Hydrogen production and storage

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OUTLINE

- Brief overview of energy storage and conversion systems
- Hydrogen storage
 - o Types
 - $\circ~$ Physical storage
 - Chemical storage metal hydrides
 - Example
- Hydrogen production
 - o Means
 - Water splitting (HER)
 - Examples on metals and alloys
- Hydrogen fuel to electricity coversion
 - The proton exchange membrane fuel cell (PEMFC)
 - Components
 - Durability issues
- Conclusions

Overview of energy storage and conversion technologies

Discharge time as a function of system size



Hydrogen has the largest potential for large-scale energy storage, which for chemical storage is far out of the scale in the figure.

H is the most abundant element and accounts for ~15 mol% on the surface of earth, e.g. in water, fossil fuel, and biomass.

K. T. Möller et al. Prog. Nat. Sci. 27 (2017) 34

Joint EPS-SIF International School on Energy

Hydrogen storage



Very low density: 1 kg of H₂(g) occupies 11 m³ at RT and atmospheric pressure

Storage density must be increased







H₂-binding materials



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J. Andersoon and S. Grönkvist, Int. J. Hydrog. Energy 44 (2019) 11901

*based on the nature of the interaction between the stored hydrogen and the storage vessel or material

Physical storage of $H_2(g)$ and $H_2(l)$

The one currently employed on any significant scale

Examples: H₂(I) in space industry Large salt cavity caverns in Texas (USA) and Teeside (UK)







A. Ozarslan, Int. J. Hydrog. Energy 37 (2012) 14265

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NASA

Storage of compressed H₂(g)

- Large amounts of H₂(g) are usually NOT stored at p>100 bar in aboveground vessels and p>200 bar in underground storages.
- At 100 bar and 20 °C, the density of H₂(g) is ~7.8 kg/m³.
- First FCVs utilized an onboard storage pressure of 700 bar.
- Alternatives to salt cavity storages are metallic pipes.



G. Sdanghi et al. *Renew. Sust. Energ. Rev.* 102 (2019) 150

Storage of liquid H₂(g)

- The density of pure hydrogen may also be increased by <u>liquefaction</u> (condensation).
- At 100 bar and 20 °C, the density of H₂(g) is ~7.8 kg/m³. The density of sat. H₂(l) at 1 bar is 70 kg/m³ → distribution medium
- Drawback: liquefaction is energyintensive
 - \circ T_b = -253 °C at 1 bar
 - Precooling with N₂(l) since H₂ does not cool down during throttling processes at T>73 °C



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- Evaporation should be minimized following storage
 - Loss of energy
 - Pressure build-up inside the storage vessel → venting
 - Loss of stored H₂ over time: boil-off. It is quantified as the % of stored H₂ lost per day (boil-off rate)
 - Cold boil-off gas from the storage vessel(s) may be injected back into a late stage of the liquefaction process using an ejector

Storage of liquid H₂(g)



Cape Canaveral 230–270 t

NASA release on Dec 19. 2018



in the metal hydrides \rightarrow chemical bonds stronger than physical bonds

- Stronger bonding allows storing at high density even at ambient conditions.
- ΔE is needed to release the chemically bonded hydrogen.
- Release achieved by:
 - Heating (thermolysis)
 - Endo, reversible in same cases, solid state phase, elevated T
 - MgH₂, AlH₃
 - Reaction with water (hydrolysis)
 - Exo, irreversible, in solution, might be spontaneous at RT
 - NaBH₄

Example: MgH₂

Advantages

- High theoretical hydrogen storage capacity: 7.6% wt.%
- Mg⁰ is widely available at low cost

× Drawbacks

- ΔH dehydrogenation is ~75 kJ/mol
- Kinetics of both hydrogenation and dehydrogenation reactions are sluggish → T > 300 °C must be applied to dehydrogenate pure MgH₂ at a reasonable rate

Improvements

- Nanoconfinement
- Particle size reduction by ball milling
- Alloying
- Addition of TM additives
- Compaction with expanded natural graphite (ENG) to improve *k*









