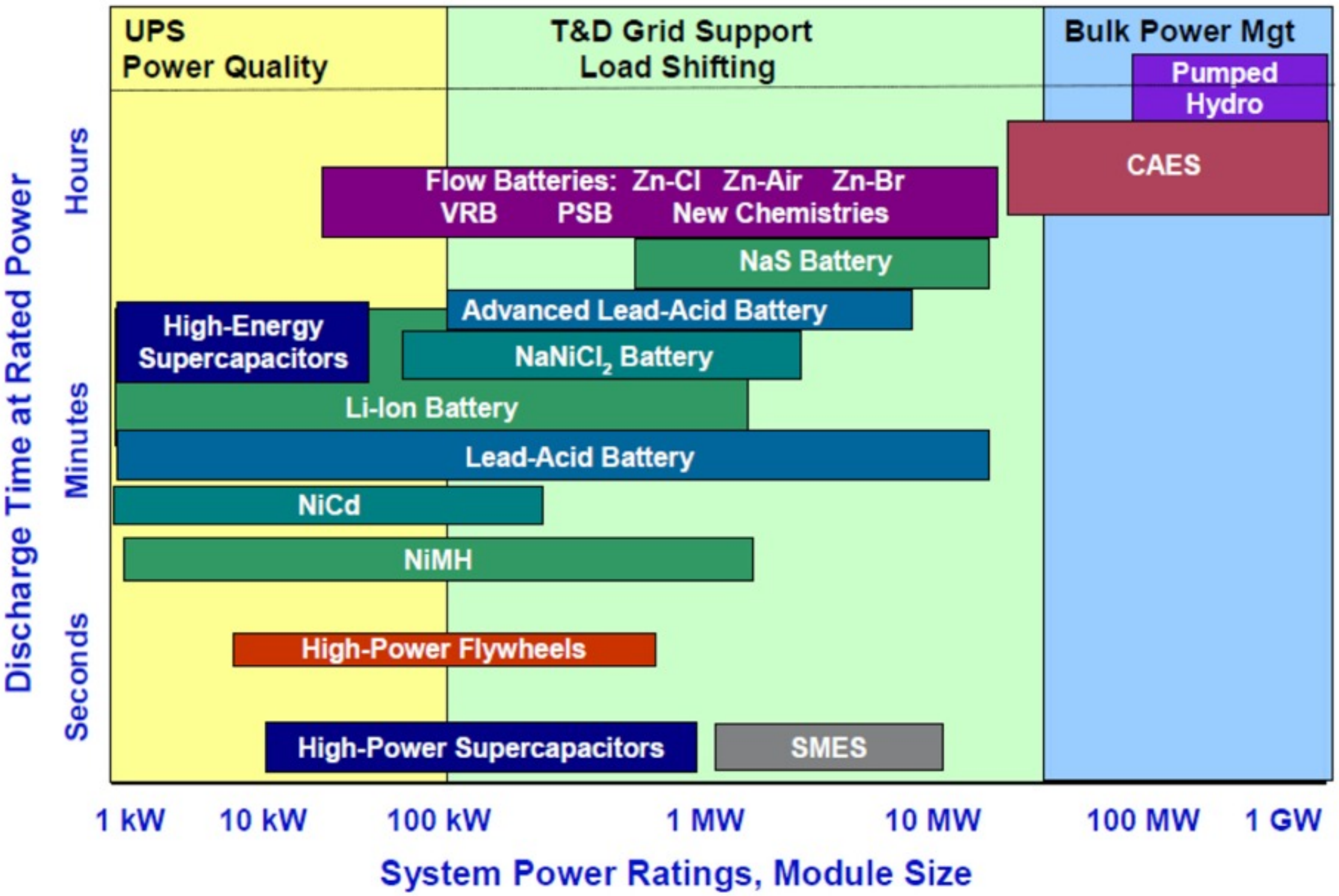
Learning objectives

- Electricity storage state-of-the-art
- Overview of H_2 uses, actual and potential
- Thermodynamics and efficiency of electrolysis
  - various technologies (water (H^+ / OH^-), steam)
  - heat integration
- Storage of H_2

Current situation in electricity storage

Possible technologies for electricity storage

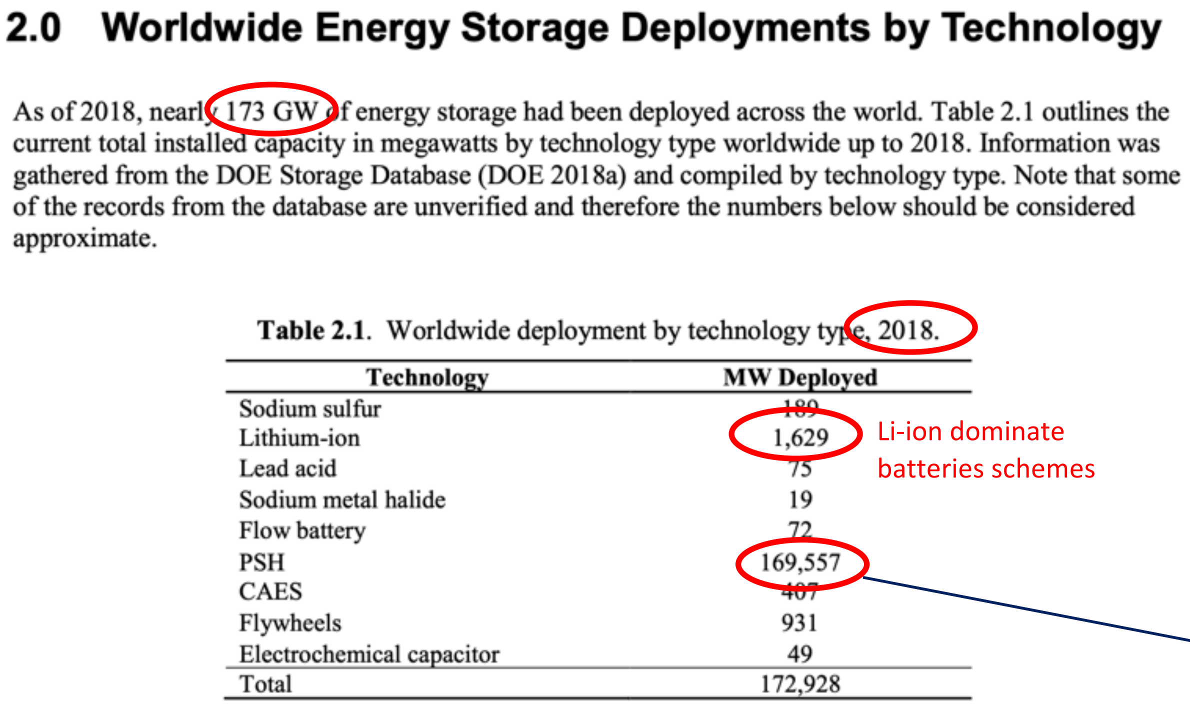
A.Z. AL Shaqsi, K. Sopian and A. Al-Hinai / Energy Reports 6 (2020) 288–306 293



Existing storage capacity

2018: 173 GWe, of which
98% pumped hydro schemes

Energy Storage Technology and Cost Characterization Report, July 2019
K Mongird, V Viswanathan, P Balducci, J Alam, PNNL-28866
https://www.energy.gov/eere/water/hydrowires-initiative



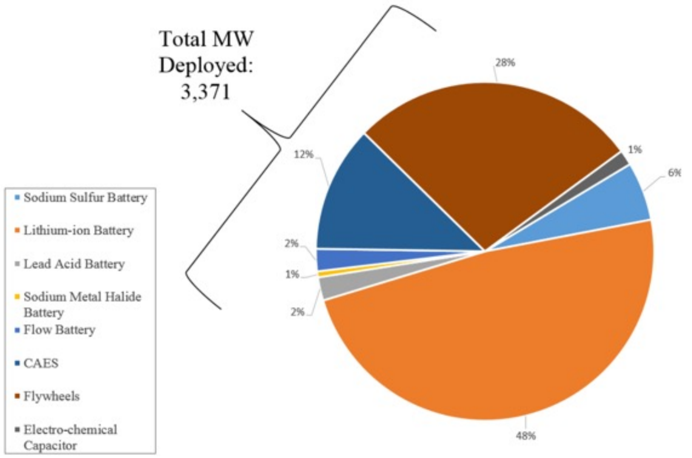
2.0 Worldwide Energy Storage Deployments by Technology

As of 2018, nearly 173 GW of energy storage had been deployed across the world. Table 2.1 outlines the current total installed capacity in megawatts by technology type worldwide up to 2018. Information was gathered from the DOE Storage Database (DOE 2018a) and compiled by technology type. Note that some of the records from the database are unverified and therefore the numbers below should be considered approximate.

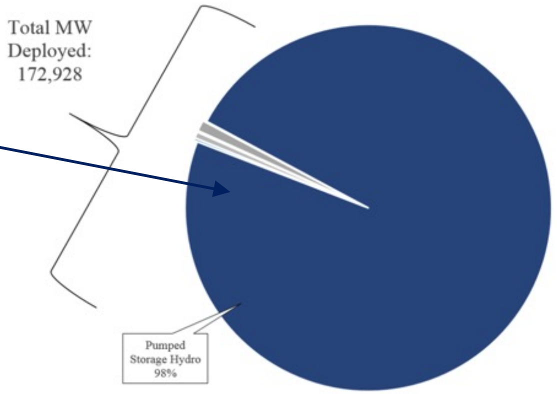
Table 2.1. Worldwide deployment by technology type, 2018.

Technology	MW Deployed
Sodium sulfur	189
Lithium-ion	1,629
Lead acid	75
Sodium metal halide	19
Flow battery	72
PSH	169,557
CAES	407
Flywheels	931
Electrochemical capacitor	49
Total	172,928

Li-ion dominate
batteries schemes



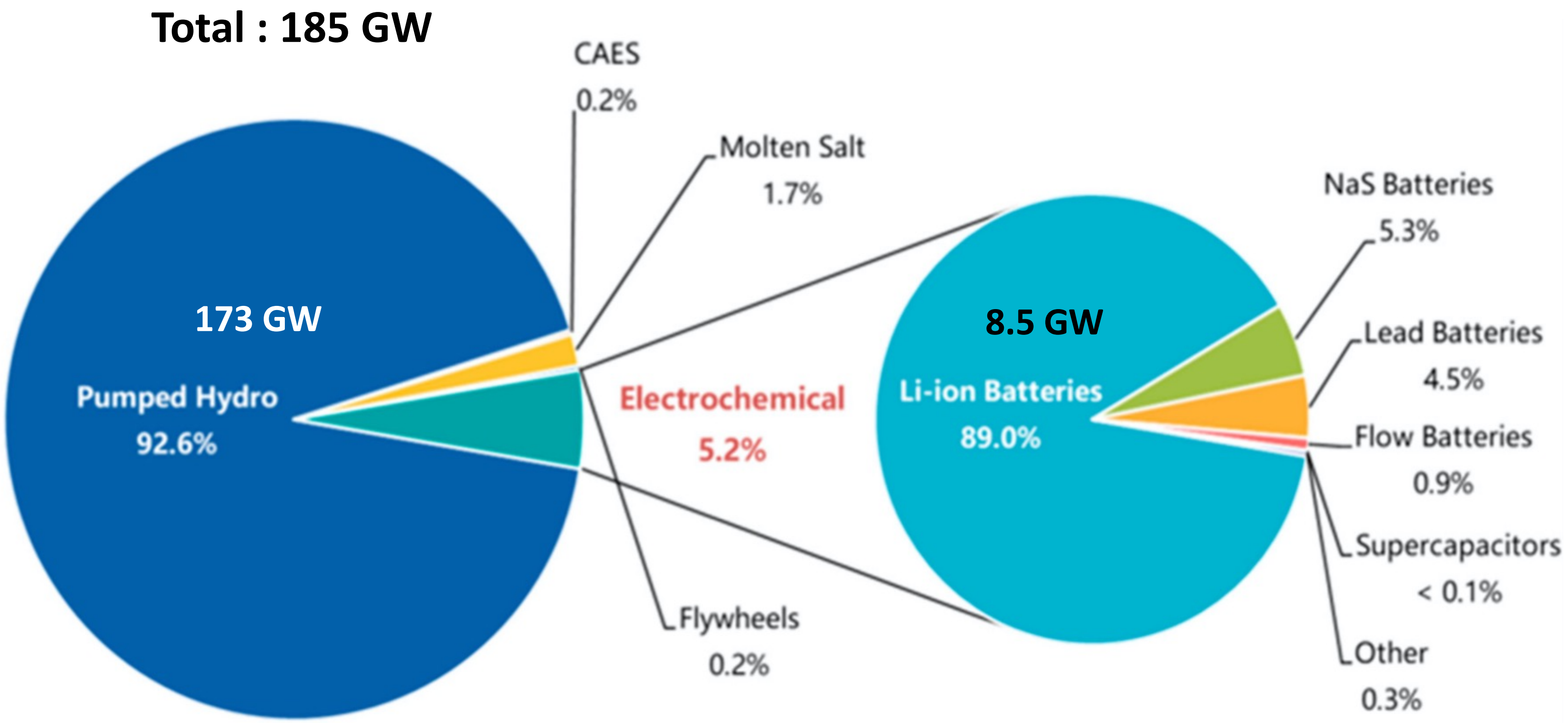
Breakdown of energy storage deployed internationally by technology type and excluding pumped storage hydro.



Proportion of megawatts of internationally deployed pumped storage hydro in comparison to other technologies.

Fast growth in storage capacity (esp. Li-ion)

March 2020



Sustainability 2020, *12*, 10511; doi:10.3390/su122410511
A Review of Energy Storage Technologies Application Potentials in Renewable Energy Sources Grid Integration
Henok Ayele Behabtu, Maarten Messagie, Thierry Coosemans, Maitane Berecibar, Kinde Anlay Fante, Abraham Alem Kebede, Joeri Van Mierlo

Cost metric: LCOS (levelized cost of storage)

$$LCOS\left[\frac{\$}{MWh}\right]=\frac{\boxed{\overset{\text{dominant cost}}{\text{Investment cost}}}+\sum_{n}^{N}\frac{\text{O\&M cost}}{(1+r)^{n}}+\sum_{n}^{N}\frac{\boxed{\overset{\text{2nd largest}}{\text{Charging cost}}}}{(1+r)^{n}}+\frac{\text{End-of-life cost}}{(1+r)^{N+1}}}{\sum_{n}^{N}\frac{Elec_{Discharged}}{(1+r)^{n}}}.$$

- = total lifetime cost of the investment in an electricity storage technology, divided by its cumulative delivered electricity
- this metric accounts for all technical and economic parameters affecting the **lifetime cost of discharging stored electricity**.
- directly comparable to the levelized cost of electricity (LCOE) for electricity generation technologies.
- key parameters that affect the LCOS of each technology, set by the respective applications, are: nominal power capacity (kW), discharge duration (h), annual cycles (number), and electricity price (€/kWhe)

Schmidt et al., Joule 3, 81–100
January 16, 2019 a 2018 Elsevier Inc.
https://doi.org/10.1016/j.joule.2018.12.008

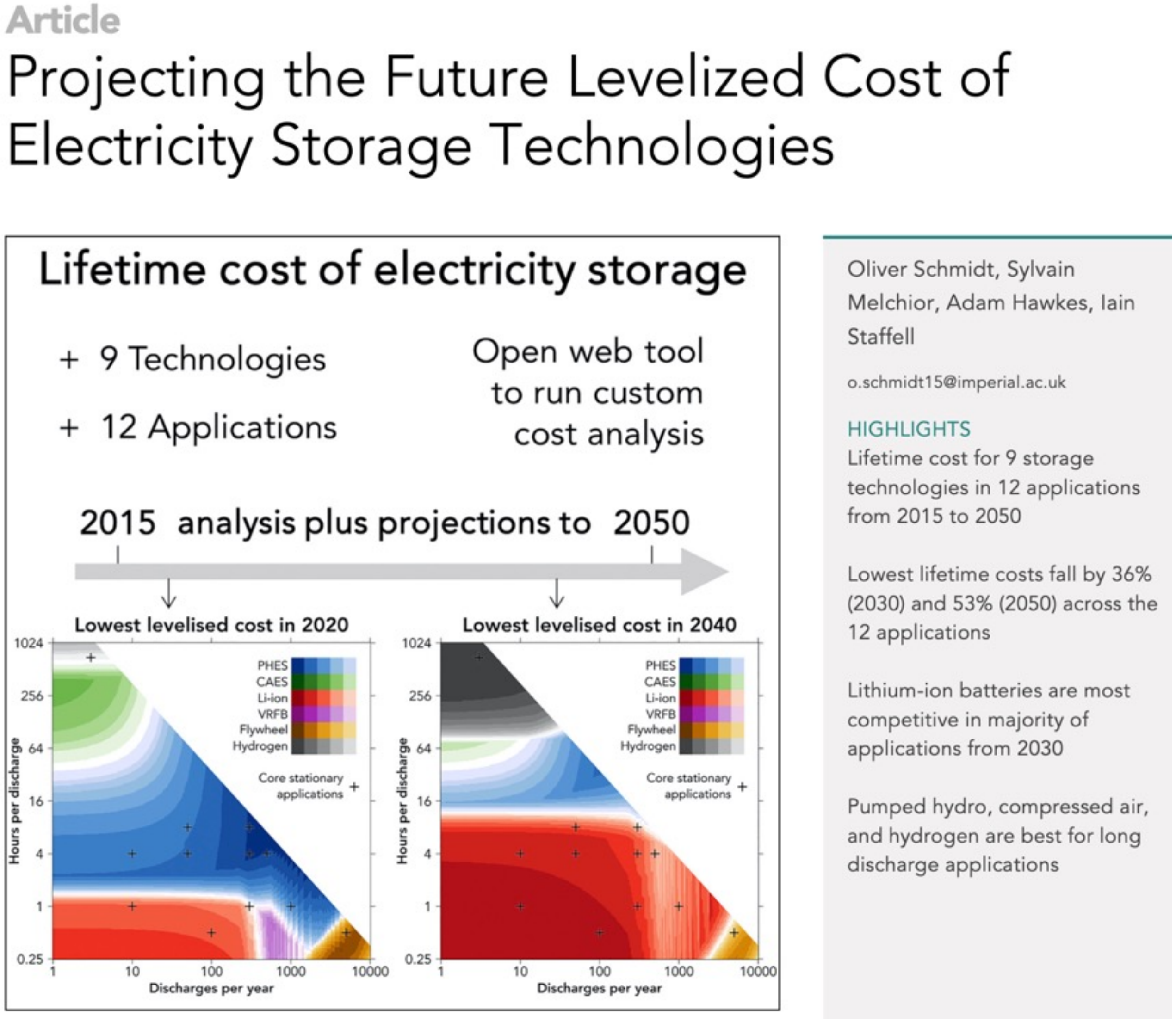
Results of LCOS study

Schmidt et al., Joule 3, 81–100
January 16, 2019 a 2018 Elsevier Inc.
https://doi.org/10.1016/j.joule.2018.12.008

PHS / CAES: ‘slow’ response time (>10 s) and large minimum sizes (>5 MWe) => not suited for primary elec.grid response and power quality and small-scale consumption.

