UNIVERSITÀ
DEGLI STUDI
DI TRIESTE

Dipartimento di
Ingegneria
e Architettura

ELECTROLYZERS

WORKING PRINCIPLES AND CHARACTERIZATION

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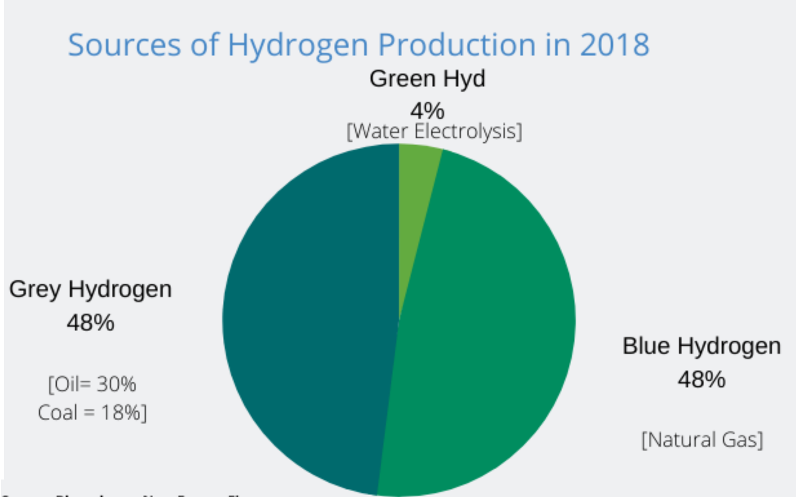
A.A. 2023-2024

HYDROGEN PRODUCTION

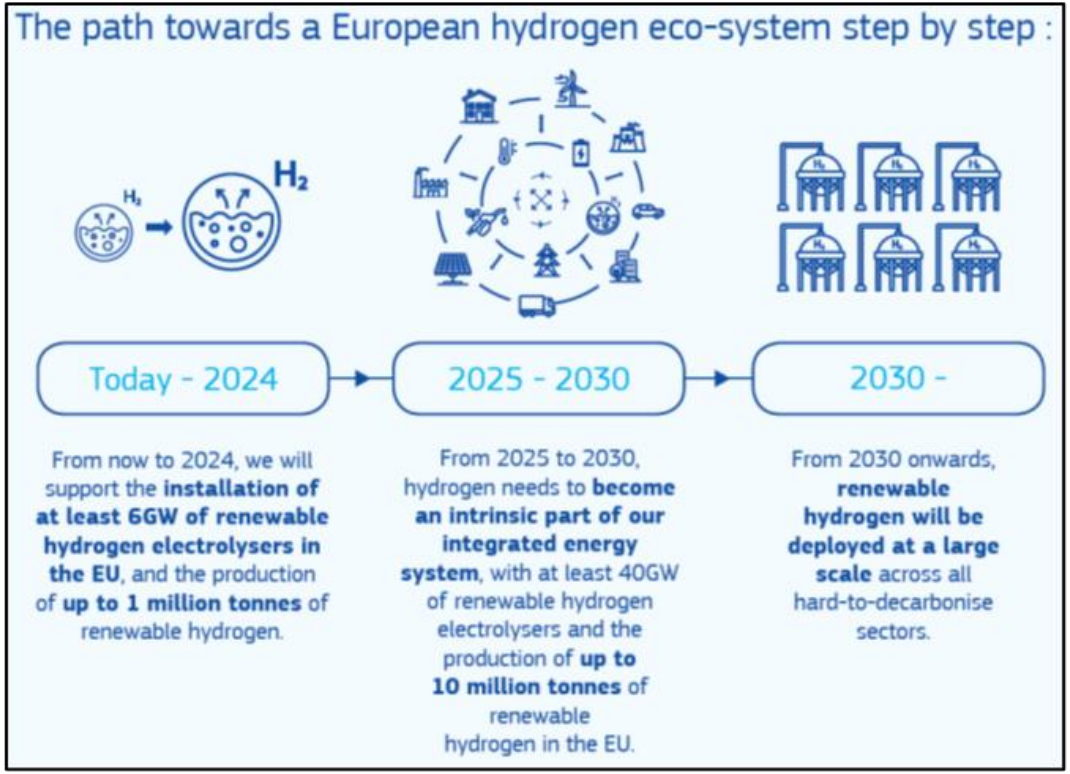
Hydrogen can be produced by both renewable and non-renewable sources of energy. Nowadays, the most predominant methods for producing hydrogen still rely on non-renewable energy sources (> 90%).
One method by which greenhouse gases emission due to hydrogen production can be minimized is by using solar or some other form of renewable energy source as the primary energy requirement for the hydrogen production.



Source: Bloombaerg New Energy Finance

Hydrocarbon (*e.g.* methane) steam reforming power supplied by non-renewable energy sources	Grey hydrogen / carbon emission released in atmosphere Blue hydrogen / carbon emissions captured and store
Derived from other production methods (mainly at prototypal stage)	Brown, Turquois, … hydrogens
Water splitting	Green hydrogen / no carbon emissions

HYDROGEN PRODUCTION – THE EU PLAN



The path towards a European hydrogen eco-system step by step :

Today - 2024 → **2025 - 2030** → **2030 -**

From now to 2024, we will support the **installation of at least 6GW of renewable hydrogen electrolysers in the EU**, and the production of **up to 1 million tonnes** of renewable hydrogen.

From 2025 to 2030, hydrogen needs to **become an intrinsic part of our integrated energy system**, with at least 40GW of renewable hydrogen electrolysers and the production of **up to 10 million tonnes** of renewable hydrogen in the EU.

From 2030 onwards, **renewable hydrogen will be deployed at a large scale** across all hard-to-decarbonise sectors.