Example: MgH₂



Example: MgH₂

Hydriding kinetics

Sample	Gravimetric capacity (wt.% H ₂)	Sorption efficiency (%)	V _{abs} , _{6%} (wt.% H ₂ /min)	v _{des,6%} (wt.% H ₂ /min)
Pure MgH ₂	7.0	92	3.00	0.41
$MgH_2 + Co_3O_4$	6.1	84	1.26	0.71
$MgH_2 + NiCo_2O_4$	6.2	85	2.72	1.66
$MgH_2 + NiO$	6.4	88	8.00	2.93

H ₂ ABSORPTION	E _{att} (KJ/mol)	57 pure MgH ₂	50 NiO-doped MgH ₂
H ₂ DESORPTION	E _{att} (kJ/mol)	345 pure MgH_2	335 NiO-doped MgH_2

M. Cabo et al. Int. J. Hydrog. Energy 36 (2011) 5400



Hydrogen production (water splitting)

H₂ production: overview (I)



H₂ production: overview (II)

The development of clean, sustainable, and cost-competitive hydrogen production processes is key to a viable future hydrogen economy. Hydrogen production technologies fall into three general categories: thermal processes, electrolytic processes, and photolytic processes.

1. Thermal Processes

- Some thermal processes use the energy in various resources, such as natural gas, coal, or biomass, to release hydrogen, which is part of their molecular structure. In other processes, heat, in combination with closed-chemical cycles, produces hydrogen from feedstocks such as water—these are known as "thermochemical" processes.
 - Reforming of Natural Gas
 - Gasification of Coal
 - Gasification of Biomass
 - Reforming of Renewable Liquid Fuels
 - High-Temperature Water Splitting

H₂ production: overview (III)

- 2. Electrolytic Processes
 - Electrolytic processes use electricity to split water into hydrogen and oxygen, a process that takes place in an electrolyzer. Hydrogen produced via electrolysis can result in zero greenhouse gas emissions, depending on the source of the electricity used. The source of the required electricity—including its cost and efficiency, as well as emissions resulting from electricity generation—must be considered when evaluating the benefits of hydrogen production via electrolysis. The two electrolysis pathways of greatest interest for wide-scale hydrogen production, which result in near-zero greenhouse gas emissions, are electrolysis using renewable sources of electricity and nuclear high-temperature electrolysis.

3. Photolytic Processes

- Photolytic processes use light energy to split water into hydrogen and oxygen. Currently in the very early stages of research, these processes offer long-term potential for sustainable hydrogen production with low environmental impact.
 - Photobiological Water Splitting
 - Photoelectrochemical Water Splitting



Electrolytic processes: HER on metal electrodes



J. Peng et al. Mater. Today Adv. 8 (2020) 100081



Electrolytic processes: HER on metal electrodes

 $2H^+(aq) + 2e^- \rightarrow H_2$ Multi-step electrochemical reaction

1) Electrochemical hydrogen adsorption (Volmer reaction)

 $H^+(aq) + M + e^- \rightarrow M - H^*$ (acid solution) $H_2O + M + e^- \rightarrow M - H^* + OH^-$ (alkaline solution)

2) Electrochemical desorption (Heyrovsky reaction)

 $M-H^* + H^+(aq) + e^- \rightarrow M + H_2 \text{ (acid solution)}$ $M-H^* + H_2O + e^- \rightarrow M + OH^- + H_2 \text{ (alkaline solution)}$

OR

3) Chemical desorption (*Tafel reaction*) $2M-H^* \rightarrow 2M + H_2$ (both acid and alkaline solutions)

1), 2), 3) depend on (electro)chemical and electronic properties of M

Electrolytic processes: HER on metal electrodes

Experimental set-up

Taken from Jaramillo's group



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Electrolytic processes: HER on metal electrodes

Taken from Jaramillo's group

Electrochemical reaction kinetics

The big question: How much current do I achieve for the amount of overpotential that I apply?

Depends on two major factors (as with any chemical reaction):

- (1) The inherent kinetics of the reaction.
- (2) Effects of mass-transfer.

