UNIVERSITÀ DEGLI STUDI DI TRIESTE

Dipartimento di Ingegneria e Architettura

WATER ELECTROLYSIS AND ELECTROLYSER TECHNOLOGIES

- PART 2 -

Prof. Marco Bogar

A.A. 2023-2024

OUTLINE

1. Alkaline Water Electrolysers
2. Anion Exchange Membrane Water Electrolysers

OUTLINE

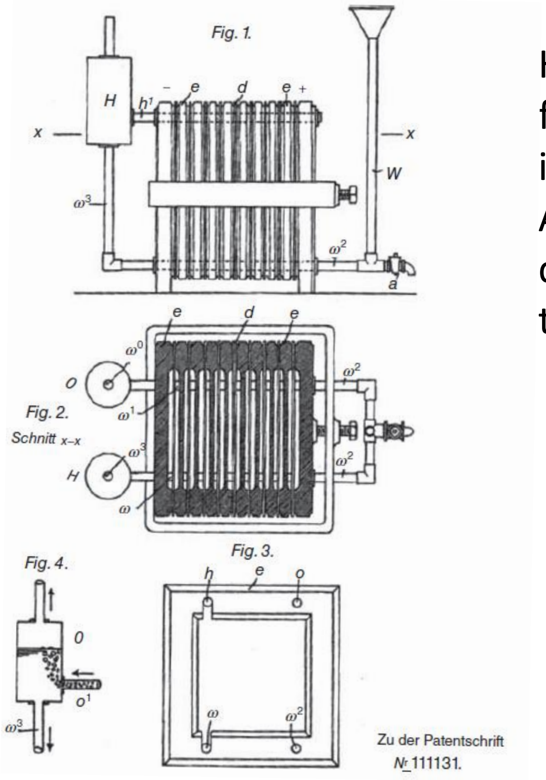
Reference	Paragraph/Pages
Hydrogen production by electrolysis, Agata Godula-Jopek, 2015 Wiley	Ch. 4

Insights	
R1	Trinke P. et al., Hydrogen Crossover in PEM and Alkaline Water Electrolysis: Mechanisms, Direct Comparison and Mitigation Strategies, J. Electrochem. Soc., 165, (2018), F502; DOI: 10.1149/2.0541807jes
R2	Bakker M.M., Vermaas D.A., Gas bubble removal in alkaline water electrolysis with utilization of pressure swings , Electrochimica Acta 319 (2019) 148-157; DOI: https://doi.org/10.1016/j.electacta.2019.06.049
R3	Khatib F.N. et al., Material degradation of components in polymer electrolyte membrane (PEM) electrolytic cell and mitigation mechanisms : A review, 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., Factors influencing the performance and durability of polymer electrolyte membrane water electrolyzer: A review, Int. J. Hyd. En., 47, 85, (2022), 35976-35989; DOI: https://doi.org/10.1016/j.ijhydene.2022.08.180
R5	Zakaria Z., Kamarudin S.K., A review of alkaline solid polymer membrane in the application of AEM electrolyzer: Materials and characterization Int J Energy Res. 2021;45: 18337 – 18354; DOI: https://doi.org/10.1002/er.6983
R6	Xu Q., et al., Anion Exchange Membrane Water Electrolyzer: Electrode Design, Lab-Scaled Testing System and Performance Evaluation, EnergyChem 4 (2022) 100087; DOI: https://doi.org/10.1016/j.enchem.2022.100087

1. ALKALINE WATER ELECTROLYSERS (AWE)

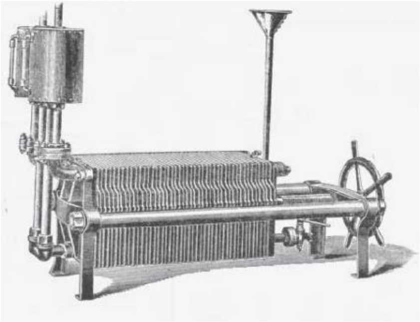
AWE: COMPOSITION

ALKALINE WATER ELECTROLYSIS

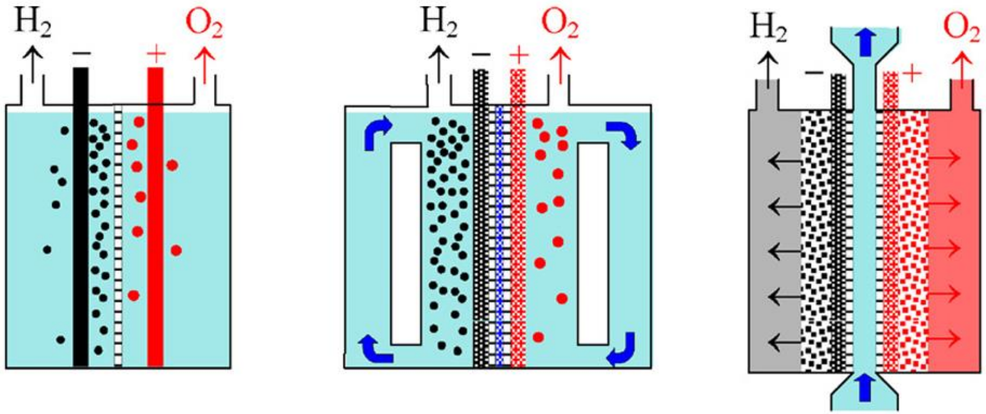


Historically, alkaline technology for water electrolysis directly derives from the fist studies made on the water splitting reaction carried out in the late XVIII and in the XIX centuries.

Alkaline electrolyzers were firstly patented in the 1900 and further developed in order to support the big hydrogen request for sustaining the Haber process for the synthesis of ammonia.



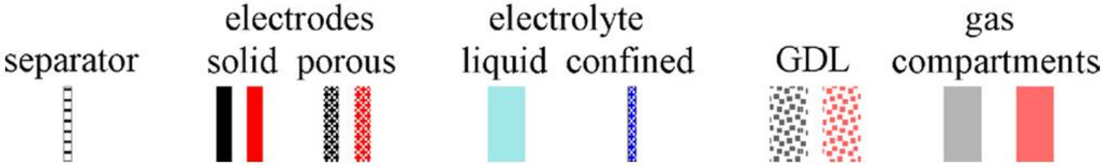
ALKALINE WATER ELECTROLYSIS



Immersion electrodes (gap cell)

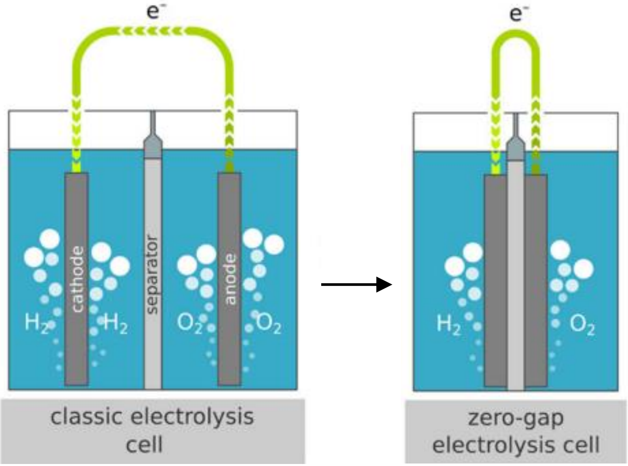
Porous electrodes, zero-gap

With gas diffusion electrodes

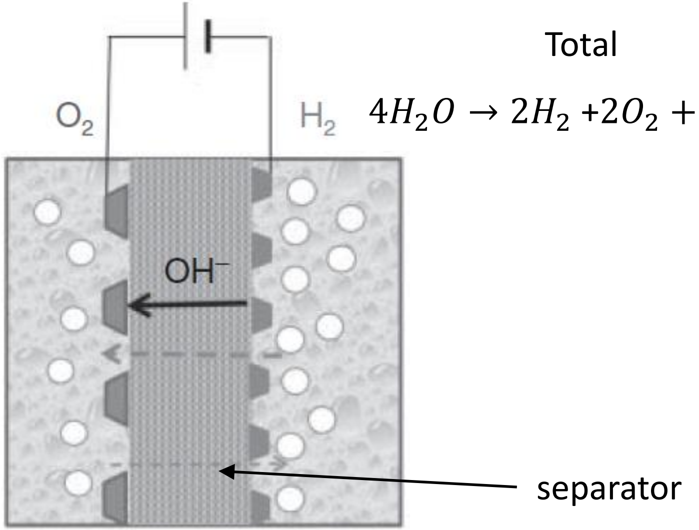


Marini S. et al., Electrochimica Acta 82 (2012) 384– 391

ALKALINE WATER ELECTROLYSIS



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



Total

$$4H_2O \rightarrow 2H_2 + 2O_2 + 2H_2O$$

Anode

$$4OH^- \rightarrow 2O_2 + 2H_2O + 4e^-$$

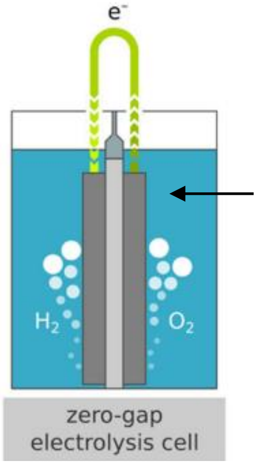
$$E^0 = 1.23\ V_{RHE}$$

Cathode

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$$

$$E^0 = 0\ V_{RHE}$$

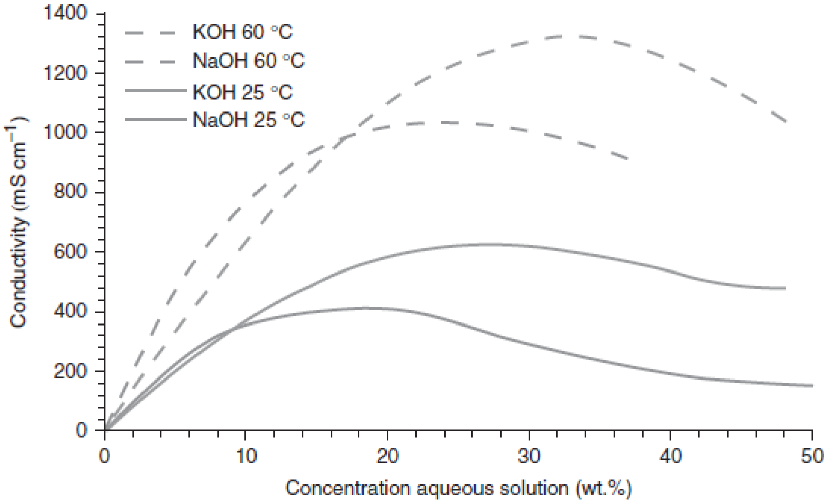
AWE: ARCHITECTURE AND COMPOSITION – THE ELECTROLYTE



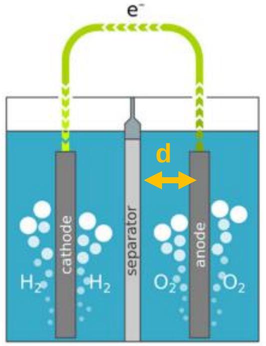
Hodges A. et al., Nature Comm. (2022) 13:1304

The electrolyte

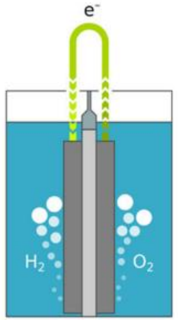
As a liquid electrolyte, a solutions of KOH usually used, because of larger conductivity with respect NaOH (which would be a suitable solution as well). For water-based KOH solutions, maximum conductivity is achieved at a weight concentration equal to 30%.