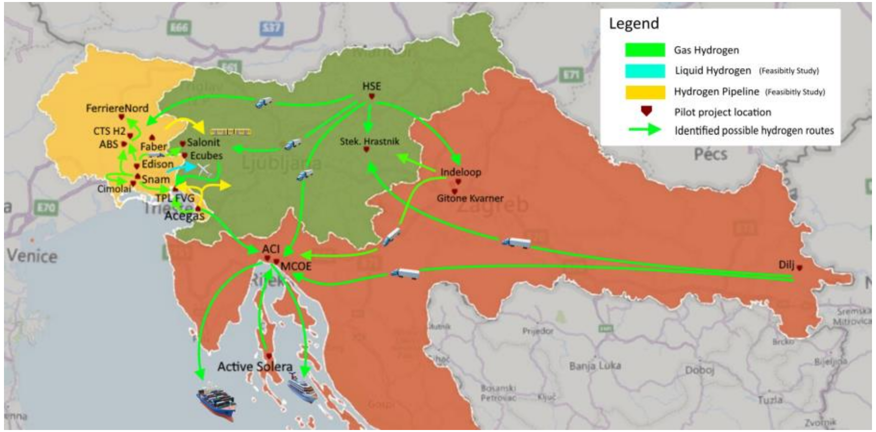
European Commission 2020

HYDROGEN PRODUCTION – THE EU PLAN – HYDROGEN VALLEYS

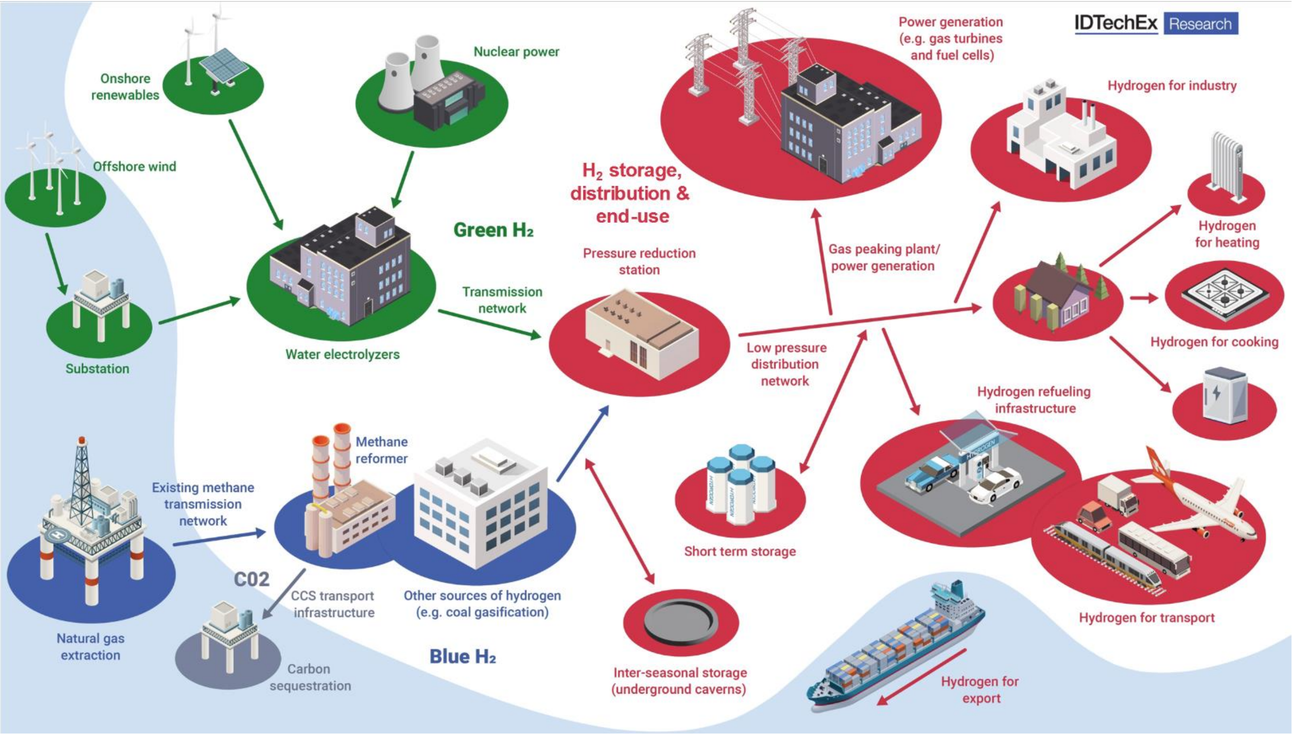
A hydrogen valley is a regional initiative that aims to develop a hydrogen ecosystem, including hydrogen **production, storage, distribution, and utilization**, within a **defined geographical area**. The idea behind a hydrogen valley is to create a localized cluster of companies, research institutions, and public authorities that work together to promote the use of hydrogen as a clean energy vector.

Weichenhain U. *et al*, (2021) Insights, Luxembourg: Publications Office of the EU

North Adriatic Hydrogen Valley



HYDROGEN PRODUCTION WITHIN THE HYDROGEN VALUE CHAIN



https://www.idtechex.com/es/research-report/hydrogen-economy-2023-2033-production-storage-distribution-and-applications/946

GREEN HYDROGEN PRODUCTION METHODS

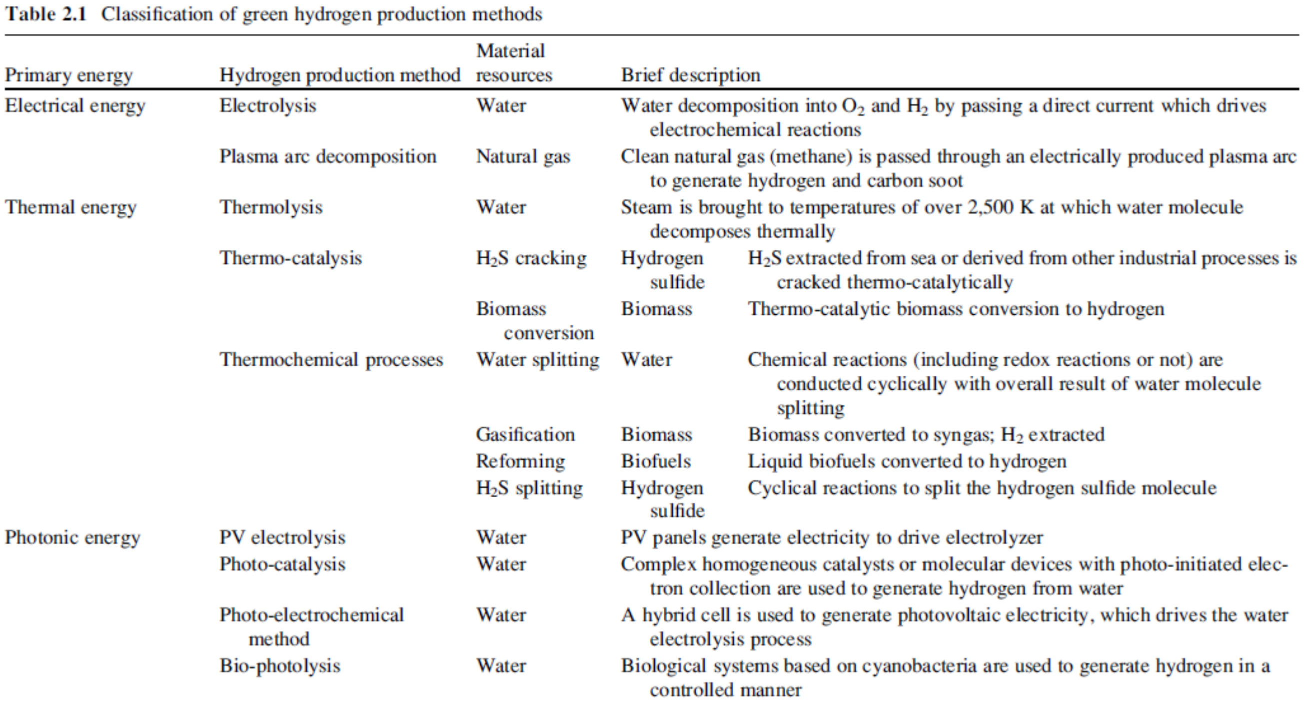
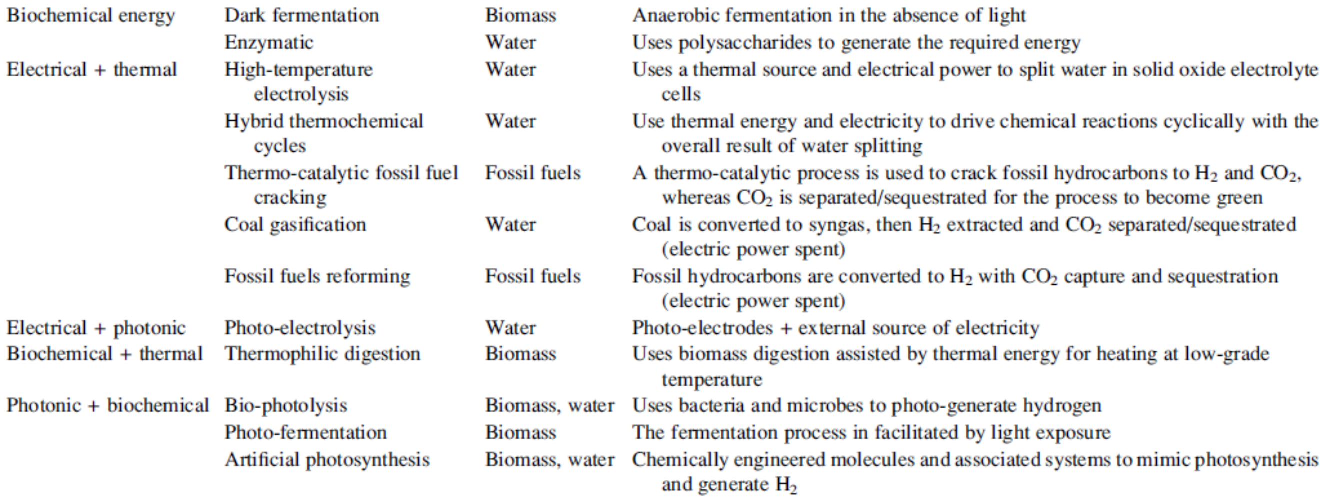


Table 2.1 Classification of green hydrogen production methods

Primary energy	Hydrogen production method	Material resources	Brief description	
Electrical energy	Electrolysis	Water	Water decomposition into O_2 and H_2 by passing a direct current which drives electrochemical reactions	
	Plasma arc decomposition	Natural gas	Clean natural gas (methane) is passed through an electrically produced plasma arc to generate hydrogen and carbon soot	
Thermal energy	Thermolysis	Water	Steam is brought to temperatures of over 2,500 K at which water molecule decomposes thermally	
	Thermo-catalysis	H_2S cracking	Hydrogen sulfide	H_2S extracted from sea or derived from other industrial processes is cracked thermo-catalytically
		Biomass conversion	Biomass	Thermo-catalytic biomass conversion to hydrogen
	Thermochemical processes	Water splitting	Water	Chemical reactions (including redox reactions or not) are conducted cyclically with overall result of water molecule splitting
		Gasification	Biomass	Biomass converted to syngas; H_2 extracted
		Reforming	Biofuels	Liquid biofuels converted to hydrogen
		H_2S splitting	Hydrogen sulfide	Cyclical reactions to split the hydrogen sulfide molecule
Photonic energy	PV electrolysis	Water	PV panels generate electricity to drive electrolyzer	
	Photo-catalysis	Water	Complex homogeneous catalysts or molecular devices with photo-initiated electron collection are used to generate hydrogen from water	
	Photo-electrochemical method	Water	A hybrid cell is used to generate photovoltaic electricity, which drives the water electrolysis process	
	Bio-photolysis	Water	Biological systems based on cyanobacteria are used to generate hydrogen in a controlled manner	

