UNIVERSITÀ DEGLI STUDI DI TRIESTE

Dipartimento di Ingegneria e Architettura

FUEL CELL TECHNOLOGIES

– PART 2 –

ALKALINE FUEL CELL TECHNOLOGIES

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OUTLINE

1. Alkaline Fuel Cells
2. Anion Exchange Membrane Fuel Cells

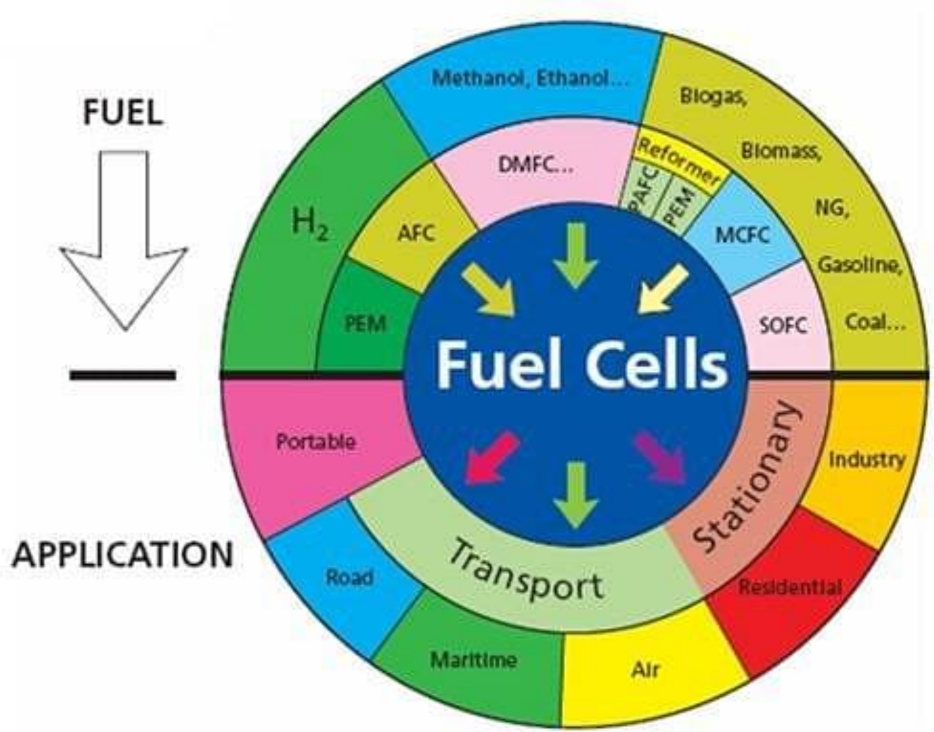
BIBLIOGRAPHY

Reference	Paragraph/Pages
Fuel Cell Systems Explained, Andrew L. Dicks, David A. J. Rand, (2018), Wiley	Ch. 5
Fuel Cell Engines, Mench M. M., (2008), Wiley	Ch. 7.4

Insights	
R1	Sahoo S. et al., Atomistic Insights into the Hydrogen Oxidation Reaction of Palladium-Ceria Bifunctional Catalysts for Anion-Exchange Membrane Fuel Cells, ACS Catalysts, 11, 5, (2021), 2460-3189; DOI: https://doi.org/10.1021/acscatal.0c04646
R2	Cheng J. et al., A mini-review on anion exchange membranes for fuel cell applications: Stability issue and addressing strategies, International Journal of Hydrogen Energy, 40, 23, (2015), 7348-7360; DOI: https://doi.org/10.1016/j.ijhydene.2015.04.040
R3	Gottesfeld S. et al., Anion exchange membrane fuel cells: Current status and remaining Challenges, Journal of Power Sources, 375, (2018), 170-184; DOI: http://dx.doi.org/10.1016/j.jpowsour.2017.08.010

