UNIVERSITÀ DEGLI STUDI DI TRIESTE

Dipartimento di Ingegneria e Architettura

WATER ELECTROLYSIS AND ELECTROLYSER TECHNOLOGIES

- PART 1 -

Prof. Marco Bogar

A.A. 2023-2024

OUTLINE

1. Electrochemical water splitting
2. PEM water electrolysers

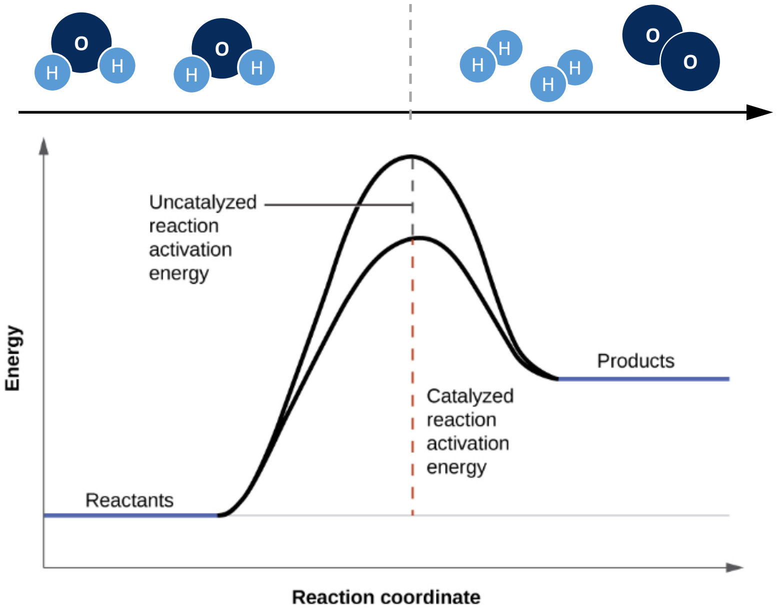
BIBLIOGRAPHY

Reference	Paragraph/Pages
Hydrogen production by electrolysis, Agata Godula-Jopek, 2015 Wiley	Ch. 2 and 3

Insights	
R1	Hodges A. et al., Nature Comm. (2022) 13:1304; DOI: https://doi.org/10.1038/s41467-022-28953-x
R2	Li X. et al., J. Mater. Chem. A, 2016,4, 11973-12000; DOI: https://doi.org/10.1039/C6TA02334G
R3	Khatib F.N. et al. Renewable and Sustainable Energy Reviews 111 (2019) 1–14; DOI: https://doi.org/10.1016/j.rser.2019.05.007
R4	Bazarah A. et al., Int. J. Hyd. En., 47, 85, (2022), 35976-35989; DOI: https://doi.org/10.1016/j.ijhydene.2022.08.180
R5	Makhsoos A. et al., Int. J. Hyd. En, 48, (2023), 15341-15370; DOI: https://doi.org/10.1016/j.ijhydene.2023.01.048

1. ELECTROCHEMICAL WATER SPLITTING

THE WATER SPLITTING REACTION



At standard T and P (298K, 1bar)

$$H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$$

$$\Delta H^0_{H_2O(l)} = +285.84\ kJ\ mol^{-1}$$

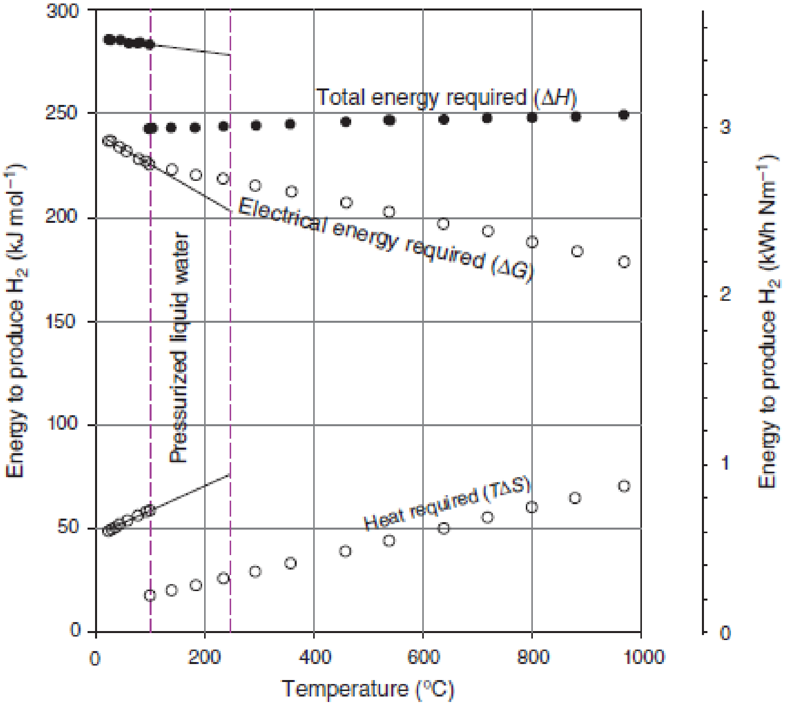
$$\Delta S^0_{H_2O(l)} = +163.15\ J\ K^{-1}\ mol^{-1}$$

$$\Delta G^0_{H_2O(l)} = \Delta H^0_{H_2O(l)} - T\Delta S^0_{H_2O(l)} = +237.22\ kJ\ mol^{-1}$$

ΔH > 0: reaction is strongly endothermic

ΔG > 0: reaction is non-spontaneous

THE WATER SPLITTING REACTION



- The total energy ΔH required to split 1 mole of water is almost constant over the entire temperature range of practical interest

- The difference among enthalpy variation:

$$\Delta H^0_{H_2O(l)} - \Delta H^0_{H_2O(g)} = +285.84 - 241.80 = +44.04\ kJ\ mol^{-1}$$

  is related to the water vaporization process.

- The ΔG > 0, but it decreases when increasing the operating temperature. ΔG becomes negative only for T >2500 K. Such a high temperature limit, is sustainable for only few if any materials, therefore, the direct thermo-dissociation of water is not considered for practical applications.

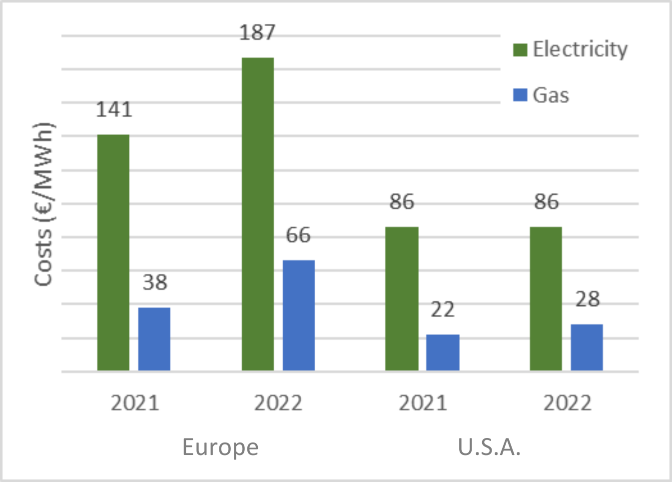
- Higher operating temperatures facilitate the water dissociation by decreasing the electrolysis voltage.

-

Temperature	Percentage of energy from water splitting from heat	Percentage of energy from water splitting from electricity
T_{room}	15	85
1000 °C	33	66

THE WATER SPLITTING REACTION – THE OPERATIVE TEMPERATURE

Thus the selection of the operative temperature is thus directly influencing the efficiency of the process.



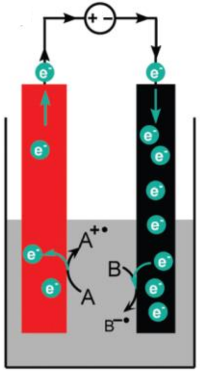
Eurostat, EIA

Nonetheless, we are going to see as high-temperature technology is less mature with respect low-temperature ones, as we are going to see.

ELECTROCHEMICAL WATER SPLITTING

From thermodynamics it is known as the water splitting reaction is non-spontaneous, but it can be driven providing energy to the system.

To sustain water splitting an electrochemical cell is used. The electrochemical cells is composed by two electrodes (half cell) and by an electrolyte. Half-cell reactions and associated mechanisms, depend on the pH of the electrolyte. For example, in an acidic media:



Schotten C., Green Chem., 2020,22, 3358-3375

1. at the anode the so-called Oxygen Evolution Reaction (OER) is promoted:

$$H_2O(l) \rightarrow 2H^+ + 2e^- + \frac{1}{2}O_2(g)$$

2. while at the cathode the Hydrogen Evolution Reaction (HER) occurs:

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

The full reaction for the water electrolysis process can be thus expressed as:

$$H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$$

ELECTROCHEMICAL WATER SPLITTING: HALF-CELL REACTION KINETICS (IN ACIDIC MEDIA)

Hydrogen Evolution Reaction (HER) has been extensively studied and only two-step-based reactions pathways are now regarded as likely to occur in acidic media. In both cases hydrogen atoms are adsorbed to the catalyst surface via electronation (that is transfer of an electron to neutral molecule with resulting anion formation).

Mechanism 1

$$H^+ + e^- + M \leftrightarrow MH_{ad}^{surface} \qquad \text{step 1}$$

$$2MH_{ad}^{surface} \leftrightarrow H_2(g) + 2M \qquad \text{step 2}$$

Mechanism 2

$$H^+ + e^- + M \leftrightarrow MH_{ad}^{surface} \qquad \text{step 1'}$$

$$H^+ + e^- + MH_{ad}^{surface} \leftrightarrow H_2(g) + M \qquad \text{step 2'}$$

This process is in competition with the Hydrogen Insertion Reaction, where protons are absorbed by catalyst atoms in sub-surface region:

$$MH_{ad}^{surface} \leftrightarrow M + H_{ab}^{sub-surface} \quad \text{step 3} \qquad \rightarrow \qquad H_{ab}^{sub-surface} \leftrightarrow H_{bulk} \quad \text{step 4}$$

An aid in promoting the occurrence of HER reaction comes from electrode morphology and composition (C-supported M-nanoparticles): in fact, diffusion path of H adatoms is limited to the nanometre scale due to the geometry of the catalytic powder, and carbon superficial diffusion is unlikely to happen due to strong carbon–hydrogen interactions and low H diffusivity.

ELECTROCHEMICAL WATER SPLITTING: HALF-CELL REACTION KINETICS (IN ACIDIC MEDIA)

Oxygen Evolution Reaction (OER) is a four-electron redox reaction and a bigger number of reaction mechanisms have been reported in literature. The most reported are the following two:

Mechanism 1 (oxide path)		Mechanism 2 (Krasil'shchikov path, IrO_2; S reaction site)	
$4Pt + 4H_2O \rightarrow 4PtOH + 4H^+ + 4e^-$	step 1	$S + H_2O \rightarrow S - OH + H^+ + e^-$	step 1
$4PtOH \rightarrow 2PtO + 2PtH_2O$	step 2	$S - OH \rightarrow S - O^- + H^+$	step 2
$2PtO \rightarrow O_2 + 2Pt$	step 3	$S - O^- \rightarrow S - O + e^-$	step 3
		$S - O \rightarrow S + 1/2O_2$	step 4

Mechanism 1 prevails on Pt electrodes; nonetheless, Pt is not a good catalyst in average for the OER (contrary with respect ORR), and in commercial devices IrO_2-based catalysts are used (which are able to provide an exchange current density thee orders of magnitude bigger than Pt-based catalysts). Here, in presence of S-reaction-sites, the mechanism 2 was reported to occur.

ELECTROCHEMICAL WATER SPLITTING: THERMODYNAMICS

Starting from the relation among variation in Gibbs free energy and electromotive force

$$\Delta G(T,P) = nFE(T,P)$$

Two different thermodynamic voltages can be defined, referring to two different variation of thermodynamic quantities; the standard potential, and the thermo-neutral potential:

$$E^0(T,P) = \frac{\Delta G(T,P)}{nF} \qquad V_{TN}(T,P) = \frac{\Delta H(T,P)}{nF}$$

E^0 V_{TN} V

$V < E^0$
Electrolysis does not start: not enough energy is supplied

$E^0 < V < V_{TN}$
There is enough electricity to initiate the process but additional heat should be fed from the extern to maintain isothermicity. Current densities are low.

$V > V_{TN}$
Both supplied potential and heat are enough to sustain the overall process. Large current densities can be managed

ELECTROCHEMICAL WATER SPLITTING: THERMODYNAMICS

In standard conditions (298K, 1 bar):

$$\Delta G^0(H_2O) = +237.22\ kJ\ mol^{-1}$$

$$\Delta H^0(H_2O) = +285.84\ kJ\ mol^{-1}$$

Thus the standard potential (of formation) is:

$$E^0 = \frac{\Delta G^0(H_2O)}{2F} = 1.2293\ V \cong 1.23\ V$$

While the thermoneutral voltage (of formation):

$$V^0 = V_{TN}^0 = \frac{\Delta H^0(H_2O)}{2F} = 1.4813\ V \cong 1.48\ V$$

But, if water is fed in form of vapour: $E^0 = 1.18$ V.

ELECTROCHEMICAL WATER SPLITTING: THERMODYNAMICS AND pH DEPENDENCE

Acidity of the media has influence on reaction voltages. For a generic medium, **acidity** can be defined as its tendency to act as a proton donor. To evaluate the effects of the acidity on the water splitting reaction, let's start from analysing the behaviour of water electrolysis carried out in an acidic media. Here, half-cell reactions have been shown being:

$$H_2O(l) \rightarrow 2H^+ + 2e^- + \frac{1}{2}O_2(g) \qquad\qquad 2H^+ + 2e^- \rightarrow H_2(g)$$

By means of the Nernst equation, the half-cell potentials can be calculated as:

$$E^+ = E^0_{OER} + \frac{RT}{nF}\ln\left(\frac{a^2_{H^+}\cdot f^{1/2}_{O_2}}{a_{H_2O}}\right) \qquad\qquad E^- = E^0_{HER} + \frac{RT}{nF}\ln\left(\frac{a^2_{H^+}}{f_{H_2}}\right)$$

Where: $a^2_{H^+}$ is the proton activity in the electrolyte, $f^{1/2}_{O_2}$ is the oxygen fugacity in the anodic compartment, and a_{H_2O} is the water activity.