GREEN HYDROGEN PRODUCTION METHODS



Biochemical energy	Dark fermentation	Biomass	Anaerobic fermentation in the absence of light
	Enzymatic	Water	Uses polysaccharides to generate the required energy
Electrical + thermal	High-temperature electrolysis	Water	Uses a thermal source and electrical power to split water in solid oxide electrolyte cells
	Hybrid thermochemical cycles	Water	Use thermal energy and electricity to drive chemical reactions cyclically with the overall result of water splitting
	Thermo-catalytic fossil fuel cracking	Fossil fuels	A thermo-catalytic process is used to crack fossil hydrocarbons to H_2 and CO_2, whereas CO_2 is separated/sequestrated for the process to become green
	Coal gasification	Water	Coal is converted to syngas, then H_2 extracted and CO_2 separated/sequestrated (electric power spent)
	Fossil fuels reforming	Fossil fuels	Fossil hydrocarbons are converted to H_2 with CO_2 capture and sequestration (electric power spent)
Electrical + photonic	Photo-electrolysis	Water	Photo-electrodes + external source of electricity
Biochemical + thermal	Thermophilic digestion	Biomass	Uses biomass digestion assisted by thermal energy for heating at low-grade temperature
Photonic + biochemical	Bio-photolysis	Biomass, water	Uses bacteria and microbes to photo-generate hydrogen
	Photo-fermentation	Biomass	The fermentation process in facilitated by light exposure
	Artificial photosynthesis	Biomass, water	Chemically engineered molecules and associated systems to mimic photosynthesis and generate H_2

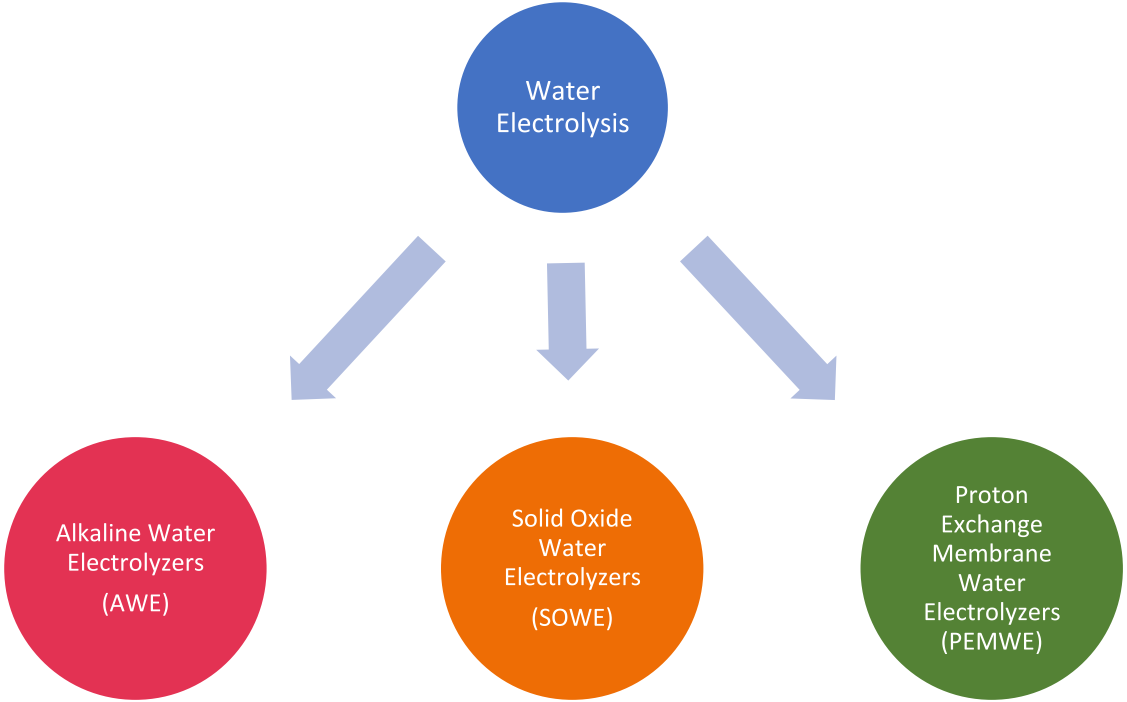
ELECTROLYSIS

Electrolysis is a technique that uses direct electric current to drive an otherwise non-spontaneous chemical reaction.

It is already used for different industrial purposes:

- In metallurgy, for extracting metals from ores, for metal purification, for metal deposition, for metal manufacturing, etching or polishing.
- For production of chemical compounds, such as NaOH, $NaClO_3$, $KClO_3$, or perfluorinated organic compounds, in example.
- For hydrogen production, starting from H_2O.

WATER ELECTROLYSIS



Water Electrolysis

Alkaline Water Electrolyzers

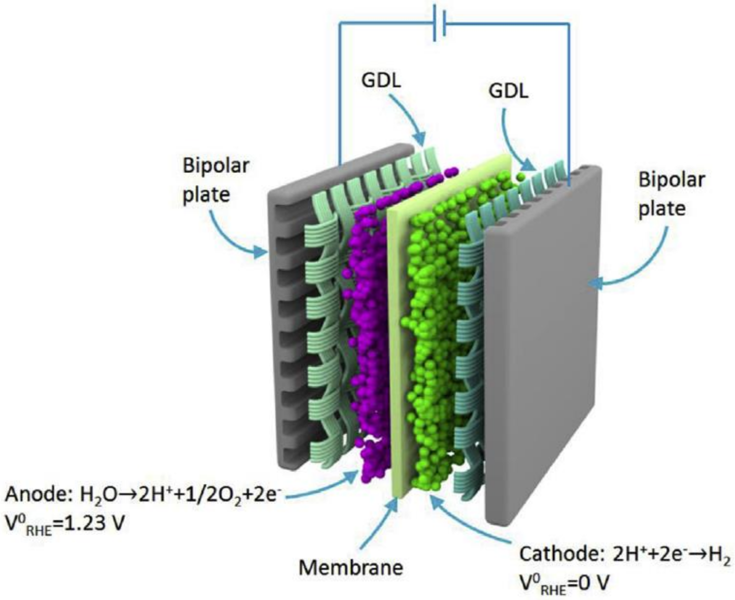
(AWE)

Solid Oxide Water Electrolyzers

(SOWE)

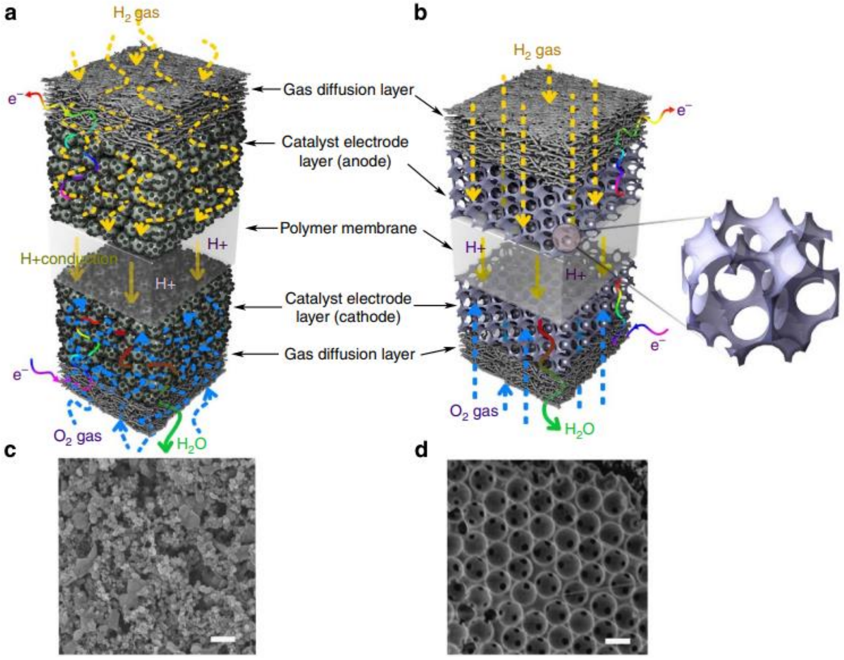
Proton Exchange Membrane Water Electrolyzers (PEMWE)