AWE: ARCHITECTURE AND COMPOSITION – THE ELECTROLYTE



classic electrolysis cell



zero-gap electrolysis cell

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

The electrolyte

In AWE with gap architecture, the volume of electrolyte between the electrodes ranges among a millimetre and some centimetres.

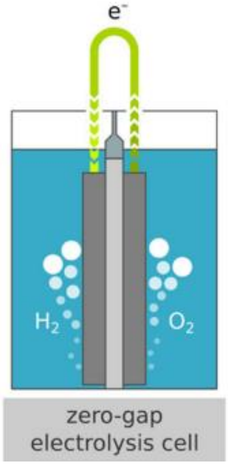
The electrode-separator distance need to be optimized in order:

(i) to reduce the ohmic-type conduction resistance of the anions in the electrolyte, and

(ii) avoid sudden reactant concentration variations which take place when the electrolyte volume is too small.

For any architecture, the electrolyte needs to be continuously stirred and its concentration adjusted, due to the fact that impurities which accumulate into it (from corrosion of metallic parts, degradation of the electrodes and separator).

AWE: ARCHITECTURE AND COMPOSITION – THE SEPARATOR (DIAPHRAGM)



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

The separator (diaphragm)

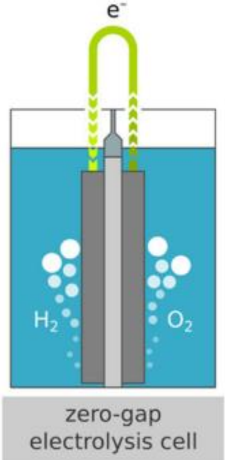
They consist of a porous and electrically insulating material separating the electrodes of different polarity to prevent any short circuit.

They should have a high ionic conductivity for OH^- ions transportation from the cathode to the anode, and prevent the H_2-O_2 recombination by avoiding gas crossover.

They must be chemically stable in the standard conditions of operation of electrolysers (such as 30 wt% KOH, 80 °C, highly oxidizing anodic environment, reducing cathodic at the cathode).

Hydrogen and fuel cells
Prof. Marco Bogar

AWE: ARCHITECTURE AND COMPOSITION – THE SEPARATOR (DIAPHRAGM)



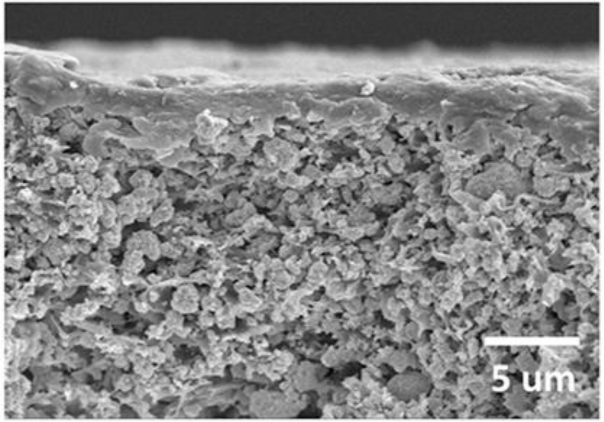
Hodges A. et al., Nature Comm. (2022) 13:1304

The separator (diaphragm)

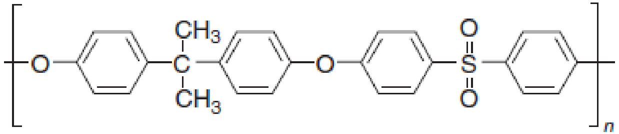
As material asbestos was used at first, later replaced by cernet-supported oxide-ceramic materials (such as YSZ, $NiTiO_3/NiO$, $BaTiO_3/ZrO_2/K_2Ti_6O_{13}$ in example), which were expensive due to the difficulty to obtain large surface areas in produced separators.

To date, Zirfon® is the brand name for the composite material used for diaphragms, where a polysulphone-network is used as a matrix material for an inorganic filler made by zirconium oxide.

Zirfon® microstructure

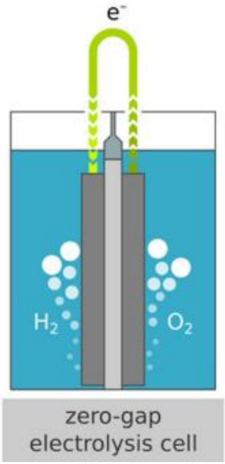


H.I. Lee et al., J. Mem. Sci., 616, (2020), 118541



AWE: ARCHITECTURE AND COMPOSITION – THE SEPARATOR (DIAPHRAGM)

R.1



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

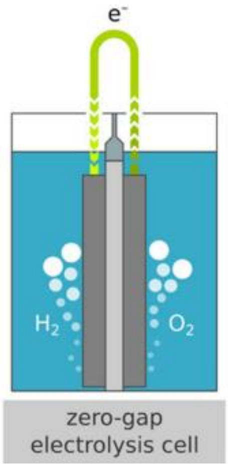
The separator (diaphragm)

Gas crossover evolves by diffusion of dissolved gases in the electrolyte, as diffusion in the solid phase of Zirfon can be considered negligible (one order of magnitude less). Moreover, in alkaline electrolysis, the diffusion coefficient of oxygen in basic solution is about one third of the diffusion coefficient of hydrogen. The hydrogen permeation flux ($N_{H_2,p}$) can be calculated from the equation relating it to the (water-free) hydrogen anodic fraction (ϕ_{H_2}), and considering that the anodic oxygen evolving flux ($N_{O_2,a}$) can be related to the current by the Faraday's law:

$$\phi_{H_2} = \frac{N_{H_2,p}}{N_{O_2,a}+N_{H_2,p}} \qquad N_{O_2,a} = \frac{i}{4F} \qquad N_{H_2,p} = \frac{i}{4F}\frac{\phi_{H_2}}{1-\phi_{H_2}}\frac{A_{el}}{A_{sep}}$$

Where the ratio A_{el}/A_{sep} is the ratio among the electrode surface and the surface of the separator.

AWE: ARCHITECTURE AND COMPOSITION – THE SEPARATOR (DIAPHRAGM) R.1



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

Thus the hydrogen permeation flux is related to the gradient in dissolved hydrogen concentration (Δc_{H_2}) and separator thickness (δ) according to the Fick's law: $N_{H_2,p} = D_{H_2,eff}\frac{\Delta c_{H_2}}{\delta}$

Where the effective hydrogen diffusivity ($D_{H_2,eff}$) is related to the morphological parameters of the separator (porosity, ε, and tortuosity, τ): $D_{H_2,eff} = \frac{\varepsilon}{\tau}D_{H_2}$

And because hydrogen concentration in the anode can be considered negligible with respect the concentration of hydrogen in the cathode: $\Delta c_{H_2} = c_{H_2,c} - c_{H_2,a} \approx c_{H_2,c} = S_{H_2}p_{H_2,c}$

Where S_{H_2} is the hydrogen solubility in the electrolyte and $p_{H_2,c}$ the hydrogen cathodic partial pressure. Summarizing:

$$N_{H_2,p} = D_{H_2}S_{H_2}\frac{\varepsilon}{\tau}\frac{p_{H_2,c}}{\delta}$$

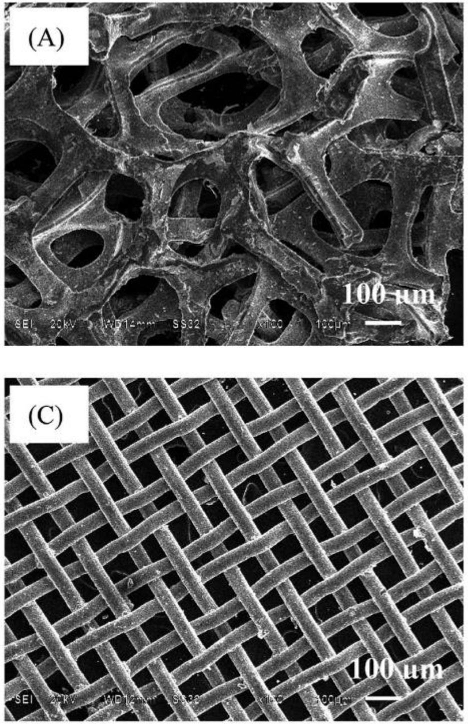
AWE: ARCHITECTURE AND COMPOSITION – ELECTRODES AND CATALYSTS

The catalysts

In alkaline environment **transition metals** show comparable performances with respect noble metals and adequate chemical an mechanical stability. **Nickel and NiFe alloy** are nowadays recognized as one of the best materials catalysing the anodic reaction, offering a rather good resistance to corrosion in alkaline solutions, a good electrochemical activity, and a reasonable cost. Other Ni-based bimetallic alloys and trimetallic ones are currently under investigation.