ELECTROCHEMICAL WATER SPLITTING: THERMODYNAMICS AND pH DEPENDENCE

$a_{H^+}^2$ is the proton **activity** in the electrolyte

In chemical thermodynamics it represents a measure of the effective concentration of a species in a mixture, which is treated as a dimensionless quantity.

For pure substances in condensed phases (solid or liquids) activity is normally taken equal to 1.

a_{H_2O} is the water **activity**

Activity depends on temperature, pressure and composition of the mixture, among other things. For gases, the activity is the effective partial pressure, and is usually referred to as *fugacity*.

$f_{O_2}^{1/2}$ is the oxygen **fugacity** in the anodic compartmen

ELECTROCHEMICAL WATER SPLITTING: THERMODYNAMICS AND pH DEPENDENCE

Both of the expressions can be simplified under the following assumptions:

- the acid electrolyte is sufficiently diluted, thus proton activity coefficient can be approximated by the molar concertation of protons, that is pH: $a_{H^+}^2 \rightarrow pH$
- as a further consequence, water activity is close to unity because of the electrolyte dilution $a_{H_2O} \cong 1$
- the effects due to saturated water vapour can be neglected due to the fact that pure oxygen is evolved during electrolysis, that is $f_{O_2}^{1/2}$ is equal to the partial pressure (1 bar)

Thus, with a hydrogen pressure equal to 1 bar, and at standard conditions:

$$E^- = E_{HER}^0 + \frac{RT}{nF}\ln\left(\frac{a_{H^+}^2}{f_{H_2}}\right) \rightarrow E^- \cong \frac{RT}{nF}\ln\left(a_{H^+}^2\right) \cong -0.06pH$$

And

$$E^+ = E_{OER}^0 + \frac{RT}{nF}\ln\left(\frac{\left(a_{H^+}^2\right)\left(f_{O_2}^{1/2}\right)}{a_{H_2O}}\right) \cong E^0 + \frac{RT}{nF}\ln\left(a_{H^+}^2\right) \rightarrow E^+ \cong 1.23 - 0.06pH$$

ELECTROCHEMICAL WATER SPLITTING: THERMODYNAMICS AND pH DEPENDENCE

Consequently:

$$E_{cell} = E^+ - E^- = 1.23\ V$$

That is that the standard potential is independent on the pH of the surrounding environment. The same result is obtained when switching to alkaline media:

$$anode\ (+):\quad 2OH^- \rightarrow H_2O(l) + \frac{1}{2}O_2(g) + 2e^- \quad OER$$

$$cathode\ (-):\quad 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^- \quad HER$$

By means of the Nernst equation, and under the same assumptions made before the half-cell potentials result:

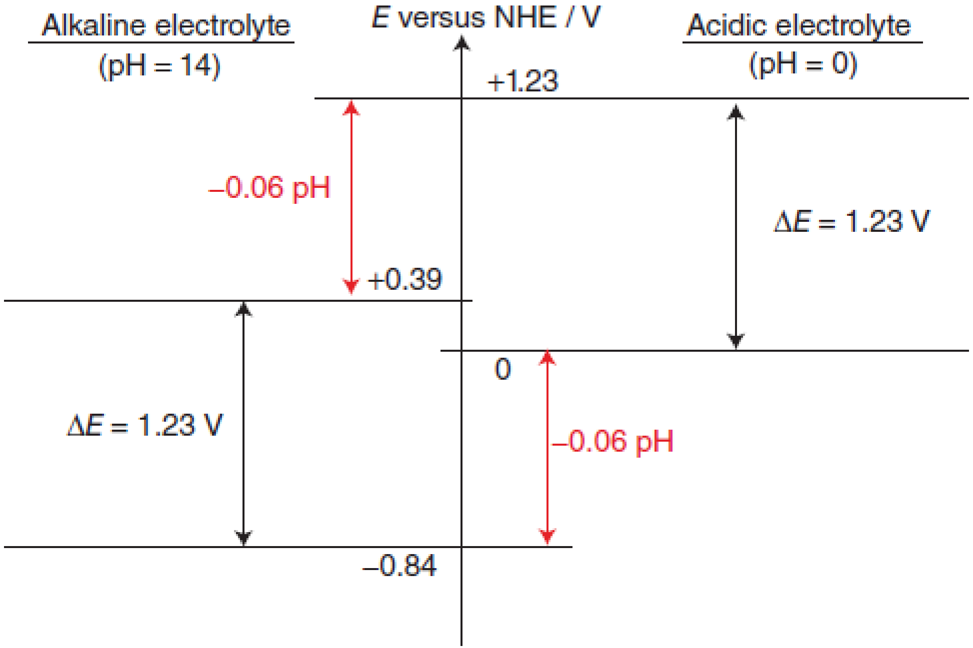
$$E^+ = E^0_{OER} + \frac{RT}{nF}\ln\left(\frac{\left(a_{H_2O}\right)\left(f_{O_2}^{1/2}\right)}{a^2_{HO^-}}\right) \cong 1{,}23 + pKe - 0.06pH$$

$$E^- = E^0_{HER} + \frac{RT}{nF}\ln\left(\frac{a^2_{H_2O}}{f_{H_2}a^2_{HO^-}}\right) \cong pKe - 0.06pH$$

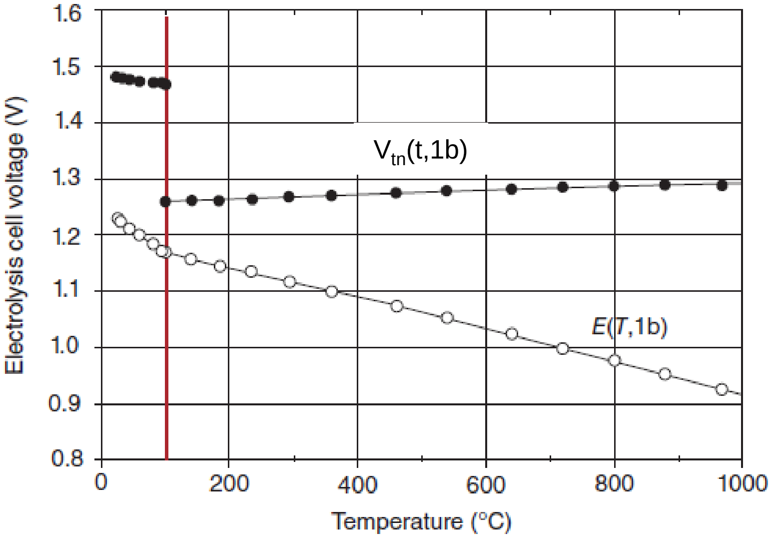
And:

$$E_{cell} = E^+ - E^- = 1.23\ V$$

ELECTROCHEMICAL WATER SPLITTING: THERMODYNAMICS AND pH DEPENDENCE



ELECTROCHEMICAL WATER SPLITTING: TEMPERATURE DEPENDENCE



$$E(T,P=1bar)=\frac{\Delta G(T,P=1bar)}{nF}$$

$$V_{tn}(T,P=1bar)=\frac{\Delta H(T,P=1bar)}{nF}$$

T (°C)	E(T,P=1bar) (V)
25	1.23
100	1.18
1000	0.9

In conclusion, operating at high temperatures allow to improve the electrochemical performances of water electrolysis, by simply managing the excess of pressurization which would be needed to adopt to face water vaporization. Thus, the operative boundaries of every technology are only due to the materials constituting the device and not from thermodynamic reasons.

ELECTROCHEMICAL WATER SPLITTING: PRESSURE DEPENDENCE

Starting from the definition of the Gibbs free energy:

$$G = U + PV \ - TS$$

In differential form, it can be expressed as:

$$dG = dPV - dTS = \left(\frac{\partial G}{\partial P}\right)_T dP - \left(\frac{\partial G}{\partial T}\right)_P dT$$

Where

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

Thus, the dependence of the standard potential E, can be related to a change in the molar volume, $\Delta\bar{V}$, as:

$$\left(\frac{\partial E}{\partial P}\right)_T = \frac{1}{nF}\left(\frac{\partial \Delta G}{\partial P}\right)_T = \frac{\Delta\bar{V}}{nF}$$

By considering that the compression effects on $\Delta\bar{V}$ are small (thus negligible) for condensed (liquid) phase, in thermodynamic analysis, $\Delta\bar{V}$ can be related only to the gaseous phase.

ELECTROCHEMICAL WATER SPLITTING: PRESSURE DEPENDENCE

By considering a mixture of gases, each characterized by a partial pressure p_i and a stoichiometric factor v_i, the molar volume variation can be expressed by the sum:

$$\Delta\bar{V} = \sum_i \nu_i \frac{RT}{p_i}$$

meaning that the variation of the standard potential in function of pressure (at a constant value of temperature) becomes equal to the sum of the potential due to the variation of the partial pressures of the single specimens involved in the reaction:

$$\left(\frac{\partial E}{\partial P}\right)_T = \frac{\Delta\bar{V}}{nF} = \sum_i \nu_i \frac{RT}{nFp_i} \equiv \sum_i \left(\frac{\partial E}{\partial p_i}\right)_T$$

ELECTROCHEMICAL WATER SPLITTING: PRESSURE DEPENDENCE

Finally, by integrating the equation:

$$\left(\frac{\partial E}{\partial P}\right)_T = \sum_i \nu_i \frac{RT}{nFp_i}$$

The following formulation of the standard potential can be found:

$$V = E^0 + \sum_i \nu_i \frac{RT}{nF} \ln\left(\frac{p_i}{p^0}\right)$$

Where p^0 is the starting of partial pressure of each specimen.

ELECTROCHEMICAL WATER SPLITTING: PRESSURE DEPENDENCE

The so-retrieved equation, $V = E^0 + \sum_i \nu_i \frac{RT}{nF} \ln\left(\frac{p_i}{p^0}\right)$, Can be applied to the water electrolysis reaction, leading to:

$$V = E^0 + \frac{RT}{2F} \ln\left(\frac{p_{H_2}}{p^0}\sqrt{\frac{p_{O_2}}{p^0}}\right)$$

Because water electrolysis produces H_2 and O_2 with high purity degrees, the presence of: spurious water saturation (at temperature of operation), traces of cross-permeation of gases, and the eventual traces of KOH (if the reaction is carried out in alkaline environment), can be neglected. By considering a device operating at pressure P at both electrodes:

$$V = E^0 + \frac{RT}{2F} \ln\left(P^{3/2}\right) = E^0 + \frac{3RT}{4F} \ln(P)$$

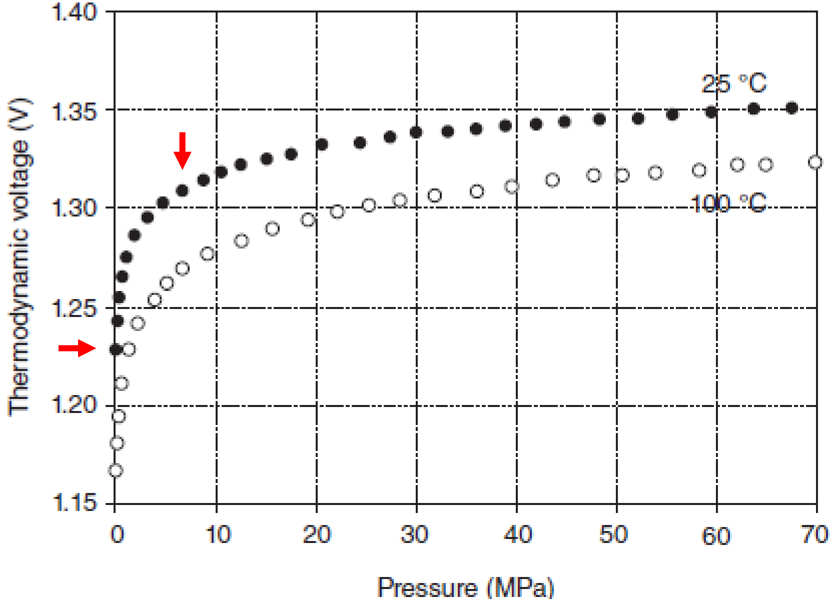
Thus, the change of operative pressure in electrolysers leads to a change in operating cell voltage, equal to:

$$V = E^0 + \frac{3RT}{4F} \ln\left(\frac{P_2}{P_1}\right)$$

And, by setting the reference operative pressure to 1bar:

$$V(T, P) = E(T, 1) + \frac{3RT}{4F} \ln(P)$$

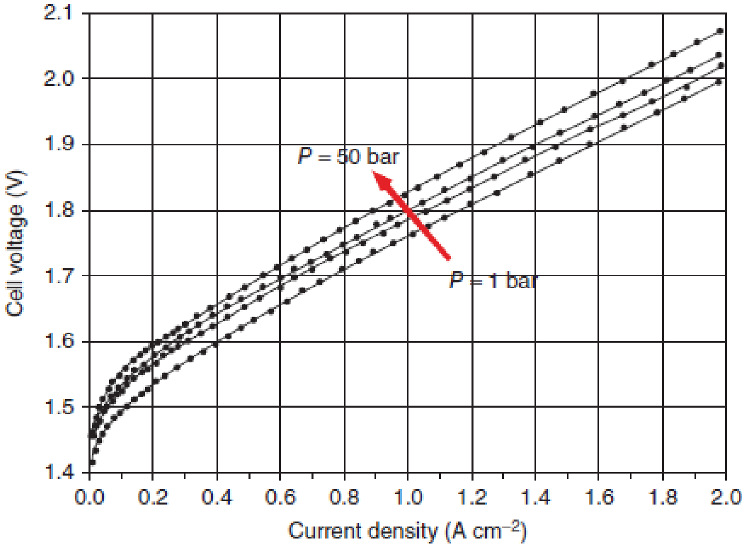
ELECTROCHEMICAL WATER SPLITTING: PRESSURE DEPENDENCE



This logarithmic dependence reflects as an increase of the operating pressure of about 0.12 V if the pressure is rose up from 1 to 6 MPa at 25°C.