Flywheels and supercapacitors : short discharge (<1 h) => not suited for longer-term power.

Seasonal storage (months, >700h): only met by technologies where energy storage capacity is fully independent of power capacity. **(PtG, H_2)**


Article

Projecting the Future Levelized Cost of Electricity Storage Technologies

Lifetime cost of electricity storage

+ 9 Technologies
+ 12 Applications

Open web tool to run custom cost analysis

2015 analysis plus projections to 2050

Oliver Schmidt, Sylvain Melchior, Adam Hawkes, Iain Staffell

o.schmidt15@imperial.ac.uk

HIGHLIGHTS

Lifetime cost for 9 storage technologies in 12 applications from 2015 to 2050

Lowest lifetime costs fall by 36% (2030) and 53% (2050) across the 12 applications

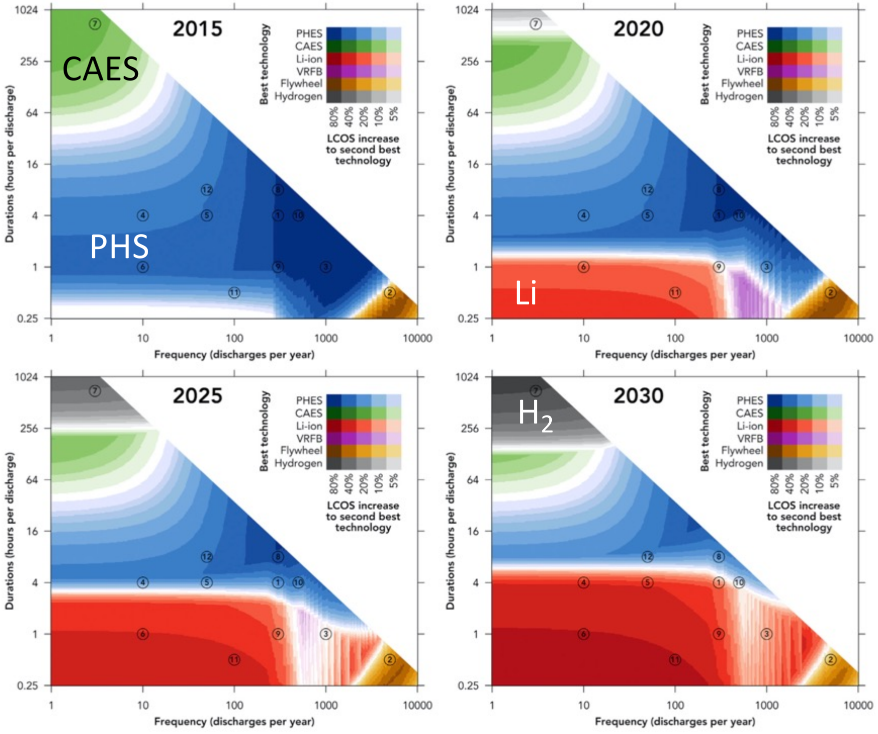
Lithium-ion batteries are most competitive in majority of applications from 2030

Pumped hydro, compressed air, and hydrogen are best for long discharge applications

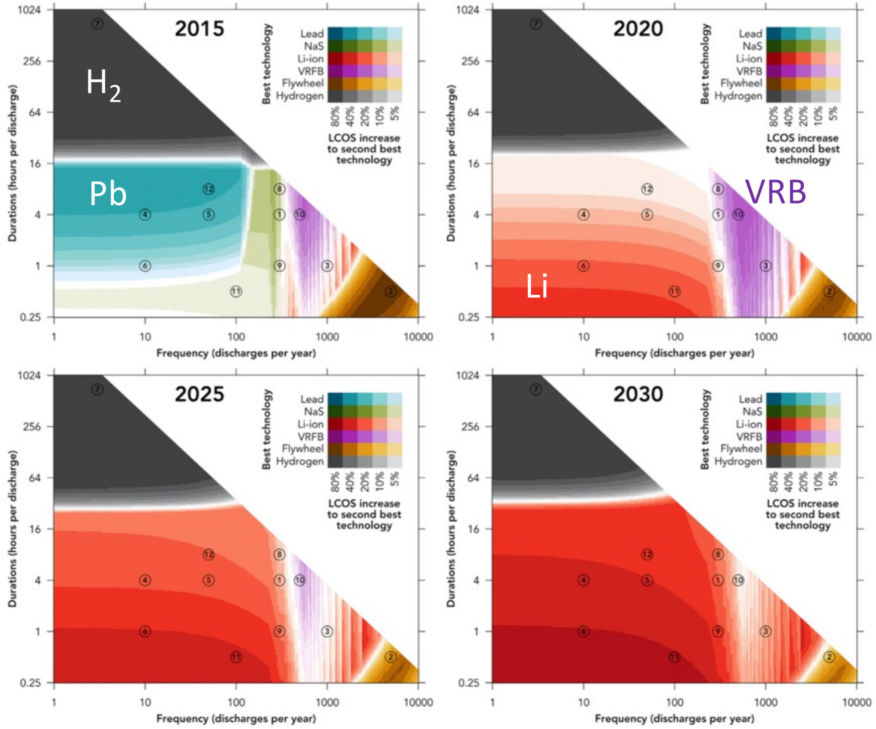
Schmidt et al., Joule 3, 81–100
January 16, 2019 a 2018 Elsevier Inc.
https://doi.org/10.1016/j.joule.2018.12.008

Excluding PHS & CAES, H_2 could be more cost-effective than batteries for discharges > 1 day

All technologies



Technologies excluding PHS / CAES



Summary on electricity storage

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

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

- Middle segment between PHS and batteries can be 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 could become economical

Hydrogen H_2 (=stored electricity) in energy and industry uses: present and future

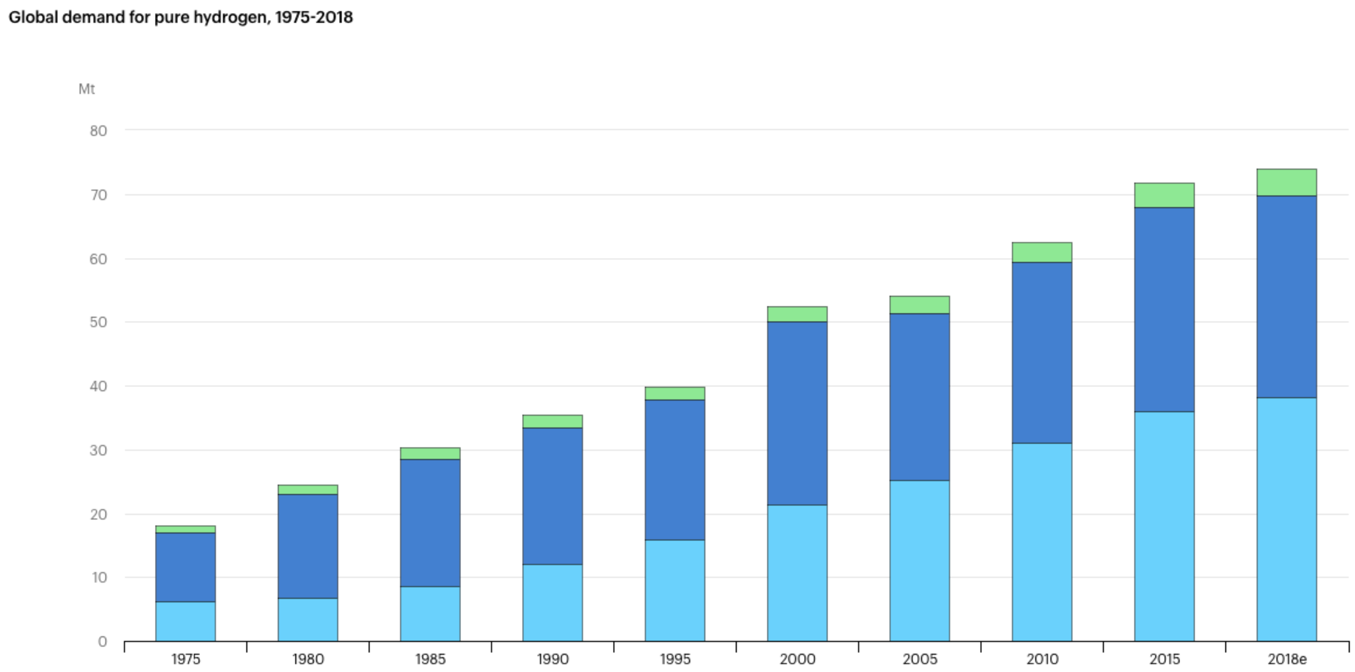
Grey, blue, green H_2

- **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

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)

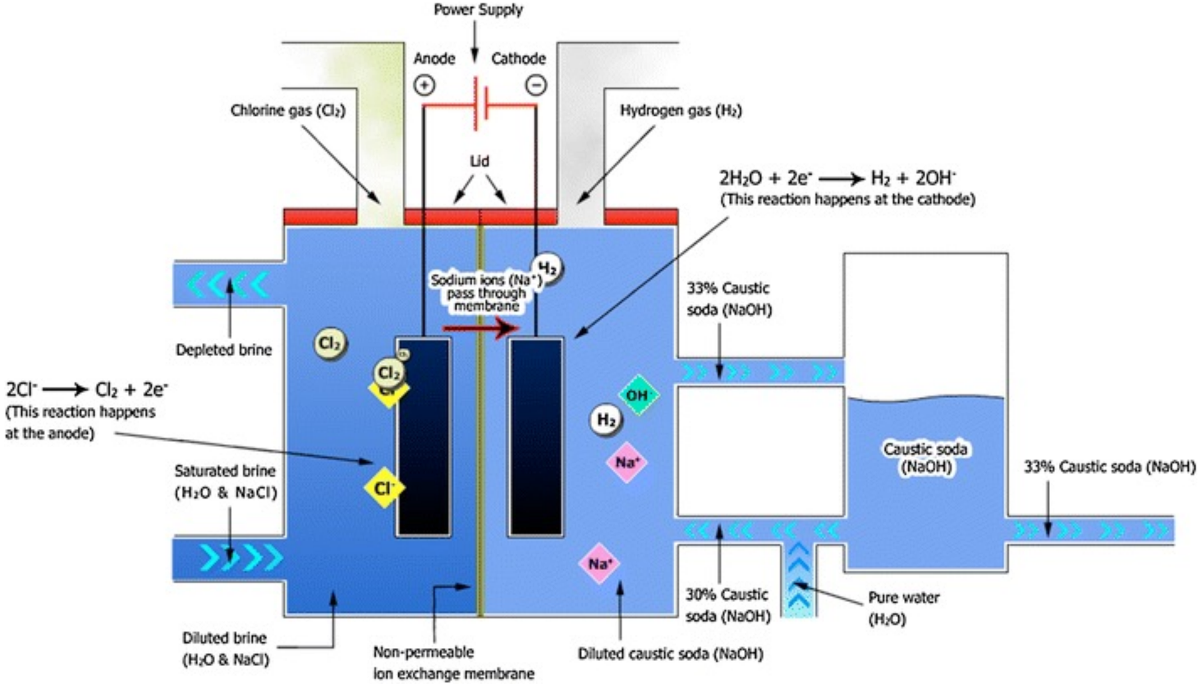
Electrolytic H_2 : e.g. chlor-alkali-industry

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

  ≈ **25-30 GWe** worldwide
- ≈0.5% of world electricity (30 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/

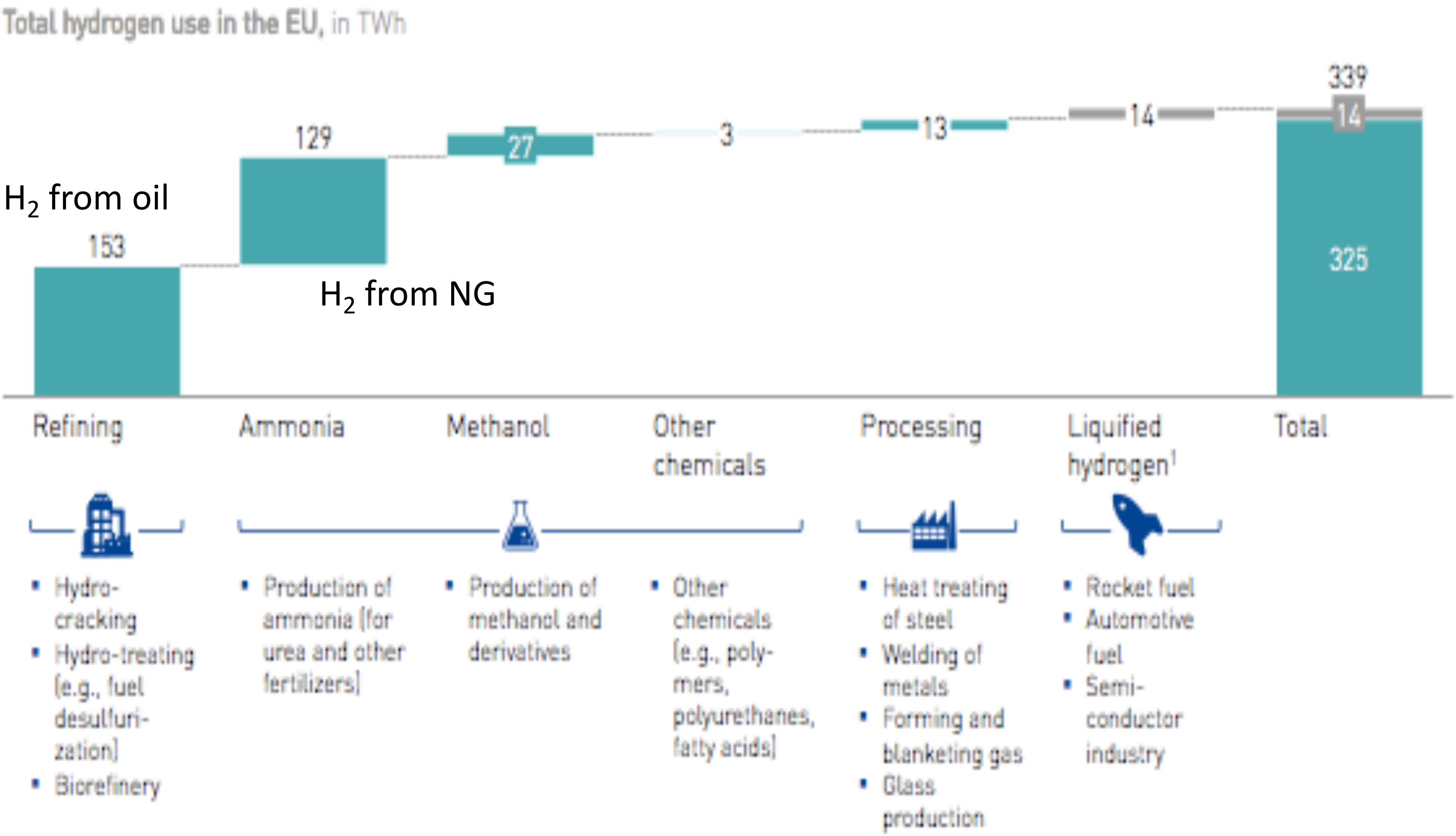
Lakshmanan, S. & Murugesan, T. Clean Techn Environ Policy (2014) 16: 225. https://doi.org/10.1007/s10098-013-0630-6

(Grey) H_2 production from fossil fuels

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

Process	Reaction	ΔH (kJ/mol)	T (°C)	P (bar)	Efficiency (% HHV)
Steam reforming	$CH_4 + H_2O \rightarrow 3\,H_2 + CO$	+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	-

Current uses of H_2 (EU)