To increase the electrochemical active surface area (ECSA) of the electrodes, catalyst layer porosity is enhanced, by depositing the catalyst on a porous structure, or by using Ni-Fe alloys. As an alternative Ni-foams have been proposed.

Stainless steel meshes are commonly used as cathode catalyst for cathodic reaction.



Hu X. et al., RSC Adv., 2019, 9, 31563

AWE: OPERATION AND LIMITS

TEMPERATURE EFFECTS ON IONIC CONDUCTION

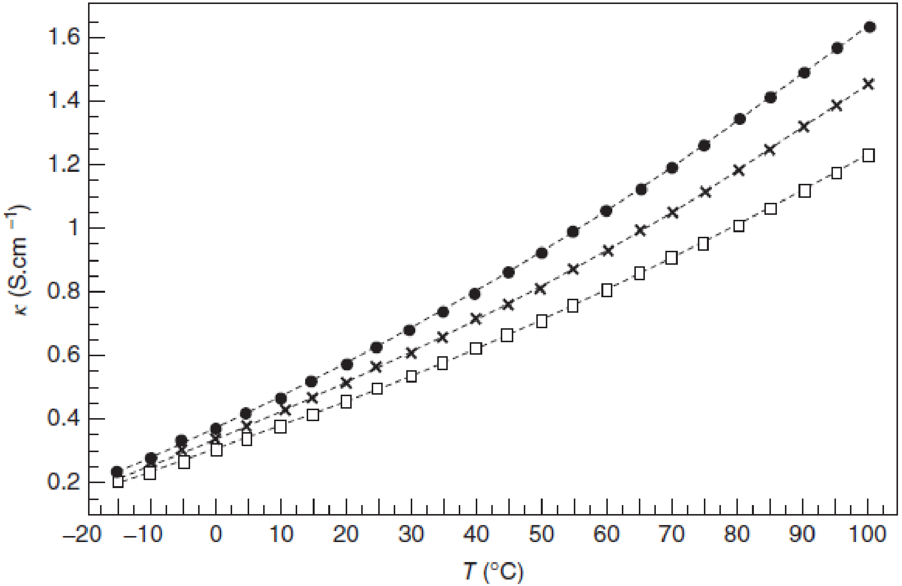


Figure 4.25 Variation of specific conductivity *k*, with temperature *T* (•) 15 mass%; (x) 20 mass%; (full square) 25 mass% KOH [11].

In selecting the most proper temperature of operation, from a thermodynamic point of view, higher temperatures lead to an increase of ionic conductivity, overall in between 70 and to 150 °C. Nonetheless, the chemical stability of the electrolyser components is a key parameter and working at temperature higher than 100 °C also necessitates the use of pressurized electrolysers that negatively impacts capital expenses. For these reasons AWE are usually operated from 70 to 90 °C.

PRESSURIZED AWE: PRESSURIZATION

To operate at pressures higher than 5 bar, mechanical compression is needed. The compression work required for an isothermal compression process is given by the simple following equation:

$$W = P_0 V_0 \ln \frac{P_1}{P_0}$$

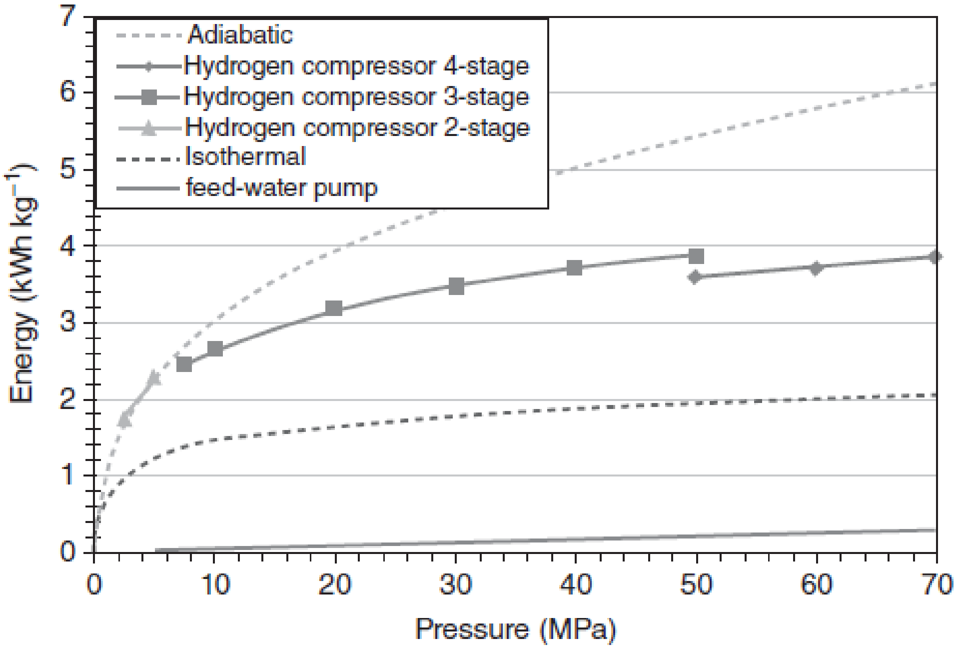
Where P_0 and V_0 are the initial pressure and specific volume (m^3/kg), and P_1 is the final pressure.

In adiabatic conditions, the compression induces an increase of temperature and:

$$W = \left(\frac{n}{n-1}\right) P_0 V_0 \left[\left(\frac{P_1}{P_0}\right)^{\frac{n}{n-1}} - 1\right]$$

Where n is the adiabatic coefficient (ratio of the specific heats) and is equal to 1.41 for hydrogen.

PRESSURIZED AWE: PRESSURIZATION



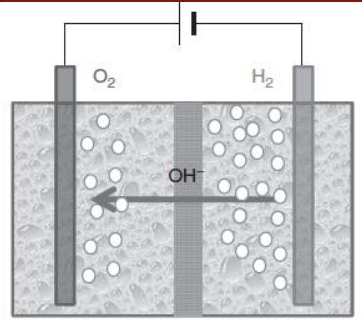
Multistage compressors equipped with intercoolers (used to evacuate excess heat) operate somewhere between the isothermal and adiabatic condition limits.

Increasing the operating pressure of the electrolyser has a major effect on the energy consumption of the hydrogen purification unit but it only slightly modifies the energy consumption for splitting the water molecule

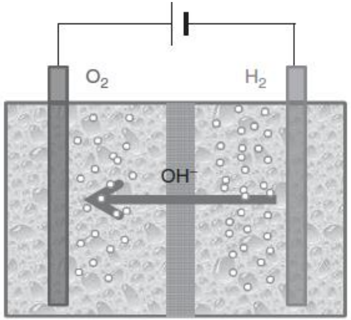
PRESSURIZED AWE: MAIN ADVANTAGES

Nonetheless, by operating at bigger pressures:

- Gas bubbles size tends to decrease, and a larger amount of gases are dissolved into the electrolyte, leading to a reduction of the resistance of the ohmic cell, due to the fact that the ‘shadow effect’ due to the presence of non-conductive gas bubbles in the electrolyte is less pronounced.
- It is easier to dry the hydrogen when produced at high pressure because the ratio among the amounts of water-to-be-removed-to-hydrogen is reduced.

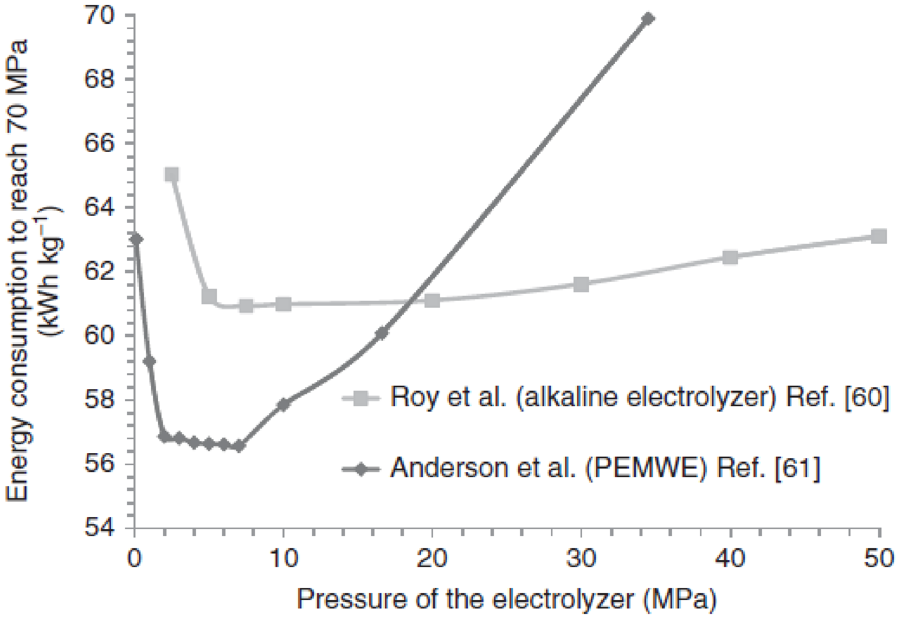


High electrical resistance of the electrolyte



Lower electrical resistance of the electrolyte

PRESSURIZED AWE: MAIN ADVANTAGES



Combining the best performance of pressurized electrolysers and mechanical compressors, is evident as the reduction of energy consumption to reach 70 MPa of hydrogen is reached for an alkaline electrolyser operating at a pressure between 5 and 10MPa and it extends for a wide pressure range.

PRESSURIZED AWE: MAIN DRAWBACKS

Nonetheless, pressurization has also some drawbacks, such as:

- The partial pressure of each gas in the compartments increases, also the partial pressure of gases in each compartment rises, leading to a proportional increase in gas crossover, and a consequent reduction of Faradaic efficiency of about 5%.
- The large number of bubbles and microbubbles created make more probable both electrode and diaphragm clogging to occur.

PRESSURIZED AWE: MAIN DRAWBACKS

Gas crossover

Also in AWE, gas cross-permeation cannot be avoided completely, as the porous diaphragm, is not perfectly impermeable to the reaction products and gases partly dissolve in the electrolyte, diffusing according to the Fick's law $\left(N_{H_2,p} = D_{H_2} S_{H_2} \frac{\varepsilon}{\tau} \frac{p_{H_2,c}}{\delta}\right)$.