ELECTROCHEMICAL WATER SPLITTING: PRESSURE AND TEMPERATURE

Summarizing, temperature and pressure have opposite effects on the electrochemical standard potential: increasing pressure makes the potential increase (at an approximate rate of $+0.3 \mathrm{mVbar^{-1}}$), while increasing temperature leads to voltage reduction (of about $-0.8 \mathrm{mV°C^{-1}}$).



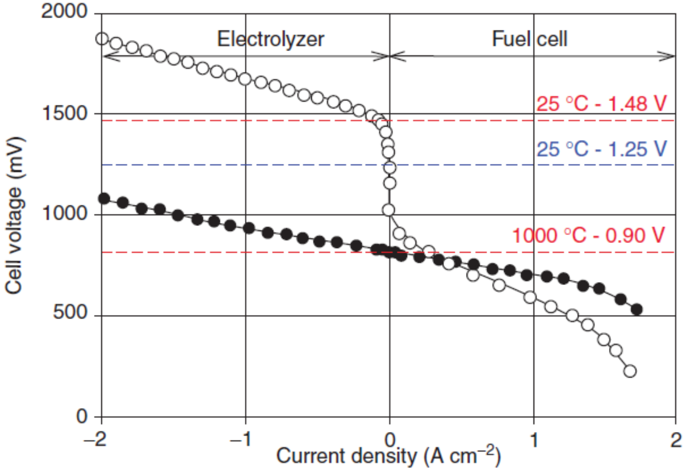


Figure 2.13 Experimental water electrolysis polarization curves measured at (o) 90 °C and (•) 1000 °C.

ELECTROCHEMICAL WATER SPLITTING: PRESSURE AND TEMPERATURE

Nonetheless, by paying more attention to the temperature dependence, it can be noticed as, by rising the temperature also the reversibility of the process is increased.

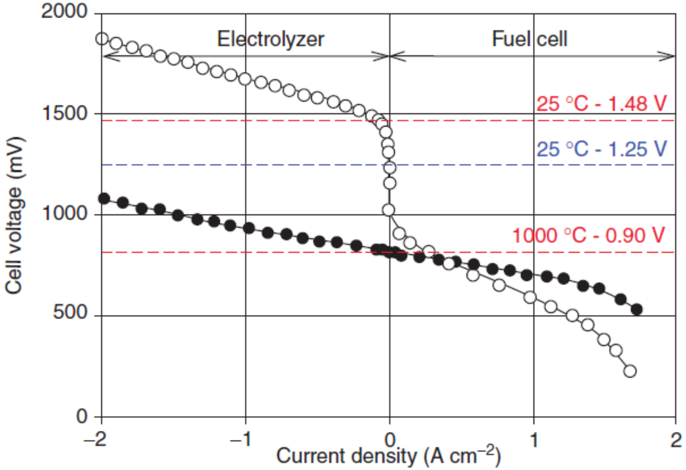


Figure 2.13 Experimental water electrolysis polarization curves measured at (o) 90 °C and (•) 1000 °C.

ELECTROCHEMICAL WATER SPLITTING: THERMODYNAMIC EFFICIENCY

Water splitting reaction efficiency is defined as the ratio among the theoretical (W_t) to real (W_r) amount of energy required to split 1 mol of water, at defined temperature T and pressure:

$$\varepsilon = \frac{W_t}{W_r}$$

The real energy can be easily calculated from the product among cell operating voltage and current: $W_r = VIt$.

In parallel, W_t can be either defined by means of the standard potential, either via the thermo-neutral voltage:

$$W_{t,\Delta G} = EIt, \quad W_{t,\Delta H} = V_{TN}It$$

Being E and V_{TN} dependent on the operating temperature and pressure, and because V is also a function of the operating current density j, two different cell efficiencies can also be defined as:

$$\varepsilon_{\Delta G}(T,P,j) = \frac{E(T,P)}{V(T,P,j)} \qquad \varepsilon_{\Delta H}(T,P,j) = \frac{V_{TN}(T,P)}{V(T,P,j)}$$

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ELECTROCHEMICAL WATER SPLITTING: FARADAIC EFFICIENCY

The Faradaic efficiency measure the efficiency of the charge transport across the cell, highlighting the presence of phenomena hampering the current flow. The Faradaic efficiency can be separately measured for each electrode:

$$\varepsilon_{F,anode} = \frac{F}{i}\frac{dn_{O_2}}{dt} \qquad \varepsilon_{F,cathode} = \frac{F}{i}\frac{dn_{H_2}}{dt}$$

Faradaic efficiency is increased by means of a separation layer used to prevent spontaneous recombination of hydrogen and oxygen (which would lead to release of Gibbs free energy in form of heat).

In reality, gas solubility in the electrolyte is not zero and mass transport across the electrolyte can take place at high current density and/or high operating pressure.

The Faradaic efficiency influences the yield of the gas production:

$$\dot{n}_{produced} = \varepsilon \frac{I}{nF}$$

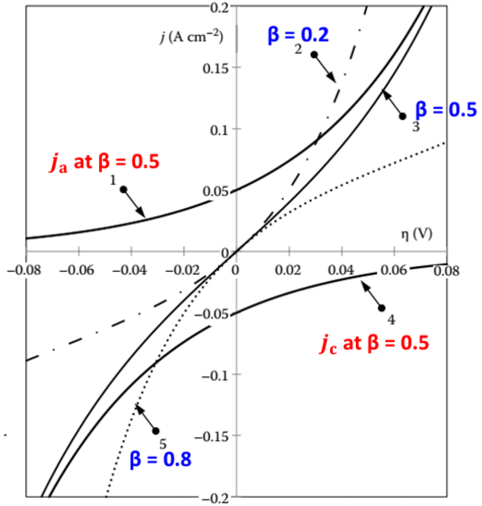
ELECTROCHEMICAL WATER SPLITTING: REACTION KINETICS

The rate of reaction influences the amount of current produced by an electrolyzer. The reaction among the kinetics of the charge transfer processes at the metal/electrolyte interface, in absence of mass transport limitations, can be described by the Butler–Volmer relationship:

$$i = i_f - i_r = i_0\left[e^{\frac{\beta nF}{RT}\eta} - e^{-\frac{(1-\beta)nF}{RT}\eta}\right]$$

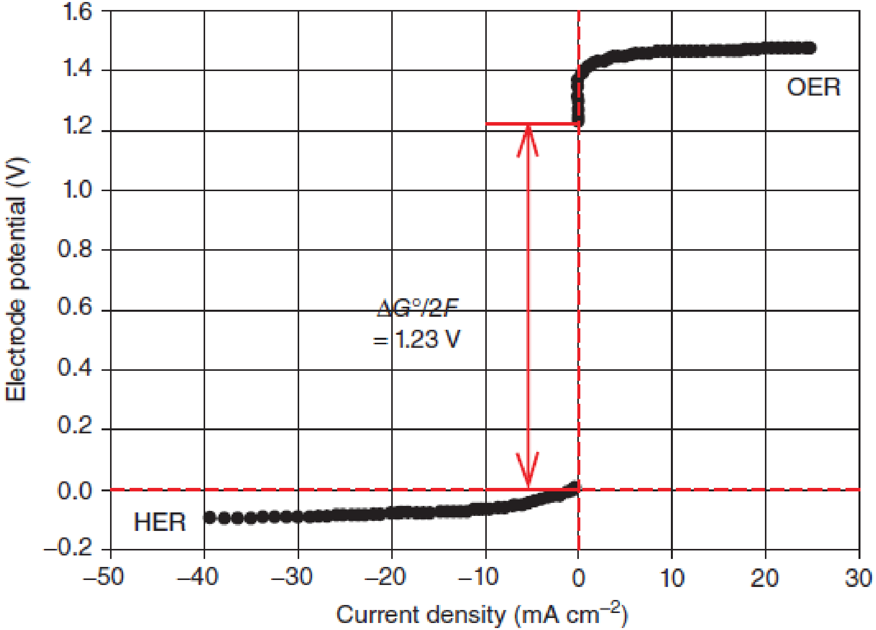
Where the subscripts *f* and *r* respectively highlight the forward and the reverse reactions, while: i_0 is the exchange current density, β is the so-called symmetry factor, and η represents the activation overpotential. For the water splitting reaction n = 2.

The main kinetic parameter which determines the efficiency of charge transfer processes is the exchange current density, i_0. The higher the current density, the more reversible is the reaction and the more efficient the charge transfer process.



Introduction to Electrochemical Science and Engineering, S. N. Lvov; CRC press 2014

ELECTROCHEMICAL WATER SPLITTING: FINAL REMARKS



From the analysis of reaction kinetics, it turns out as the HER reaction occurs much faster than OER; as a consequence:

$$\frac{i_{0,HER}}{i_{0,OER}} \approx 10^3$$

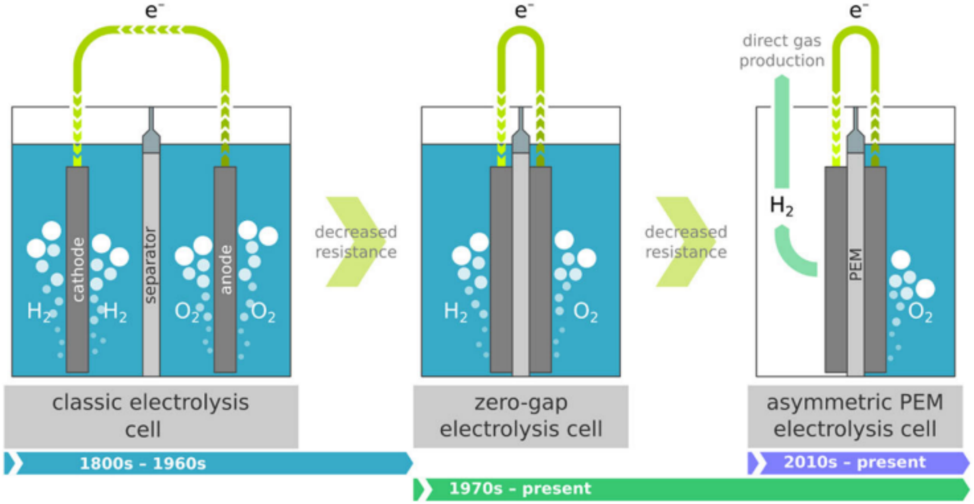
the OER constitutes the main bottleneck in limiting the performances of water electrolysers.

The velocity of occurrence of the HER reaction (by means of Butler-Volmer equations, neglecting the reverse contribution) also reflects on the HER voltage, which value is close to zero, and can be thus taken as a reference for the whole cell potential.

CELL ARCHITECTURE FOR THE WATER SPLITTING REACTIONS

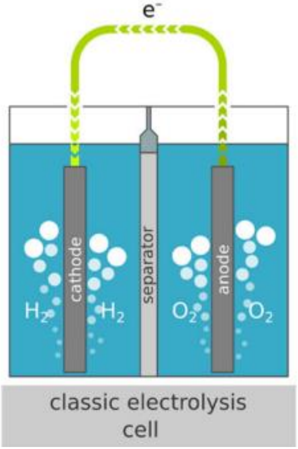
Historically, three types of cell architectures were developed:

1 – The Gap cell
2 – The Zero-gap cell
3 – The Proton Exchange Membrane (PEM) cell



Hodges A. et al., Nature Comm. (2022) 13:1304

CELL ARCHITECTURE FOR THE WATER SPLITTING REACTIONS



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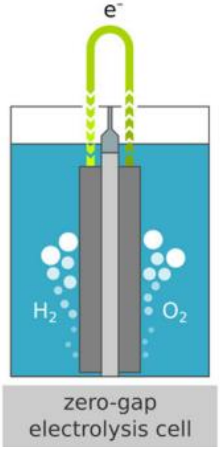
The gap cell

Two planar electrodes are placed face to face in a liquid electrolyte.

A separator (usually a porous diaphragm impregnated with the electrolyte) is introduced in the interpolar gap to prevent the spontaneous recombination of reaction products.

The distance between electrodes and diaphragm must be sufficiently large to let gases evolve freely but not too large to reduce ohmic losses. When bubble concentration increases, there is a tendency to form continuous and highly resistive gaseous films over electrode surfaces and therefore the maximum operating current density is usually limited in this kind of cell.

CELL ARCHITECTURE FOR THE WATER SPLITTING REACTIONS



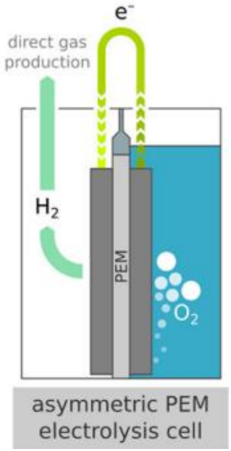
Hodges A. et al., Nature Comm. (2022) 13:1304

The zero-gap cell

Porous electrodes are pressed directly onto the separator, to reduce as much as possible the distance between the anode and the cathode (and corresponding ohmic losses).

Gaseous products are released through the pores at the backside. Significantly larger current densities can be reached without significant extra voltage losses.

CELL ARCHITECTURE FOR THE WATER SPLITTING REACTIONS



Hodges A. et al., Nature Comm. (2022) 13:1304

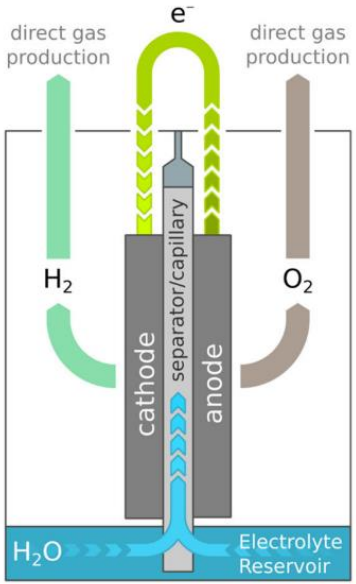
The Proton Exchange Membrane (PEM) cell

There is no liquid electrolyte in circulation in this kind of cell.

The cell separator is a thin ion-conducting polymeric film that is used for the double purpose of conveying electric charges (protons in the case of PEM water electrolysis) from the anode to the cathode and separating gas products.