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

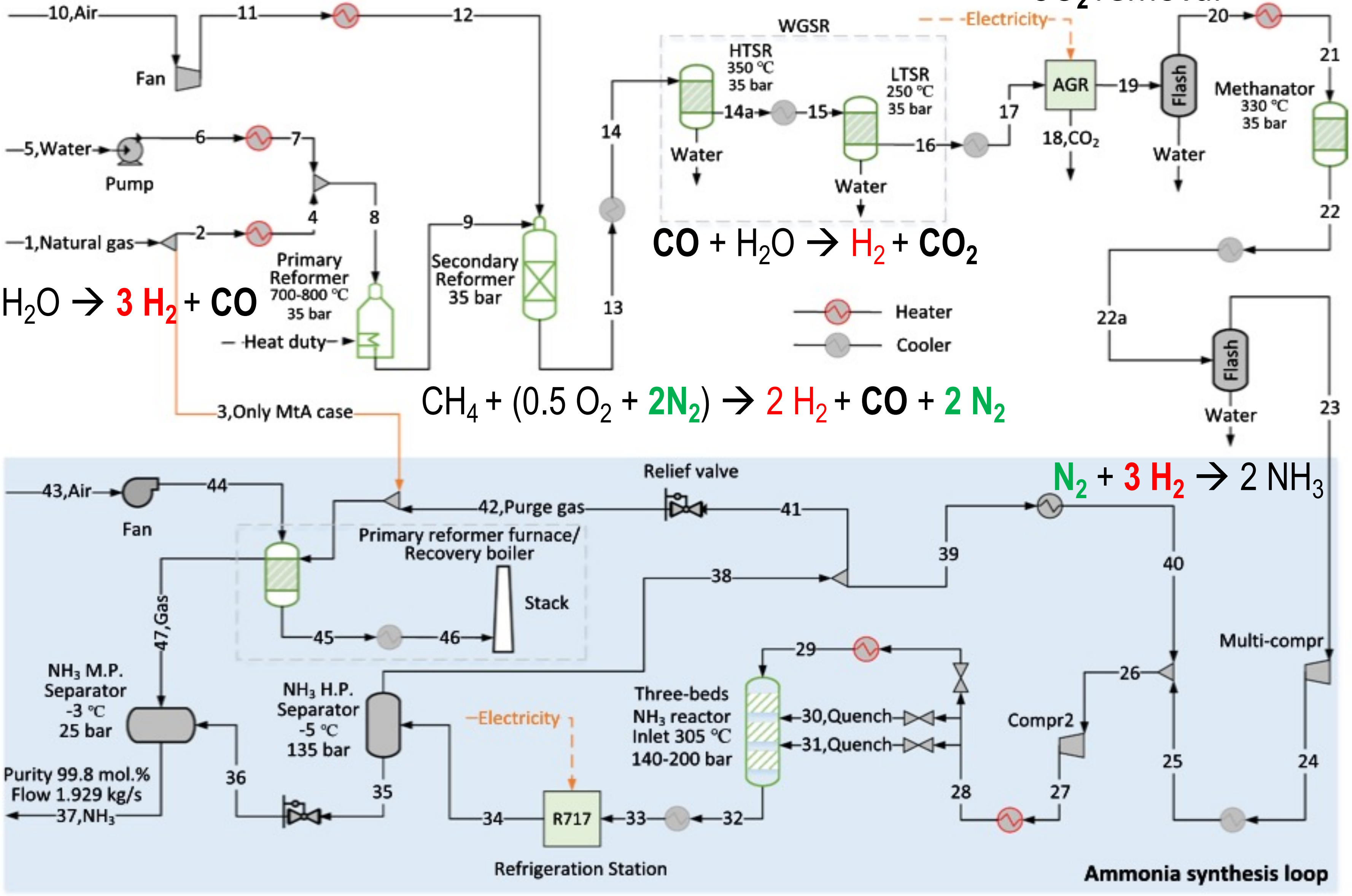
FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

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

H_2 current uses

- Refineries (47%): hydrodesulphurisation (HDS), hydro-cracking to multiple useful oil fractions
- 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)

Example: ammonia synthesis plant



CO_2 removal

$CH_4 + H_2O \rightarrow 3\ H_2 + CO$

$CO + H_2O \rightarrow H_2 + CO_2$

$CH_4 + (0.5\ O_2 + 2N_2) \rightarrow 2\ H_2 + CO + 2\ N_2$

$N_2 + 3\ H_2 \rightarrow 2\ NH_3$

Techno-economic comparison of green ammonia production processes, Fig. 1
H Zhang, L Wang, J Van herle, F Maréchal, U Desideri, *Applied Energy* **259, 114135 (2020)**

Planned 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 (metal, glass, food,..)

Example: oil refinery

https://refhyne.eu/

Rheinland refinery (Shell) (D)

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

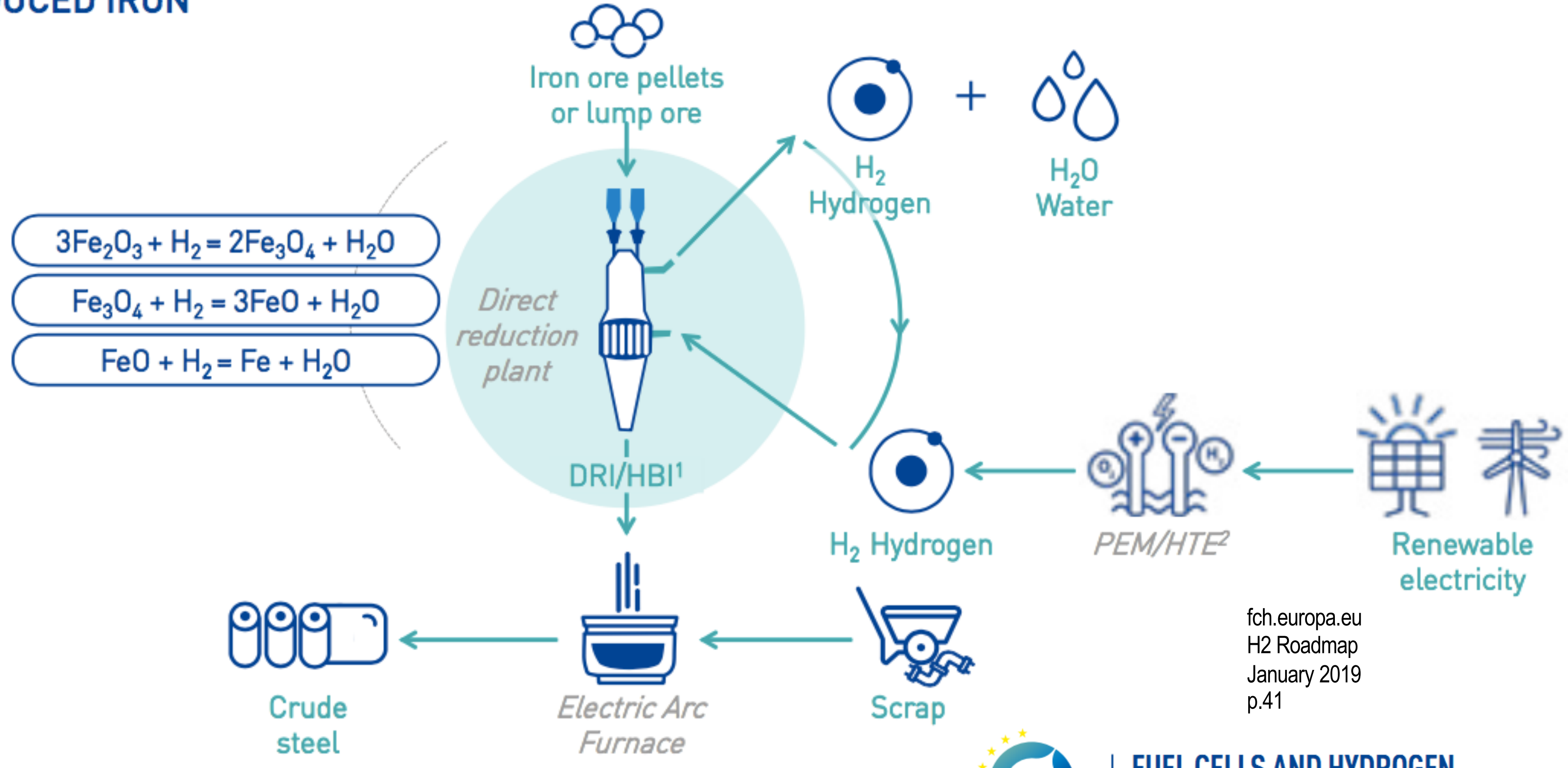
10 MWe PEM-electrolyser:
=> supplies **1300 t H_2** / yr (<1% !!)

REFHYNE CLEAN REFINERY HYDROGEN FOR EUROPE 2018-2022

FUEL CELLS AND HYDROGEN JOINT UNDERTAKING 10 M€

H_2 for steel making : DRI (direct reduced iron)

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



$3Fe_2O_3 + H_2 = 2Fe_3O_4 + H_2O$

$Fe_3O_4 + H_2 = 3FeO + H_2O$

$FeO + H_2 = Fe + H_2O$

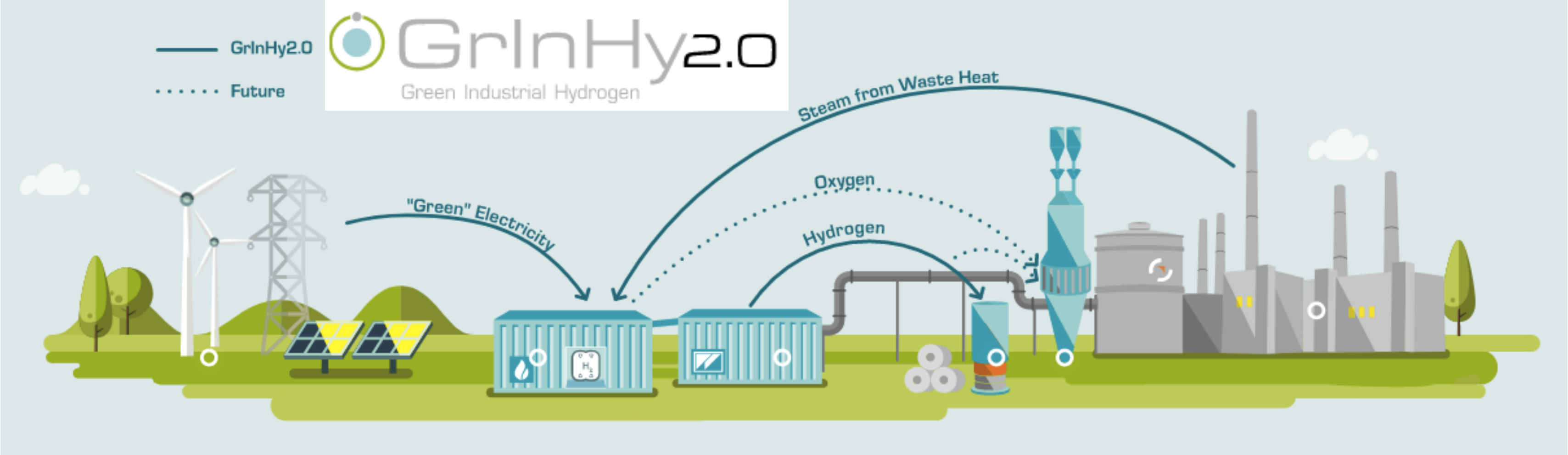
fch.europa.eu
H2 Roadmap
January 2019
p.41

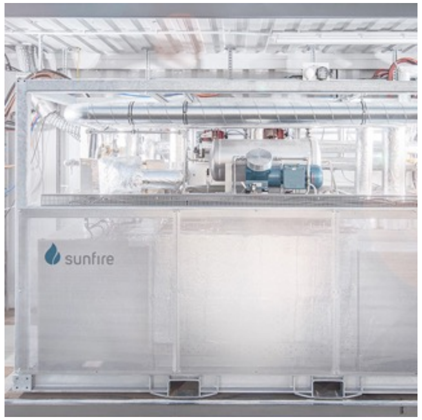
FUEL CELLS AND HYDROGEN
JOINT UNDERTAKING

[1] Direct reduced iron/hot briquetted iron
[2] Polymer electrolyte membrane electrolysis/high temperature electrolysis