In order to reduce gas crossover the electrodes of alkaline electrolyzers can be run at the same pressure in order to avoid as much as possible the formation to a concentration dependent from pressure gradients.

PRESSURIZED AWE: MAIN DRAWBACKS

Sudden changes in current

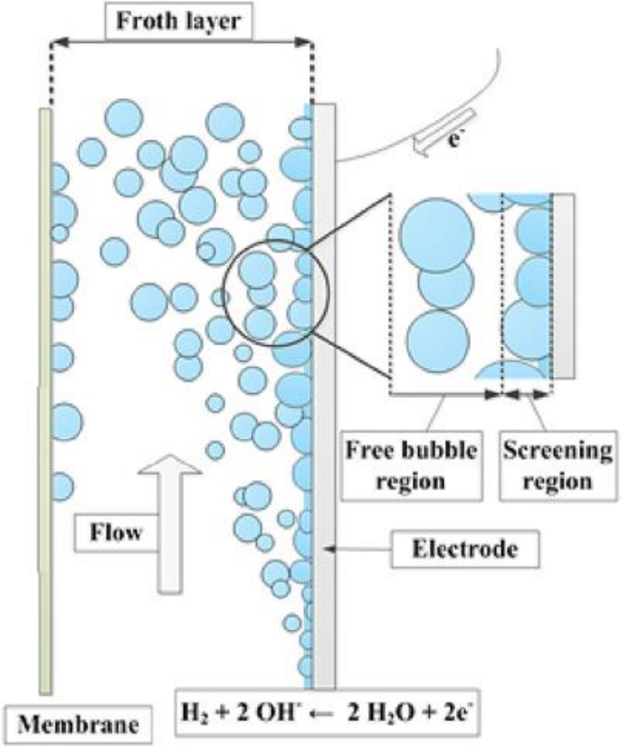
In case of very rapid rise in current, a large amount of gas is produced very quickly. Consequently, there is a risk that the electrolyte could be expelled from the compartments towards the outlets of the system. The evacuation of a substantial portion of the electrolyte would lead to a significant deficiency of the electrolyser and could potentially damage the system.

In other words, alkaline water electrolysers require stationary operating conditions and are not totally well-adapted for operation with transient power sources.

AWE: LIMITATIONS

Gas clogging

In regular operation, bubbles detachment is consequent to a bubble growth process taking place at the electrode surface. Their growth occurs via diffusion and coalescence with neighbouring bubbles and stop after a limit radius is reached. At this point, the buoyancy and lift forces (due to electrolyte flow) are large enough to overtake the force of interfacial tension, and bubbles detach from the electrode surface.



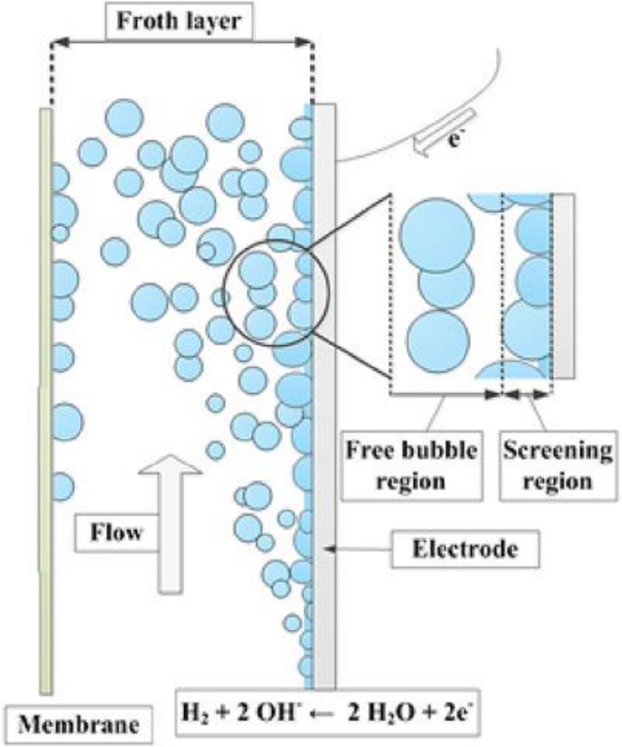
Bakker M.M., Vermaas D.A., Electrochimica Acta 319 (2019) 148-157

AWE: LIMITATIONS

Gas clogging

The bubble froth layer can be divided into two separate layers: the free bubble region and the screening layer, containing adhered bubbles. Both layers contribute in a different way to the resistance for the transport of ions, and hence to the electrical resistance.

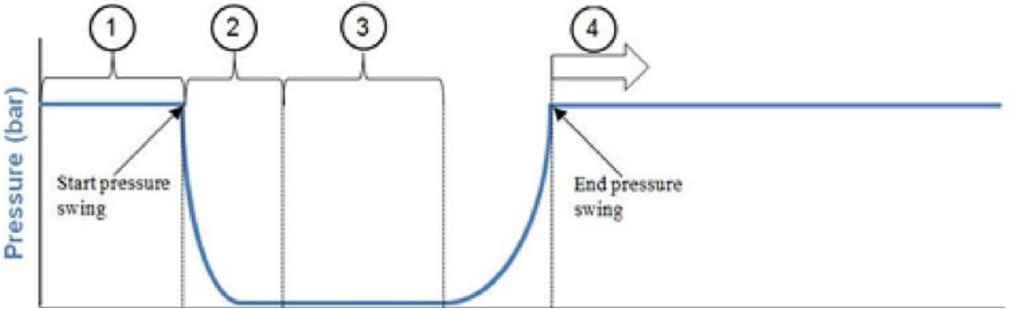
The screening region (which extends for about 0.1 ÷ 1 mm) is the region in which reactant diffuse toward the electrode surface: here bubble volume fraction ranges in between 0.65 ÷ 0.80, several factors higher than in the bulk. Moreover, the presence of screening bubbles strongly influences adsorption kinetics.



Bakker M.M., Vermaas D.A., Electrochimica Acta 319 (2019) 148-157

AWE: GAS CLOGGING AND PRESSURE SWING

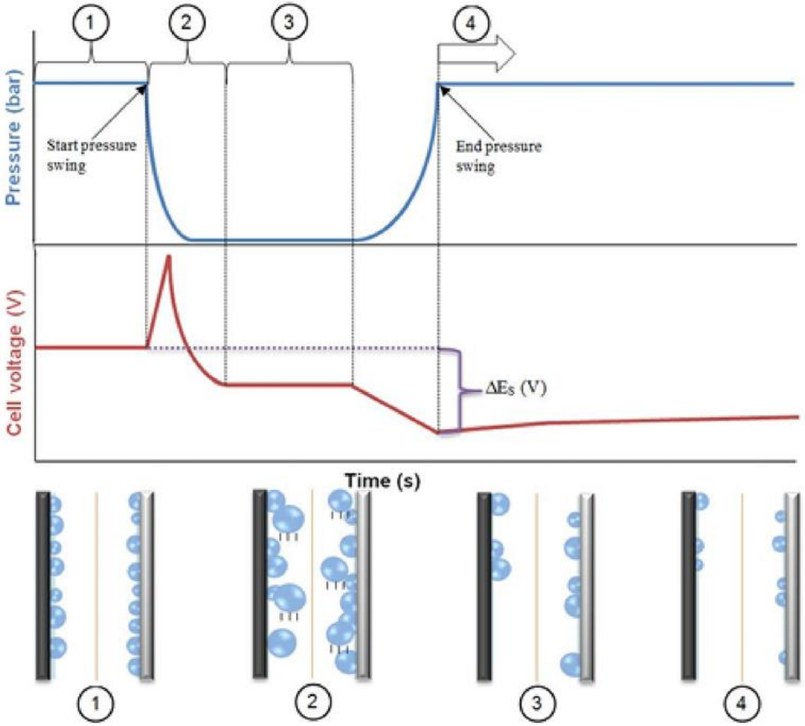
By pressurizing electrolysis it helps in reducing gas bubble size (and consequently the associated resistance). In correspondence of a rapid increase of current, the screening region may be saturated by water bubbles, leading to the overall resistance of the device. Pressure swing, consists in a temporary reduction of operating pressure can thus be used for speeding up bubble detachment.



Bakker M.M., Vermaas D.A., Electrochimica Acta 319 (2019) 148-157

AWE: GAS CLOGGING AND PRESSURE SWING

The applied depressurization is used to suddenly increase the bubble size (according to the ideal gas law), electrode resistance, and cell potential. Bigger bubbles then detach from the electrode surface, freeing some space at the electrode interface, consequently reducing cell potential. Finally pressure is restored to the starting operative value. Voltage reaches its minimum value from which it starts to increase again over time.



Bakker M.M., Vermaas D.A., Electrochimica Acta 319 (2019) 148-157

AWE: GAS CLOGGING AND PRESSURE SWING

The overpotential related to gas bubble formation is expressed as the sum of the concentration overpotential caused by diffusional gas transport (η_c), and the Ohmic contribution associated to the bubble dispersed electrolyte resistance in the screening layer (η_d), where:

$$\eta_c = \frac{RT}{nF} \ln \frac{C_{g,s}}{C_{g,0}} \qquad\qquad \eta_d = j\,\frac{\delta_S}{k_e}(1-f)^{-1.5}$$

where $C_{g,x}$ are the supersaturated (S) and saturated (0) gas concentration, δ_S is the thickness of the screening layer, k_e the conductivity of the bubble-free electrolyte, and f is the gas fraction in the screening layer.