PEM is the most efficient but its implementation is also limited by geometrical and technical constrains which are making this technology more expensive.

CELL ARCHITECTURE FOR THE WATER SPLITTING REACTIONS: FUTURE POSSIBILITIES



Hodges A. et al., Nature Comm. (2022) 13:1304

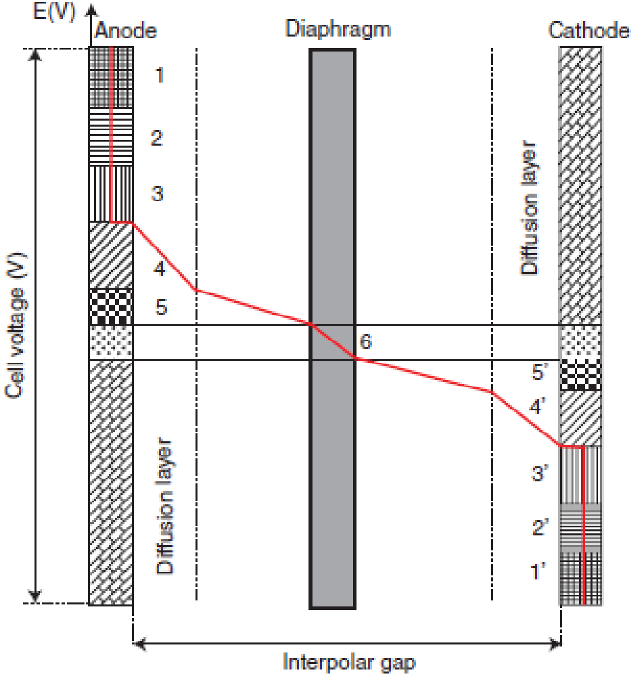
The capillary-fed electrolysis cell

Novel design (published on 2022): its possibilities have still to be investigated

The aqueous electrolyte is constantly supplied to the electrodes by a spontaneous capillary action through the separator, while gases are produced directly in gas collection chambers.

In this design, the cell avoids bubbles masking the electrodes and maintains access to the catalytic sites on the electrodes, and it ensures that water flow to an electrode does not counteract gas flow away from the electrode

WATER ELECTROLYZING CELLS: EFFICIENCY



Investigating and optimizing the cell architecture is fundamental for maximizing the efficiency of the reaction at a cell level. In fact, while the most significant part of electricity supplied to an electrolysis cell is used for the Gibbs free energy change of the reaction of interest, there are several sources of energy degradation (electricity into heat), as we will later investigate.

By now it can be observed as potential drops are located inside bulk electrodes due to internal resistance (1, 1′), across electroactive layers which are not always good electronic conductors (2, 2′), at interfaces where charge transfer processes take place (3, 3′), in solution, across the diffusion layers close to the electrode surface when mass transport phenomena are involved or gaseous species are formed (4, 4′), by transport of ions in the bulk electrolyte (5, 5′) and across the cell separator (6). As we are going to discover, most of these processes are in common among all water electrolyzer technologies.

2. PROTON EXCHANGE MEMBRANE WATER ELECTROLYSERS (PEMWE)

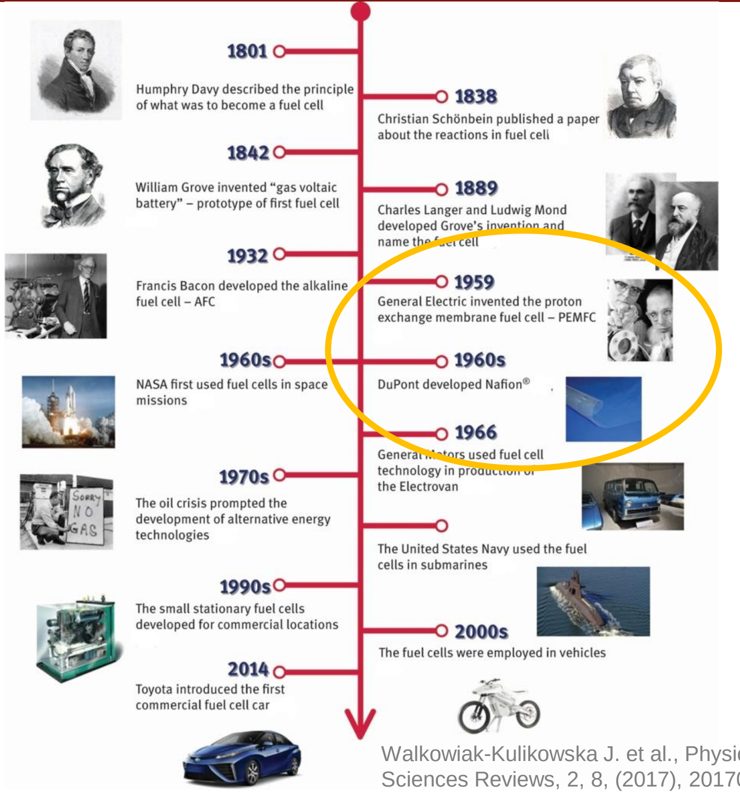
PEMWE: COMPOSITION

PROTON EXCHANGE MEMBRANE TECHNOLOGY

The interest in using PEM technology for water electrolysis, is due to the fact that:

- It allows to realize compact electrolyzers able to operate with current densities about several A cm^{-2}.
- Electrolyser are characterized by a high efficiency; moreover, with respect other technologies they more efficient in the high current densities regime because heat can be managed more easily.
- Electrolysers are safer, as they don’t use corrosive electrolyte and can be operated more safely under pressure.
- They have a good dynamic response, and they cansustain repetitive on/off cycles and transient loads; they are therefore well-suited for water splitting using intermittent power sources.

FROM ALKALINE TO PROTON-EXCHANGE-MEMBRANE (PEM) TECHNOLOGY



1801
Humphry Davy described the principle of what was to become a fuel cell

1838
Christian Schönbein published a paper about the reactions in fuel cell

1842
William Grove invented "gas voltaic battery" – prototype of first fuel cell

1889
Charles Langer and Ludwig Mond developed Grove's invention and name the fuel cell

1932
Francis Bacon developed the alkaline fuel cell – AFC

1959
General Electric invented the proton exchange membrane fuel cell – PEMFC

1960s
NASA first used fuel cells in space missions

1960s
DuPont developed Nafion®

1966
General Motors used fuel cell technology in production of the Electrovan

1970s
The oil crisis prompted the development of alternative energy technologies

The United States Navy used the fuel cells in submarines

1990s
The small stationary fuel cells developed for commercial locations

2000s
The fuel cells were employed in vehicles

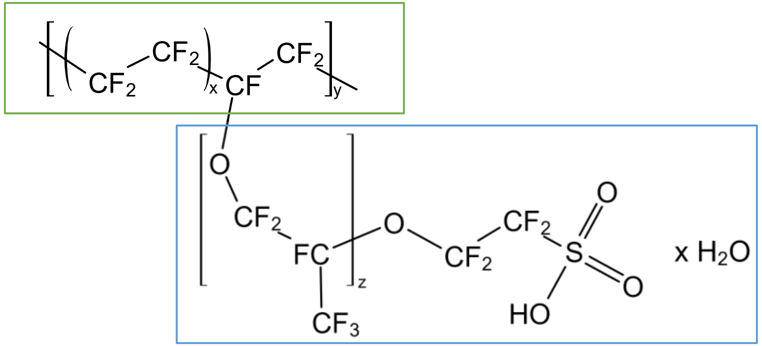
2014
Toyota introduced the first commercial fuel cell car

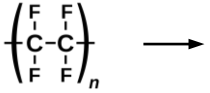
Walkowiak-Kulikowska J. et al., Physical Sciences Reviews, 2, 8, (2017), 20170018

NAFION

Nafion® is the brand name of a polymer belonging to the family of perfluoro-sulfonic acid (PFSA) polymers. It is represented by the chemical formula: $C_7HF_{13}O_5S \cdot C_2F_4$, and, more in depth, it can be defined as a sulfonated tetrafluoroethylene-based fluoropolymer-copolymer.

It is composed by a hydrophobic backbone and an hydrophilic sulfonated chain. The average distance between the side chains along the backbone defines the equivalent weight (EW) of the formulation, which is describing the number of grams of dry polymer per mole of SO_3 groups. This parameter is crucial in defining the abilities of water uptake and retention of the polymer.





Teflon, $(C_2F_4)_n$

$$EW = 800 \div 1500 \; g \; mol^{-1}$$

NAFION

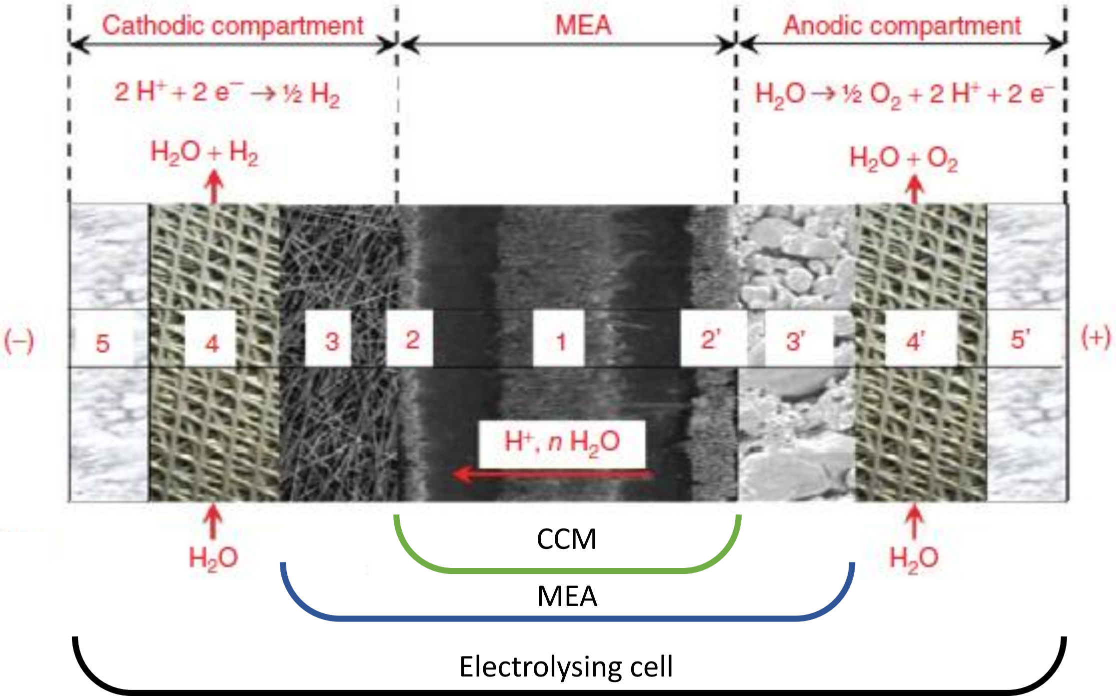
Nafion is characterized:

- By a range of operative temperature up to 100°C
- A high proton conductivity
- An excellent chemical and mechanical stability.

In PEM technology Nafion is used as solid electrolyte.

To date, depending on the application, Nafion membrane thickness ranges from usually 50 to 250 µm.

THE PROTON-EXCHANGE-MEMBRANE (PEM) ARCHITECTURE



1. Electrolyte
2. Catalyst layer
3. (3) Gas Diffusion Layer /
   (3') Porous Transport Layer
4. Separator (optional)
5. Bipolar plates

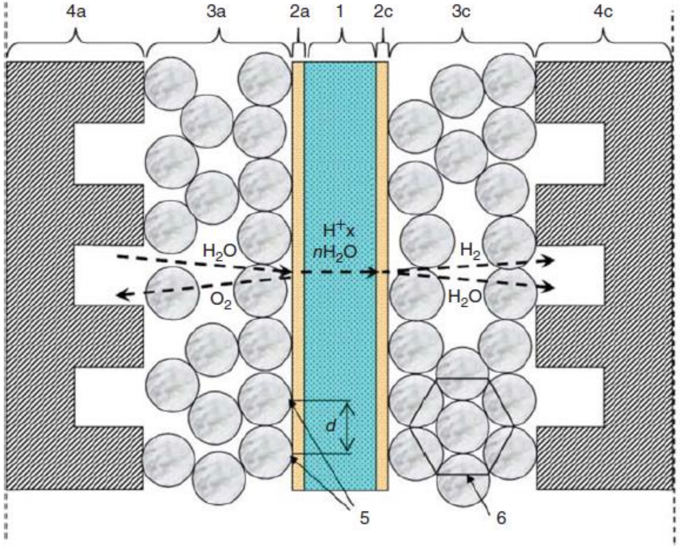
CCM: Catalyst Coated Membrane

MEA: Membrane Electrode Assembly

PEMWE: CELL DESIGN

The optimal cell design aims to:

1. Reducing as much as possible the electronic resistance of bipolar plates and current distributors and the resistance among the catalyst layer and the charge collectors (5)
2. Reducing as much as possible the pressure drop in pumping the liquid water through the anodic compartment.
3. Ensuring a homogeneous water transfer to the anode catalyst by optimizing electrode porosity, allowing at the same time, gaseous oxygen flow counterclockwise from the anode to the anodic bipolar plate.



PROTON EXCHANGE MEMBRANE TECHNOLOGY: THE ELECTROLYTE

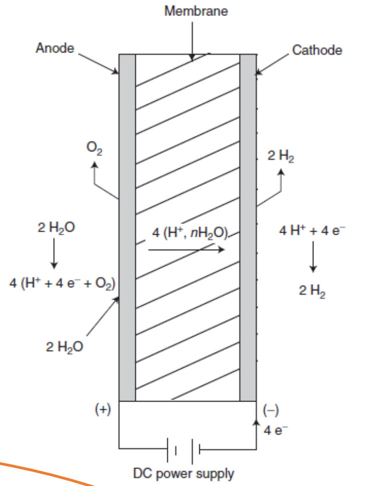
Electrolyte

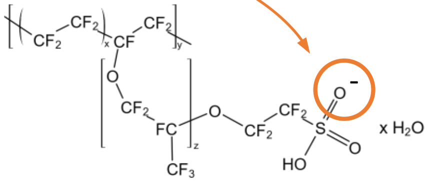
The central component of the cell is an about ≈0.2÷0.1 mm thick membrane of a proton-conduction polymer electrolyte; here Nafion is used to fulfil two main tasks:

- Sustain ionic transport by carrying ionic charges (solvated protons) via the sulfonated functional groups.
- Separate the produced gases.