PEMWE CELL / CONSTITUENTS



Feng Q., et al., Journal of Power Sources, 366, 2017, 33-55

PEMWE CELL / CL

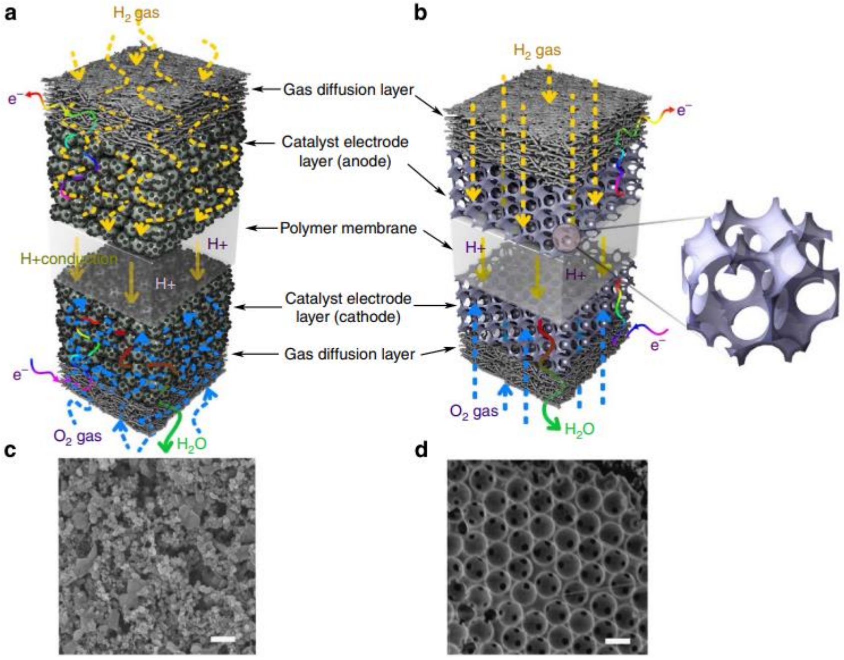


Kim *et al.* *Nat Commun* 4, 2473 (2013).

The CL has to be electronically conductive, chemically stable, its morphology has to promote gas diffusion. There have been three progressive improvements in MEA architecture:

1. CL on GDL (ease of manufacturing, reduced stability of catalyst nanoparticles)
2. Catalyst-coated-membrane-MEA (precious metal utilization is optimized and proton conductive resistance is reduced) – standard
3. Long-distance-ordered-structure-support for hosting the catalyst

PEMWE CELL / CL



Kim *et al. Nat Commun* 4, 2473 (2013).

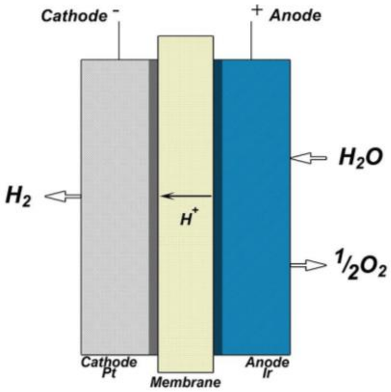
The GDL should be:

- flat to make GDL contact CL closely, leading to uniform dispersion of the current on the electrode
- porous to provide enough mass transfer channels
- mechanically stable and made of certain elastic to meet the requirements of seal and assembly
- of low resistance for reducing current loss;
- anti-oxidative to enhance the durability of the MEA

Common materials used:

PROTON EXCHANGE MEMBRANE WATER ELECTROLYZER (PEMWE)

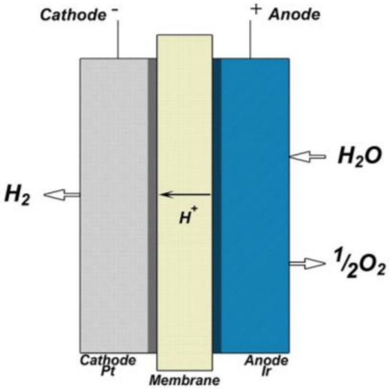
- PEM is usually constituted by Nafion, which is able to support high proton conductivities
- Catalysts are still expensive: Pt/C (HER), IrO_2 (OER)
- Cathode (HER): $4H^+ + 4e^- \rightarrow 2H_2$
- Anode (OER): $2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$
- Total: $2H_2O \rightarrow O_2 + 2H_2$



https://en.wikipedia.org/wiki/Polymer_electrolyte_membrane_electrolysis

PROTON EXCHANGE MEMBRANE WATER ELECTROLYZER (PEMWE)

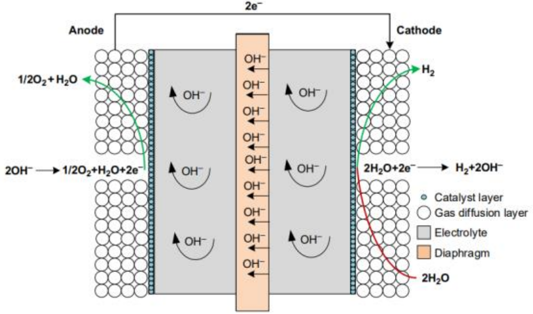
- They operate at low T (50-80°C) and P (20-50 bar).
- They operate at high current densities: 1 – 2 A/cm^2 with a hydrogen rate (per stack, around 400 Nm^3/h)
- Specific energy consumption is around 4 – 6.5 kWh/Nm^3
- Efficiency in commercial stacks is around 70% with a system efficiency around 50%.
- Stack lifetime can reach up to 100 kh with performance losses around 0.5-2.5%/year
- Investment cost: 1500-3800 $/kW, with annual maintenance cost about 4% of the initial investment



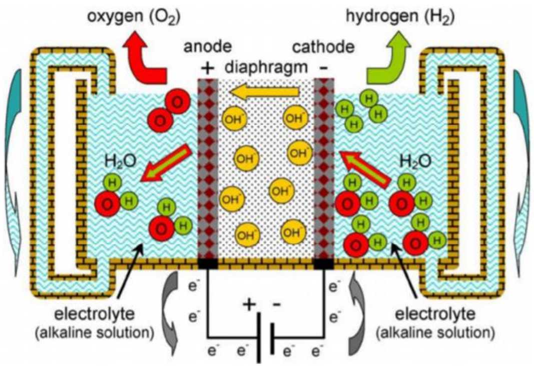
https://en.wikipedia.org/wiki/Polymer_electrolyte_membrane_electrolysis

ALKALINE WATER ELECTROLYZER (AWE)

- A OH⁻-conducting diaphragm is needed for separating the anode and cathode.
- Electrolyte: KOH solution; keeps hydrogen and oxygen separated to prevent their recombination.
- Ni and Fe are used as catalysts for cathode and anode, respectively.
- Cathode (HER): $4H_2O(l) + 4e^- \rightarrow 2H_2(g) + 4OH^-(aq)$
- Anode (OER): $4OH^-(aq) \rightarrow O_2(g) + 2H_2O + 4e^-$
- Total: $2H_2O \rightarrow O_2 + 2H_2$



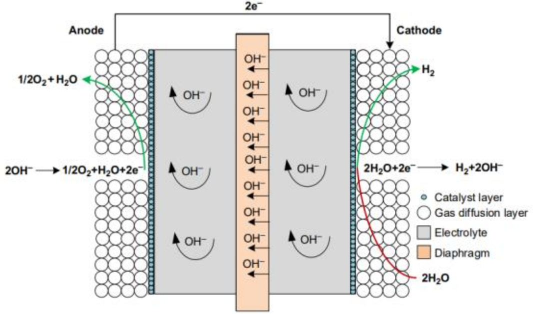
Solar Hydrogen Production, 2019, Academic press, chapter 9



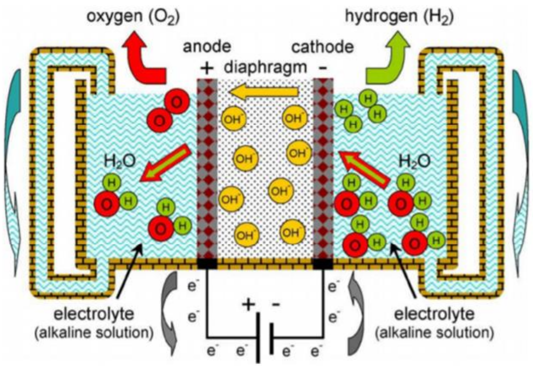
Chowdhury, American Journal of Renewable and Sustainable Energy Vol. 4, No. 3, 2018, pp. 40-46

ALKALINE WATER ELECTROLYZER (AWE)

- They operate at low T (60-90°C) and P (10-30 bar).
- They operate at low current densities: 0.2 – 0.6 A/cm^2 with a high produced hydrogen rate (per stack, around 1400 Nm^3/h)
- Specific energy consumption is around 4 – 6 kWh/Nm^3
- Efficiency in commercial stacks is around 70% with a system efficiency around 50%.
- The electrolyte is corrosive at operating temperatures: this strongly limits their lifetime
- Stack lifetime can reach up to 120 kh with performance losses around 0.25-1.5%/year
- Investment cost: 850-1500 $/kW, with annual maintenance cost about 2% of the initial investment