 $i = i_o \{ \exp\left[\frac{\alpha_a n F \eta}{RT}\right] - \exp\left[-\frac{\alpha_c n F \eta}{RT}\right] \}$ i = current density i_o = exchange current density i_o = exchange current density n = # of electrons transferred a = transfer coefficient (anodic or cathodic) F = Faraday's constant: 96,485 C/mol n = (E - E_{equil}) = overpotential R = gas constant

- Assumes only one step is rate-determining
- If near equilibrium, both terms are important.
- If farther from equilibrium, one term dominates... can use the <u>Tafel Equation</u>!

$$i_a = i_o \exp(\frac{\eta}{b})$$
$$i_c = -i_o \exp(-\frac{\eta}{b})$$

where b = Tafel slope

T = temperature

The Butler-Volmer Equation

Electrolytic processes: HER on metal electrodes

Electrocatalyst activity: figures of merit

Taken from Jaramillo's group



Electrolytic processes: HER on metal electrodes

Tafel plots for various HER catalysts

Taken from Jaramillo's group



Chen Z, Jaramillo T.F., et al. NanoLetters 11, 10 (2011)

Electrolytic processes: HER on metal electrodes

Towards quantitative 'descriptors' for catalysis

Taken from Jaramillo's group

 Paul Sabatier (1911):
 An optimal catalyst will bind reaction intermediates moderately on its surface; not too strongly nor too weakly.

Roger Parsons (1957): The first 'qualitative' volcano in electrocatalysis, indicating that the best HER catalysts should exhibit $\Delta G_H \approx 0$ eV.



Electrolytic processes: HER on metal electrodes

Star material for HER: Platinum (high j_0 and small Tafel slope) - Activity well studied as a function of (*hkl*)

.... Drawbacks: high cost and insufficient Pt reserves imes

Other candidates: Fe, Co and Ni alloys, semiconductors (MoS₂), TMPs... \checkmark

Current trend: modify, partially or fully replace Pt while keeping a resonably high activity towards HER

-Increase of surface area (porous films, NPs, NWs...)



Electrolytic processes: HER on metal hydr(oxy)oxide electrodes Pt(111) modified with 3d-M metal hydr(oxy)oxide clusters



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HER on high surface area metallic electrodes

Copper-nickel





HER on high surface area metallic electrodes

Copper-nickel

Theory: Metals with more unpaired electrons in the *d*band interact strongly with electron-donating adatoms or molecules

 \rightarrow Ni shoud be more active than Cu!

log (i₀ (A/cm²_{metal}))

-5

-6

-0.8

-0.6

-0.4

-0.2

∆E_u (eV)

0.0

 $H_2O + M + e^- \rightarrow M - H^* + OH^-$ (alkaline solution)



HER on high surface area metallic electrodes

Copper-cobalt-phosphorous (phosphides)



P boosted HER performance in KOH \rightarrow chemical shifting of metal–P bonds \rightarrow charge separation between the negatively charged P (δ^{-}) and positively charged Cu and Co (δ^{+}) \rightarrow decrease of HER overpotential.

Y.S. Park et al. ACS Sustainable Chem. Eng. 7 (2019) 10734

H⁺ could be trapped by the small negative charge of P atoms on the surfaces of metal phosphides



HER on high surface area metallic electrodes





HER on high surface area metallic electrodes

medium: 0.5 M H_2SO_4 2H⁺(aq) + 2 $e^- \rightarrow H_2(g)$







HER on high surface area metallic electrodes

Metallization of (commercial) macroporous foams

e.g. polyurethane, Ni, Cu, etc.



HER on high surface area metallic electrodes

Metallization of (commercial) macroporous foams



(A) Low- and (B) high-magnification SEM images of Co/CoP-NF. (C) EDS elemental mapping images of elemental Co and P in Co/CoP-NF catalyst.