ALKALINE FUEL CELL TECHNOLOGIES

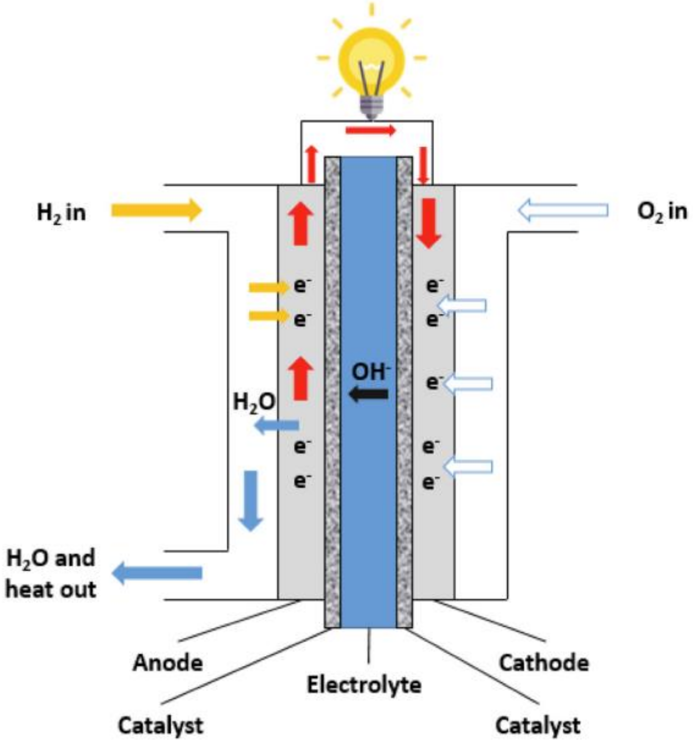
FUEL CELLS!



https://collegedunia.com/exams/fuel-cells-chemistry-articleid-152

1. ALKALINE FUEL CELLS

ALKALINE FUEL CELLS



Hamada A.T. et al., Energy Reports 9 (2023) 6396–6418

In Alkaline Fuel Cells (AFC) were developed in between 1950s and 1960s, were used for the Apollo space programme, and were tested as a powertrain for transportation among the 1960s and the 1970s, but in the following decade, they were overcome by other FC technologies. Here, ionic conduction is sustained via the anion OH^-.

At the anode:

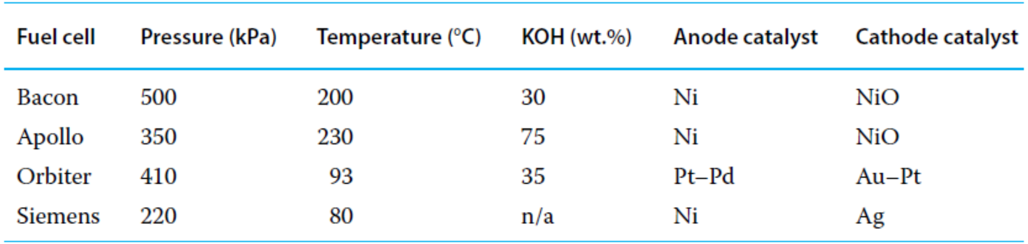
$$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^- \qquad E^0 = -0.282\,V$$

At the cathode:

$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^- \qquad E^0 = 0.400\,V$$

The main advantages lies in low activation overpotential, fast reaction kinetics, and high efficiencies.