Example: steel industry

https://www.green-industrial-hydrogen.com/





2016 - 2022

FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

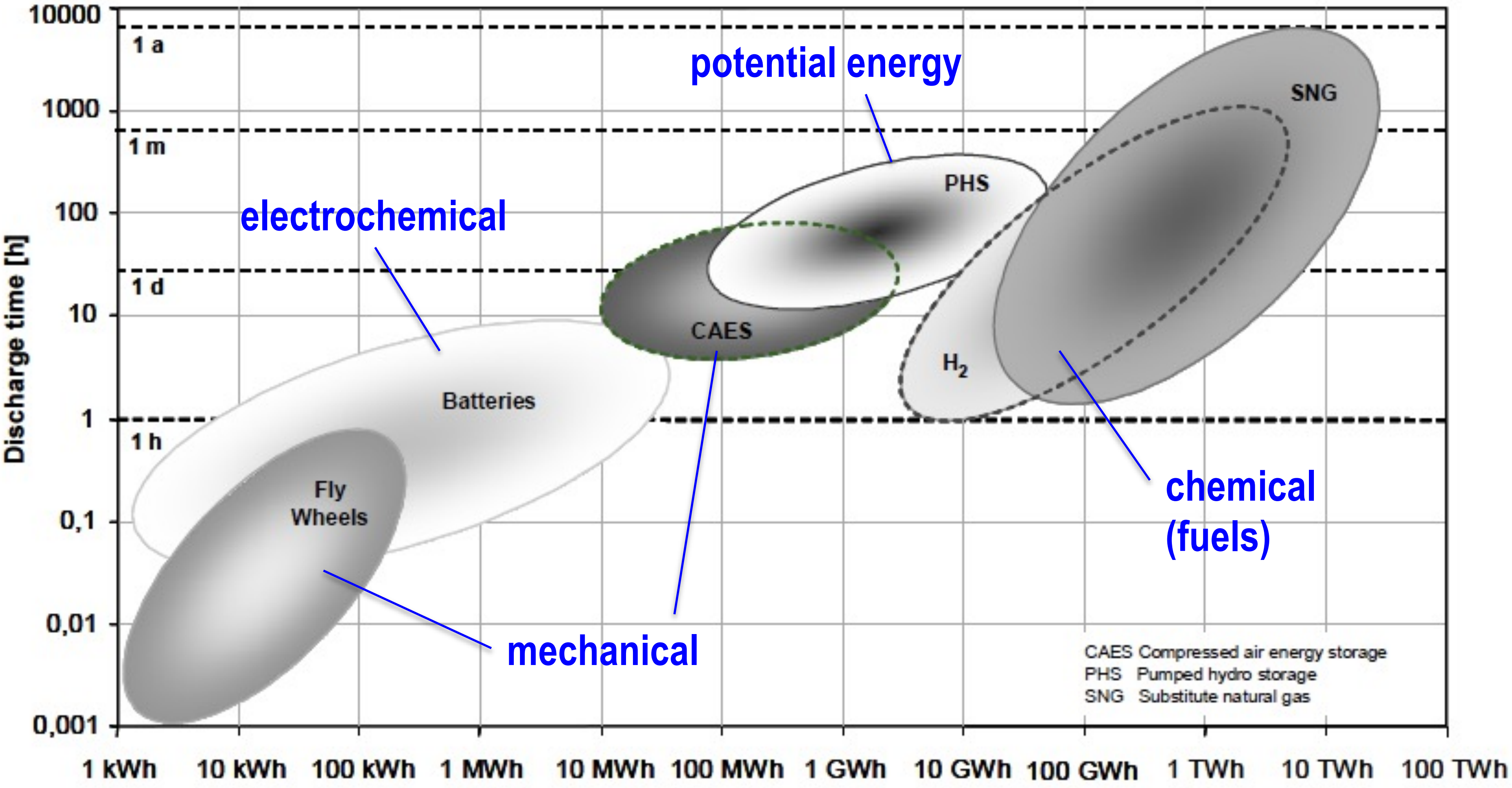
4.5 M€

720 kWe solid oxide steam electrolyser

200 Nm^3/h H_2 (84% efficiency LHV)

100 t H_2 @ < 7€/kg

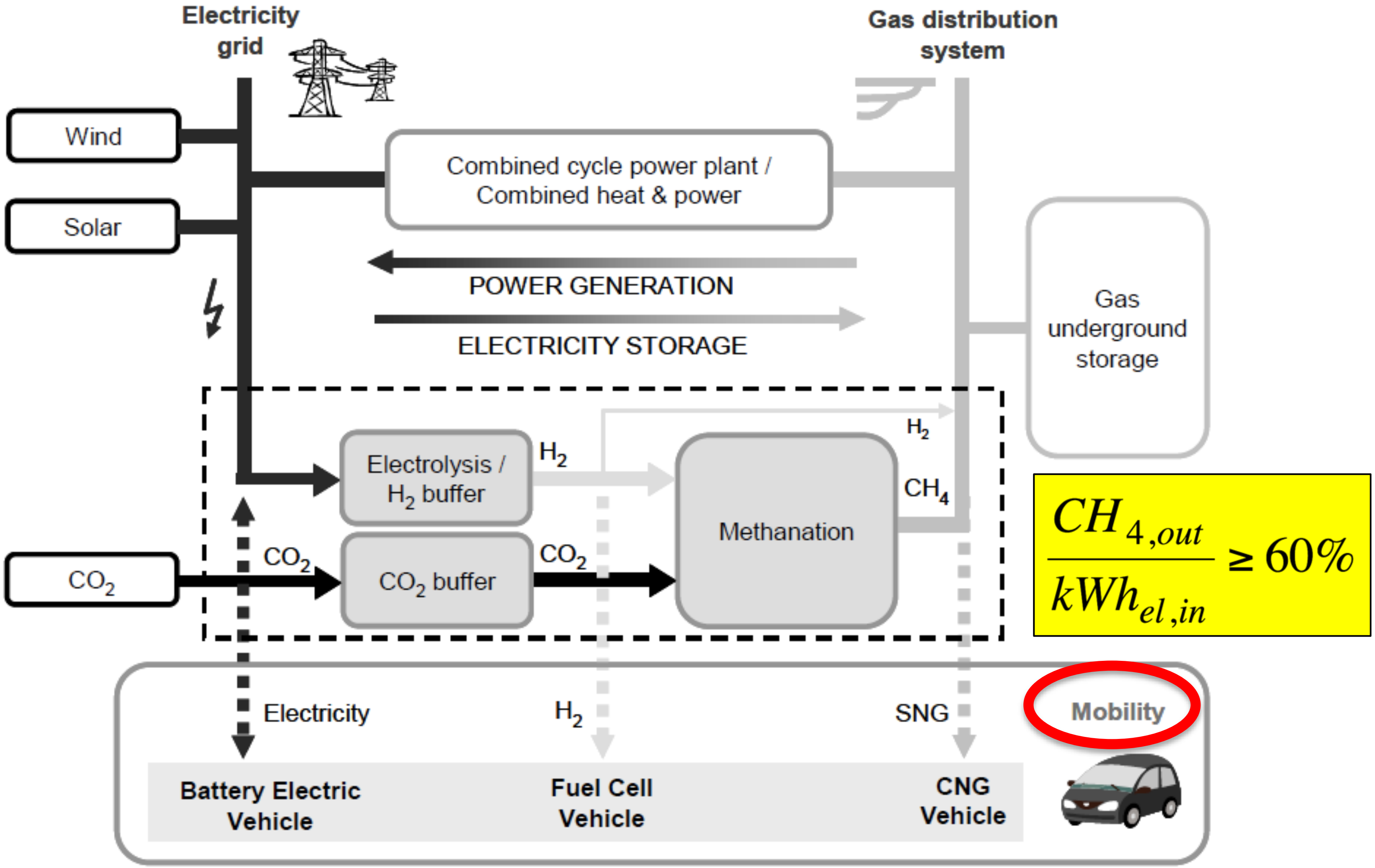
Storage schemes overview



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

‘Power-to-Gas’ concept



Electricity grid

Gas distribution system

Wind

Solar

Combined cycle power plant / Combined heat & power

POWER GENERATION

ELECTRICITY STORAGE

Gas underground storage

Electrolysis / H_2 buffer

H_2

H_2

Methanation

CH_4

CO_2

CO_2

CO_2 buffer

CO_2

Electricity

H_2

SNG

Mobility

Battery Electric Vehicle

Fuel Cell Vehicle

CNG Vehicle

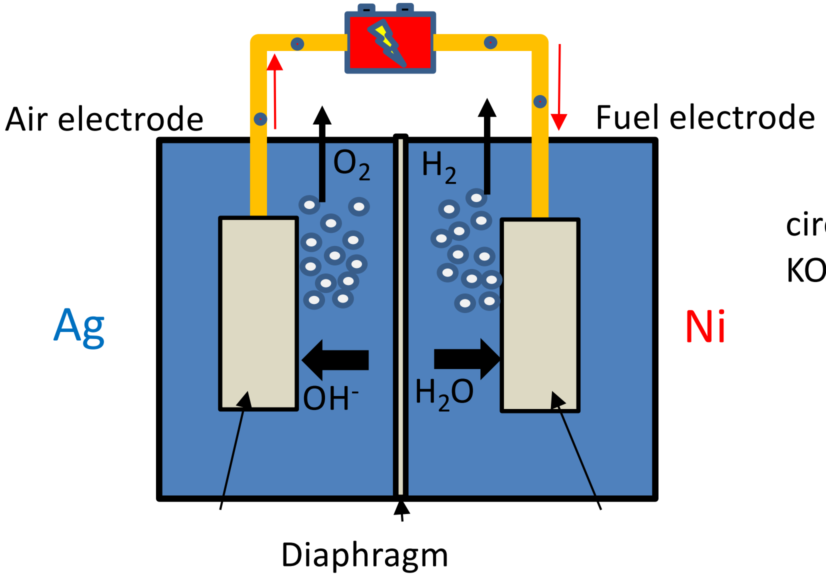
$$\frac{CH_{4,out}}{kWh_{el,in}} \geq 60\%$$

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

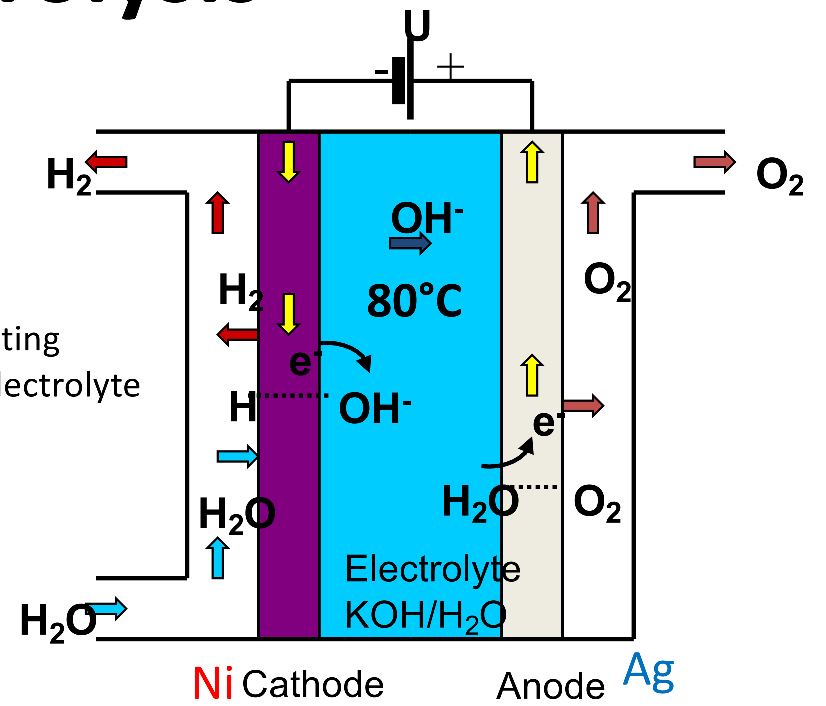
Electrolyser technologies

- AEL : alkaline water
- AEMEL : anionic exchange membrane
- PEMEL : proton exchange membrane (water)
- SOEL : solid oxide ceramic (steam)
- PCCEL : proton conducting ceramic (steam)

1. Alkaline electrolysis



circulating
KOH electrolyte



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

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

1– 30 bar

Monthey (VS)

Advantages :

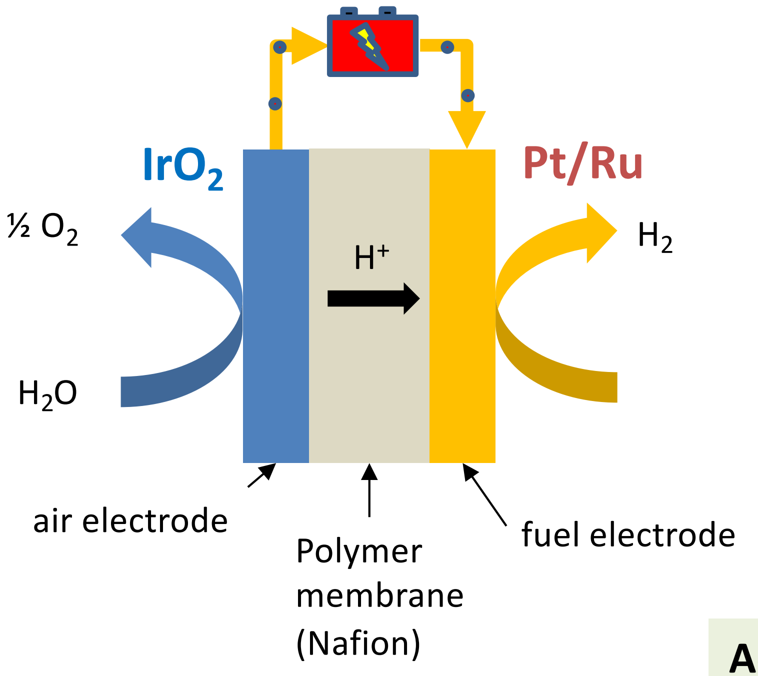
- Mature technology
- Large capacity (1400 Nm^3/h)
- Low cost
- Long life

Limitations:

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

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

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 :

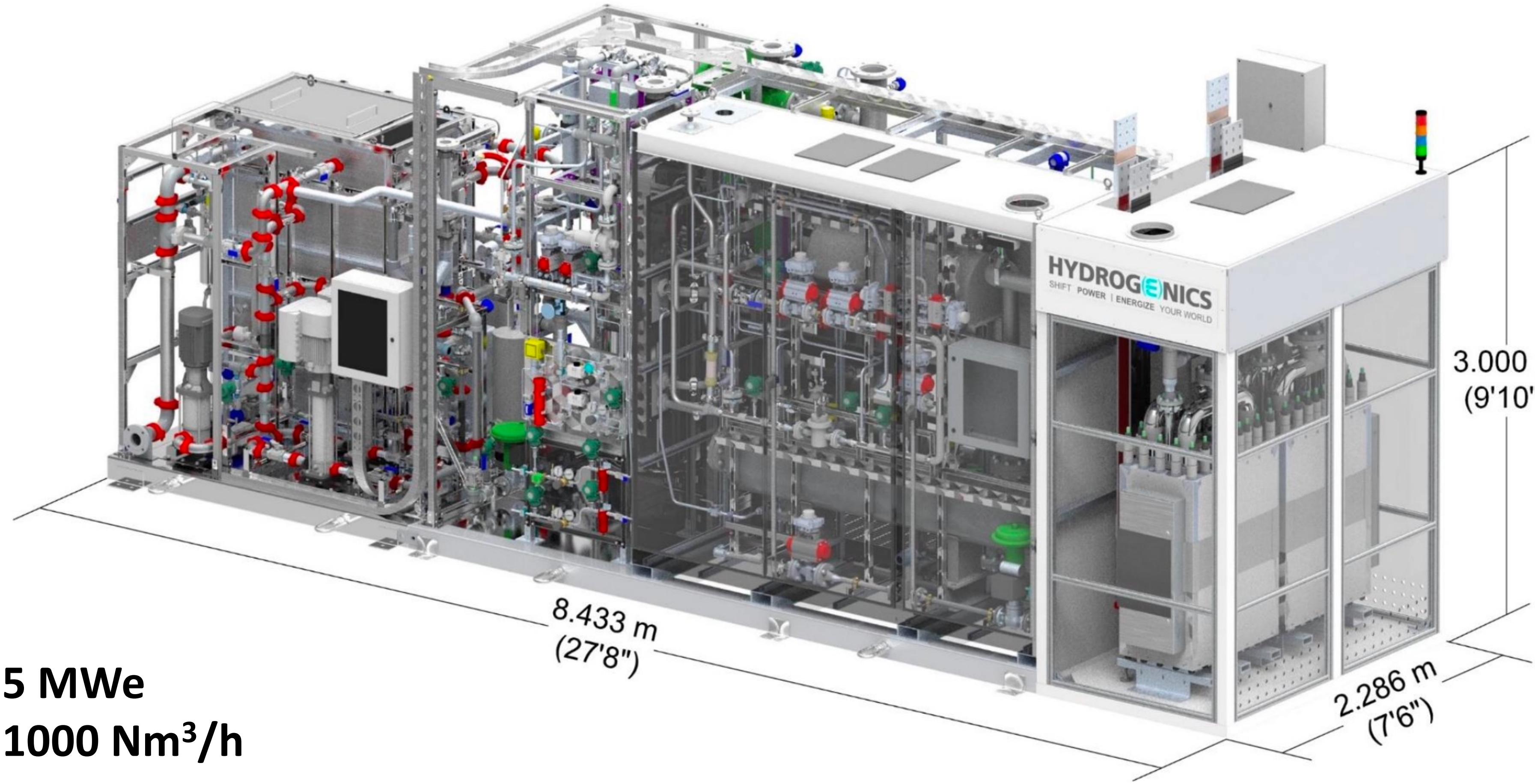
- High current density
- Wide load range
- Fast dynamics

Limitations:

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

slide from T.Macherel, EPFL

HYLYZER®-1000 ELECTROLYZER



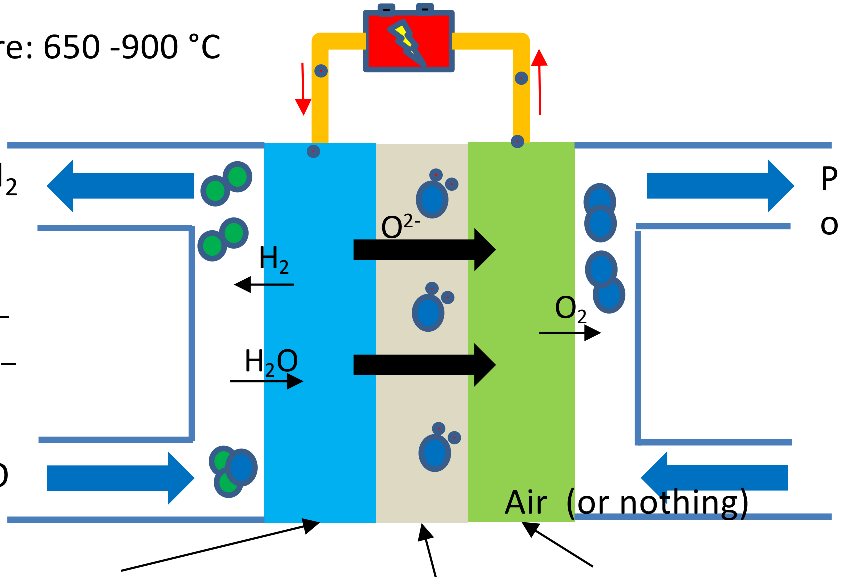
5 MWe
1000 Nm^3/h

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 -900 °C



Pure Oxygen
or Air

Fuel electrode:

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

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

Air electrode:

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

Fuel electrode

Ni

Electrolyte
($Y\text{-}ZrO_2$)

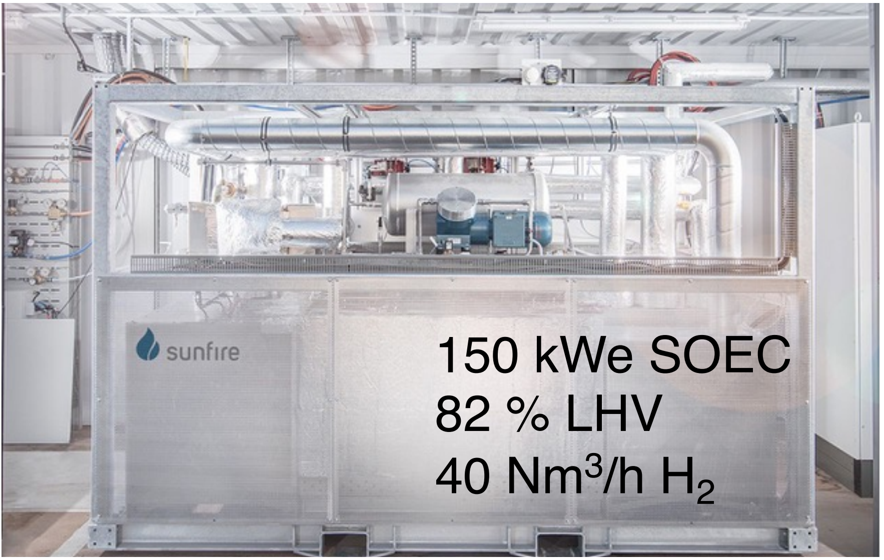
Air electrode

oxide, e.g. $LaSrCoFeO_3$

slide from T.Macherel, EPFL

Solid-oxide system development & manufacturers

SUNFIRE
POWERCORE



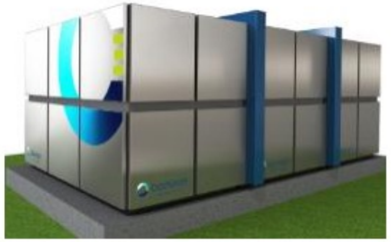
150 kWe SOEC
82 % LHV
40 Nm^3/h H_2

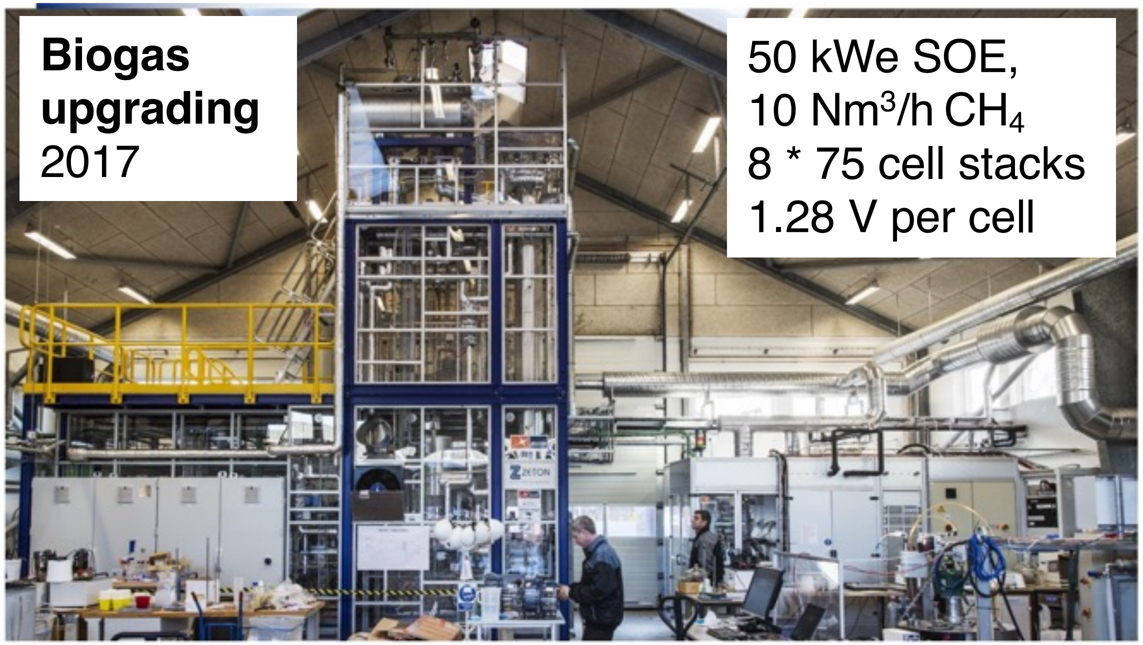
Convion C50
50kW, NG, Biogas

Validation 2015

CONVION SOFC

X00 concept
175 kWe, Biogas
ηe > 53 %
2016



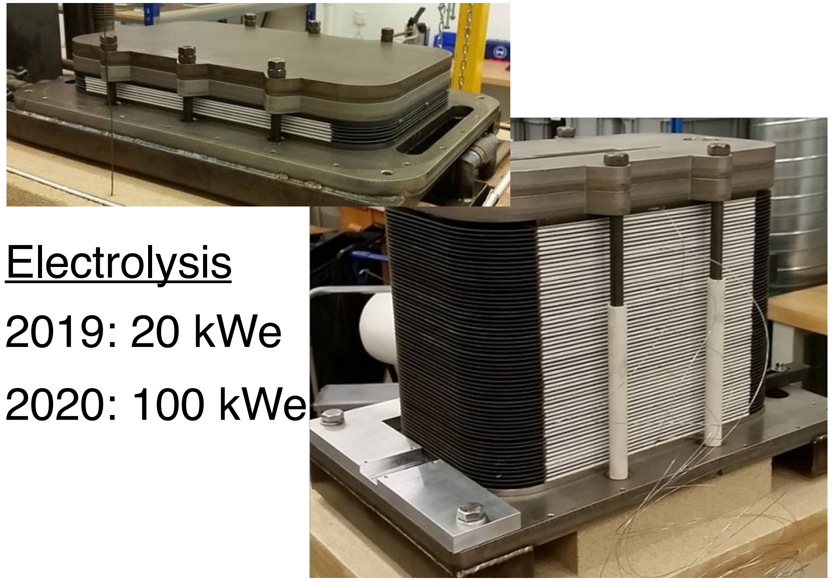


Biogas upgrading
2017

50 kWe SOE,
10 Nm^3/h CH_4
8 * 75 cell stacks
1.28 V per cell

HALDOR TOPSØE

SOLIDPower 5-kW SOFC stack



Electrolysis

2019: 20 kWe

2020: 100 kWe

Thermodynamics of splitting steam vs water

	Reaction	ΔH (kJ/mol)	MJ / Nm^3	kWh / Nm^3
Water	$H_2O(l) \Rightarrow H_2 + \frac{1}{2}O_2$	286 ↓ $-\Delta H_{evap}$	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