Bakker M.M., Vermaas D.A., Electrochimica Acta 319 (2019) 148-157

AWE: GAS CLOGGING AND PRESSURE SWING

R.2

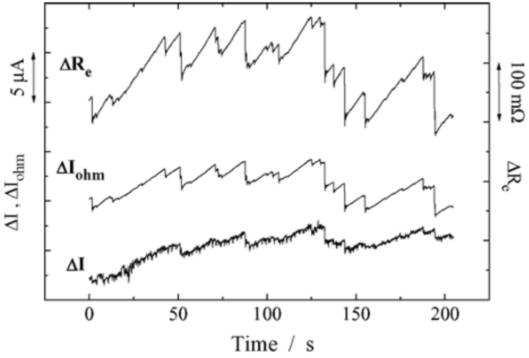
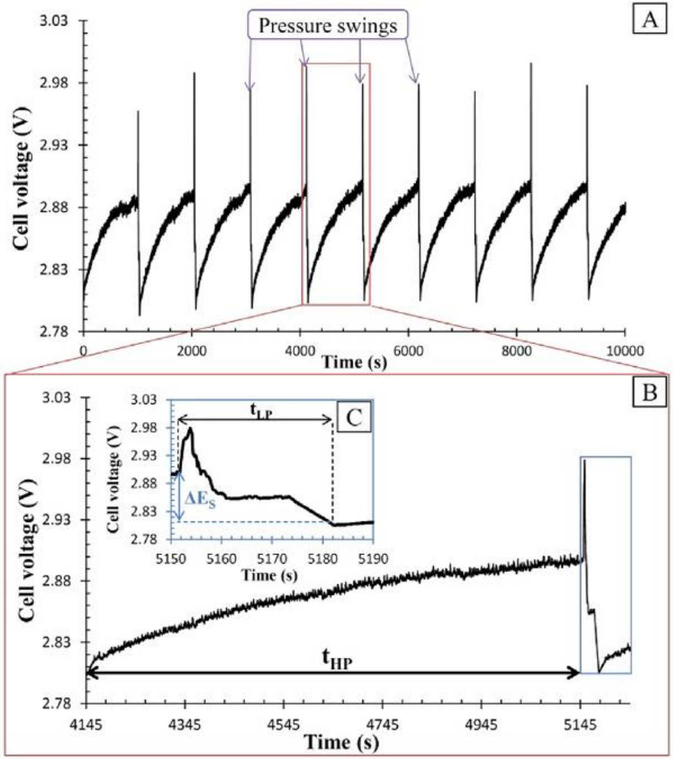


Fig. 6. Time fluctuations of the electrolyte resistance, ΔR_e, total current, ΔI, and ohmic-current, ΔI_{ohm}, caused by hydrogen evolution at a current density of $-1\ \mathrm{mA\ cm^{-2}}$ in 1 M NaOH. Arbitrary time origin. Sampling rate: 10 Hz.

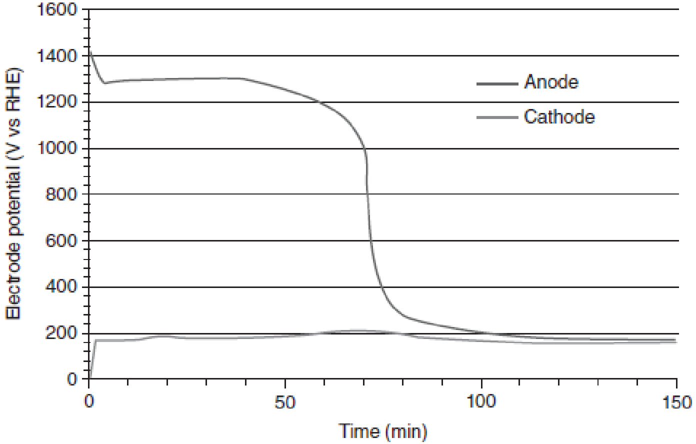
Gabrielli C., et al., Electrochimica Acta 50 (2005) 3726–3736;



AEM: FACTORS INFLUENCING THEIR PERFORMACES

The main phenomenon involved in degradation and AWE drop of performances can be highlighted as the gas evolution within the pores of the porous electrodes, leading to mechanical stress and then to crumbling or erosion of catalyst particles. For this reason it AWE are preferred to be operated under constant loads and takes always place in transient conditions.

Also startup and shutdown procedures can induce large electrode potential variations. In example, at the shutdown, the cathode potential rises quickly (within seconds) to approximately +200 mV versus RHE, and then remains stable. On contrary, anodic potential decreases rapidly, then stabilizes for a long period of time, and then falls down to the voltage value of the cathode after 80 min.



SUMMARY

R.3, R.4

Technical specifications

- Hdrogen production rate / system size:
  0.25 ÷ 760 $Nm^3_{H2}\ h^{-1}$ / 1.8 ÷ 5300 kW
- System efficiency:
  68 ÷ 77 %
- System lifetime:
  > 100 000 h
- Operating temperature:
  40 ÷ 90 °C
- Operating pressure:
  1 ÷ 30 bar
- Operating current density:
  0.3 ÷ 0.5 A cm^{-2}
- Hydrogen purity:
  99.5 % ÷ 99.9998 %
- Responding times (from min to max):
  about 10 minutes

Advantages

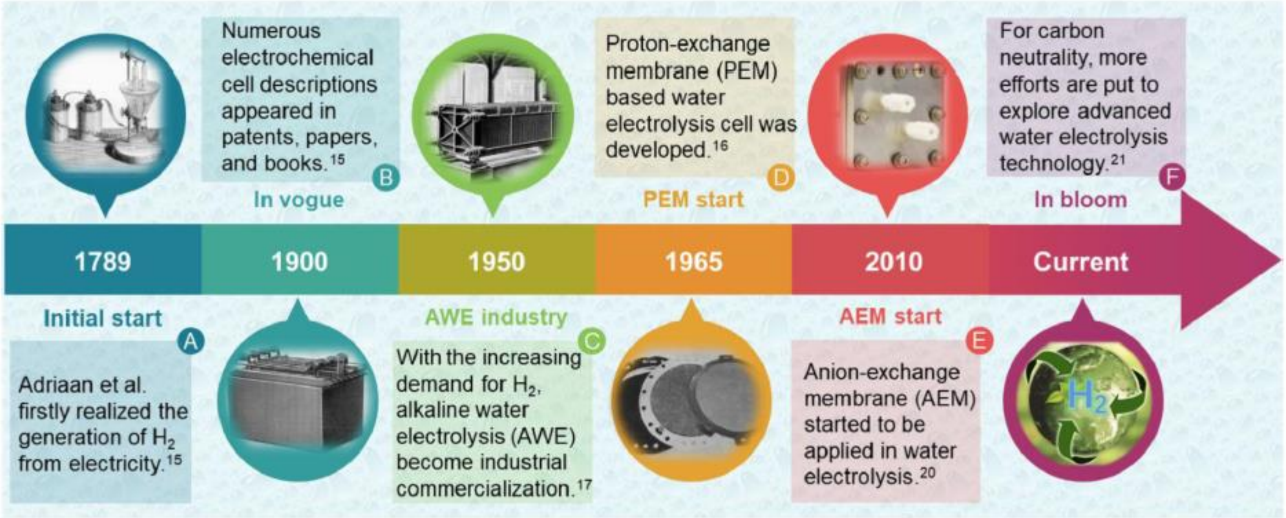
- Stacks in the MW range
- Long-term stability and stack lifetime
- Relative low cost
- Cost-effective
- Well-established technology
- Employ non-noble catalysts
- Low manufacturing cost

Disadvantages / limitations

- Low operation pressures
- Low partial load range
- Low current densities
- Corrosive (caustic) liquid electrolyte
- High probability of gas crossover

2. ANION EXCHANGE MEMBRANE WATER ELECTROLYSERS

AEMWE



Adriaan et al. firstly realized the generation of H_2 from electricity.[15]

Numerous electrochemical cell descriptions appeared in patents, papers, and books.[15]

With the increasing demand for H_2, alkaline water electrolysis (AWE) become industrial commercialization.[17]

Proton-exchange membrane (PEM) based water electrolysis cell was developed.[16]

Anion-exchange membrane (AEM) started to be applied in water electrolysis.[20]

For carbon neutrality, more efforts are put to explore advanced water electrolysis technology.[21]

Q. Xu et al. , EnergyChem 4 (2022) 100087

Developed with the aims:

- merging the benefits of PEMWE and AWE
- trying to reduce the MEA internal resistance
- sustain alkaline electrolysis at high pressures

AEMWE – THE ANION EXCHANGE MEMBRANE

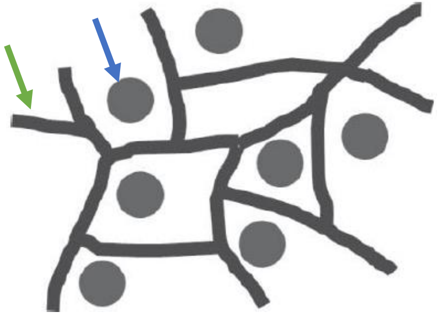
The Anion Exchange Membrane (AEM) is used to replace the diaphragm, and operate as a solid electrolyte. AEMs are usually about 50 – 90 µm thick, and need to be characterized by :

- mechanical and thermal stability in contact with water and during operation;
- insulating in regards electronic conductivity;
- high OH^- ionic conductivity;
- very low permeability to gases to avoid gas crossover between the anodic and cathodic compartments;
- low cost.

The difficulties in producing an effective membrane is mostly related to the fact that the mobility of OH^- ions about 15 times lower with respect H^+ and is thus difficult to achieve comparable performances with respect PEM technology.

AEMWE – THE ANION EXCHANGE MEMBRANE

It is typically synthesized by modifying the polymeric backbone with grafted cationic functional groups to the formed alkaline solid polymeric membrane. AEM can be classified in three classes:



Heterogeneous materials.

They are made of an anion exchange material embedded in an inert compound, providing mechanical resistance.

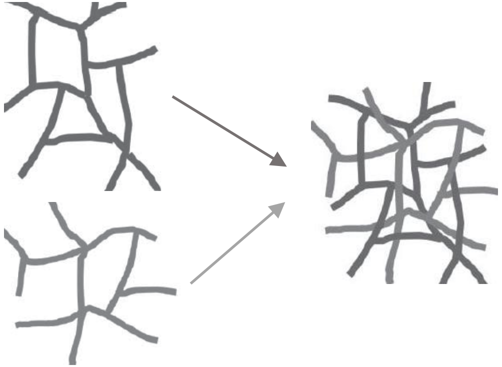
To operate properly, such membranes must be thick (250 ÷ 600 µm), and thus homogeneous dispersions of the anion exchange material are difficult to be achieved. The electrical contact between the ionic exchange groups in the membrane and the electrodes is generally poor and, under long-term operation, a slow extraction of the anionic exchange groups takes place, leading to a loss of ionic conductivity.