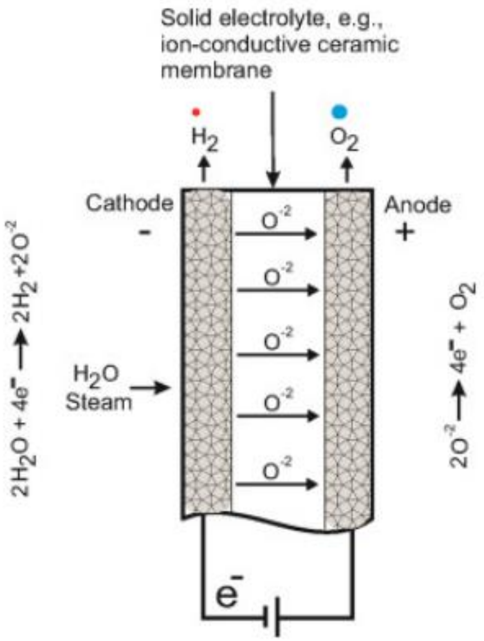


Solar Hydrogen Production, 2019, Academic press, chapter 9



Chowdhury, American Journal of Renewable and Sustainable Energy Vol. 4, No. 3, 2018, pp. 40-46

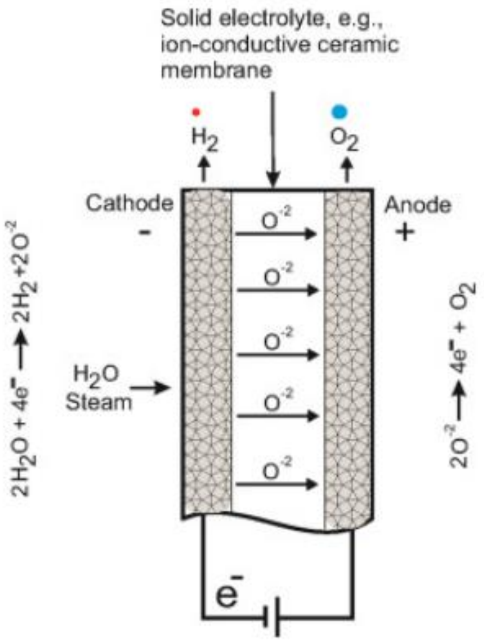
SOLID OXIDE ELECTROLYZER CELL (SOEC)



Bessarabov, Millet, 2018. PEM water electrolysis. Academic Press.

- Solid electrolyte is composed by thin film ceramics (*e.g.*, Y_2O_3 doped ZrO_2)
- Ni-doped ceramic materials are used as electrodes
- Cathode: $2H_2O + 4e^- \rightarrow 2H_2 + 2O^{-2}$
- Anode: $2O^{-2} \rightarrow O_2 + 4e^-$
- Total: $2H_2O \rightarrow O_2 + 2H_2$

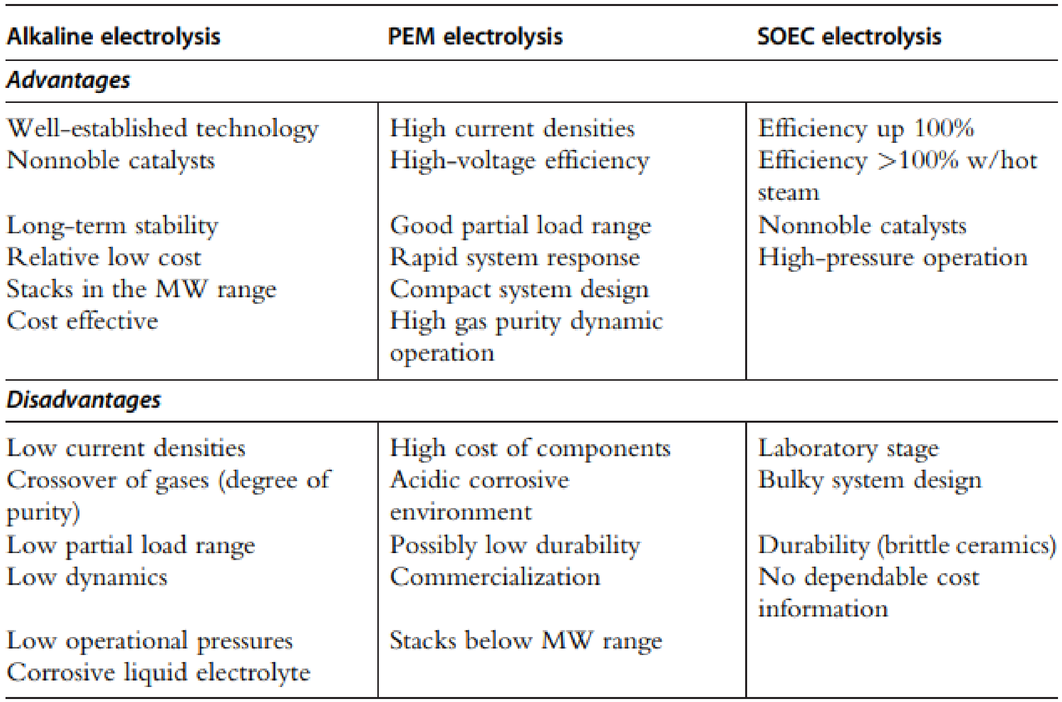
SOLID OXIDE ELECTROLYZER CELL (SOEC)



Bessarabov, Millet, 2018. PEM water electrolysis. Academic Press.

- They operate at high temperatures (700 – 1000°C) and low pressures (1-15 bar).
- Applied current density ranges between 0.3 an 1.0 A/ cm^2 with resulting low rate of produced hydrogen (per stack, around 10 Nm^3/h)
- Specific energy consumption is around 3 – 4 kWh/Nm^3
- Efficiency in commercial stacks is around 100% with a system efficiency around 80%.
- Thermal and mechanical stresses strongly jeopardize the lifetime of the device.
- Stack lifetime can reach up to 20 kh with performance losses around 3-50%/year
- Investment cost: <2200 $/kW

WATER ELECTROLYZERS / COMPARISON



Alkaline electrolysis	PEM electrolysis	SOEC electrolysis
Advantages		
Well-established technology	High current densities	Efficiency up 100%
Nonnoble catalysts	High-voltage efficiency	Efficiency >100% w/hot steam
Long-term stability	Good partial load range	Nonnoble catalysts
Relative low cost	Rapid system response	High-pressure operation
Stacks in the MW range	Compact system design	
Cost effective	High gas purity dynamic operation	
Disadvantages		
Low current densities	High cost of components	Laboratory stage
Crossover of gases (degree of purity)	Acidic corrosive environment	Bulky system design
Low partial load range	Possibly low durability	Durability (brittle ceramics)
Low dynamics	Commercialization	No dependable cost information
Low operational pressures	Stacks below MW range	
Corrosive liquid electrolyte		

PEMWE / OPERATING POINT

The operating point of an electrolyzer is defined by the thermodynamic voltage of water electrolysis.

From the relation among Gibbs free energy the standard potential, E^0:

$$\Delta G = nFE^0$$

For the water splitting reaction $\Delta G=237.22$ kJ/mol; thus, it is possible to calculate the potential needed to start the reaction:

$$E^0 = \frac{\Delta G}{nF} = 1.23V$$

PEMWE / OPERATING POINT

However, from a thermodynamic point of view, the water splitting reaction at room temperature and pressure can be expressed as :

$$H_2O + \Delta H \rightarrow 1/2O_2 + H_2$$

Where ΔH can be expressed, by means of the second law of thermodynamics as:

$$\Delta H = \Delta G + T\Delta S$$

Here, ΔG is the Gibbs free energy of the reaction and it defines the minimum energy required to induce for water splitting, while ΔS describes the variation of entropy due to temperature changes.