→

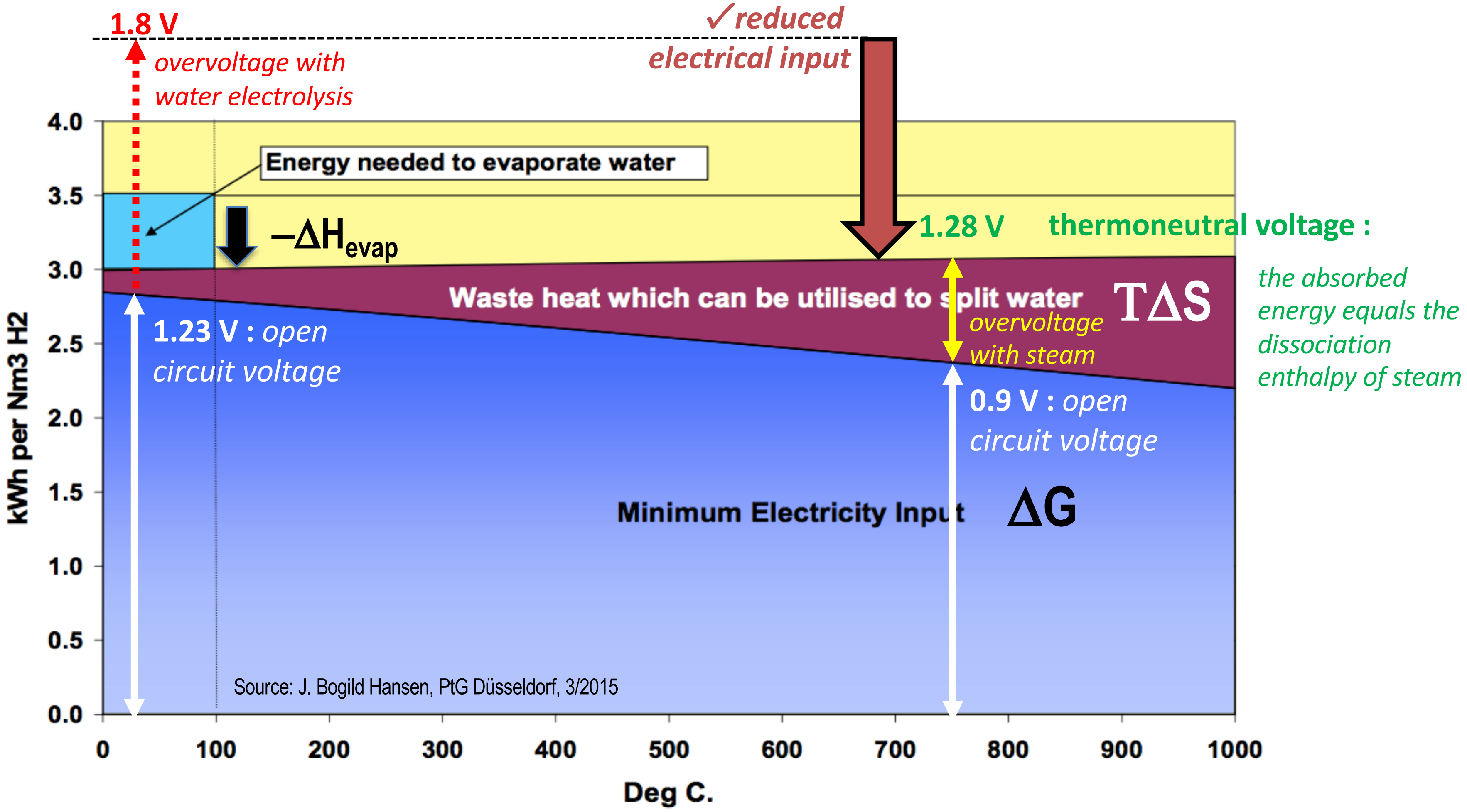
Electrolysis : energy necessary for dissociation

←

Combustion: energy liberated as heat

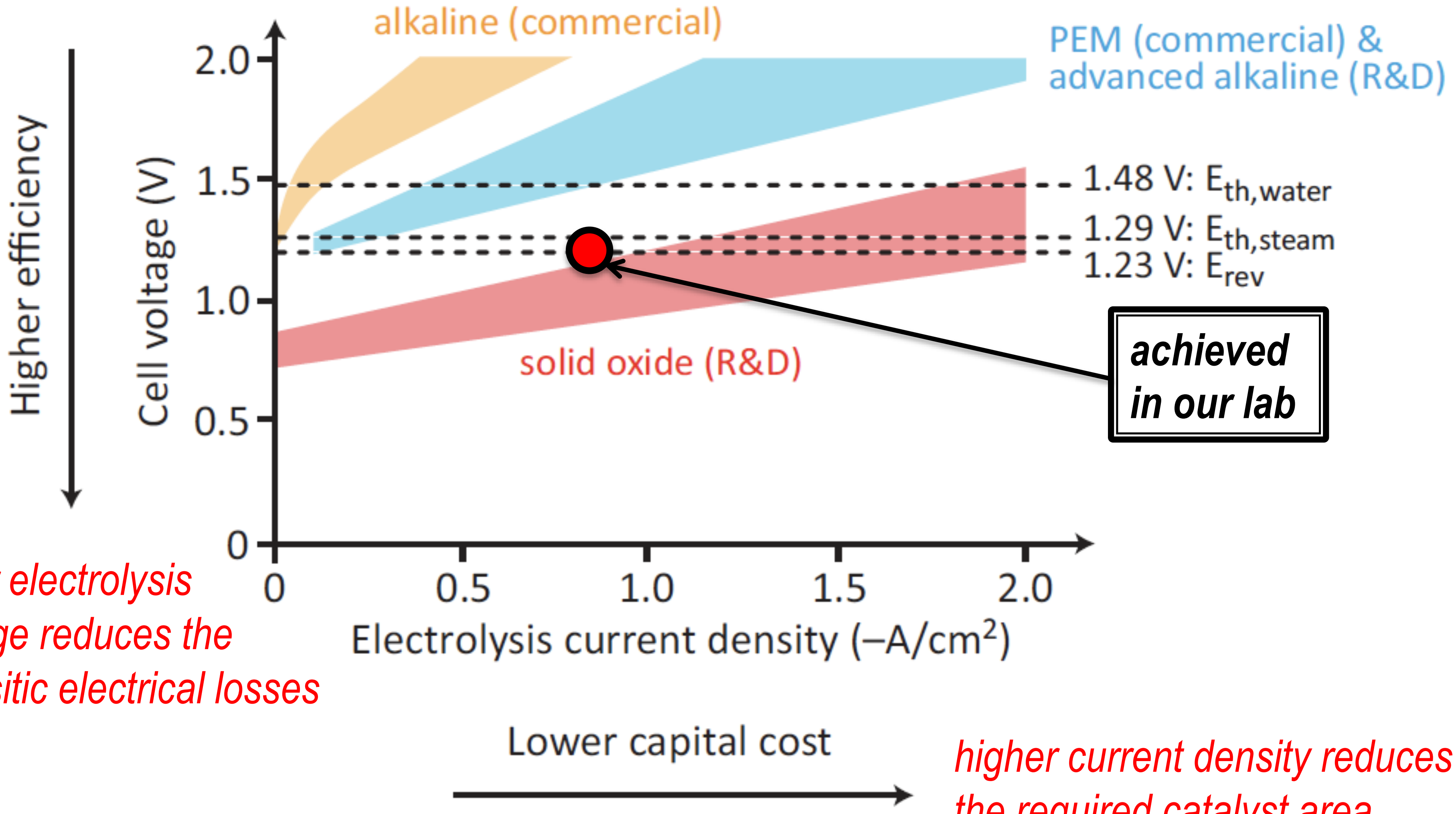
Why *steam* electrolysis?

ΔH = total energy
= electricity + heat
= ΔG + $T\Delta S$



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

Electrolysis technology comparison



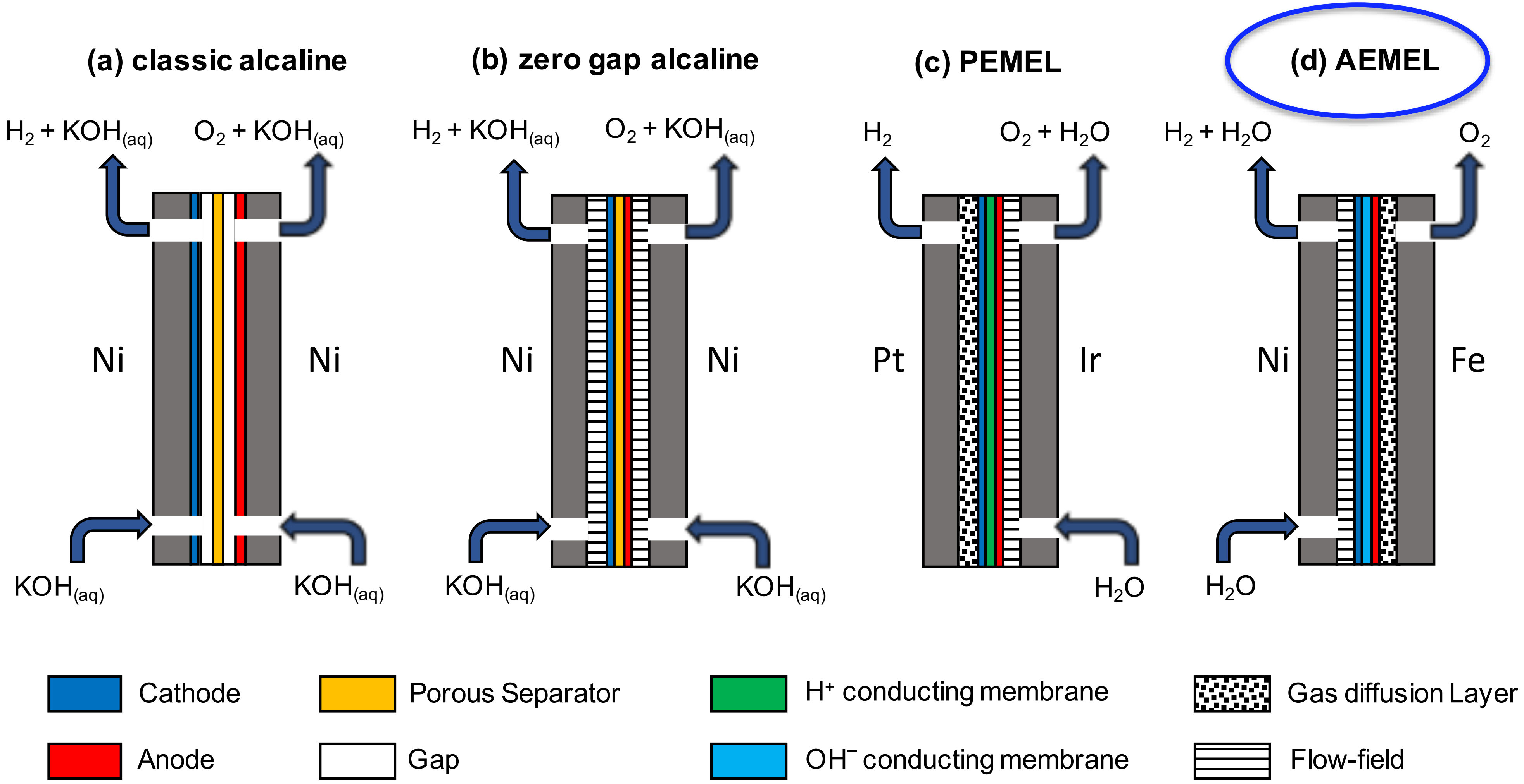
achieved in our lab

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

4. Recent : AEM (anionic exchange membrane electrolysis)

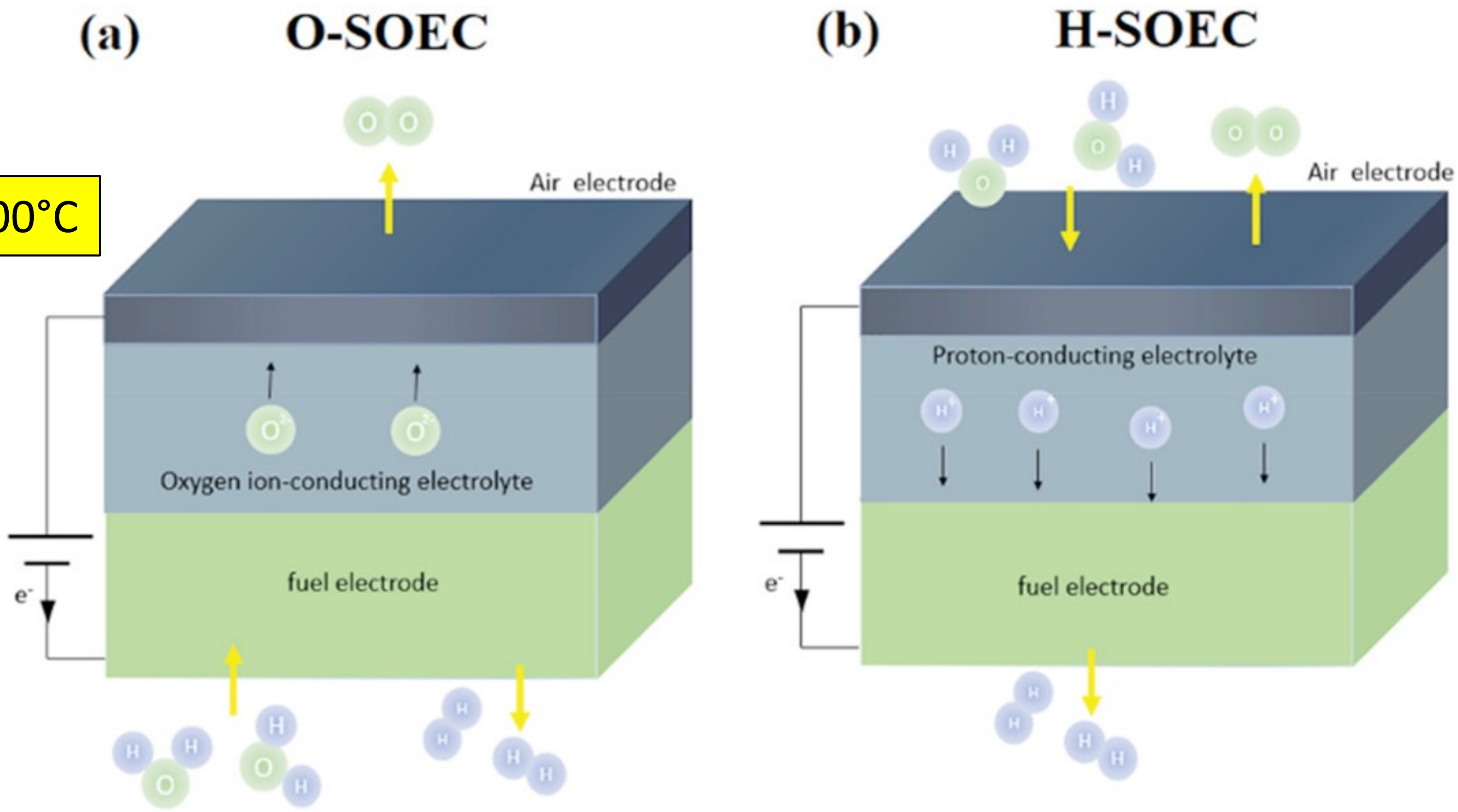


(graph : Dr Heron Vrubel)