AEMWE – THE ANION EXCHANGE MEMBRANE

Homogeneous membranes.

Ionic conductive groups are now covalently bound to the polymer backbone and distributed homogeneously over the entire polymer matrix.

They provide good performances but the large-scale production of such a class of membranes is limited by the expensive production method (radiation-induced grafting).



Interpenetrating polymer networks

Obtained by combining two polymer networks without any covalent bonds between them. Usually, a polymer matrix is used to provide thermal, chemical and mechanical properties, while a conductive polymer is used to sustain anion transport.

Because polymers are not covalently bounded, the conductive polymer can slowly diffuse out of the matrix reducing the overall conductivity over time.

AEMWE – THE ANION EXCHANGE MEMBRANE

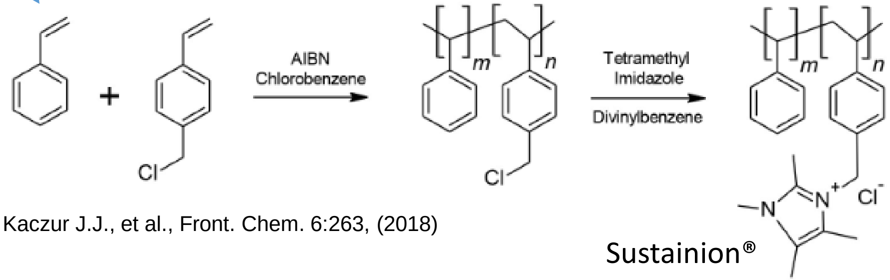
R.5

AEM base materials	Advantages	Disadvantages
FAA-3-based (polyketone or polypropylene with quaternary ammonium groups) – by Fumasep	Good electrochemical properties. Low membrane resistances. Compact structure polymeric membrane.	Limitation of ion exchange diffusion. Low mechanical stability
Polysulfone-based	Biopolymer materials. High mechanical strength. High thermal stability of the polymeric membrane.	Low ionic exchange capacity and ionic conductivity. Low water uptake due to high hydrophobic properties.
Poly (vinyl benzyl chloride)	Low cost of polymeric materials. Easy to modify in chemical process or physical process.	Low capabilities to diffuse the ionic transfer within the polymeric membranes.
Poly (vinyl alcohol)	High tendency to form thin-film. Easy to modify chemically and physically. Low-cost and biodegradable.	Low ionic exchange capacity and ionic conductivity. High swelling ratio.

AEMWE – THE ANION EXCHANGE MEMBRANE

R.5, R.6

AEM base materials	Advantages	Disadvantages
Polystyrene	High chemical stability. Easy to modify chemically. Can stand in high thermal and pressure.	Low ionic conductivity. Low water uptake. Hard to dispose.
A-201 (linear hydrocarbon backbone quaternarized with ammonium functional groups) – by Tokuyama	High conductivity in an alkaline atmosphere. Low-cost production. Can be performed in thin-film structure and minimizes the cell structure.	Requires high concentration of alkaline condition, which leads to corrosive properties to cells. High possibility of incorporation of carbonate inside the membrane



Kaczur J.J., et al., Front. Chem. 6:263, (2018)

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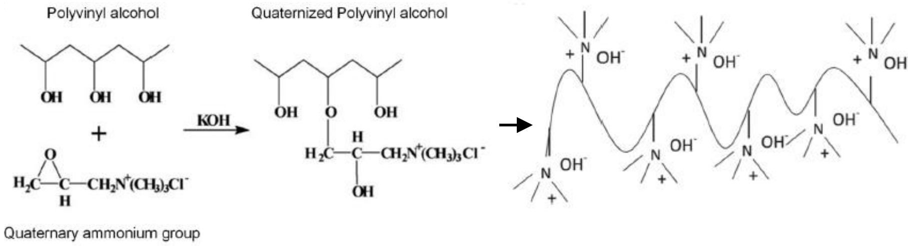


AEMWE – THE CATALYST LAYER

Cathode

Ni-based materials have been widely perceived as the most promising alternatives to commercialized PGMs due to their high reactivity and corrosion resistance in alkaline solutions.

However, by observing the cathode reaction:

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$$

Bare-Ni catalysts are not able to sustain both H_2O adsorption, H_2O dissociation and H* adsorption, which impedes the HER kinetics and efficiency.

In this extent, alloying Ni with Co, Fe, Mn, Cr, Cu and Zn, revealed to be an effective strategy to trigger the synergistic effect of multiple active sites for accelerating the alkaline cathodic reaction.

Moreover, it was also found as oxygen-incorporated Ni-based composites show high activity and durability of the electrocatalyst, due to their optimized adsorption-desorption of OH^- anion.

Hydrogen and fuel cells
Prof. Marco Bogar

AEMWE – THE CATALYST LAYER

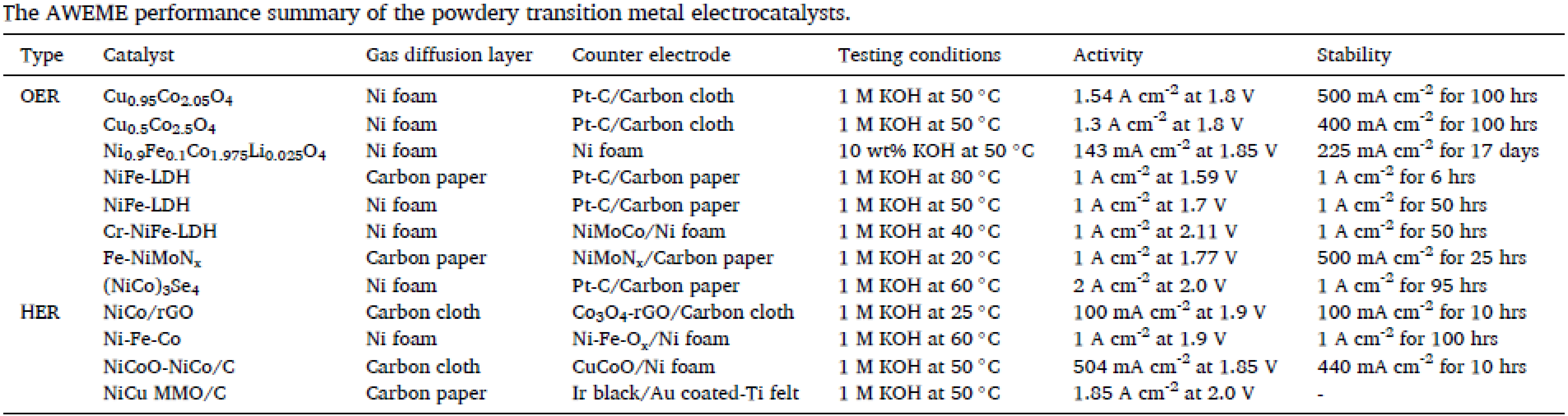
Anode

The anodic reaction ($4OH^- \rightarrow 2O_2 + 2H_2O + 4e^-$) is one of the bottlenecks of water electrolysis because of its sluggish kinetics due to the four protons coupled electrons transfer process, resulting in a large overpotential which enhances electricity consumption and limits the process efficiency.

Metals and transition metal oxides, belonging to the spinel and perovskite families were found having remarkable catalytic activity, due to their flexible oxidation states and coordination structures of metal centres. Furthermore, transition metal oxides are characterized by low cost, excellent alkali resistance, and environmental friendliness.

AEMWE – THE CATALYST LAYERS

R.6

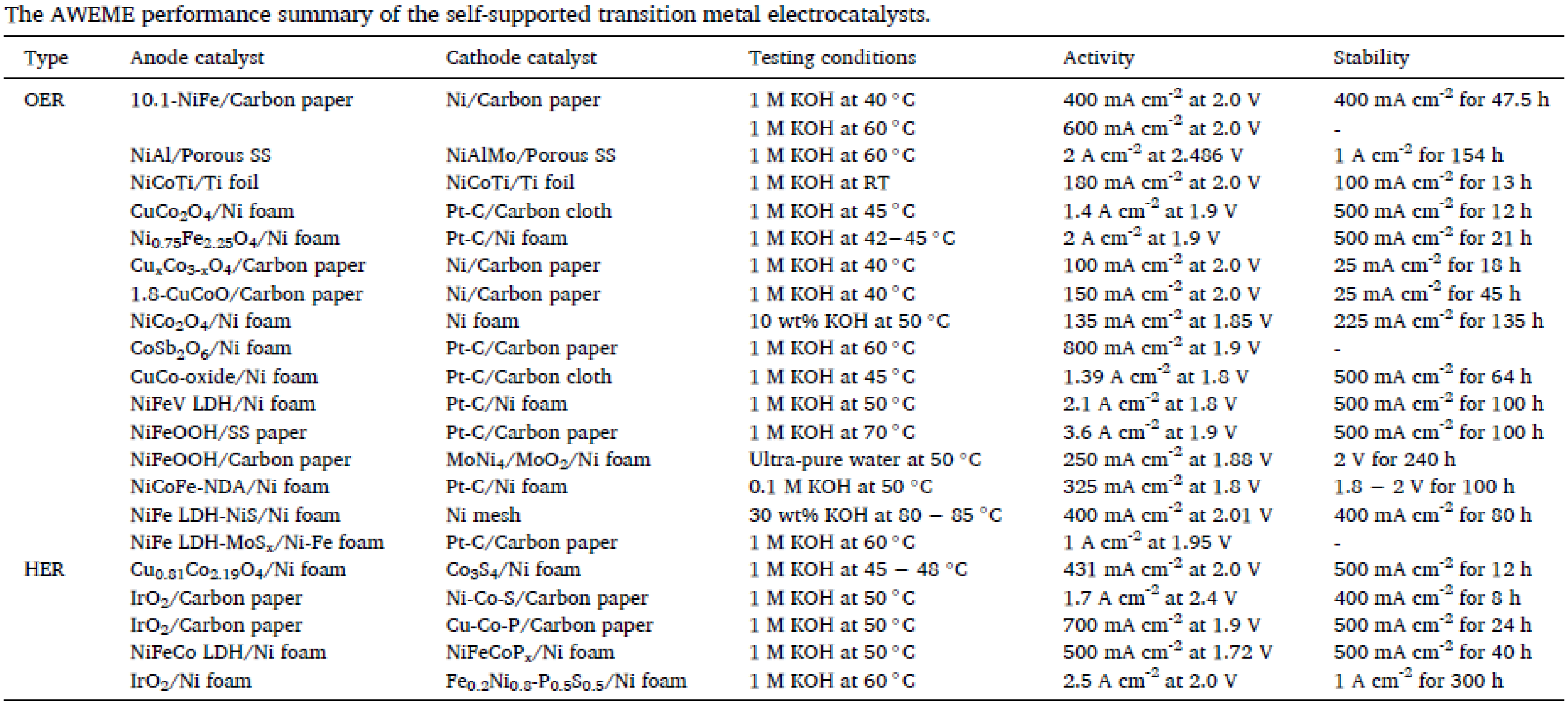


The AWEME performance summary of the powdery transition metal electrocatalysts.