For liquid water, ΔS =163.15 J/(mol K), ΔH=285.840 J/(mol K), leading to the definition of the so-called thermo-neutral voltage:

$$E_{TN} = \frac{\Delta H}{nF} = \frac{\Delta G + T\Delta S}{nF} = 1.48V$$

PEMWE / OPERATING POINT

Generally the applied voltage has to be higher than the voltage defined form theoretic calculation:

$$V = V_{TN} + V_{ACT} + V_{OHM} + V_{TRN}$$

Where V_x are different types of voltage losses:

V_{ACT}: losses due to the activation overpotential

V_{OHM}: losses due to ohmic overpotential

V_{TRN}: losses due to mass transport

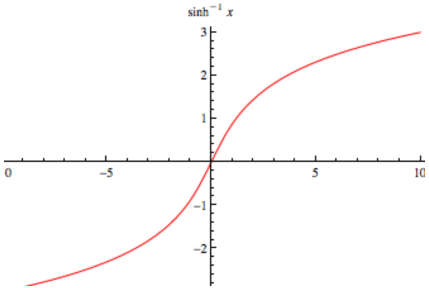
PEMWE / ACTIVATION LOSSES

Activation overpotential

- Related to the additional energy which has to be provided at the system in order to start the HER and the OER
- Directly affected by the temperature, catalyst material, utilization, and loading
- The can be modelled by means of a simplified version Butler-Volmer equation

$$V_{ACT} = \frac{RT}{\alpha} \operatorname{arcsinh}\left(\frac{i}{i_0}\right)$$

Where α is the charge transfer coefficient and i_0 is the exchanged current density



PEMWE / OHMIC LOSSES

Ohmic losses

Related to electronic and ionic transport; it is due to the resistance to the flow of electrons through the current collectors and separator plates, as well as the conduction of protons through the membrane. They can be described by means of the Ohm’s law:

$$V_{OHM} = R_{TOT} I + \frac{\delta_m}{A\sigma_m} I$$

Where δ_m is the membrane thickness and σ_m its proton conductivity

PEMWE / MASS TRANSPORT LOSSES

Mass transport losses

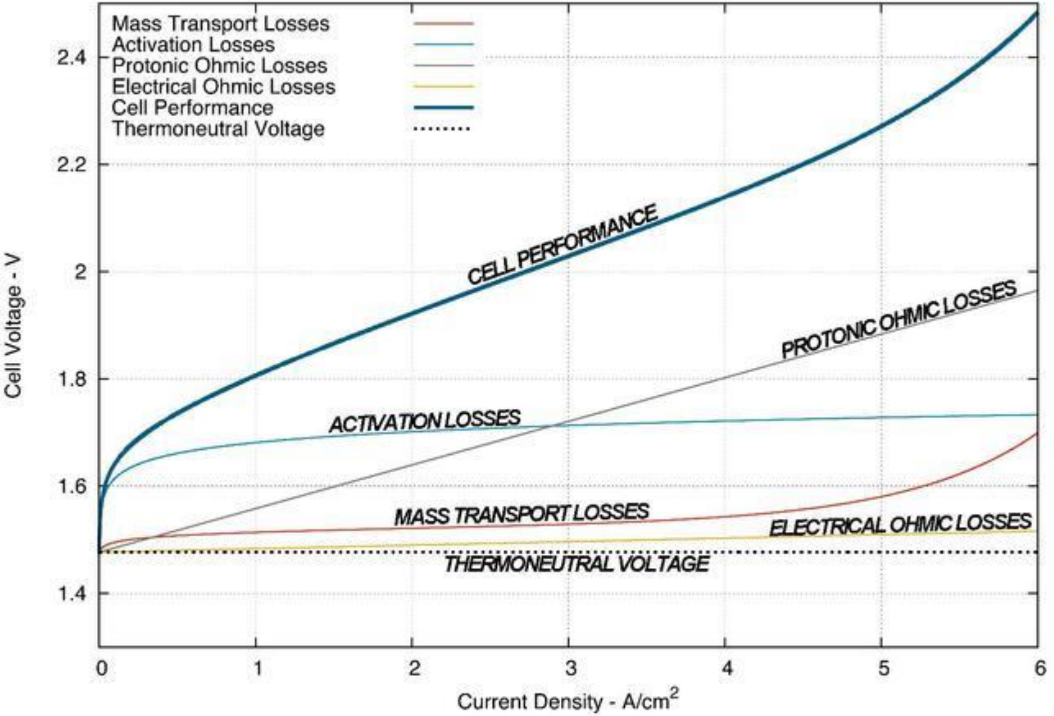
They are related to matter flow through a porous media and can be related to different phenomena:

- flow restriction to the catalyst sites
- gas bubbles formation from the reaction products
- surplus of reaction products at the catalyst sites blocking the reactant diffusion.

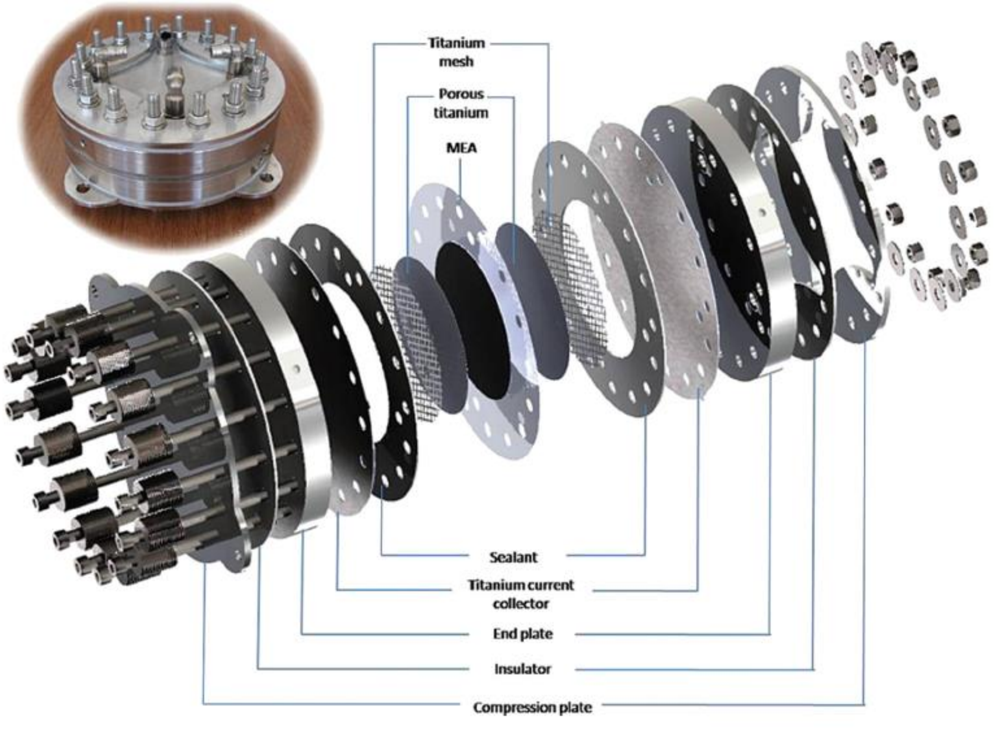
Diffusion is described by the Fick's law: $J = -D_{eff}\left(\frac{\partial C_i}{\partial x}\right)$, where J is the diffusion flux, D is the diffusion coefficient and C the specimen concentration. Mass transport losses are related to the variation of specimen concentration at the membrane-electrode-interface (C_{mei}) by means of the Nernst equation:

$$V_{TRN} = \frac{RT}{nF}\ln\left(\frac{C_{i,mei}}{C_{i,mei,0}}\right)$$

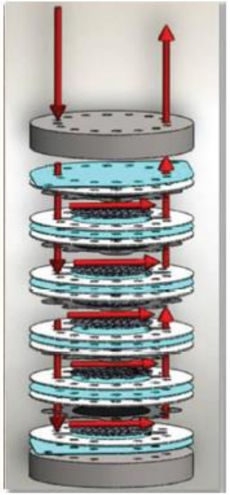
ELECTROLYZERS / OPERATING CONDITIONS



PEMWE CELLS


Titanium mesh
Porous titanium
MEA
Sealant
Titanium current collector
End plate
Insulator
Compression plate