AEMEL : combination of PEMEL and classical alcaline

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

5. Recent: proton conducting ceramic electrolyser (PCCEL)



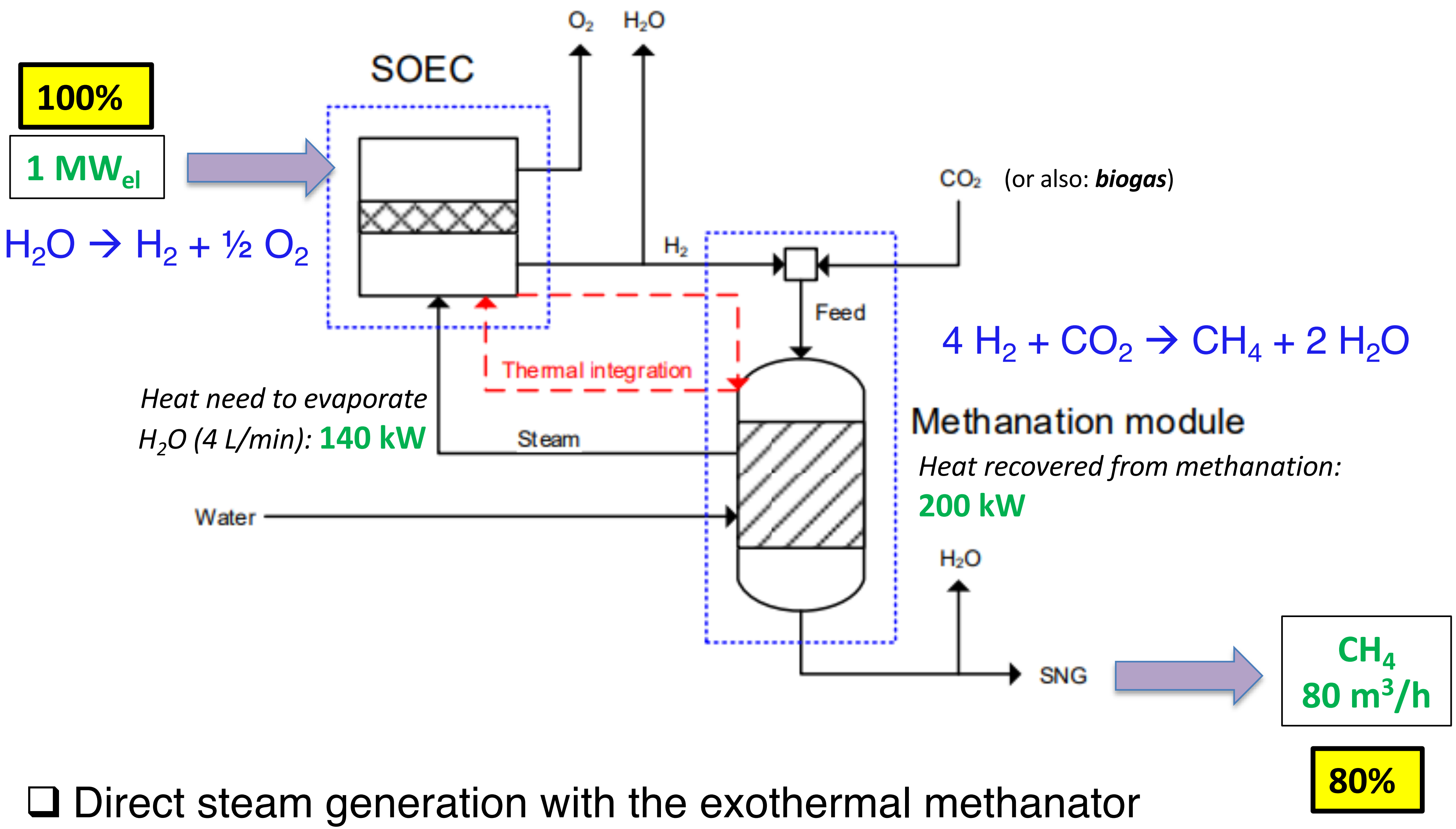
700°C

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 production of dry H_2

SOE (Solid Oxide Electrolysis) based Power-to-CH_4



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%

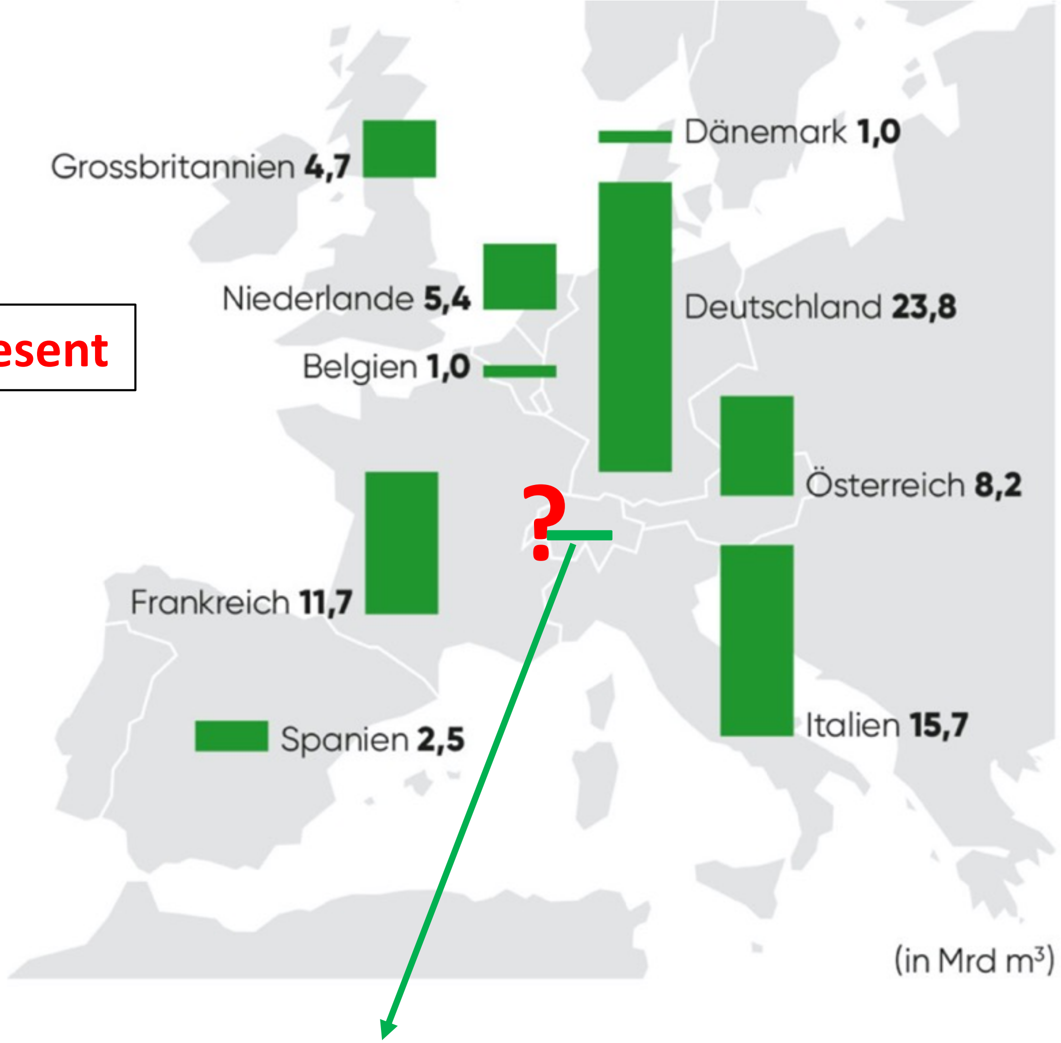
❑ Direct steam generation with the exothermal methanator

P2G : H_2 or CH_4?

H_2	CH_4
• 1-step synthesis • mobility without CO_2	• 2-step synthesis • Need CO_2 source • Heat management
• Limited injection in gas grid • Compression & transport loss • Difficult to store	• No limit for gas grid injection • Low compression/transport loss

Seasonal gas storage in Switzerland?

no NG storage at present



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

10 TWh of NG require 14 TWhe of electricity, expected to be coverable from future 30 TWhe of PV and 40 TWhe of hydro (summer excess)

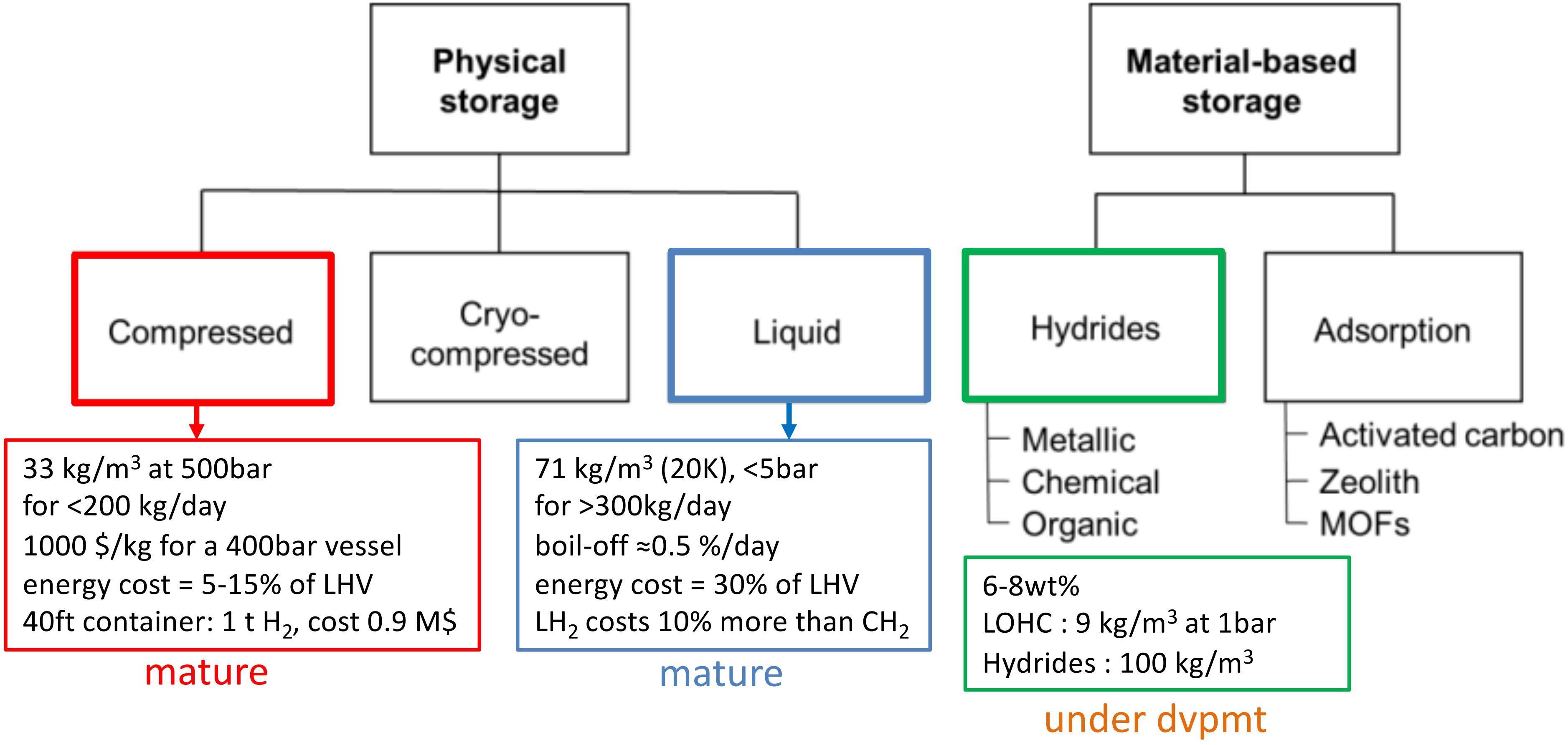
with 1 bio m^3 gas (10 TWh), the Swiss winter electricity gap would be covered (i.e. a deficit of ~1 TWhe / month).

H_2 storage methods

- as compressed H_2 gas (=> 1000 bar)
- as liquid H_2 (1 bar)
  - optional: further cryocompression of liq H_2
- as physically adsorbed H_2-layer on high surface area materials
  - sorption increases at low T
- as chemical H in hydrides
  - solid solution → hydride H (interstitial H, up to intermetallics)
  - complex hydrides (e.g. $NaBH_4$)
- as H in other chemical compound
  - LHOC (liquid hydrogen organic carrier)
  - NH_3

H_2 storage overview

(figure: Leonardo Gant)



Physical storage

Compressed

Cryo-compressed

Liquid

Material-based storage

Hydrides
- Metallic
- Chemical
- Organic

Adsorption
- Activated carbon
- Zeolith
- MOFs

33 kg/m^3 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/m^3 (20K), <5bar
for >300kg/day
boil-off ≈0.5 %/day
energy cost = 30% of LHV
LH_2 costs 10% more than CH_2

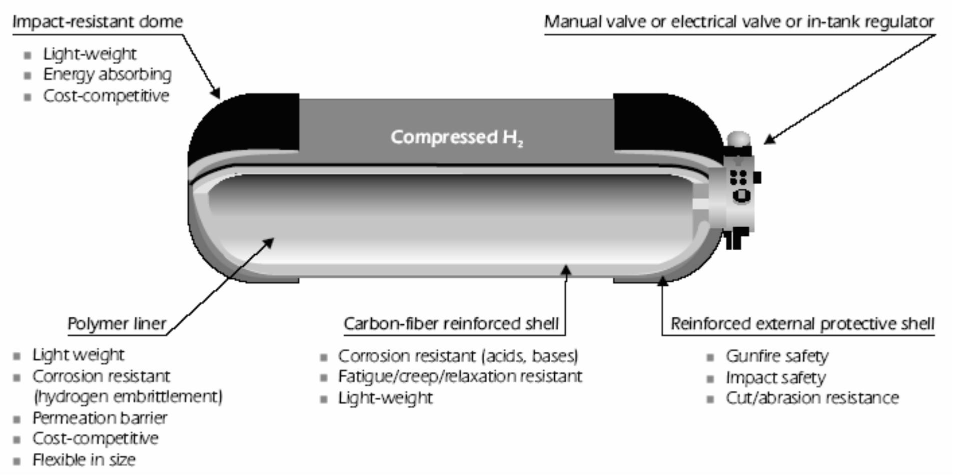
mature

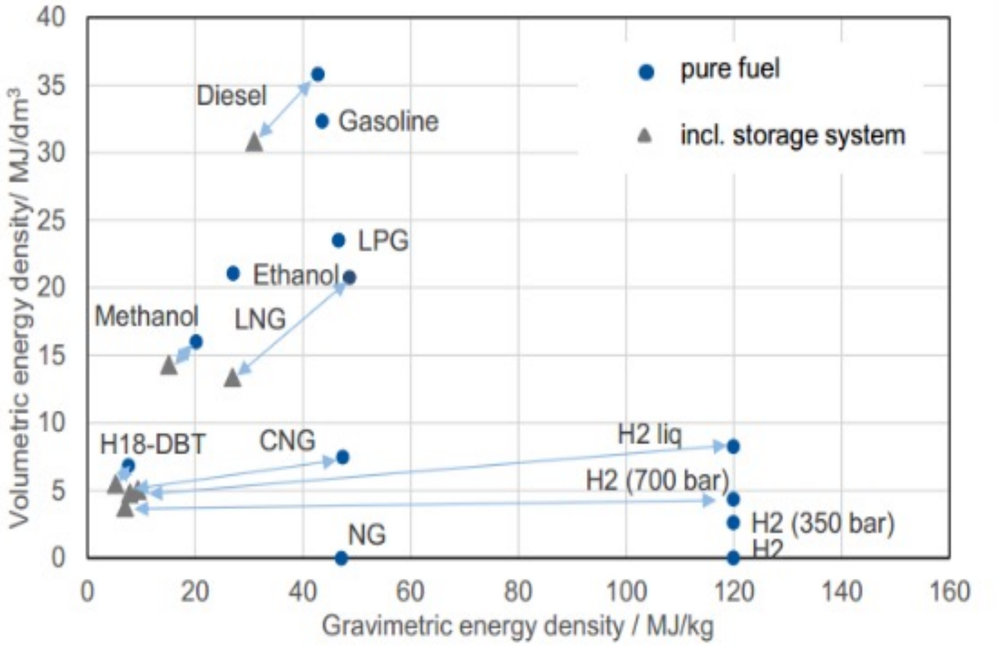
6-8wt%
LOHC : 9 kg/m^3 at 1bar
Hydrides : 100 kg/m^3

under dvpmt

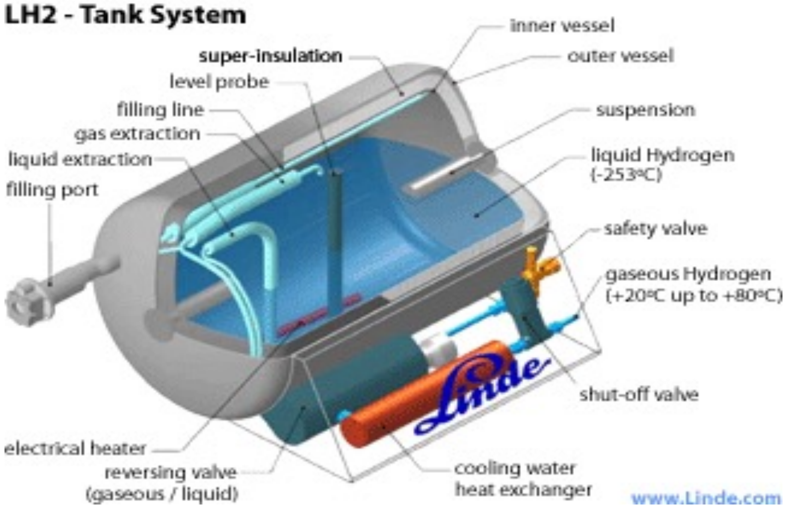
H_2 storage : compressed gas, and liquid