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NF = Ni foam
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N. Bai et al. ACS Appl. Mater. Interfaces 8 (2016) 29400



HER on high surface area metallic electrodes

• 0D (nanoparticles) and 1D (nanorods, nanowires) structures



HER on high surface area metallic electrodes

Durability





K. Hu et al. ACS Energy Lett.3 (2018) 1539

H₂ production: photolytic processes

Photoelectrochemical water splitting





Advantages:

O. Khaselev et al. Science 280 (1998) 425

- no wires / external electronics
- low-cost semiconducting absorbers
- direct energy storage in chemical bonds
- H₂ for fuel cells, turbines, liquid-fuel synthesis from CO₂
- closed-loop cycle

Disadvantages: Difficult to find right materials and to scale.

Proton exchange membrane fuel cells (energy conversion device)

The fuel cell (FC) Negative electrode (or anode) H_2 is fed to the anode sunlight 02 hydrolysis H_2 Water/ Heat H₂O Hydrogen -0 000 Öxygen **Fuel Cell** hydrogen hydrogen fuel cells storage Positive electrode (or cathode) Air is fed to the cathode 49





Table 1

Specifications for the latest FCEV models currently in production.

FCEV	Launch date	Mass (kg)	Fuel cell/ motor power (kW)	Power density (kW/L)	Acceleration time (s) 0–60 mph (100 km/h)	Fuel tank capacity (kg) (wt%)	Fuel pressure (MPa)	Estimated range (miles-km)	Fuel economy (kg hydrogen / 100 km)	Fuel consumption (mpg gasoline equivalent) ^a
Hyundai Nexo	2018	1873	95/120	3.10	9.5 (10)	6.33 (7.18 wt%)	70	370-595	0.84	57–61
Honda Clarity	2016	1875	103/130	3.12	9.2 (9.7)	5.46 (6.23 wt%)	70	366-589	0.97	67
Hyundai ix35 FCEV or Tucson FCEV	2014	1980	100/100	1.65	12.5 (13.2)	5.64 (6.43 wt%)	70	369-594	0.95-1.0	66
Toyota Mirai	2014	1850	90/114	3.10	9 (9.5)	5.0 (5.70 wt%)	70	312-502	0.76	67

FCEV, fuel cell electric vehicle.

For other FCEVs, see Pollet et al and Cano et al [1,2].

^a Compared with sales-weighted average fuel economy in the USA of 25-43 mpg, depending on the vehicle class.

B. J. Pollet et al. Curr. Op. Electrochem. 16 (2019) 90–95

Electrochemical energy storage and conversion (EESC) devices

Comparison of various electrochemical energy storage and conversion devices (*Ragone plots*)



Note that they are at the same time energy storage and conversion systems e.g. energy stored in the battery is converted to traction power for use by an AC motor with the aid of an onboard DC/AC converter.

M.E. Plonska-Brzezinska et al. J. Mater. Chem. 1 (2013) 13703

Electrochemical energy storage and conversion (EESC) devices



The electrical energy contained within a **battery** is either from the factory where it was made, or from charging the battery via an outlet. If your battery dies, you are dependent on either being near a source of electricity to re-charge, or near a store to buy a new one. A **fuel cell** takes an energy source, such as propane, diesel or natural gas, and converts it into electrical energy. As long as you have access to your energy source, you have access to electricity any time you need it.



S.P.S. Badwal et al. Front. Chem. 2 (2014) 79

Proton exchange membrane fuel cells – Electrode materials



Proton exchange membrane fuel cells – Electrode materials



Proton exchange membrane fuel cells – Electrode materials

Electrode structure



Proton exchange membrane fuel cells – Electrode materials



Proton exchange membrane fuel cells – Electrode materials

The catalyst

CO poisons the anode reaction through preferentially adsorbing to the Pt surface and blocking active sites:



S. Prass et al. *Molecules* 24 (2019) 3514

 Search for new materials to improve PEMFC efficiency → catalyst that is less susceptible to poisoning by CO, especially in low temperature fuel cell developments that use hydrogen coming from an alcohol or hydrocarbon fuel. Proton exchange membrane fuel cells – Electrode materials

The catalyst

Methods to mitigate the effect of CO poisoning:

- the use of a Pt alloy catalyst
- higher cell operating temperature or pressure
- introduction of oxygen into the fuel gas flow \rightarrow oxygen bleeding



Proton exchange membrane fuel cells – Electrode materials

The catalyst

In addition, oxygen reduction reaction (ORR) is more sluggish in PEMFCs than hydrogen oxidation and requires 3 to 5 times as much Pt. The high cost and scarcity of Pt have driven efforts to reduce Pt usage.