PEMWE STACKS

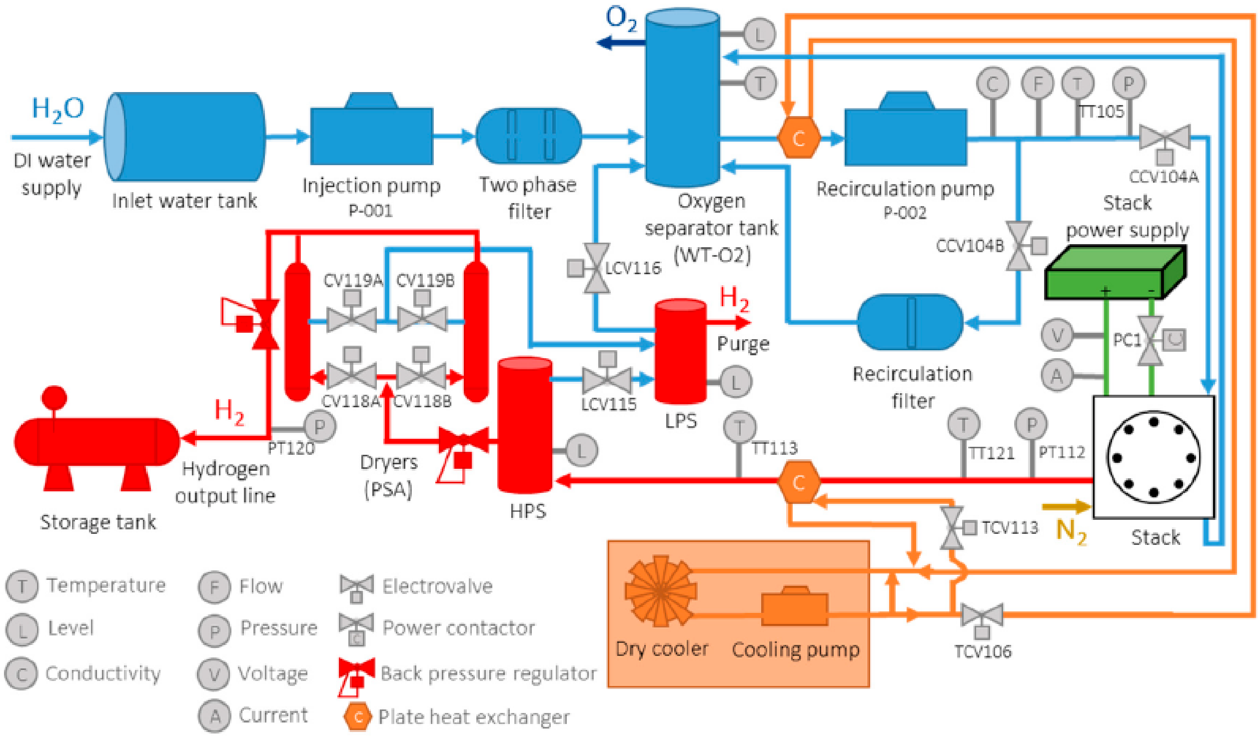


While designing a PEMWE stack, homogeneous water and current distribution and appropriate compression in the cell and stack must be obtained. The stack must be compressed with an appropriate pressure to make sure the cell sealed and to avoid gas leak, or MEA crack resulted by lower or higher torque, as well as Ohmic losses due contact resistance decreases the stack efficiency

PEMWE SYSTEM

https://www.ise.fraunhofer.de/en/business-areas/hydrogen-technologies-and-electrical-energy-storage/electrolysis-and-power-to-gas.html

BALANCE OF PLANT



Composition:

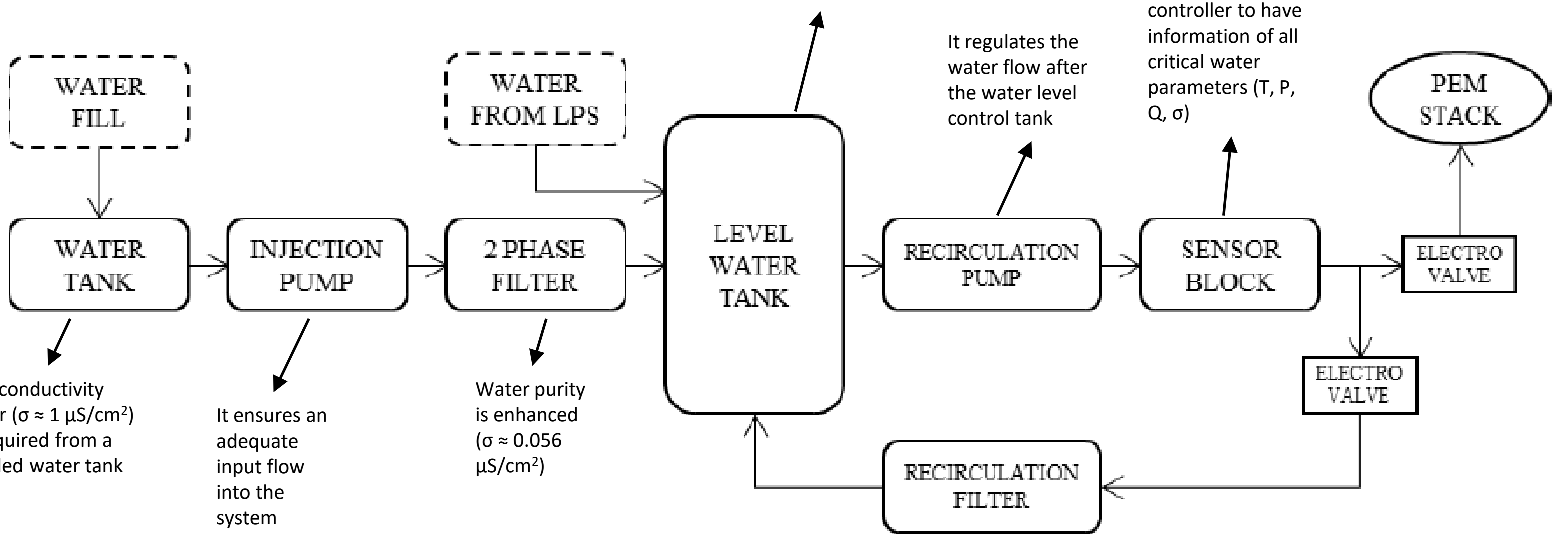
H_2O subsystem

H_2 subsystem

Cooling subsystem

Control subsystem

BALANCE OF PLANT / WATER SUBSYSTEM



Low-conductivity water (σ ≈ 1 μS/cm^2) is acquired from a distilled water tank

It ensures an adequate input flow into the system

Water purity is enhanced (σ ≈ 0.056 μS/cm^2)

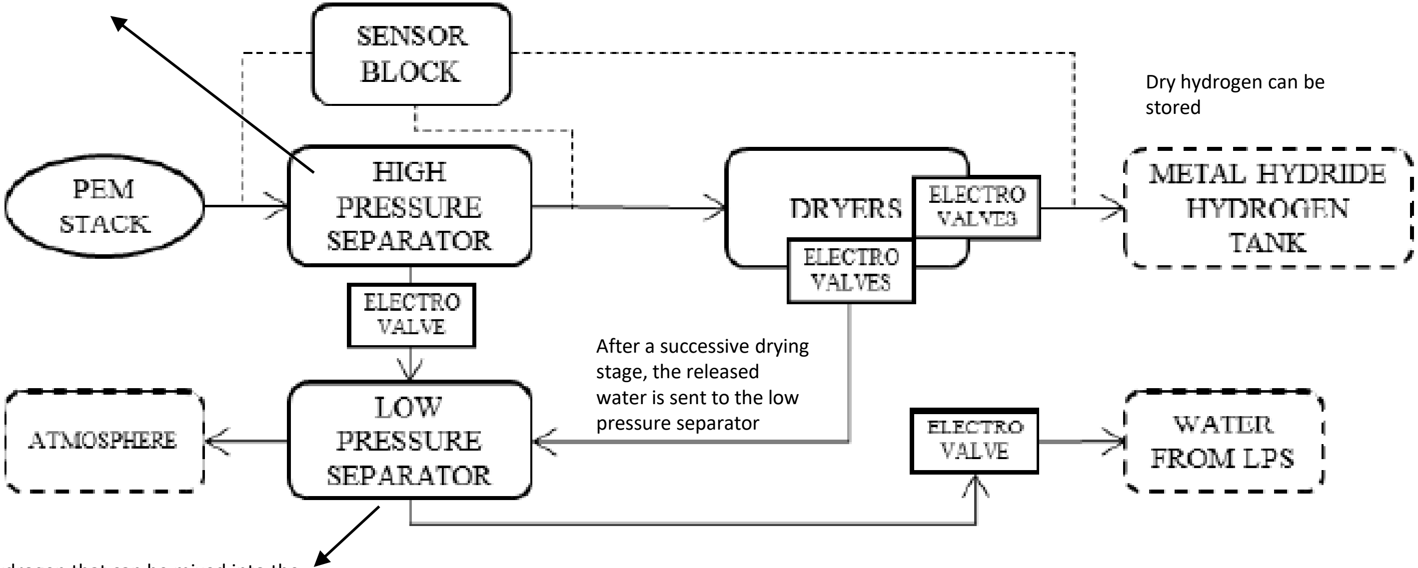
It carries out two tasks:
1. Is a buffer with the aim to adjust the water flow inside the circuit
2. Acts as a sink collecting the water obtained in the drying stages of the hydrogen produced

It regulates the water flow after the water level control tank

Used by the controller to have information of all critical water parameters (T, P, Q, σ)

BALANCE OF PLANT / HYDROGEN SUBSYSTEM

It takes advantage by the pressure difference in water contained in the form of moisture to dry the hydrogen. Once a high humidity gradient is reached in the high pressure separator, the wet (*dirty*) hydrogen flows into the low pressure separator, while the dry (*clean*) hydrogen continues to the dryers' stage