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





loss 0.1 – 3% / day



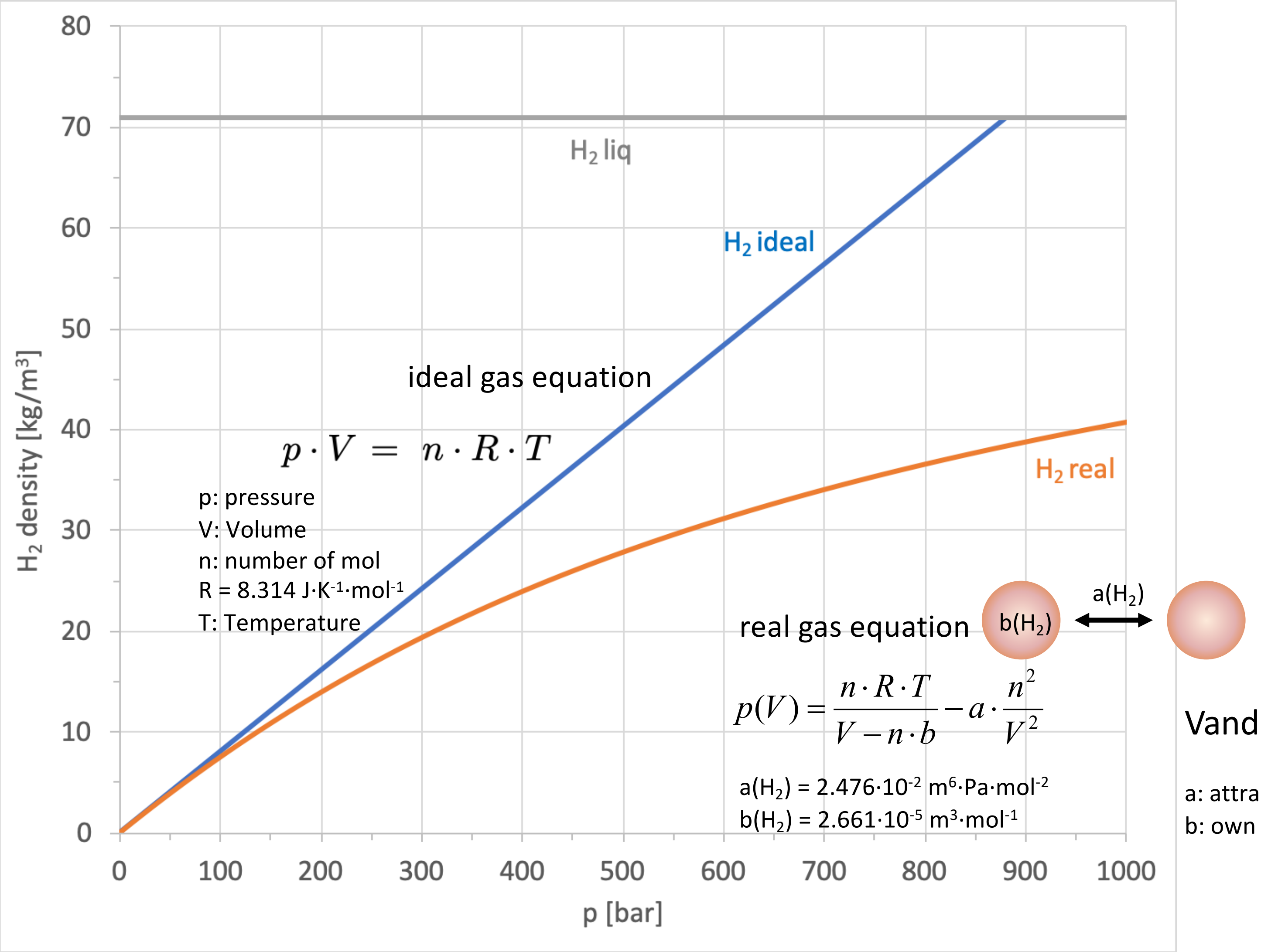
fuel density (kg^{-1}) alone is high;
not when adding storage medium weigth

(figures: Leonardo Gant)

Pressurized H_2

1 bar = 2 g / 22.4 L = 90 g /m^3
ideal gas: 1000 bar = 90 kg/m^3

(water : 1000 kg/m³ !)



ideal gas equation

$$p \cdot V = n \cdot R \cdot T$$

p: pressure
V: Volume
n: number of mol
R = 8.314 J·K^{-1}·mol^{-1}
T: Temperature

real gas equation

$$p(V) = \frac{n \cdot R \cdot T}{V - n \cdot b} - a \cdot \frac{n^2}{V^2}$$

a(H_2) = 2.476·10^{-2} m^6·Pa·mol^{-2}
b(H_2) = 2.661·10^{-5} m^3·mol^{-1}

VanderWaals gas

a: attraction term btw molecules
b: own volume of the molecules

slide from Prof A Züttel, EPFL

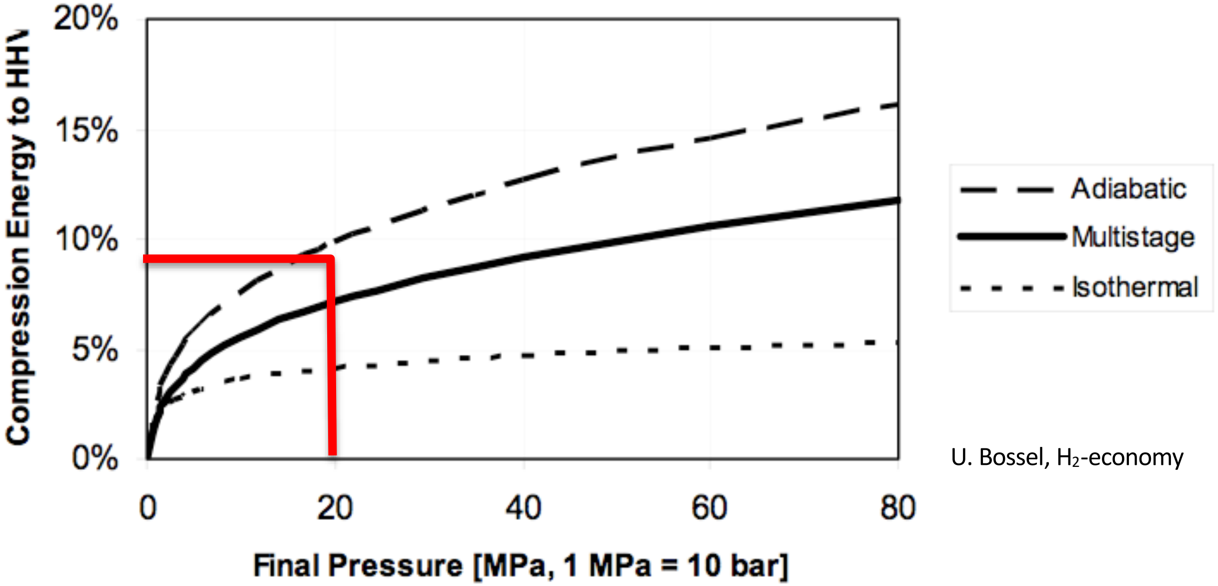
Compression work

- ideal isothermal work$_{id}$ (J/kg) = $p_0 V_0 \ln(p_1/p_0)$
- adiabatic work$_{ad}$ = $(\gamma/\gamma-1)\, p_0 V_0 \left((p_1/p_0)^{(\gamma-1)/\gamma}-1\right)$

V_o initial volume(m^3/kg) (11.11 m^3/kg for H_2, 1.39 m^3/kg for CH_4)

p_0 initial pressure, p_1 final pressure, $\gamma = C_p/C_v$ (1.41 for H_2, 1.31 for CH_4)

- @200 bar (W_{ad}): for CH_4 2 MJ/kg (2% HHV), for H_2 14 MJ/kg (10% HHV)



U. Bossel, H_2-economy

Joule-Thomson coefficient

isenthalpic expansion/compression:

$$\boxed{\mu_{J-T} = \left(\frac{dT}{dP}\right)_{\boldsymbol{H}} = -\frac{(\alpha T - 1)V}{C_P}}$$

α : expansion coefficient at const. P

C_P : heat capacity at const. P

$$\boxed{\mu_{J-T} > 0}$$

positive J-T-coefficient

@ low P:
the gas cools upon expansion

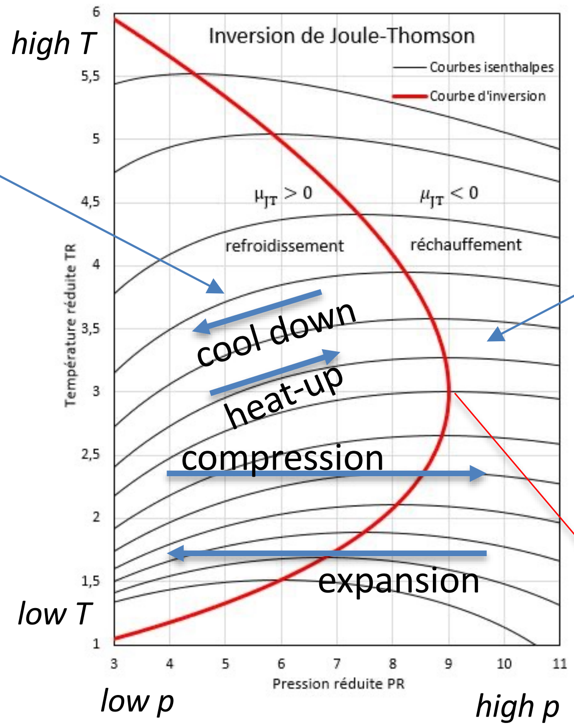
μ_{J-T} = 0 for an ideal gas
no T-change during J-T-expansion

$$\boxed{\mu_{J-T} < 0}$$

negative J-T-coefficient

@ high P:
the gas heats upon expansion

(expansion accelerates the molecules,
$h_{total} = h_{static} + c^2/2$; due to high speed of light molecules,
friction heating dominates the expansion cooling)



The gas can therefore be cooled (and eventually liquified), only

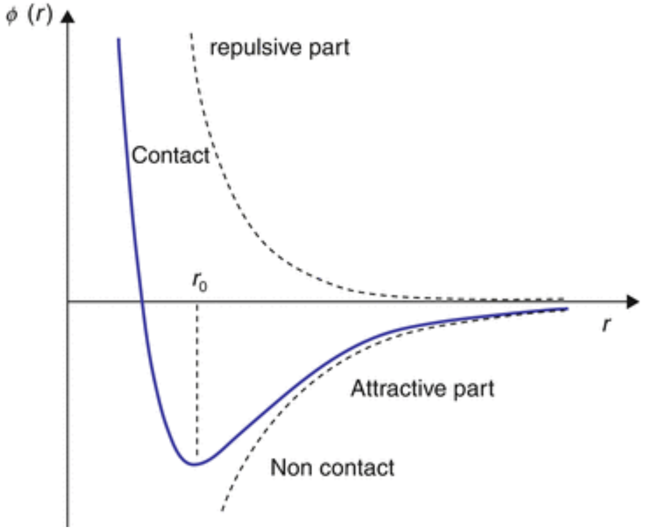
- by expansion if $\mu_{J-T} > 0$
- by compression if $\mu_{J-T} < 0$

⇒ for H_2-filling (400 bar=>350 bar), cooling is needed !

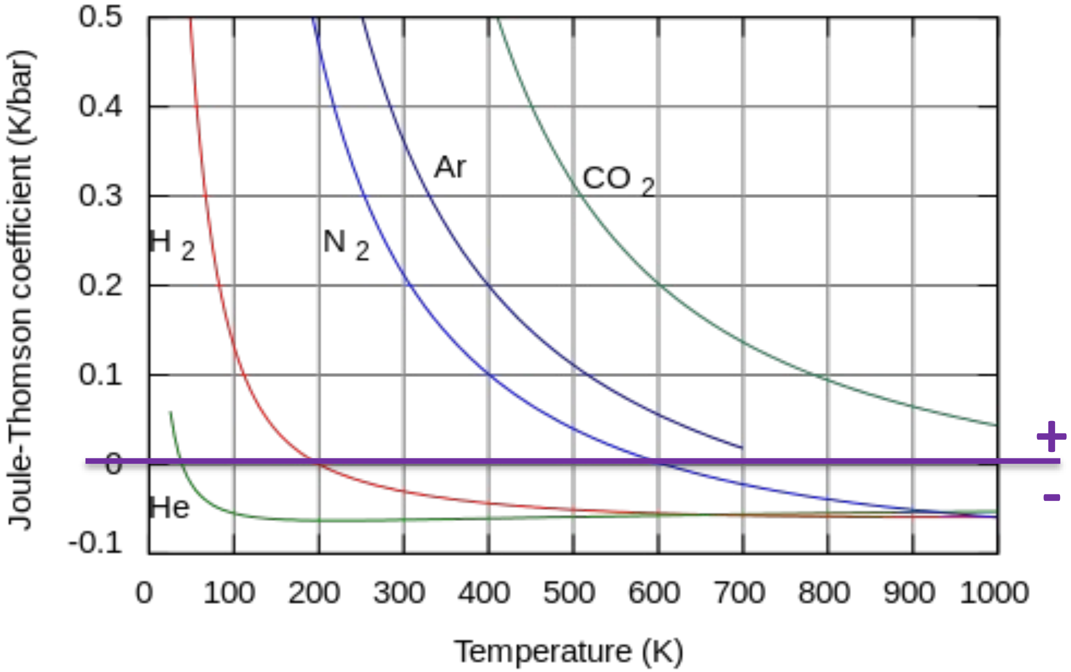
The inversion curve crosses the maxima of all isenthalpic curves

Joule-Thomson Effect

$$\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial p}\right)_H$$



Van der Waals



$$\mu_{\mathrm{JT}} = \frac{1}{C_p} \cdot \left(\frac{2a}{RT} - b\right) \qquad T_{\mathrm{inv}} = \frac{2a}{Rb}$$

$a(H_2) = 2.476 \cdot 10^{-2}\ m^6 \cdot Pa \cdot mol^{-2}$
$b(H_2) = 2.661 \cdot 10^{-5}\ m^3 \cdot mol^{-1}$
$R = 8.314\ J \cdot K^{-1} \cdot mol^{-1}$

=> T_{inv} = 200K

At ambient T (300K), H_2 must be cooled for filling (expansion), and heated when compressing. At cryo-conditions (e.g. 77K and lower), it is the opposite.

For light gases (H_2, He,..), i.e. smallest molecules, the inversion T is low. This T increases for larger/heavier molecules. One needs to go to very low T, i.e. slow down the speed of the molecules enough, so that H_2 and He become positive in their J-T coefficient and behave like 'normal' gases.

slide from Prof A Züttel, EPFL

Review of hydrogen compression technologies

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

@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 compression technologies overview

- 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 (‘pack, distribute, store, deliver’), 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 1-2wt% @250 bar (steel), 6wt% @700 bar (composite), and 30g H_2/L
(US-DOE targets : 40 g/L and 5.5wt%)

Non-mechanical compressors

- Cryogenic compression of liquefied H_2
- Electrochemical compression
- Thermally driven:
  - Adsorption of H_2 on high surface materials
  - Metal-hydride

Liquefaction work

As Carnot cycle with a heat sink at 300 K, the ideal work of liquefaction is W_L = 13 MJ kg^{-1} (3.6 kWh kg^{-1}) for LH_2

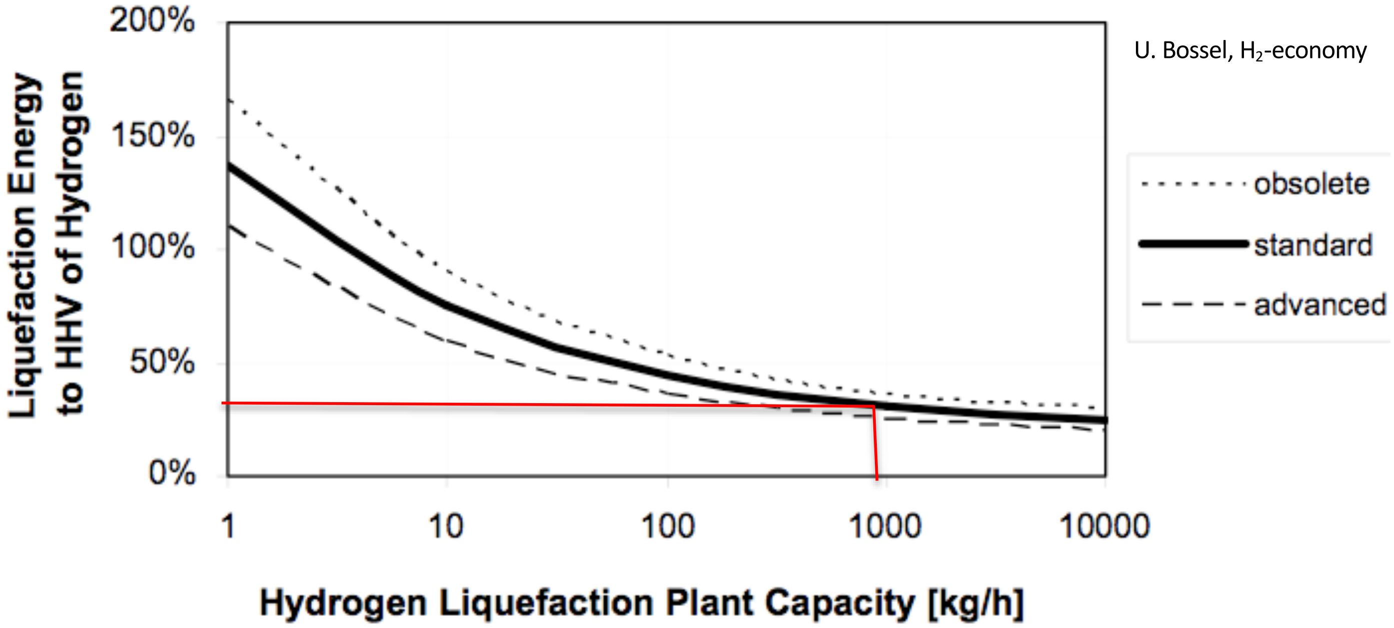
300K

$$W_L = \Delta H \frac{(T_a - T_e)}{T_e}$$

20K

225 kJ/kg (evap)
+703 kJ/kg (ortho-para hydrogen)