ALKALINE FUEL CELLS

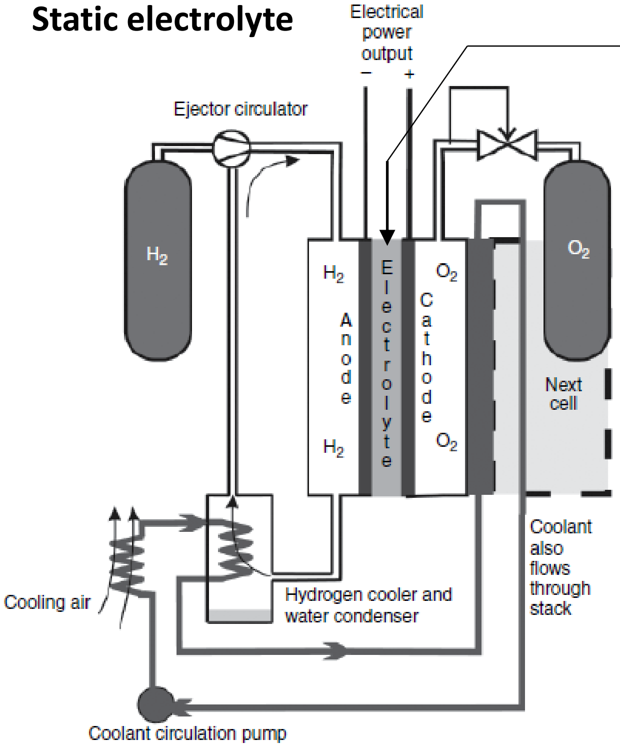


Fuel cell	Pressure (kPa)	Temperature (°C)	KOH (wt.%)	Anode catalyst	Cathode catalyst
Bacon	500	200	30	Ni	NiO
Apollo	350	230	75	Ni	NiO
Orbiter	410	93	35	Pt–Pd	Au–Pt
Siemens	220	80	n/a	Ni	Ag

- Anion conductivity is directly dependant on operating temperature is increased, and AFC have been historically run at higher temperatures.
- The KOH solution, having a freezing point below zero allows to start the fuel cells in cold conditions. Concentrated (85 %) KOH solutions allow to operate up to 230 °C with a liquid electrolyte.

ALKALINE FUEL CELLS – STATIC AND CIRCULATING ELECTROLYTE

Static electrolyte



Each fuel cell has its own liquid electrolyte layer (solution held into a matrix material) in between GDLs.

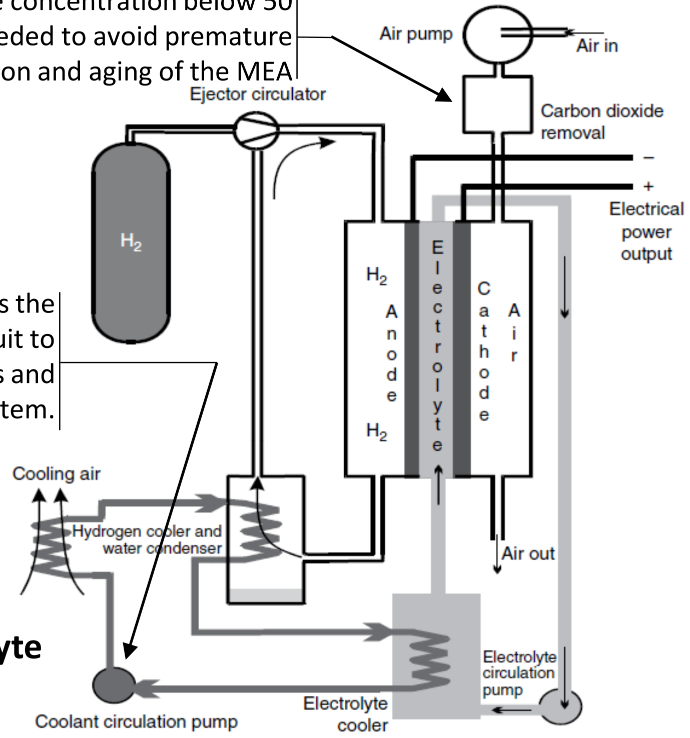
Main issues:

1. Intrinsically subjected to electrolyte poisoning by carbonate formation
2. Additional cooling is required.
3. High purity gases are needed

ALKALINE FUEL CELLS – STATIC AND CIRCULATING ELECTROLYTE

carbon dioxide concentration below 50 ppm is needed to avoid premature degradation and aging of the MEA

A circulation pump makes the electrolyte flow in the circuit to sustain the redox reactions and cooling down the system.



Circulating electrolyte

Main drawback:

Additional hardware is required, thus the system complexity is higher.

ALKALINE FUEL CELLS – STATIC AND CIRCULATING ELECTROLYTE

Advantages:

1. The flowing fluid allows to use it as a cooling medium.
2. The electrolytic solution can be continuously stirred and mixed. In fact, when focusing to the redox reactions taking place at the electrodes:

   Anode $2H_2 + 4OH^- \rightarrow H_2O + e^-$ Cathode $O_2 + e^- + 2H_2O \rightarrow 4OH^-$

   It can be noticed as the cathodic reaction is characterized by twice water consumption with respect the produced water in the anodic reaction. This phenomenon, would lead to excessive concentration of KOH in the electrolyte, and can be simply attenuated by stirring the solution and/or by diluting the solution fed at the cathode.
3. The external circuit allows to easily replace the electrolyte when needed
4. Start-up and shutdown in cold conditions are more simple, as only the electrolyte would need to be heated instead of the whole stack.