Proton exchange membrane fuel cells – Catalyst degradation

Simplified representation of suggested degradation mechanisms for Pt particles on a carbon support in fuel cells:



J. C. Meier, Beilstein J. Nanotechnol. 5 (2014) 44

Proton exchange membrane fuel cells – Carbon corrosion

Corrosion of C support causes pronounced detachment of Pt NPs and massive ECSA losses \rightarrow can be followed by Raman spectroscopy and differential electrochemical mass spectrometry (DEMS)

DEMS: Current versus potential curves were recorded simultaneously with the mass intensity versus potential curves, for selected values of the mass/charge (m/z) ratio.



Subject to accelerated stress test (AST) protocols mimicking load-cycling or start-up/shutdown events in a PEMFC

L. Castanheira et al, ACS Catal. 5 (2015) 2184



Degradation maximal for Pt/HSAC

The CO_2 produced during the carbon oxidation reaction is monitored at m/z = 44 (CO_2^+)

Proton exchange membrane fuel cells – Catalyst degradation

Activity loss during long-term operation caused by:

Pt agglomeration and particle growth (e.g. by Ostwald ripening)





TEM images of Pt/Vulcan 3–4 nm catalyst before and after 5000 potential cycles between 0.4 and 1.4 VRHE in 0.1 M $HClO_4$ (scan rate 1 V s⁻¹, room temperature). Green circles indicate examples for agglomeration of Pt nanoparticles. The particle size distributions before and after 5000 degradation cycles indicate both particle growth and dissolution to occur.

J. C. Meier, Beilstein J. Nanotechnol. 5 (2014) 44

Proton exchange membrane fuel cells – Catalyst degradation

Activity loss during long-term operation caused by:

- Pt agglomeration and particle growth (e.g. by Ostwald ripening)
- Pt loss and migration
- Active sites contamination (poisonous effects aroused by contaminants)

The redistribution of Pt nanoparticles is actually a complex process involving (1-3):

(2)

Platinum dissolution :
$$Pt_{(s)} \rightarrow Pt_{(*)}^{2+} + 2e^{-}$$
 (1)

The process of Pt dissolution most likely occurs on the cathode side.

Platinum oxide formation :
$$Pt_{(s)} + H_2O \rightarrow PtO_{(s)} + 2H_{(*)}^+ + 2e^-$$

Platinum oxide dissolution : $PtO_{(s)} + 2H_{(*)}^{+} \rightarrow Pt_{(*)}^{2+} + H_2O$ (3)

$$Pt_{(*)}^{z+} + \frac{z}{2}H_{2(g)} \to Pt_{(s)} + zH_{(*)}^{+}$$
 (

Pt^{z+} species are chemically and
 electrochemically reduced to Pt particles by H₂ that has crossed over the PEM and cathode.

* Denotes ionic species present in water or in the ionomer phase.

Proton exchange membrane fuel cells – Catalyst degradation

Activity loss during long-term operation caused by:

Active sites contamination (poisonous effects aroused by contaminants)

Gas contaminates from the fueland the air CH_4 , CO, CO_2 , H_2S , NH_3 , NO, NO_2 , SO_2 , SO_3 , and O_3



System-derived contaminants Trace amounts of metallic ions or silicon from system components (e.g., bipolar metal plates, membranes, and sealing gaskets)

Physical/chemical and electrochemical investigation methods employed during the catalyst degradation research