While the fluorinated backbone allows:

- To promote the ionization of the ending sulphonic groups (achieving an acidity level similar to 1M aqueous sulphuric acid solutions when the membrane is hydrated)
- And to provide appropriate chemical stability, especially on the anodic side where severe oxidizing conditions are found.

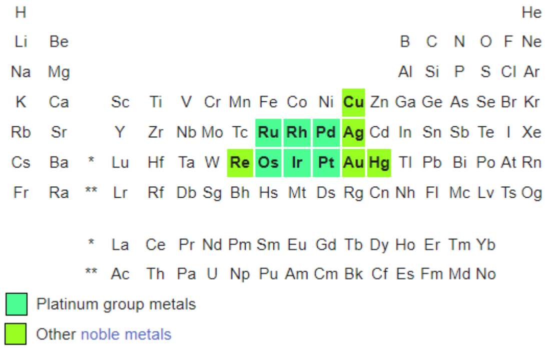




PROTON EXCHANGE MEMBRANE TECHNOLOGY: THE ELECTRODES

Electrodes

Electrodes are connected to an external DC power source, which provide the electrical work for the reaction. Both electrode share the same morphological architecture, consisting in a microporous support hosting a dispersion of metallic nanoparticles. As materials metals belonging to the platinum group metals are used. Their scarcity and high costs, is the main factor limiting the diffusion of PEM technology.

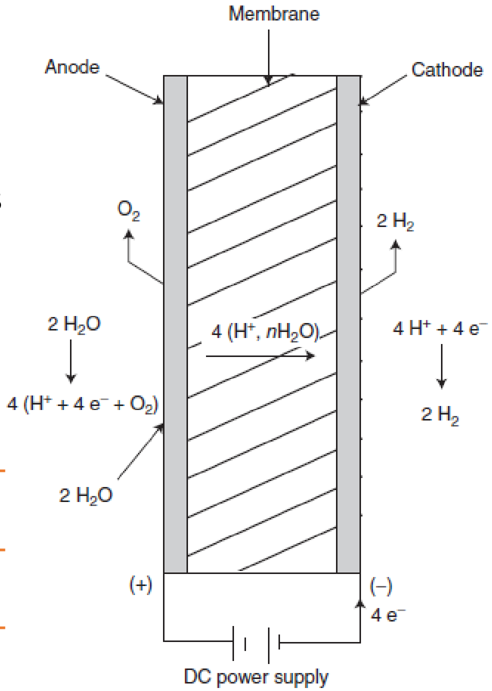


H																		He
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	**Cu**	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr		Y	Zr	Nb	Mo	Tc	**Ru**	**Rh**	**Pd**	**Ag**	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Lu	Hf	Ta	W	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
		*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
		**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

🟩 Platinum group metals

🟩 Other noble metals

Anode (OER)	$H_2O(l) \rightarrow 2H^+ + 2e^- + \frac{1}{2}O_2(g)$
Cathode (HER)	$2H^+ + 2e^- \rightarrow H_2(g)$
Full reaction	$H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$



PEMWE: THE CATALYST LAYER – THE CATHODE ELECTRODE

Cathode (HER)	$2H^+ + 2e^- \rightarrow H_2(g)$

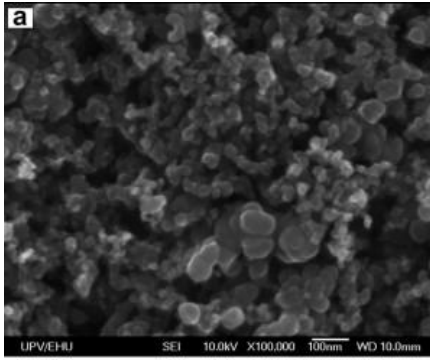
As previously introduced, catalyst layers are composed by metallic nanoparticles dispersed on a microporous support.

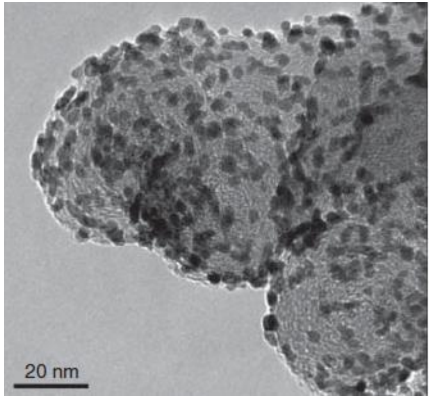
As a support, the standard is set by electro-conductive carbon blacks, such as Vulcan® (Cabot Co.), in example. Carbon black is realized by means of thermal decomposition or partial oxidation of hydrocarbons.

Carbon blacks contain very small particles (10 ÷ 40 nm thick), which, during the synthesis, tend to form 20 ÷ 100 nm wide aggregates.

The pore network includes the pores of the particles themselves and the pores formed by the aggregation of these particles.

For the HER, platinum is commonly used as catalyst material because is the most efficient and stable HER electrocatalyst in acidic or alkaline electrolytes.



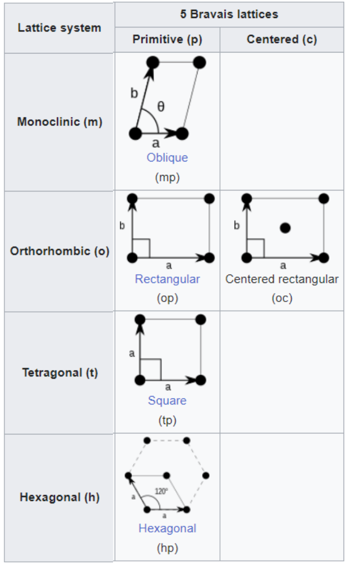


Antxustegi M. et al., Int. J. of Hydrogen Energy (2014), 39, 8, 3978-3983

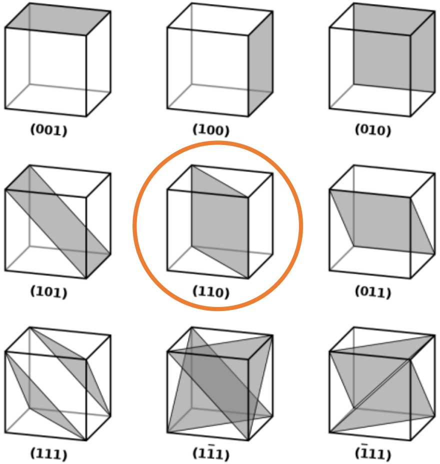
PEMWE: THE CATALYST LAYER – THE CATHODE ELECTRODE

To reduce Pt consumption and increase the efficiency of its use, three strategies have been developed:

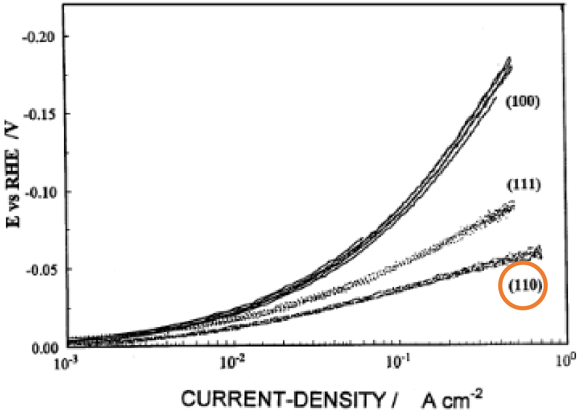
1. Increase the number of reactive sites by fabricating Pt nanoparticles exposing as much as possible the [1 1 0] crystallographic plane



Lattice system	5 Bravais lattices	
	Primitive (p)	Centered (c)
Monoclinic (m)	Oblique (mp)	
Orthorhombic (o)	Rectangular (op)	Centered rectangular (oc)
Tetragonal (t)	Square (tp)	
Hexagonal (h)	Hexagonal (hp)	



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

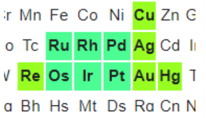


B.E. Conway, B.V. Tilak / Electrochimica Acta 47 (2002) 3571-3594

https://en.wikipedia.org/wiki/Bravais_lattice#In_2_dimensions

PEMWE: THE CATALYST LAYER – THE CATHODE ELECTRODE

R.2



r	Mn	Fe	Co	Ni	Cu	Zn	G
o	Tc	Ru	Rh	Pd	Ag	Cd	I
V	Re	Os	Ir	Pt	Au	Hg	T
a	Bh	Hs	Mt	Ds	Rg	Cn	N

2. Tune catalyst design: Pt-coating of low-cost PGM, or creating bi- (or tri-) metallic alloys
3. Improve the degree of order of the support-catalyst complex

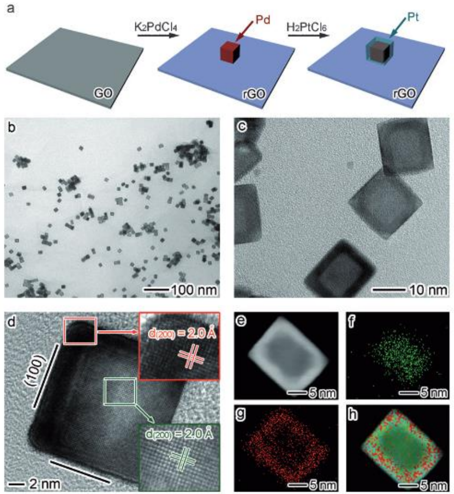
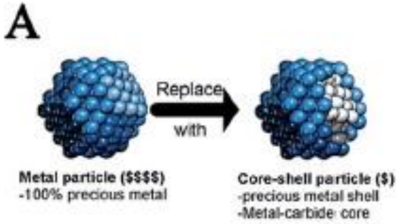


Figure 1. a) Schematic illustration for the synthesis of Pt–Pd–rGO structures. b,c) TEM images of the Pt–Pd–rGO structure (namely Pt–Pd–rGO II). d) HRTEM image of a Pt–Pd nanocrystal on the rGO. e) STEM image and f–h) EDS mapping profiles of a single Pt–Pd nanocrystal on the rGO, element profiles for f) Pd (green), g) Pt (red), and h) Pt–Pd-STEM overlay.

Bai S., et al., Angew. Chem. Int. Ed.2014,53, 12120 –12124



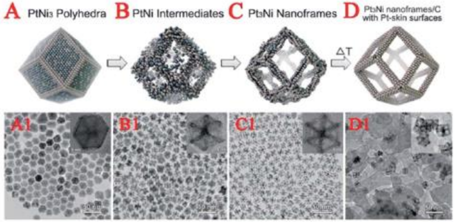


Fig. 3 Schematic and corresponding TEM images of the synthesis of the samples. (A and A1) Initial $PtNi_3$ polyhedra. (B and B2) PtNi intermediates. (C and C1) Pt_3Ni hollow nanoframes. (D and D1) Annealed Pt_3Ni nanoframes. Reprinted with permission from ref. 49 copyright 2014, American Association for the Advancement of Science.

Li, J. et al., Mater. Chem. A, 2016, 4, 11973–12000

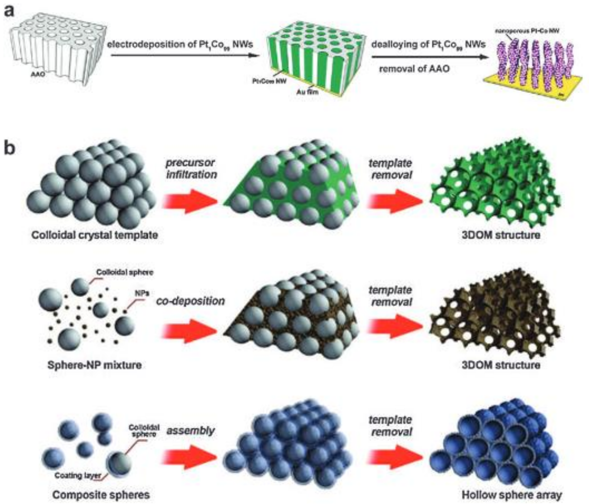


Fig. 2 (a) Schematic illustration of the fabrication process of nanoporous Pt–Co alloy nanowires. Reprinted with permission from ref. 10. Copyright 2009 American Chemical Society. (b) Three pathways of preparing periodic porous structures by colloidal crystal templating. Reprinted with permission from ref. 12. Copyright 2008 American Chemical Society.

Xu, Y., et al.,Chem. Soc. Rev., 2014, 43, 2439-2450

PEMWE: THE CATALYST LAYER – THE ANODE ELECTRODE

Anode (OER)	$H_2O(l) \rightarrow 2H^+ + 2e^- + \frac{1}{2}O_2(g)$

On the anode side, there are few if any supporting electronic carriers available, due to the harsh potential at which the reaction takes place (> 1.5 V) where most of materials oxidize and corrode. Iridium (metal or oxide) is the most efficient and stable catalyst for the OER. Ir can be deposited on different supports and a current hot topic in research is the formulation of the most proper support able to withstand for long operating times at working conditions.