ALKALINE FUEL CELLS – SUMMARY

The development of such technology is on standby as other fuel cell technologies were found more performant or easier to be employed. The main advantaged characterising AFC can be summarised as:

- Low polarization voltages for the ORR, leading to higher operating efficiencies with respect of PEM technology.
- Cheap technology, as using low-cost electrolyte, Ni-based catalyst materials, and materials constituting the stack.

Nonetheless:

- CO_2 poisoning is a serious problem, as its presence at the cathode inlet induces formation of potassium carbonite:

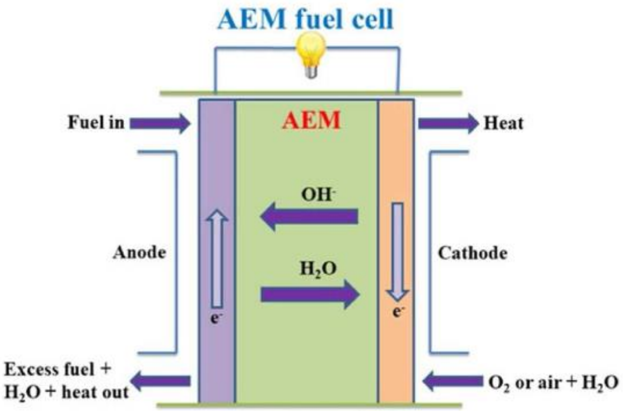
$$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$$

  Lowering ionic conductivity (by decreasing OH^- concentration and reducing reaction kinetics), oxygen solubility, increasing electrolyte viscosity and clogging the porosities within the MEA (thus limiting mass transport). To avoid such a problem, additional equipment is needed (CO_2 removal equipment, additional filtering in the recirculation plant).

- Liquid electrolyte management increases system complexity.

2. ANION EXCHANGE MEMBRANE FUEL CELLS

ANION EXCHANGE MEMBRANE FUEL CELLS



Feng Z. et al., International Journal of Hydrogen Energy, 48, (2023), 25830-25858

AEMFC have been developed as an upgrade of alkaline fuel cells, where the liquid electrolyte is replaced by a solid polymeric membrane able to sustain anion transport. Such an architecture (which is the alkaline-analogous of acidic-PEM technology), has the great advantage of using a CO_2-tolerant electrolyte, able to extend the lifetime of the device.

Anode (HOR) $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

Cathode (ORR) $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Overall $2H_2 + O_2 \rightarrow 2H_2O$

ANION EXCHANGE MEMBRANE FUEL CELLS

In alkaline media the HOR is a more complex reaction which can evolve via a combination of three possible elementary steps:

1. Hydrogen adsorption and decomposition:

$$2H_2 + 2* \rightarrow 2(* - H_{ad})$$

2. Hydrogen dissociative ionization (involving the electron transfer with the catalyst material):

$$H_2 + OH^- + * \rightarrow (* - H_{ad}) + H_2O + e^-$$

3. Oxidative desorption of adsorbed hydrogen:

$$(* - H_{ad}) + OH^- \rightarrow * + H_2O + e^-$$

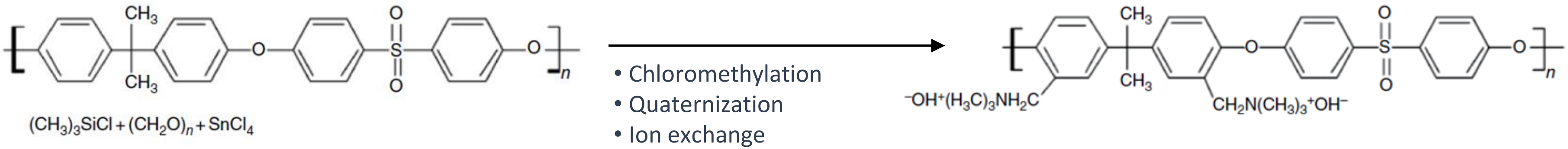
Where * denotes the active site on the catalyst surface. Discussion is still open for identifying the right and/or predominant mechanism(s).