	Technologies	Characteristics	Information of the catalyst layer
	TEM (transmission electron microscopy) SEM or FEG-SEM or SEM-EDS (scanning electronic microscopy or Field-emission gun scanning electron microscopy or scanning electron microscopy combined	Morphology or Pt distribution analysis	Topography investigation and particle size distribution Topography investigation and elemental distribution analysis of a cross section of an MEA or CL
hysical/chemical methods	with energy dispersive spectroscopy) AFM (atomic force microscopy) or CP-AFM (conductive probe atomic force microscopy) Optical micrography 3-D X-ray CT (3D X-ray computer tomography)		Morphology of the surface of the carbon substrate Dispersion of Pt/C catalyst on glassy carbon disk electrodes Investigate changes in the internal morphology, Pt distribution and
	EPMA (electron probe micro-analysis)		carbon content, etc. Characterize the Pt content through the cross-section of the MEA
	AAS (atomic adsorption spectroscopy) ICP or ICP-AES or ICP-MS (inductively coupled plasma or inductively coupled plasma combined with atomic emission spectrometry or inductively coupled plasma combined with	Elemental content analysis	Investigate the Pt content in the Pt/C catalyst Investigate the amount of metal content
	mass spectrometry) TGA-MS (thermal gravimetric analysis coupled with on-line mass spectrometry) UV (ultraviolet spectroscopy)		Characterize the oxygen content of electrochemically oxidized Vulcan carbon support Detect the presence of Pt ²⁺ ionic species (z = 2,4) in decantation
	XAS (X-ray absorption spectroscopy)	Atomic structure analysis	Give information about the atomic structure of the catalyst, mainly of the surface atoms
	XPS (X-ray photoelectron spectroscopy)		Surface oxygen content or electronic structure change of other surface elements
	LRS (laser Raman spectroscopy)		Detect the degree of structural disorder of carbon
	XRD (X-ray diffraction)		Pt particle average sizes and crystallinity of alloy materials analysis

S. Zhang et al. *J. Power Sources* 194 (2009) 588

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Physical/chemical and electrochemical investigation methods employed during the catalyst degradation research

10

0

-10

-20

-30

0.0

Current density, mA/cm²



Cyclic voltammogram of PEM fuel cell catalyst layer for ECSA analysis by hydrogen adsorption/desorption. Conditions: Scan rate = 40 mV/s; Cell: 35 °C; 100% RH anode/cathode; 1 atm.

K.R. Cooper, Fuel Cell Magazine, Jan/Feb 2019

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Physical/chemical and electrochemical investigation methods employed during the catalyst degradation research

nemical methods	IV (polarization curve) LSV (linear sweep voltammetry)	Potential or current scanning	Characterize cell performance by potential vs. current density under specialized conditions Obtain some detailed information about the degradation mechanism
	CV (cyclic voltammetry) COSV (CO-stripping voltammetry) EIS (electrochemical impedance spectroscopy)	CV based scanning Impedance	by position shift of the potential peak Determine the ECSA of Pt by hydrogen adsorption Determine the ECSA of Pt by CO oxidation Characterize the polarization resistance (especially for ohmic resistance and charge transfer
	10		
$\frac{q_{Pt}}{r} \cdot L$	ensity, mA/cm ²	di charging k-ove	
educe a on Pt	D -20	The shaded area density due to during the rever	a is the charge H adsorption rse scan and is
; in the		used in the ECSA	A calculation

0.1

0.0

0.2

 $ECSA(cm_{Pt}^{2} / g_{Pt}) = \frac{q_{Pt}}{\Gamma \cdot L}$

Electroch

Γ: charge required to reduce a monolayer of protons on Pt (210 μ C/cm² _{Pt}) L: Pt content or loading in the electrode, in g_{Pt}/cm² _{electrode}

K.R. Cooper, Fuel Cell Magazine, Jan/Feb 2019

Potential, V vs. RE/CE

0.3

0.4

CONCLUSIONS

- Hydrogen based economy can be (or is) a reality.
- Hydrogen can be stored using different means. Physical storage still dominates but there has been an incredible progress in chemical storage pathways.
- Hydrogen production by water splitting can be entirely green if electrical energy comes from renewable sources. There is a need to find cheaper and affordable catalysts.
- The FCV is already a reality and its market will increase in the forthcoming years. Powering of other devices is anticipated.

Thank you for your attention

UAB

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