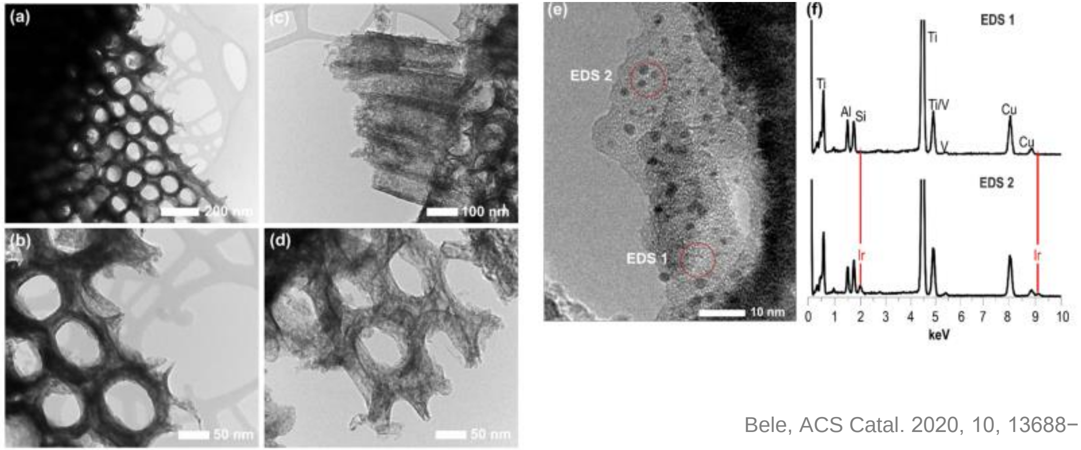


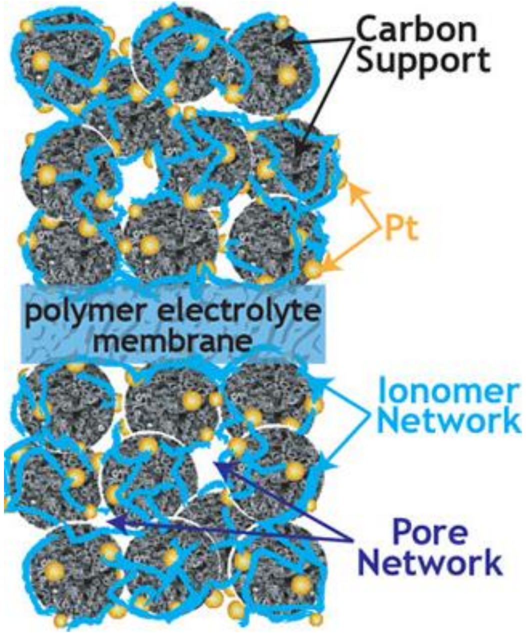
Figure 3. TEM micrographs of TiON nanotubes: (a) top-sectional view, (b) higher-magnification top-sectional view, (c) cross-sectional view, and (d) high-magnification top-sectional view. Figure (e) shows the TEM micrograph of the TiON nanotube with deposited Ir nanoparticles, whereas the corresponding EDS analyses of a part with no Ir nanoparticles (EDS 1) and a part with Ir nanoparticles (EDS 2) are shown in (f).

Bele, ACS Catal. 2020, 10, 13688−13700

PEMWE: THE CATALYST LAYER

Different coating approaches have been developed in order to search for the most up-scalable production method able to confer the better stability to the catalyst layer. The catalyst solution (composed by a solvent, catalyst nanoparticle, ionomer and support) is then deposited with spray coating techniques onto a support. The evaporation of the solvent leads to the formation of the solid electrode. This method is also preferred to be used because easier to be upscaled at an industrial level.

For catalyst formulations dedicated to research activities also method of physical vapour deposition (such as sputtering) can be used.



PEMWE: GAS DIFFUSION AND POROUS TRANSPORT LAYERS

To maximise charge transport to the electrode, catalyst supported nanoparticles need to be in contact with a surface of the current collectors, which act as gas diffusion layers too.

Also here, the anodic compartment is more difficult to handle, because of the counterflow of water and oxygen molecules which are respectively diffusing towards the catalyst layer and towards the bipolar plate.

To date, the current collector layers are usually made of sintered titanium particles.

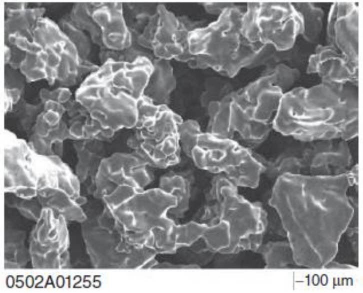


Figure 3.10 SEM image of a porous Ti current collector with homogeneous particle size.

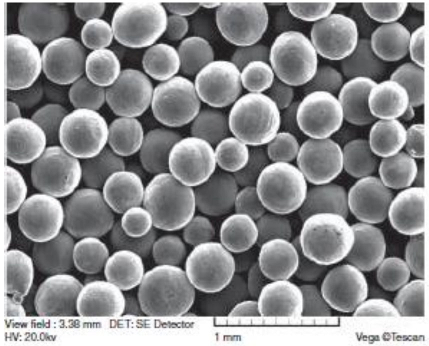


Figure 3.13 SEM image of a porous Ti current collector with spherical particles.

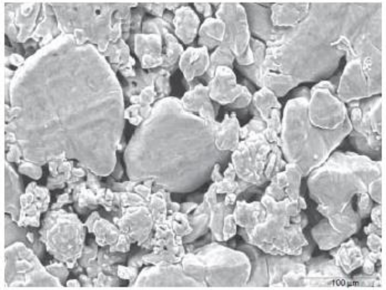


Figure 3.11 SEM image of a porous Ti current collector with heterogeneous particle size.

PEMWE: GAS DIFFUSION AND POROUS TRANSPORT LAYERS

Thickness and porosity need here to be finely tuned in order to:

- optimize the mass transport between the bipolar plates and the catalytic layers
- homogeneously distribute the current lines at the interface with the catalyst layer
- guarantee homogeneous compression distribution to enhance homogeneous diffusion and mechanical stability

Higher porosity leads to better mass transport but poorer charge transport, due to the reduction of the contact points with the catalyst layer

PEMWE: SPACER

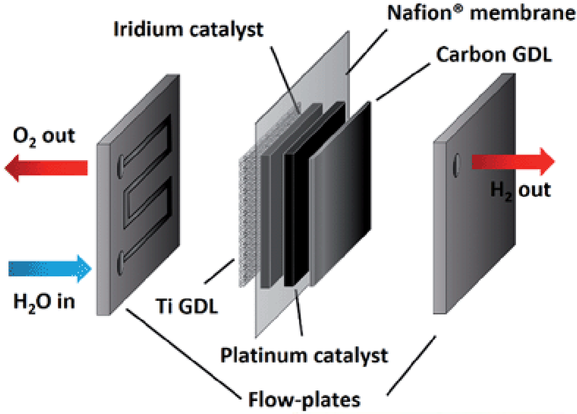
A spacer can be additionally displaced in between GDLs and bipolar plates to define a region in which liquid water can be pumped and where gaseous reaction products are collected.

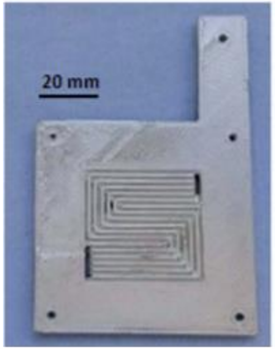
Figure 3.15 Photograph of a grid spacer installed in a srack + details of water injection/gas collection.

PEMWE: THE BIPOLAR PLATES

The bipolar plates are the two covers which are enclosing the MEA. They are usually made out of titanium, because of its electronic and thermic favourable conduction properties, and moreover because of its chemical stability with respect the specimens involved in the water splitting reaction and the range of operative voltages too. While operating, the Ti is passivated by an oxide layer (TiO_2); to reduce the parasitic contact resistance, Ti bipolar plates can be coated with noble metals (Au, Pt), TiC or TiN.

Bipolar plates then host the flow field, that is a set of grooved channels made to homogeneously distribute water to the MEA surface and homogeneously collect reaction products.

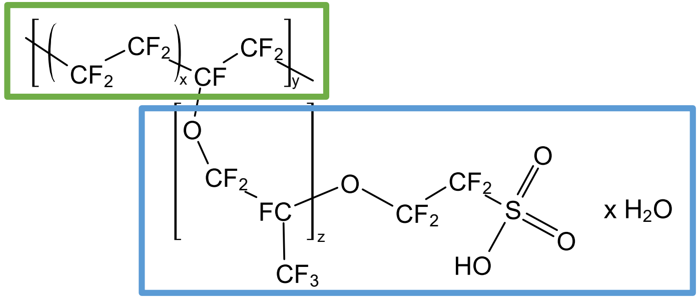


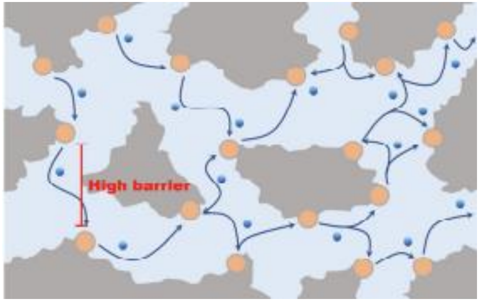


Chisholm G. et al.,
Energy Environ. Sci.,
2014, 7, 3026–3032

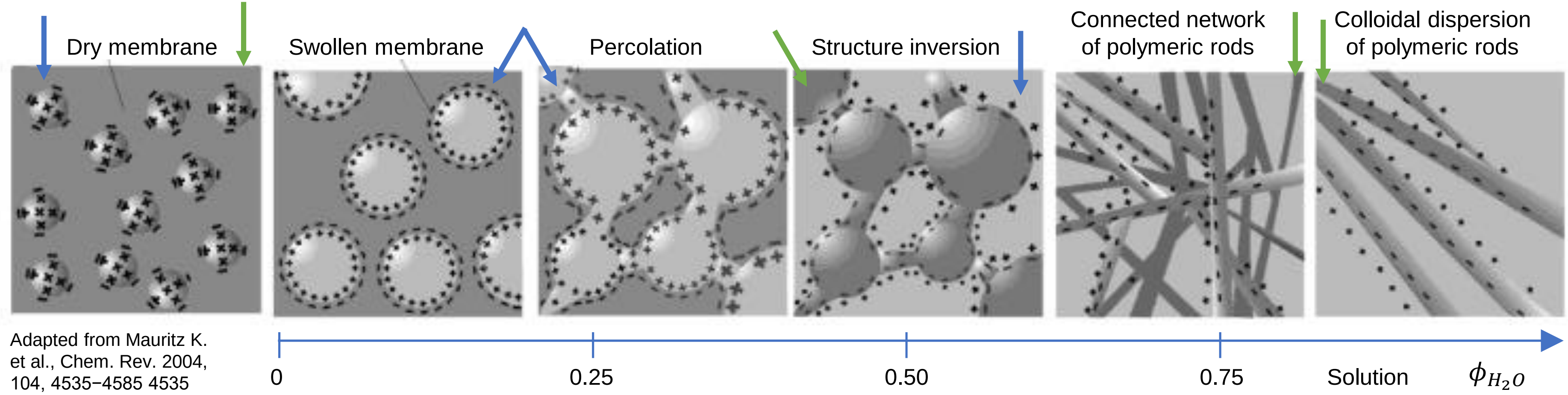
PEMWE: OPERATION AND LIMITS

NAFION AND IONIC CONDUCTION





Hwang S. *et al.*,
Int. J. Mol.
Sci. 2022, 23(22)



Adapted from Mauritz K.
et al., Chem. Rev. 2004,
104, 4535−4585 4535

CROSS-PERMEATION IN NAFION

The gas permeability (P^m) in Nafion is pressure dependent:

$$P^m = \frac{\nu}{\Delta P}\frac{L}{A}$$

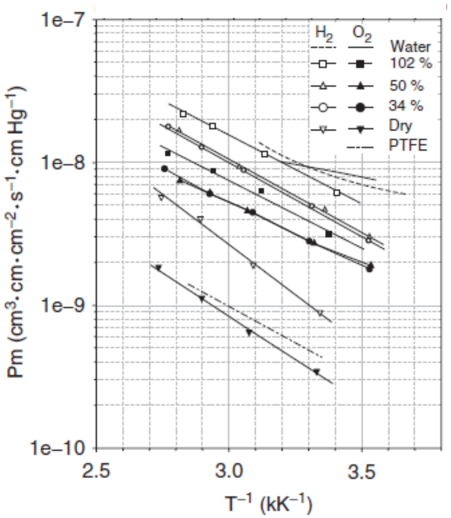
Where ν is the rate of gas permeation ($cm^3\ s^{-1}$), ΔP is the difference of pressure (Pa), L is the membrane thickness (cm) and A its cross-sectional area (cm^2).

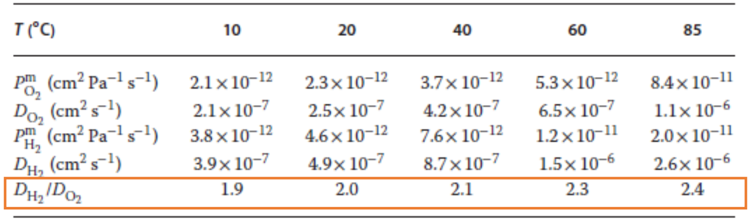
Because PEMWE operate with liquid water, Nafion is fully hydrated and, therefore, H_2 and O_2 permeabilities are at their maximum, diffusing according to the Fick's law :

$$D_i = P_i^m RTC_i$$

Where D is the diffusion coefficient ($cm^2\ s^{-1}$) and C the specimen solubility.

In the operating regime of PEMWEs hydrogen cross permeation is double with respect oxygen one.