298 K → 20 K	MJ need per kg liquid H_2	Reference
theoretical requirement	13 (10% of HHV)	Carnot
usual scale	54	182 kg / h, Linde plant (D)
large scale	36	2000 kg / h, USA
ultimate scale	30-25	12000 kg/h, study case

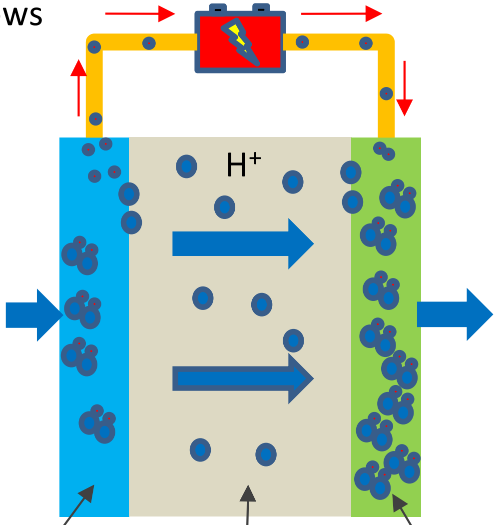


U. Bossel, H_2-economy

Liquifaction of H_2 is very energy intense (about 30% lost)

Electrochemical 'pump'

using a proton exchange membrane (PEM) and Pt catalysts



At LP electrode:

$H_2(LP) \rightarrow H^+ + 2e^-$ splitting

At HP electrode:

$H^+ + 2e^- \rightarrow H_2(HP)$ recombining

Minimum voltage:

$$E_{rev} = \frac{RT}{zF} \ln(\frac{p_{HP}}{p_{LP}})$$

z=2 electrons

13mV

Theoretically only 84 mV needed to raise from 1 to 700 bar. (ln(700)=6.55) However, ohmic drop and overpotentials increase the voltage. Achieved: 140 mV for 50 bar @0.2A/cm^2
=> 0.3 kWh/Nm^3 v. low consumption

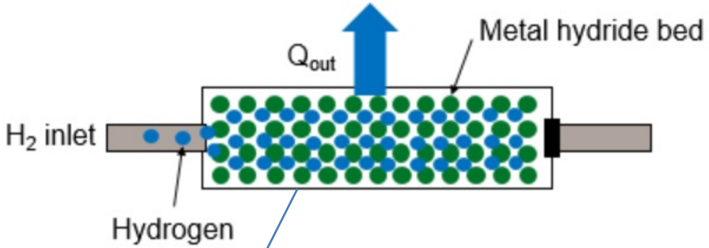
slide from T Macherel, EPFL

see HY-ET company (NL):
1000 bar in 1 step !

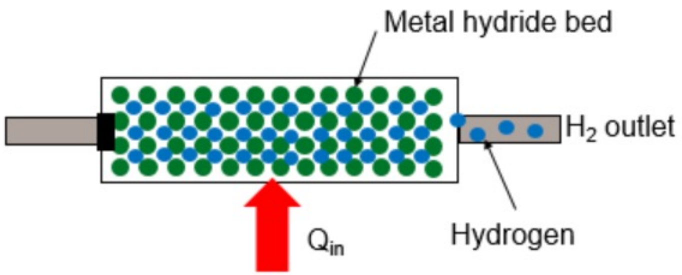
Metal hydride compression

$$M_{(s)} + \frac{x}{2}H_{2(g)} \overset{abs}{\underset{des}{\leftrightarrow}} MH_x + Q$$

Hydride heats up during absorption
=> needs heat removal



Steel tank.
Tubular for easy heat/mass transfer



Heat supply increases the storage pressure

slide from T Macherel, EPFL

see GRZ Technologies company

H_2 compression 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

Linde AG presentation at EFCF : Industrial perspective on H_2 purification, compression, storage and distribution

Chemical H-storage

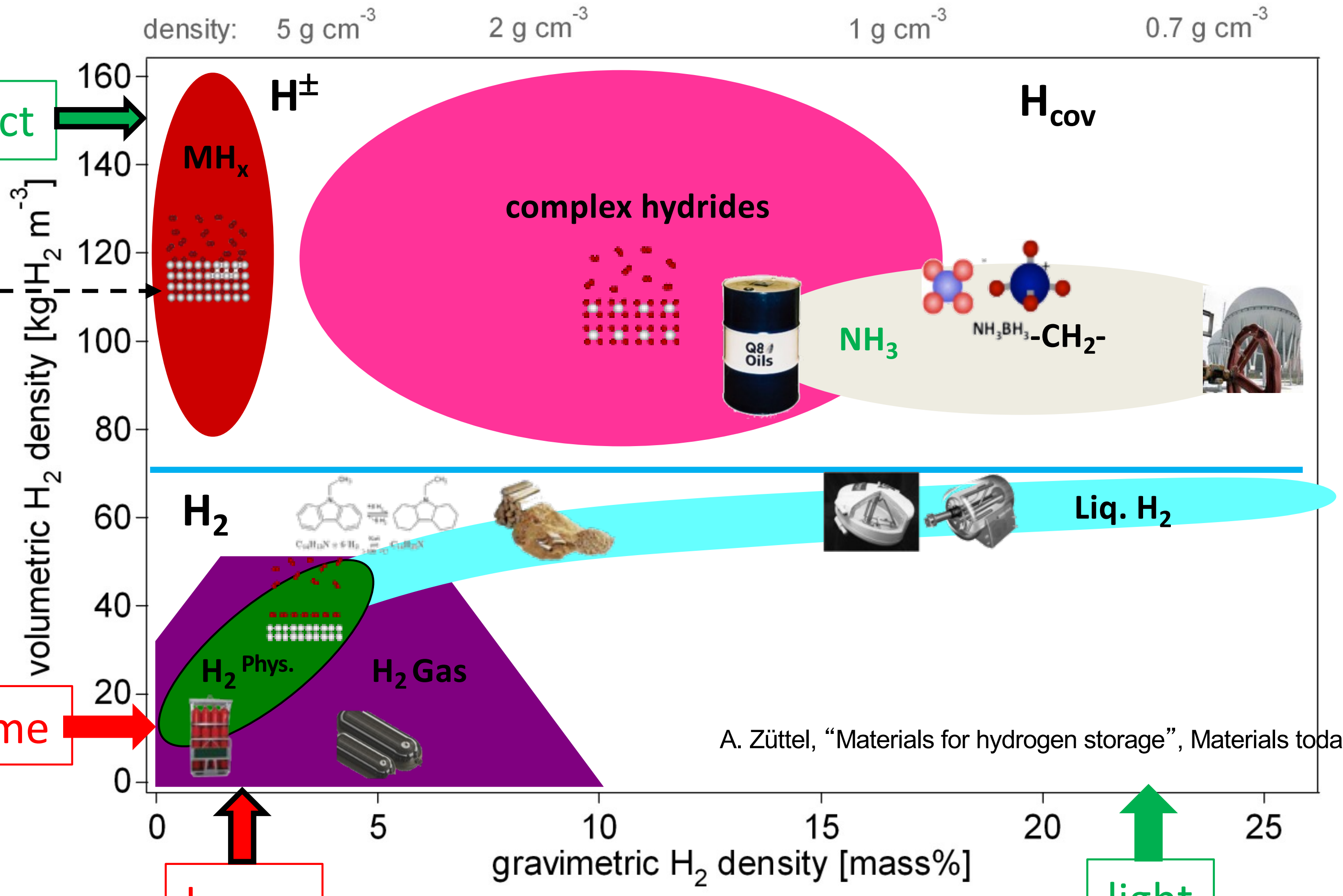
- Formic acid or formate ($HCOOH_{liq} = H_2 + CO_2$)
- NH_3 (3x more energy dense than liq. H_2)
- LOHC (liquid organic hydrogen carriers)
- …

Hydrogen Storage Density comparison

compact

MH:
high volumetric, but
low gravimetric density

large volume



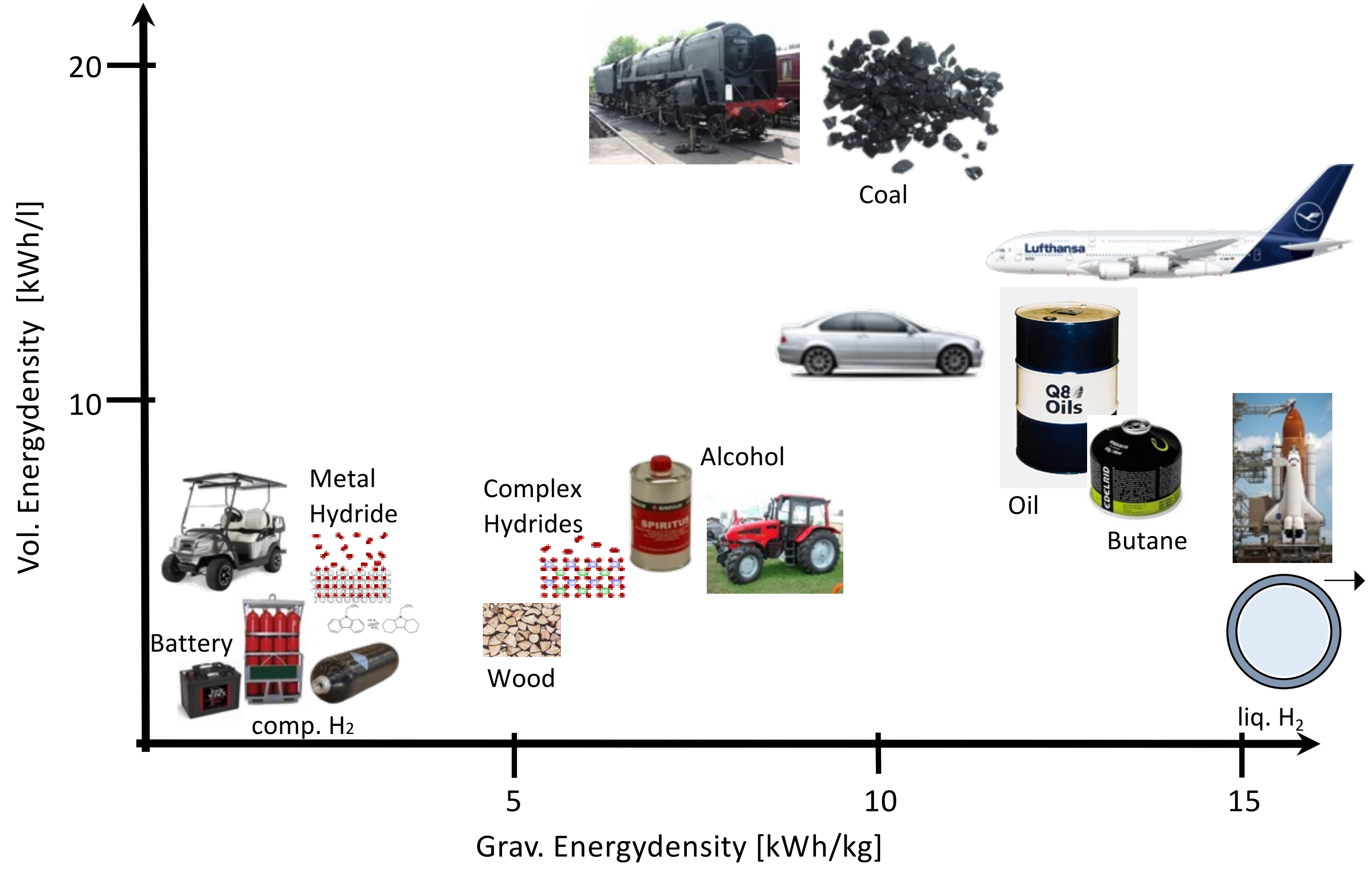
A. Züttel, “Materials for hydrogen storage”, Materials today, Sept 2003, pp. 18-27

heavy

light

slide from Prof A Züttel, EPFL

Energy density of fuels overall



slide from Prof A Züttel, EPFL

Comparison H_2 storage

	$c\text{-}H_2(g)$	LH_2	LOHC	MOFS	M-hydride	Complex hydrides	Salt hydrides
ρ (kg /m^3)	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 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

Linde AG presentation at EFCF: Industrial perspective on H_2 purification, compression, storage and distribution

Summary on H_2

- Regarded as important intermediate energy vector, because:
  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 interest now for **heavy duty** mobility and **heavy** industry
- Different electrolyser technologies will co-exist. The main challenges are:
  1. large scale deployment (TWe capacity is needed) : manufacturing, materials, footprint
  2. storage, and transport, of H_2 (volume, weight)
  3. Compression and liquefaction are very energy intense; alternative compression technologies specific to H_2 are being developed. H_2 as very light gas has a negative Joule-Thomson coefficient at ambient T.

A potential roadmap of Power-to-X technologies

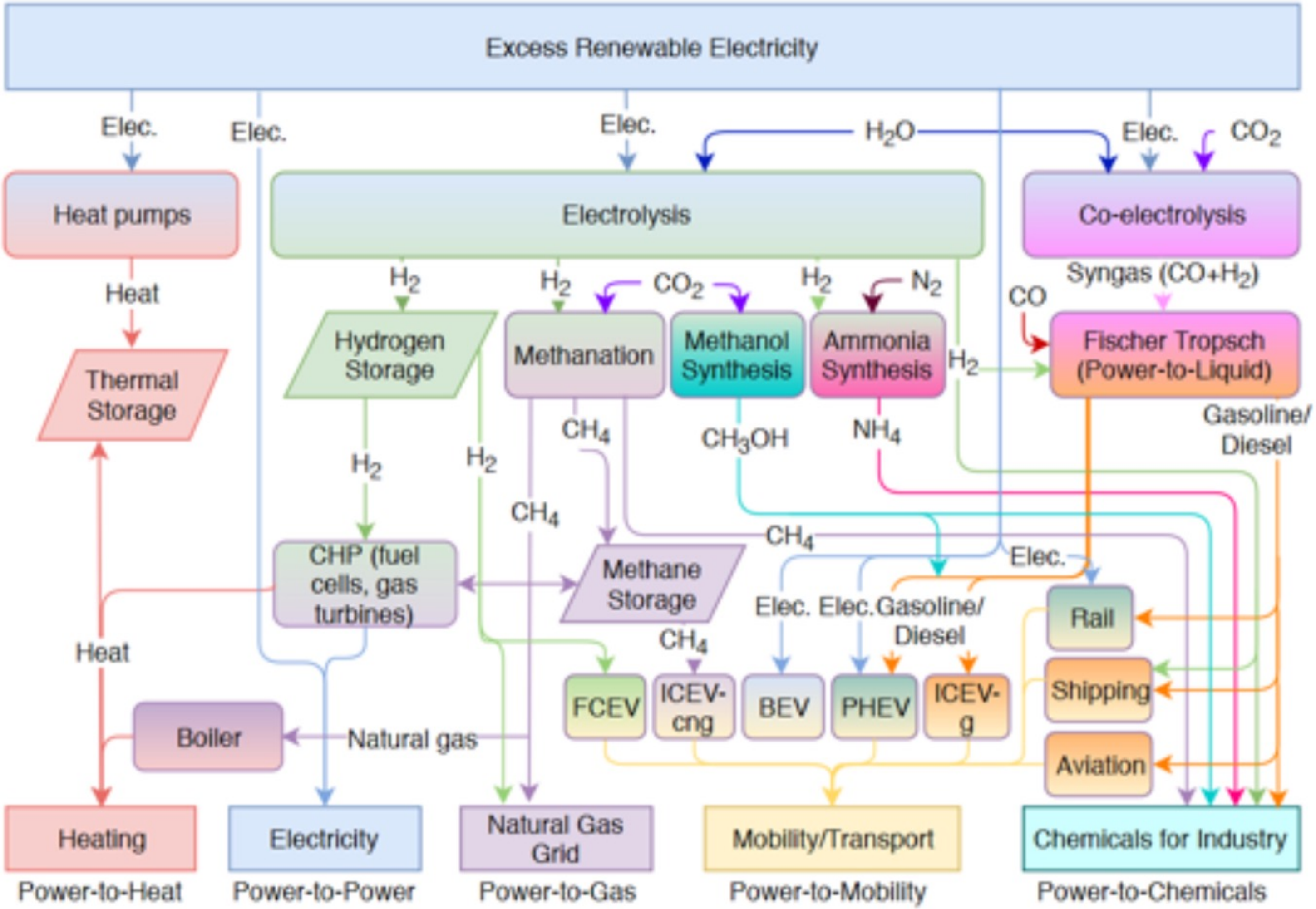


Figure 1.1 – Schematic representation of the power-to-X concept. Reprinted from [1].

Portia Murray. The Role of Power-to-X Technologies in Decentralised Multi-Energy Systems. Doctoral Thesis, ETH Zurich, 2020. URL https://www. research-collection.ethz.ch/handle/20.500.11850/403923. Accepted: 2020-03- 09T10:43:39Z.

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