Storage and Power-to-Gas

Learning objectives

- Electricity storage state-of-the-art
- Overview of H₂ uses, actual and potential
- Thermodynamics and efficiency of electrolysis
 - various technologies (water (H⁺ / OH⁻), steam)
 - heat integration
- Storage of H₂

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

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	Li-ion dominate
Lead acid	75 batteries schemes
Sodium metal halide	19
Flow battery	72
PSH	169,557
CAES	407
Flywheels	931
Electrochemical capacitor	49
Total	172,928

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



- = 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)

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, H₂)

Article

Projecting the Future Levelized Cost of **Electricity Storage Technologies**



Oliver Schmidt, Sylvain Melchior, Adam Hawkes, Jain

o.schmidt15@imperial.ac.uk

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

Excluding PHS & CAES, H₂ could be more cost-effective than batteries for discharges > 1 day



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%)
 - <u>maximal</u> 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 H₂ (=stored electricity) in energy and industry uses: present and future

Grey, blue, green H₂

- Grey H₂ : made from fossil sources
- Blue H₂ : made from fossil sources but including carbon capture
- **Green H**₂ : made from renewable sources

Annual H₂ production

≈75 Mt/yr ≈ 830 10⁹ m³ /yr ≈ 10 EJ (2800 TWh) = 2% of world energy

Global demand for pure hydrogen, 1975-2018

- 49% from natural gas
- 29% from oil
- 18% from coal
- 4% from electrolysis





 By comparison: natural gas 4000 10⁹ m³ /yr = 140 EJ (24% of world energy – 580 EJ)

Electrolytic H₂ : e.g. chlor-alkali-industry

- Production 2017: 58 Mton Cl₂ (650 plants)
- Elec. consumption: 2.1 3.4 kWhe / kg Cl₂
- (assume avg of 2.5 kWhe / kg Cl₂) => 150 TWhe
 ≈ 25-30 GWe worldwide
- ≈0.6% of world electricity (25 PWh)
- this co-produces 1.6 Mt H₂ = 54 TWh H₂, accounting for > $\frac{1}{2}$ of all electrolytic H₂

Chlor-alkali process (1888) 2NaCl + $2H_2O => 2NaOH + Cl_2 + H_2$



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

(Grey) H₂ production from fossil fuels



Linde, Texas, STR, HT-shift, PSA NG, 110000 m³/h, 99.99% pure H₂

Process	Reaction	∆H (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 H₂ (EU)

Total hydrogen use in the EU, in TWh





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

H₂ current uses

- Refineries (47%): hydrodesulphurisation (HDS), hydro-cracking to multiple useful oil fractions
- 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 (glass floating on liquid tin baths)
 - food (fats hydrogenation)
- 325 TWh or 1.2 EJ (2% of final EU energy)



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 H₂ uses

- Mobility : fuel cell vehicles
- Residential heating : natural gas network admixing, and/or H₂ pipelines
- Industry:
 - industry heating: replacing coal, natural gas
 - industry feedstock:
 - refineries
 - ammonia, methanol, other industries
 - steel making
 - light industries

Example: oil refinery

Rheinland refinery (Shell) (D)

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

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





https://refhyne.eu/



H₂ for steel making : DRI (direct reduced iron)



2 Polvmer electrolvte membrane electrolvsis/high temperature electrolvsis

Example: steel industry

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





2016 - 2022



| **FUEL CELLS AND HYDROGEN** 4.5 M€

720 kWe solid oxide steam electrolyser

200 Nm³/h H₂ (84% efficiency LHV)

100 t H₂ @ < 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

\rightarrow converting electricity to fuel gives the largest capacities

'Power-to-Gas' concept



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)





Monthey (VS)

Advantages :

- Mature technology
- Large capacity (1400 Nm³/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



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) :

$$H_2 O_{(l)} \rightarrow \frac{1}{2} O_{2(g)} + 2H^+ + 2e^-$$

At fuel electrode (cathode) :

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

Advantages :

- High current density
- Wide load range
- Fast dynamics

Limitations:

- scarce and expensive materials

(noble metal catalysts; treated Ti interconnect)

- gas crossover



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



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, CO₂)



Solid-oxide system development & manufacturers



HALDOR TOPSOE

Thermodynamics of splitting steam vs water

	Reaction	∆H (kJ/mol)	MJ / Nm ³	kWh / Nm³
Water	$H_2 O(l) \Longrightarrow H_2 + \frac{1}{2}O_2$	286	12.77	3.55
Steam	$H_2O(g) \Rightarrow H_2 + \frac{1}{2}O_2$	—ΔH _{evap} 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



Electrolysis technology comparison



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)



AEMEL : combination of PEMEL and classical alcaline

(graph : Dr Heron Vrubel)

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

5. Recent: proton conducting ceramic electrolyser (PCCEL)



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 H₂ product

SOE (Solid Oxide Electrolysis) based Power-to-CH₄



P2G : H₂ or CH_4 ?

H ₂	CH ₄
 1-step synthesis mobility without CO₂ 	 2-step synthesis Need CO₂ 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?

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



with 1 bio m³ gas (10 TWh), the Swiss winter electricity gap would be covered (i.e. a deficit of ~1 TWhe / month).