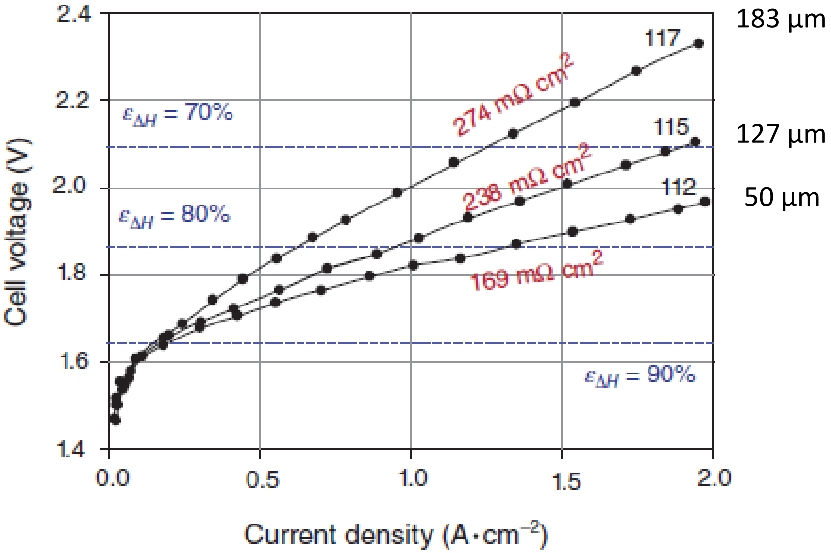


T (°C)	10	20	40	60	85
$P^m_{O_2}$ ($cm^2\ Pa^{-1}\ s^{-1}$)	2.1×10^{-12}	2.3×10^{-12}	3.7×10^{-12}	5.3×10^{-12}	8.4×10^{-11}
D_{O_2} ($cm^2\ s^{-1}$)	2.1×10^{-7}	2.5×10^{-7}	4.2×10^{-7}	6.5×10^{-7}	1.1×10^{-6}
$P^m_{H_2}$ ($cm^2\ Pa^{-1}\ s^{-1}$)	3.8×10^{-12}	4.6×10^{-12}	7.6×10^{-12}	1.2×10^{-11}	2.0×10^{-11}
D_{H_2} ($cm^2\ s^{-1}$)	3.9×10^{-7}	4.9×10^{-7}	8.7×10^{-7}	1.5×10^{-6}	2.6×10^{-6}
D_{H_2}/D_{O_2}	1.9	2.0	2.1	2.3	2.4

CROSS-PERMEATION AND ELECTROLYSER PRESSURIZATION

Cross-permeation is mainly dependant on two parameters:

1. Thickness of the Nafion membrane (thicker membranes allow to reduce gas permeation but they are also characterized by higher ionic conduction resistance).



CROSS-PERMEATION AND ELECTROLYSER PRESSURIZATION

2. Operating pressure

The larger the operating pressure, the larger the cross permeability.

To better embed electrolysers into the hydrogen value chain, in particular, many practical applications require pressurized hydrogen, such as:

- hydrogen storage in metal hydrides (P > 1.2MPa with <5 ppm O_2 and H_2O);
- hydrogen transport in pipelines (H_2 into CH_4 and biogases – power to gas): 1.3 ÷ 8.2 MPa;
- hydrogen filling in tube trailers (22 MPa);
- hydrogen storage in car tanks (35 ÷ 70 MPa);
- hydrogen storage in hydrogen refuelling stations (90 MPa).

CROSS-PERMEATION AND ELECTROLYSER PRESSURIZATION

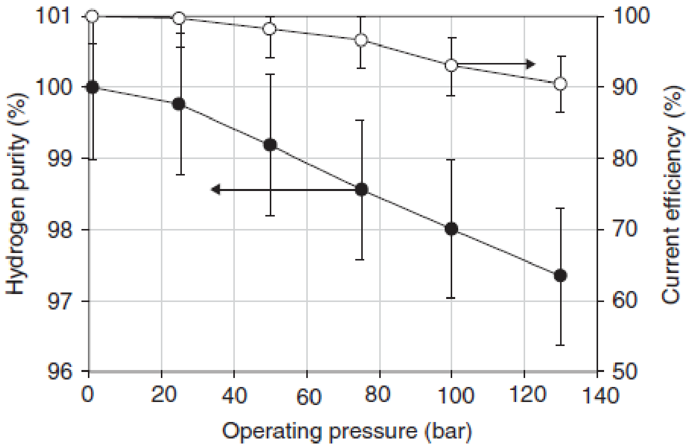


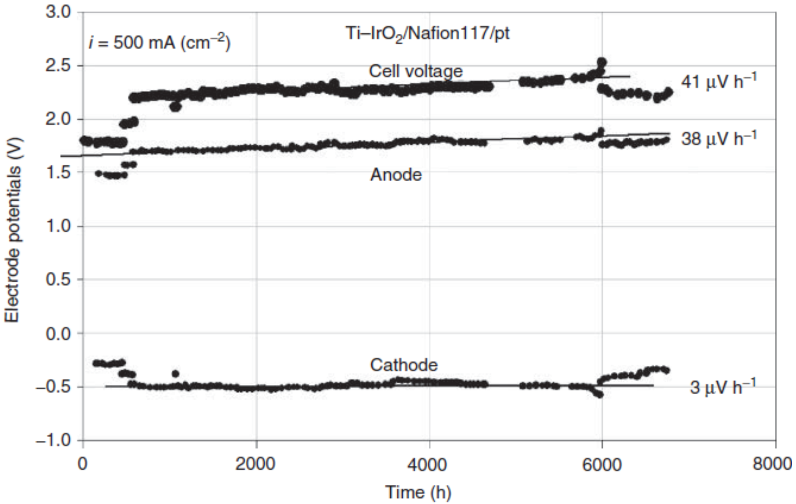
Figure 3.34 Hydrogen purity (•, vol%) in the cathodic compartment and current efficiency (○, %) as a function of operating pressure.

More in depth, gas cross-permeation is at the base of the reduction of hydrogen purity and faradaic efficiency when pressure is rose.

To date, for trying to reduce the cross-correlation, some functionalization of the ionomeric membrane was tried (by adding inorganic fillers to reduce diffusivity or by adding fillers able to promote gas recombination), leading to an overall reduction of mechanical stability and ionic conductivity.

PEMWE: DURABILITY

In electrolysis plants, durability is directly related to capital expenses. Durability is expressed in terms of hours of operation and the current standard for PEMWE is set at 50000 h.
Durability is affected by the development of degradation processes which are mainly inducing a loss of activity at the anode. At a cell and system level, degradation can be expressed in terms of voltage loss per hour (μV h^{-1}). To date, the the largest drop of performances occurred after the first 500 - 1000 h of operation.



PEMWE: FACTORS INFLUENCING THEIR PERFORMANCES

Degradation is still a central problem which is reducing catalyst performances and lifetime. The main processes involved in catalyst degradation involve all of the components of the MEA; concerning the catalyst layer:

Catalyst dissolution: found to be due to the formation of soluble iridium complexes at the operating voltages (Ir dissolution starts at about 1.1 V, thus an operative voltage of 1.5 – 1.8 V is demanding).

Catalyst poisoning: dissolved Na and Ca can deposit on the catalyst layer, increasing the charge transfer resistance and the activation overpotential.

Catalyst migration: operating the electrolyser for longer hours leads to agglomeration at both at the anode and cathode. The main result is the increase in particle size and reduction of electrochemically active surface area end electrode performances. It was also detected that Ir agglomeration can be also triggered by ionomer degradation.

Catalyst passivation: catalyst oxidation results in a formation of nonconductive layer which makes the overall contact resistance increase.

PEMWE: FACTORS INFLUENCING THEIR PERFORMANCES

Concerning the proton exchange membrane it can be subjected to:

Chemical degradation: which leads to the thinning of the membrane (increasing in example the rate of the gas cross-over, and reducing the lifetime of the membrane).

Membrane poisoning from cations (such as Na^+, Li^+, Ca^{2+}, Cu^{2+}, Ni^{2+}, Fe^{3+}) reduces the liquid phase conductivity of membrane by settling on the sites supporting ion conduction.

Thermally induced degradation: hydrothermal breakdown of the sulphonated chains and fluorine release can be thermally promoted if the operating temperature is ranging from 55 ÷ 150 °C

PEMWE: STACKING

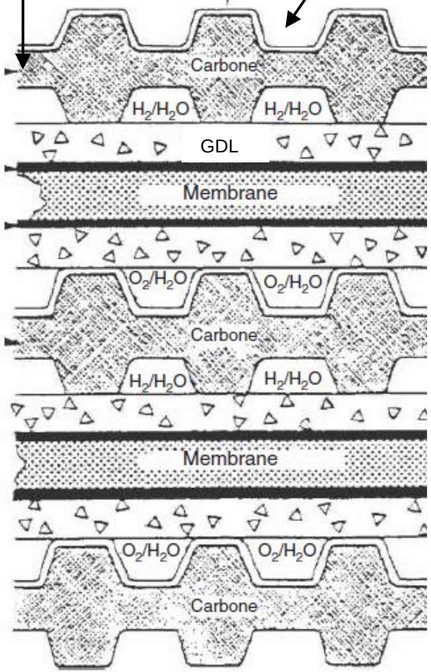
STACKING PEMWES

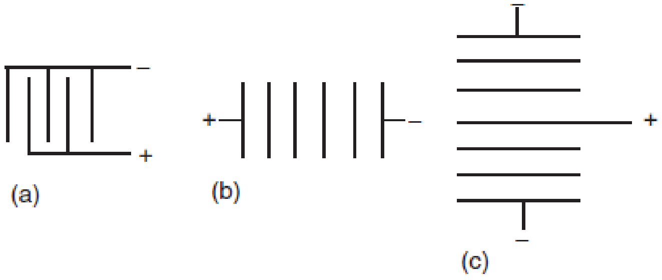
The stacking procedure consists in assembling together a set of electrochemical cells in order to build a device able to deal with larger power.

Stacking needs to be carefully done in order to:

- ensure a homogeneous distribution of **reactants** to the single cells and of products of reaction, which needs to be collected and properly conveyed to the subsequent steps.
- ensure a homogeneous distribution of **current** and **heat management**
- ensure an even **compression force** in order to delineate the volumes of individual cells, as well as to support the different of pressure between the cells and the atmosphere.
- in pressurized electrolyzers, pressurized inert gas is best to be flown across the pressurization vessel during electrolysis, in order to remove traces of leaking hydrogen and/or oxygen that would otherwise tend to accumulate inside the vessel.

STACKING PEMWE





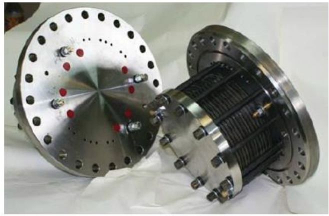
Monopolar design

Bipolar design

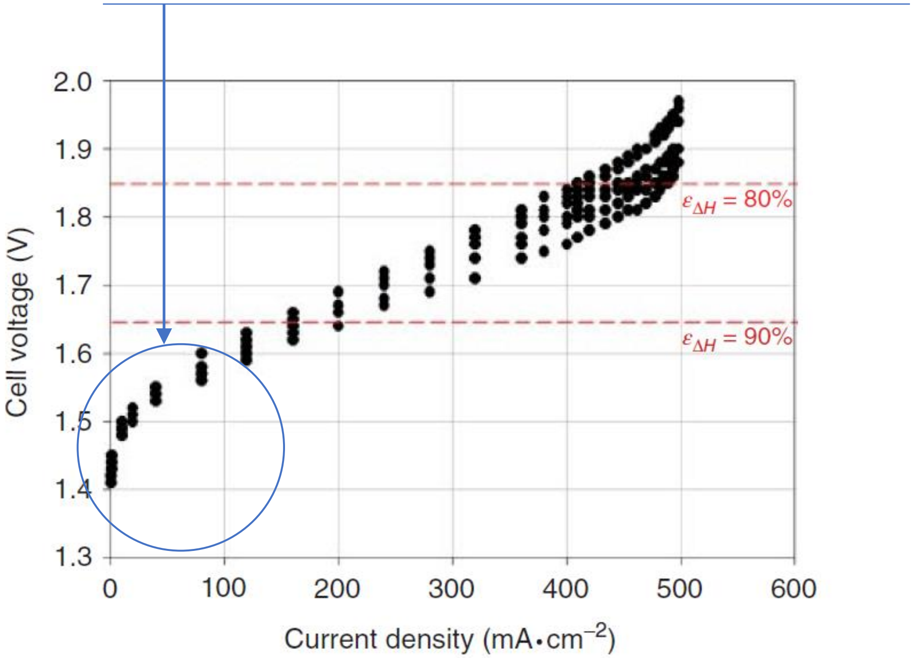
Design with central anode

STACKING PEMWE

The most basic tool for checking the stack condition is measuring the polarization curve from the single cells composing it.

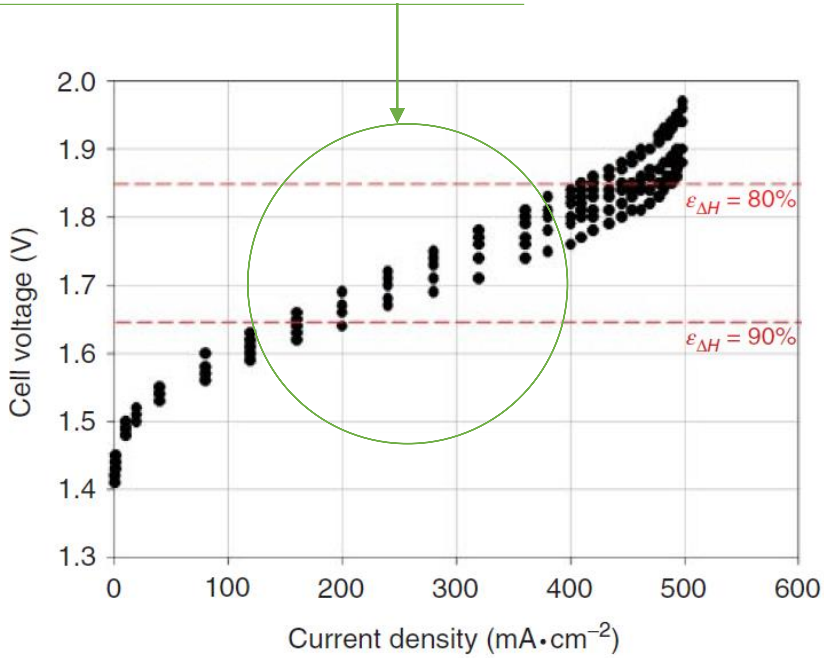


Spotted differences at low current densities are the first indication that MEAs do not operate homogeneously.