Type	Catalyst	Gas diffusion layer	Counter electrode	Testing conditions	Activity	Stability
OER	$Cu_{0.95}Co_{2.05}O_4$	Ni foam	Pt-C/Carbon cloth	1 M KOH at 50 °C	1.54 A cm^{-2} at 1.8 V	500 mA cm^{-2} for 100 hrs
	$Cu_{0.5}Co_{2.5}O_4$	Ni foam	Pt-C/Carbon cloth	1 M KOH at 50 °C	1.3 A cm^{-2} at 1.8 V	400 mA cm^{-2} for 100 hrs
	$Ni_{0.9}Fe_{0.1}Co_{1.975}Li_{0.025}O_4$	Ni foam	Ni foam	10 wt% KOH at 50 °C	143 mA cm^{-2} at 1.85 V	225 mA cm^{-2} for 17 days
	NiFe-LDH	Carbon paper	Pt-C/Carbon paper	1 M KOH at 80 °C	1 A cm^{-2} at 1.59 V	1 A cm^{-2} for 6 hrs
	NiFe-LDH	Ni foam	Pt-C/Carbon paper	1 M KOH at 50 °C	1 A cm^{-2} at 1.7 V	1 A cm^{-2} for 50 hrs
	Cr-NiFe-LDH	Ni foam	NiMoCo/Ni foam	1 M KOH at 40 °C	1 A cm^{-2} at 2.11 V	1 A cm^{-2} for 50 hrs
	Fe-NiMoN$_x$	Carbon paper	NiMoN$_x$/Carbon paper	1 M KOH at 20 °C	1 A cm^{-2} at 1.77 V	500 mA cm^{-2} for 25 hrs
	$(NiCo)_3Se_4$	Ni foam	Pt-C/Carbon paper	1 M KOH at 60 °C	2 A cm^{-2} at 2.0 V	1 A cm^{-2} for 95 hrs
HER	NiCo/rGO	Carbon cloth	Co_3O_4-rGO/Carbon cloth	1 M KOH at 25 °C	100 mA cm^{-2} at 1.9 V	100 mA cm^{-2} for 10 hrs
	Ni-Fe-Co	Ni foam	Ni-Fe-O$_x$/Ni foam	1 M KOH at 60 °C	1 A cm^{-2} at 1.9 V	1 A cm^{-2} for 100 hrs
	NiCoO-NiCo/C	Carbon cloth	CuCoO/Ni foam	1 M KOH at 50 °C	504 mA cm^{-2} at 1.85 V	440 mA cm^{-2} for 10 hrs
	NiCu MMO/C	Carbon paper	Ir black/Au coated-Ti felt	1 M KOH at 50 °C	1.85 A cm^{-2} at 2.0 V	-

10.1016/j.enchem.2022.100087

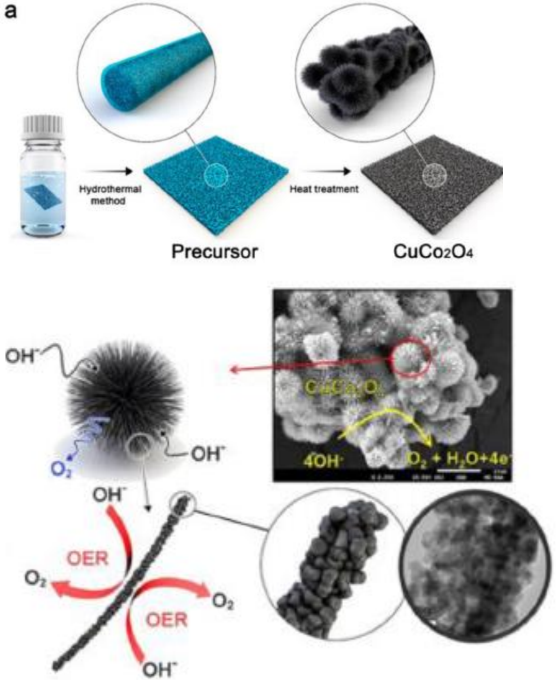
AEMWE – THE CATALYST LAYERS

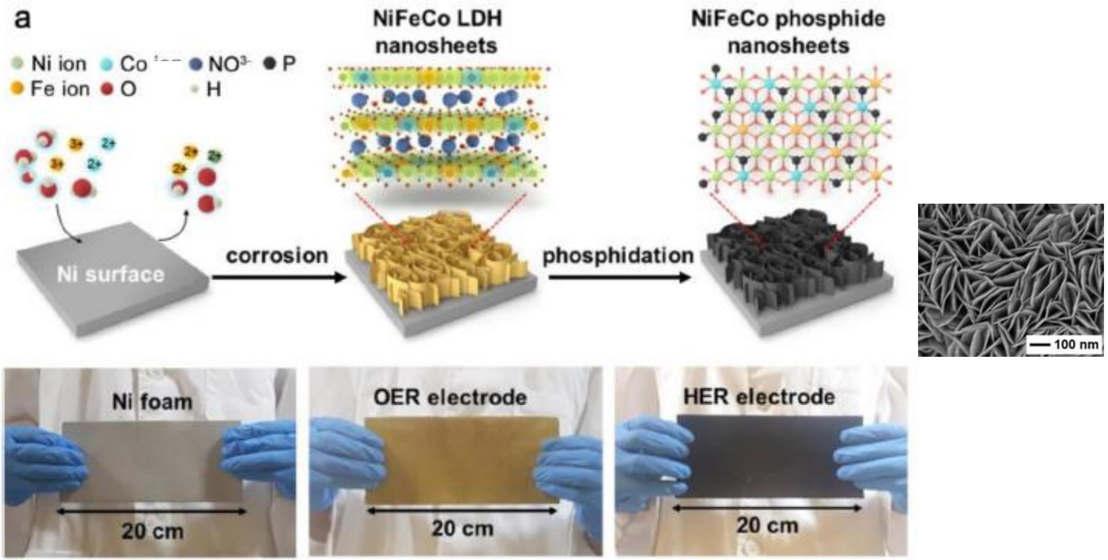


The AWEME performance summary of the self-supported transition metal electrocatalysts.

Type	Anode catalyst	Cathode catalyst	Testing conditions	Activity	Stability
OER	10.1-NiFe/Carbon paper	Ni/Carbon paper	1 M KOH at 40 °C	400 mA cm^{-2} at 2.0 V	400 mA cm^{-2} for 47.5 h
			1 M KOH at 60 °C	600 mA cm^{-2} at 2.0 V	-
	NiAl/Porous SS	NiAlMo/Porous SS	1 M KOH at 60 °C	2 A cm^{-2} at 2.486 V	1 A cm^{-2} for 154 h
	NiCoTi/Ti foil	NiCoTi/Ti foil	1 M KOH at RT	180 mA cm^{-2} at 2.0 V	100 mA cm^{-2} for 13 h
	$CuCo_2O_4$/Ni foam	Pt-C/Carbon cloth	1 M KOH at 45 °C	1.4 A cm^{-2} at 1.9 V	500 mA cm^{-2} for 12 h
	$Ni_{0.75}Fe_{2.25}O_4$/Ni foam	Pt-C/Ni foam	1 M KOH at 42−45 °C	2 A cm^{-2} at 1.9 V	500 mA cm^{-2} for 21 h
	$Cu_xCo_{3-x}O_4$/Carbon paper	Ni/Carbon paper	1 M KOH at 40 °C	100 mA cm^{-2} at 2.0 V	25 mA cm^{-2} for 18 h
	1.8-CuCoO/Carbon paper	Ni/Carbon paper	1 M KOH at 40 °C	150 mA cm^{-2} at 2.0 V	25 mA cm^{-2} for 45 h
	$NiCo_2O_4$/Ni foam	Ni foam	10 wt% KOH at 50 °C	135 mA cm^{-2} at 1.85 V	225 mA cm^{-2} for 135 h
	$CoSb_2O_6$/Ni foam	Pt-C/Carbon paper	1 M KOH at 60 °C	800 mA cm^{-2} at 1.9 V	-
	CuCo-oxide/Ni foam	Pt-C/Carbon cloth	1 M KOH at 45 °C	1.39 A cm^{-2} at 1.8 V	500 mA cm^{-2} for 64 h
	NiFeV LDH/Ni foam	Pt-C/Ni foam	1 M KOH at 50 °C	2.1 A cm^{-2} at 1.8 V	500 mA cm^{-2} for 100 h
	NiFeOOH/SS paper	Pt-C/Carbon paper	1 M KOH at 70 °C	3.6 A cm^{-2} at 1.9 V	500 mA cm^{-2} for 100 h
	NiFeOOH/Carbon paper	$MoNi_4/MoO_2$/Ni foam	Ultra-pure water at 50 °C	250 mA cm^{-2} at 1.88 V	2 V for 240 h
	NiCoFe-NDA/Ni foam	Pt-C/Ni foam	0.1 M KOH at 50 °C	325 mA cm^{-2} at 1.8 V	1.8 − 2 V for 100 h
	NiFe LDH-NiS/Ni foam	Ni mesh	30 wt% KOH at 80 − 85 °C	400 mA cm^{-2} at 2.01 V	400 mA cm^{-2} for 80 h
	NiFe LDH-MoS_x/Ni-Fe foam	Pt-C/Carbon paper	1 M KOH at 60 °C	1 A cm^{-2} at 1.95 V	-
HER	$Cu_{0.81}Co_{2.19}O_4$/Ni foam	Co_3S_4/Ni foam	1 M KOH at 45 − 48 °C	431 mA cm^{-2} at 2.0 V	500 mA cm^{-2} for 12 h
	IrO_2/Carbon paper	Ni-Co-S/Carbon paper	1 M KOH at 50 °C	1.7 A cm^{-2} at 2.4 V	400 mA cm^{-2} for 8 h
	IrO_2/Carbon paper	Cu-Co-P/Carbon paper	1 M KOH at 50 °C	700 mA cm^{-2} at 1.9 V	500 mA cm^{-2} for 24 h
	NiFeCo LDH/Ni foam	$NiFeCoP_x$/Ni foam	1 M KOH at 50 °C	500 mA cm^{-2} at 1.72 V	500 mA cm^{-2} for 40 h
	IrO_2/Ni foam	$Fe_{0.2}Ni_{0.8}$-$P_{0.5}S_{0.5}$/Ni foam	1 M KOH at 60 °C	2.5 A cm^{-2} at 2.0 V	1 A cm^{-2} for 300 h