H₂ storage methods

- as compressed H₂ gas (=> 1000 bar)
- as liquid H_2 (1 bar)
 - optional: further cryocompression of liq H_2
- as physically adsorbed H₂-layer on high surface area materials
 - sorption increases at low T
- as H in hydrides
 - solid solution \rightarrow hydride H (interstitial H up to intermetallic)
 - complex hydrides (e.g. NaBH₄)
- as H in other chemical compound
 - LHOC (liquid hydrogen organic carrier)
 - NH_3 etc.

H₂ storage overview

(figure: Leonardo Gant)



under dvpmt

H₂ storage : compressed gas, and liquid



(figures: Leonardo Gant)

Pressurized H₂

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

(water : 1000kg/m³ !)



slide from Prof A Züttel, EPFL

Compression work

- ideal isothermal work_{id} $(J/kg) = p_0V_0 \ln(p_1/p_0)$
- adiabatic work_{ad} = $(\gamma/\gamma 1) p_0 V_0 ((p_1/p_0)^{(\gamma-1)/\gamma} 1)$

V_o initial volume(m³/kg) (11.11 m³/kg for H₂, 1.39 m³/kg for CH₄) p₀ initial pressure, p₁ final pressure, $\gamma = C_p/C_v$ (1.41 for H₂, 1.31 for CH₄)

@200 bar (W_{ad}): for CH₄ 2 MJ/kg (2% HHV), for H₂ <u>14</u>
 MJ/kg (10% HHV)



Joule-Thomson coefficient

isenthalpic expansion/compression:



Joule-Thomson Effect



At ambient T, H₂ must be cooled for filling (expansion), and heated when compressing. At cryo-conditions (e.g. 77K and lower), it is the opposite.

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: lowest volumetric density:

140 MJ/**kg** 0.011 MJ/**L**

(496.0 moles) (1/22.4th of a mole = 0.0446 mole)

H₂ compression technologies overview

- Mechanical: volume flow for H₂ is confined by a displacement device
 - 1. reciprocating piston
 - 2. diaphragm
 - 3. linear (magnetic)
 - 4. ionic liquid
- Non-mechanical : specifically designed for H₂ application
 - 1. cryogenic
 - 2. electrochemical (mass flow)
 - 3. adsorption (thermal)
 - 4. metal-hydride (thermal)

In terms of H₂-economy ('pack, distribute, store, deliver'), the cheapest solution today is: H₂-gas compression + truck-delivery (for small stations); in carbon-/glass fiber storage tanks to reduce weight: best values 1-2wt% @250 bar (steel), to 6wt% @700 bar (composite), and 30g H₂/L (still below the US-DOE targets of 40 g/L and 5.5wt%)

Non-mechanical compressors

- Cryogenic compression of liquefied H₂
- Electrochemical compression
- Thermally driven:
 - Adsorption of H₂ on high surface materials
 - Metal-hydride

Liquefaction work

300K

+703 kJ/kg (ortho-para)

 $(T_{\rm a}-T_{\rm e})$

 $T_{\rm e}$

20K

As Carnot cycle with a heat sink at 300 K, the ideal work of liquefaction is $W_{\rm L} = \Delta H$ W_L = 13 MJ kg⁻¹ (3.6 kWh kg⁻¹) for LH₂ 225 kJ/kg (evap)

298 K \rightarrow 20 KMJ need per kg liquid H2Referencetheoretical requirement13 (10% of HHV)Carnotusual scale54182 kg / h, Linde plant (D)large scale362000 kg / h, USAultimate scale30-2512000 kg/h, study case



Hydrogen Liquefaction Plant Capacity [kg/h]

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

Electrochemical 'pump'



At LP electrode:

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

At HP electrode:

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

Minimum voltage:



Theoretically only 84 mV needed to raise from 1 to 700 bar. (In(700)=6.55) However, ohmic drop and overpotentials increase the voltage. Achieved: 140 mV for 50 bar @0.2A/cm² => 0.3 kWh/Nm³ v. low consumption

Metal hydride compression



slide from T Macherel, EPFL

see GRZ Technologies company

H₂ compression overview

	Piston	Membrane	Screw	Electro- chemical	Metal- hydride	lonic 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 EFCF July 2019: Industrial perspective on H₂ purification, compression, storage and distribution

Chemical H-storage

- Formic acid or formate
- NH₃
- LOHC (liquid organic hydrogen carriers)
- . . .

Hydrogen Storage Density comparison



Energy density of fuels overall



Comparison H₂ storage

	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 (NaAlH₄)	7.7 (MgH ₂)
Т	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 EFCF July 2019: Industrial perspective on H₂ purification, compression, storage and distribution

Summary on H₂

- 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 likely co-exist. The main challenges are:
 - 1. large scale deployment (TWe capacity will be 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.

Reminder about the exam

- Saturday June 28th 9h15-12h15 sorry 100
- Room CE 1 6
- Only bring the formula memento, a calculator and a pen
 - do not write anything extra on the formula memento
- No electronic communication devices
- Multiple choice questions on general understanding (principles, pro's/con's, comparisons, applications)
 - Wrong answers are not counted negative
 - the exception is when there are multiple correct answers possible in a question (to avoid that you tick too many boxes to increase 'chances')
- ~short calculation exercices
- Know the scales (orders of magnitudes) and efficiencies (%)
- Know how to handle and convert energy units (PJ, kWh, oilequivalent,...)

have a look at our website for semester/master projects 🤐

gem.epfl.ch