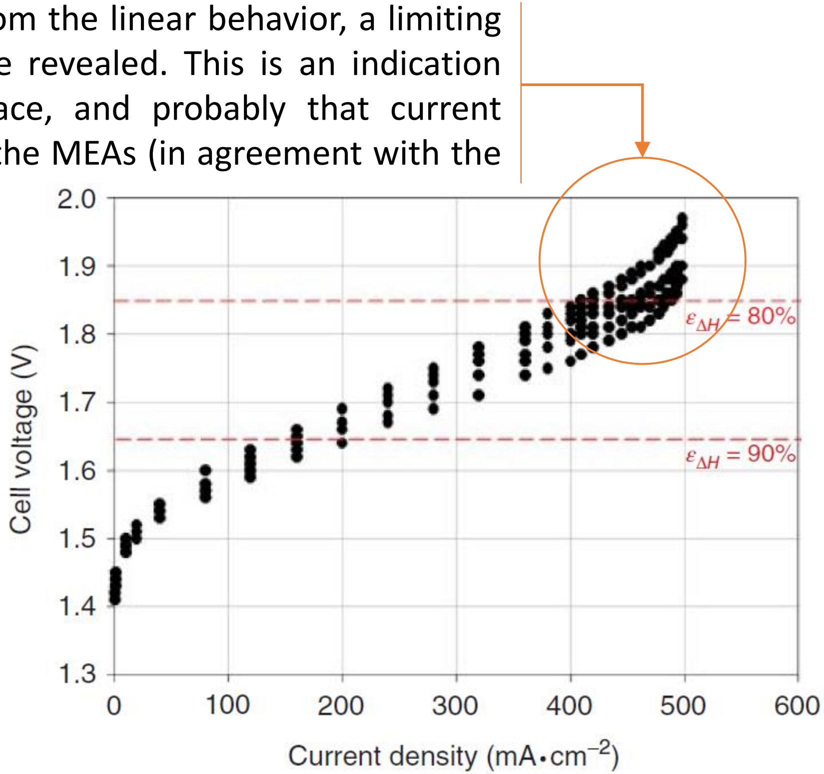
STACKING PEMWE

In the intermediate regime, the V/I curves exhibit different ohmic slopes, that is cell resistances are different. This may be due to surface oxidation of some Ti cell components or more or in less resistive MEAs.

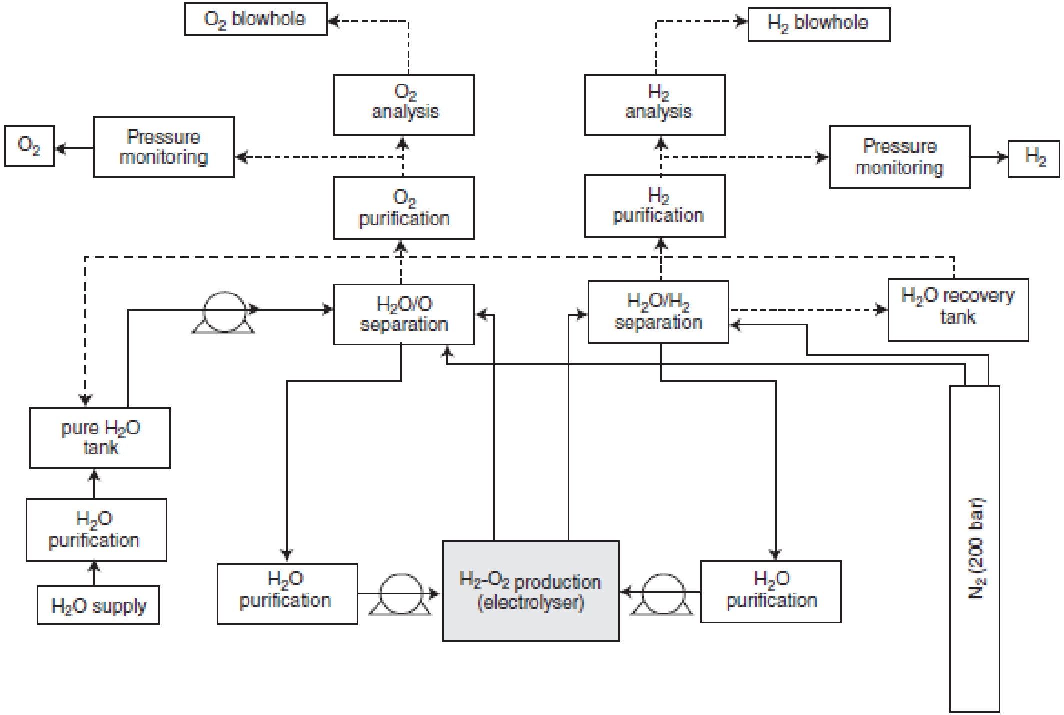


STACKING PEMWE

At high current densities , the deviation from the linear behavior, a limiting current density of 450–500mAcm^{-2} can be revealed. This is an indication that gas screening effects are taking place, and probably that current distributors are not firmly pressed against the MEAs (in agreement with the recorded strong ohmic slopes).



BALANCE OF PLANT OF A PEMWE SYSTEM



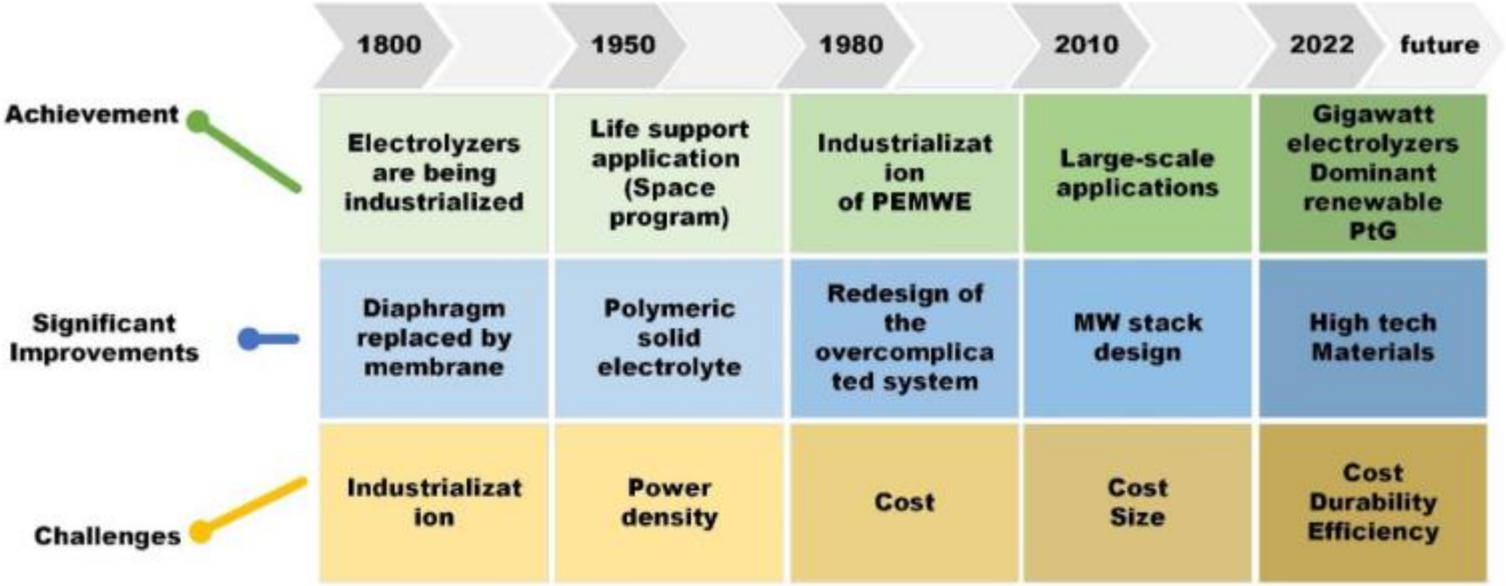
https://www.ise.fraunhofer.de/en/business-areas/hydrogen-technologies-and-electrical-energy-storage/electrolysis-and-power-to-gas.html

SUMMARY AND PERSPECTIVES

R.3, R.4

Technical specifications	Advantages	Disadvantages / limitations
• Hdrogen production rate / system size: $1.1 \div 240\ \mathrm{Nm}^3_{\mathrm{H2}}\ \mathrm{h}^{-1}$ / $0.2 \div 1150$ kW • System efficiency: $62 \div 77$ % • System lifetime: ≈ 400 000 h • Operating temperature: $50 \div 90$ °C • Operating pressure: $1 \div 300$ bar ($0.1 \div 30$ MPa) • Operating current density: $1 \div 2\ \mathrm{A\ cm}^{-2}$ • Hydrogen purity: $99.9\ \% \div 99.9999\ \%$	• Efficient (in terms of reaction and system) • Produces highly pure hydrogen • It does not need corrosive and leaking (liquid) electrolytes • Safe pressurized operation • Well-adapted to operate with transient power loads offering a rapid system response • Fast heat-up and cool-off time and a compact system design	• Stacks below MW range • Acidic corrosive environment • Possible low durability • High manufacturing cost • Expensive noble metal catalysts

SUMMARY AND PERSPECTIVES



	1800	1950	1980	2010	2022 future
Achievement	Electrolyzers are being industrialized	Life support application (Space program)	Industrialization of PEMWE	Large-scale applications	Gigawatt electrolyzers Dominant renewable PtG
Significant Improvements	Diaphragm replaced by membrane	Polymeric solid electrolyte	Redesign of the overcomplicated system	MW stack design	High tech Materials
Challenges	Industrialization	Power density	Cost	Cost Size	Cost Durability Efficiency

Makhsoos A. et al., Int. J. Hyd. En. 48 (2023) 15341–15370

SUMMARY AND PERSPECTIVES

- Although there has been some progress, further study of the new chemical compounds for catalysts remains essential.
- Material science is expected to increase electrolyzers efficiency by improving the electrode design at the nanoscale.

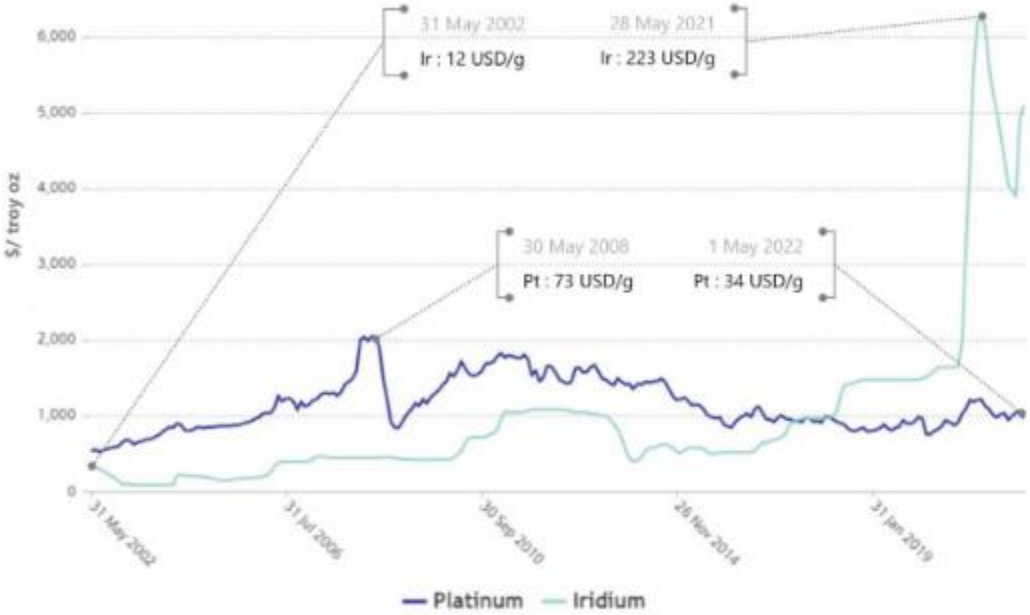


Fig. 5 – PEMWE catalysts (PGM)prices [97].

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SUMMARY AND PERSPECTIVES

- PEMWE technology in renewable energy storage is in its infancy and has much potential. So it is a valuable
- The technological hybridization at a systemic level still need to be fully explored
- Future studies should be also addressed to maximize the entire system's efficiency by balancing the use of both electric and thermal energy.

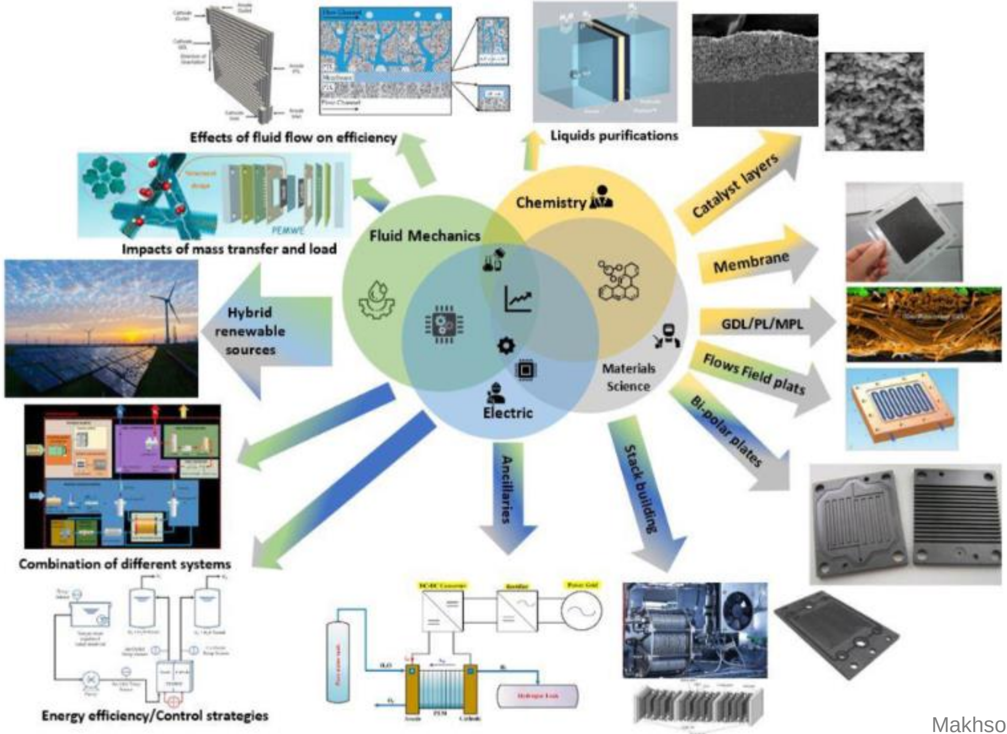

Fig. 6 – Various science branches that can increase different parts of PEMWE efficiency.

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