AEMWE – THE CATALYST LAYERS





AEMWE

An alkaline solution of KOH 30 wt% in water is provided at both electrodes or at the anode side only. In this latter configuration, the permeability of the AEM allows water to reach the cathode side. Here, the cathode reaction consists in the HER:

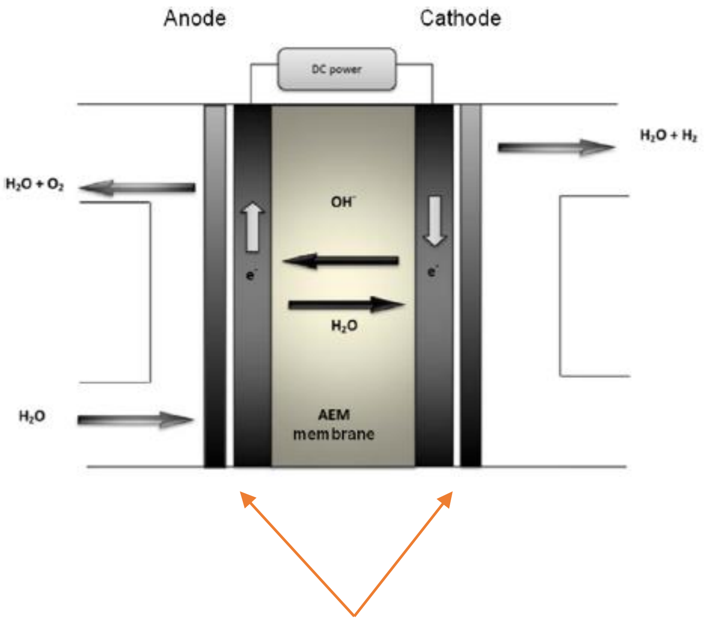
$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \quad E^0 = 0.401\ V$$

Subsequently, the OH^- spontaneously diffuses across the AEM to the anode side, where the OER takes place:

$$4OH^- \rightarrow\ O_2 + 2H_2O + 4e^- \quad E^0 = -0.828\ V$$

Overall:

$$2H_2O \rightarrow 2H_2 + O_2 \quad E^0 = 1.23\ V$$



Ni plates as current collectors

SUMMARY AND FUTURE PERSPECTIVES

R.

Technical specifications

Hdrogen production rate / system size:
--- Nm^3_{H2} h^{-1} / 2.5 kW

- System efficiency:
  52 ÷ 67 %
- System lifetime:
  > 5 000 h
- Operating temperature:
  40 ÷ 60 °C
- Operating pressure:
  1 ÷ 35 bar
- Operating current density:
  0.3 ÷ 0.5 A cm^{-2}
- Hydrogen purity:
  99.9 % ÷ 99.999 %
- Responding times (from min to max):

Advantages

- Higher efficiency than AWE
- Alkaline electrolyte is not needed
- They can operate at higher current densities due to their lower ohmic resistance
- They allow electrochemical pressurization of hydrogen (as PEMWE)
- Either Pt-group free and critical raw material catalysts are not used (cheaper)
- Being the AEM non-porous (as the diaphragm is), safety is improved
- Characterized by a lower overall footprint with respect PEMWE

Disadvantages / limitations

- Still not comparable to AWE or PEMWE in terms of efficiency and performance
- Performances are strongly limited by the AEM, which still present low ionic conductivity
- Catalyst formulation still have to be tuned to optimize performances and durability

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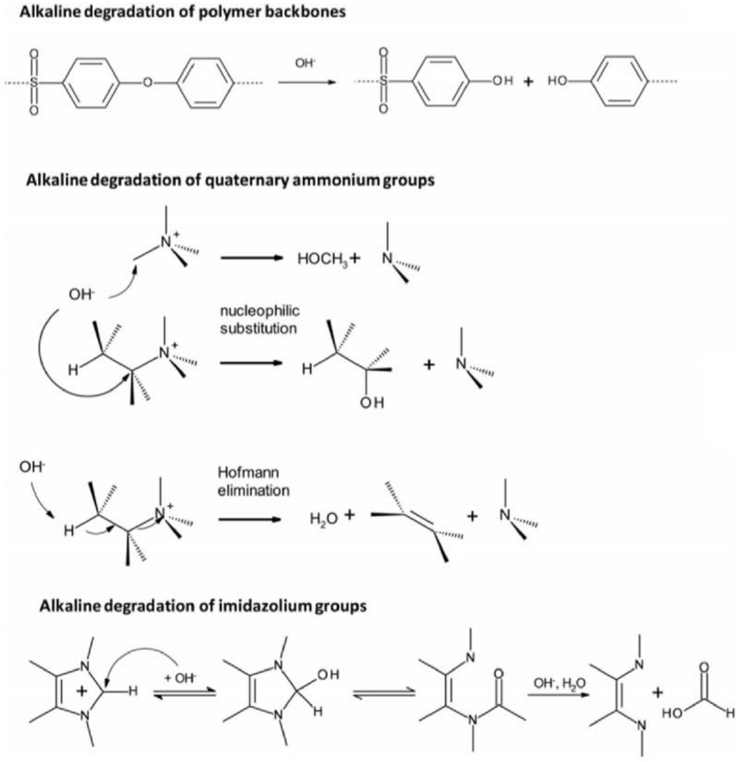
AEM – CHEMICAL STABILITY

Most of the AEMs are characterized by low chemical stability. To date, three main mechanisms have been identified eliminating the cation functional groups (and consequently reducing the number of anion exchange groups and ion conductivity):

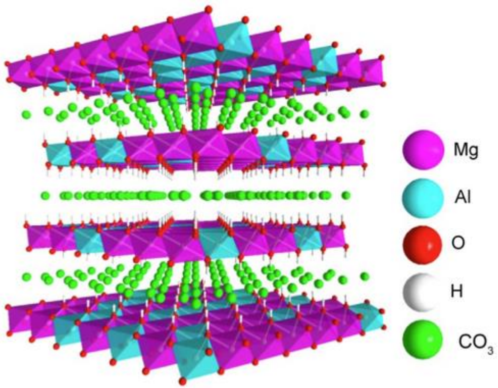
- degradation of the polymeric backbone
- nucleophilic substitution (OH^-, as electron-rich specimen replaces a functional group in an electron-deficient molecule)
- the Hoffmann elimination reaction, in which amines are transformed in alkene due to the formation of a double C-C bond and the elimination of the functional group

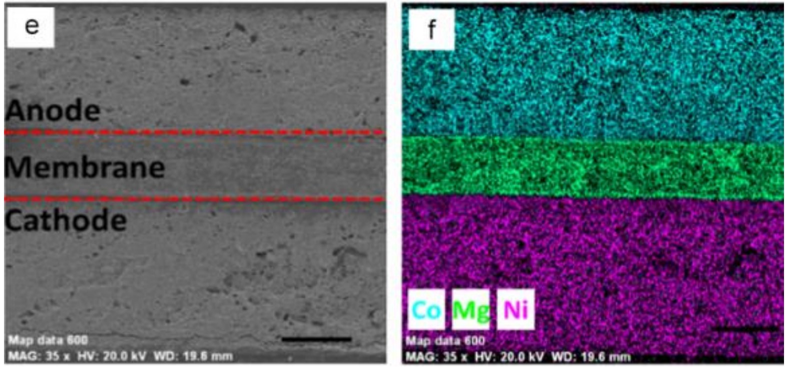


SUMMARY AND FUTURE PERSPECTIVES: AEM AND ION CONDUCTION

AEM made on inorganic materials are currently under investigation. Here crystalline layers are functionalised at the surface in order to promote OH^- transport via the Grotthuss mechanism.

In the here shown example, Mg-Al layered double hydroxides (Mg-Al LDHs) were used as hydroxide ion conductors in the membrane and catalyst layers, reaching a conductivity of 7.75 mS cm^{-1} (for A-201: 12 mS cm^{-1}).





Zheng L., Zhao T.S., Nano Energy (2015) 11, 110-118

SUMMARY AND FUTURE PERSPECTIVES

Very promising technology, allows to merge most of the benefits from both liquid alkaline and solid proton exchange membrane architectures:

- research should be addressed to alternative polymeric materials to fabricate the alkaline solid polymer membrane.
- searching for new functional groups or methods to improve functional groups stability to improve the ionic conductivity of the alkaline solid polymer electrolyte should be improved in order to reduce the ohmic resistance effect, by paying attention not to compromise reactant crossover properties.
- balancing the properties of ion conductivity, crossover, and mechanical stability. The cation functional group's high density can improve the ion conductivity, but the mechanical stability of the AEM appears to be degraded due to extra water absorption
- Reduce the sensibility to hydroxide attack, which decreases ion conductivity and mechanical stability.
- the ideal condition of the alkaline atmosphere in an AEM electrolyzer must be identified.
- optimal catalyst materials are still to be developed

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