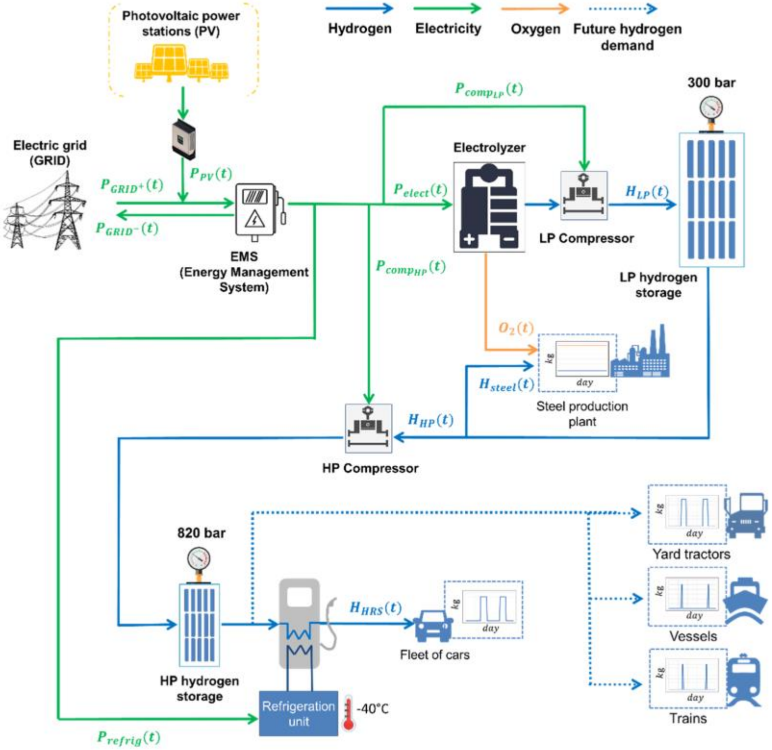


Dry hydrogen can be stored

After a successive drying stage, the released water is sent to the low pressure separator

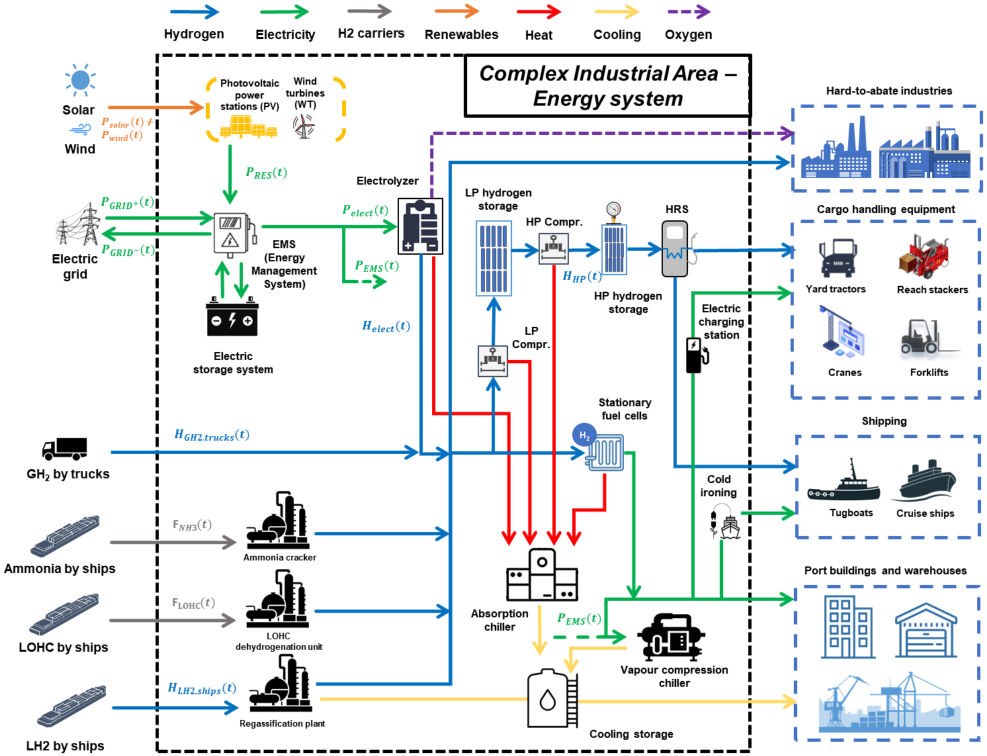
The hydrogen that can be mixed into the atmosphere is released, and the water is sent to the level water tank

WATER ELECTROLYZERS / INDUSTRIAL PERSPECTIVES



Pivetta D. et al., J. Mar. Sci. Eng. 2022, 10(2), 231; https://doi.org/10.3390/jmse10020231

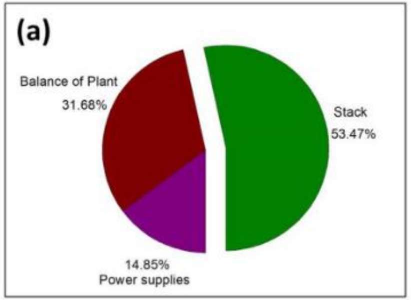
WATER ELECTROLYZERS / INDUSTRIAL PERSPECTIVES



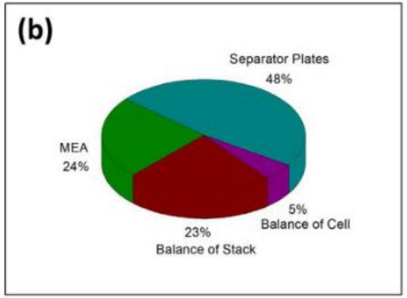
Pivetta D., PhD thesis

WATER ELECTROLYZERS / BOTTLENECKS

- Costs (both OPEX and CAPEX)
- Performance and durability
- Regulation



(a). Breakdown system cost



(b). Breakdown cell cost

PEMWE CELLS / POSSIBLE IMPROVEMENTS – MATERIAL SIDE

- **Improve the catalytic activity** for HER and OER by reducing catalyst load (in example by introducing binary, ternary or quaternary alloys with an advanced material design).
- **Improve the electrochemical active surface area**, catalyst utilization, **and stability** against corrosion. In the case of using supported catalysts, development of highly conductive supports that can sustain the corrosion environment and still provide high nanoparticle dispersion and homogeneity.
- Improve the **proton transport** across the catalytic layer, decrease gas crossover across the electrolyte and nanoparticle hindering, diminish the electronic resistance provided by the ionomer, improve the water transport across the triple-phase-boundary.

PEMWE CELLS / POSSIBLE IMPROVEMENTS (2)

- Develop low cost current collectors with tuned porous structure, high corrosion resistance, low ohmic resistance, and optimized mass transport
- Titanium-made separator plates could be replaced by using lower cost materials (e.g.: copper, graphite, stainless steel) coated with high electron transport and high corrosion resistance materials.
- Model the multi-phase transport of species through the current collectors and separator plates. This could prove to be very beneficial in the design of current collectors, especially for larger scale electrolysers.
- Develop a predictive model for the exchange current density for various catalysts. Although this task is very demanding, if successfully accomplished, modelling would prove to be a much more useful design tool capable of aiding in the design of all the individual components.

BIBLIOGRAPHY

Books/Book Chapters

- Electrochemical Water Electrolysis, Fundamentals and Technologies, 2020 Taylor & Francis Group, 78-1-138-32932-4, chapter 1 (Fundamentals of water electrolysis - Xiaoxia Yan, Rida Javed, Yanmei Gong, Daixin Ye, Hongbin Zhao)
- Erik Wolf, Electrochemical Energy Storage for Renewable Sources and Grid Balancing, Chapter 9 - Large-Scale Hydrogen Energy Storage, doi.org/10.1016/B978-0-444-62616-5.00009-7
- Solar Based Hydrogen Production Systems, Dincer, Joshi, 2013, Springer, 978-1-4614-7430-2

Optional

- Carmo, Stolten *et al.*, A comprehensive review on PEM water electrolysis, International Journal of Hydrogen Energy, 38, 12, 2013, 4901-4934, http://dx.doi.org/10.1016/j.ijhydene.2013.01.151
- Mancera, Calderón *et al.*, An Optimized Balance of Plant for a Medium-Size PEM Electrolyzer: Design, Control and Physical Implementation, Electronics 9, 5, (2020), 871, https://doi.org/10.3390/electronics9050871
- Kumar, Himabindu, 2019, Hydrogen production by PEM water electrolysis – A review, Materials Science for Energy Technologies, 2, 3, (2019), 442-454, https://doi.org/10.1016/j.mset.2019.03.002

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