AEMFC – THE ELECTROLYTE

The Anion Exchange Membrane-based technology is not a novelty: for many years anion-exchange membranes have been employed in sea-water desalination plants, in recovering metal ions from waste waters, or in processes related to bio-separation and electrodialysis.

Nonetheless, for being used to sustain fuel cells operation, the performances of the already-used membranes were not sufficient, thus proper electrolytes needed to be developed. To date this is an issue which hasn’t been solved yet, because it is difficulties related to the production process.

To date, anion exchange membranes are formed by functionalizing polysulfone polymers, resulting in addition of functional groups (quaternary ammonium groups, QA) able to sustain anion transport.



$(CH_3)_3SiCl + (CH_2O)_n + SnCl_4$

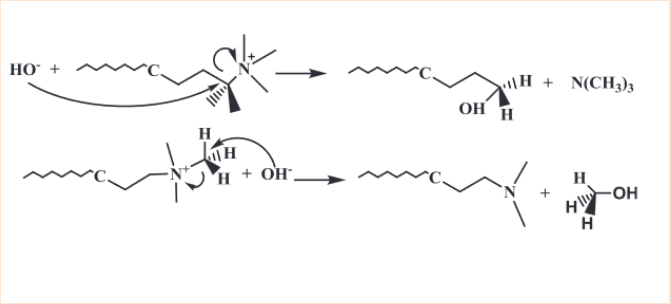
- Chloromethylation
- Quaternization
- Ion exchange

AEMFC – THE ELECTROLYTE

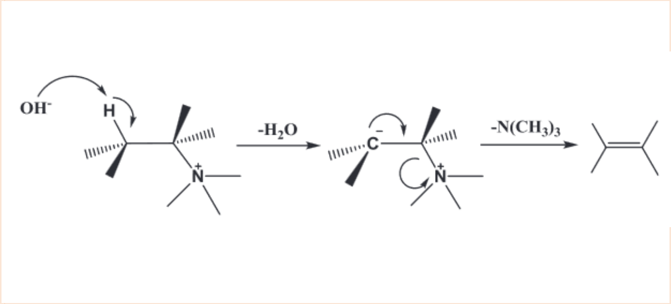
Such a class of polymers guarantee reasonable stability in alkaline environments, but are still limited by :

- Reduced conductivity: mobility of OH^- anions is typically $^1/_3$ to $^1/_2$ with respect H^+.
- The fabrication process of AEM requires materials able to withstand the final step of membrane fabrication in strong alkaline solutions, thus limiting the range of suitable materials usable for this purpose.
- The OH^- ions can intrinsically promote polymer degradation via:

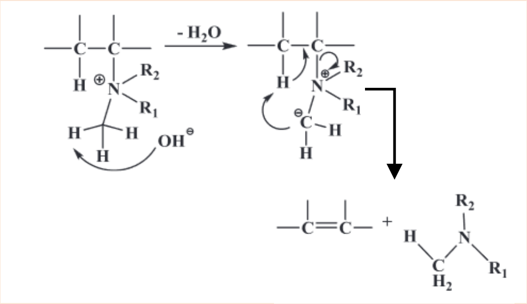
Direct nucleophilic substitution



Hofman elimination reaction



Intermediate-mediated reactions

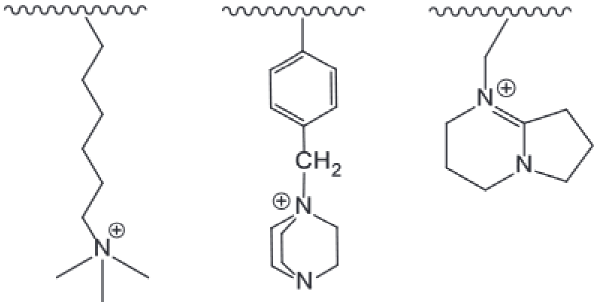


Cheng J. et al., International Journal of Hydrogen Energy , 40, 23, (2015), 7348-7360

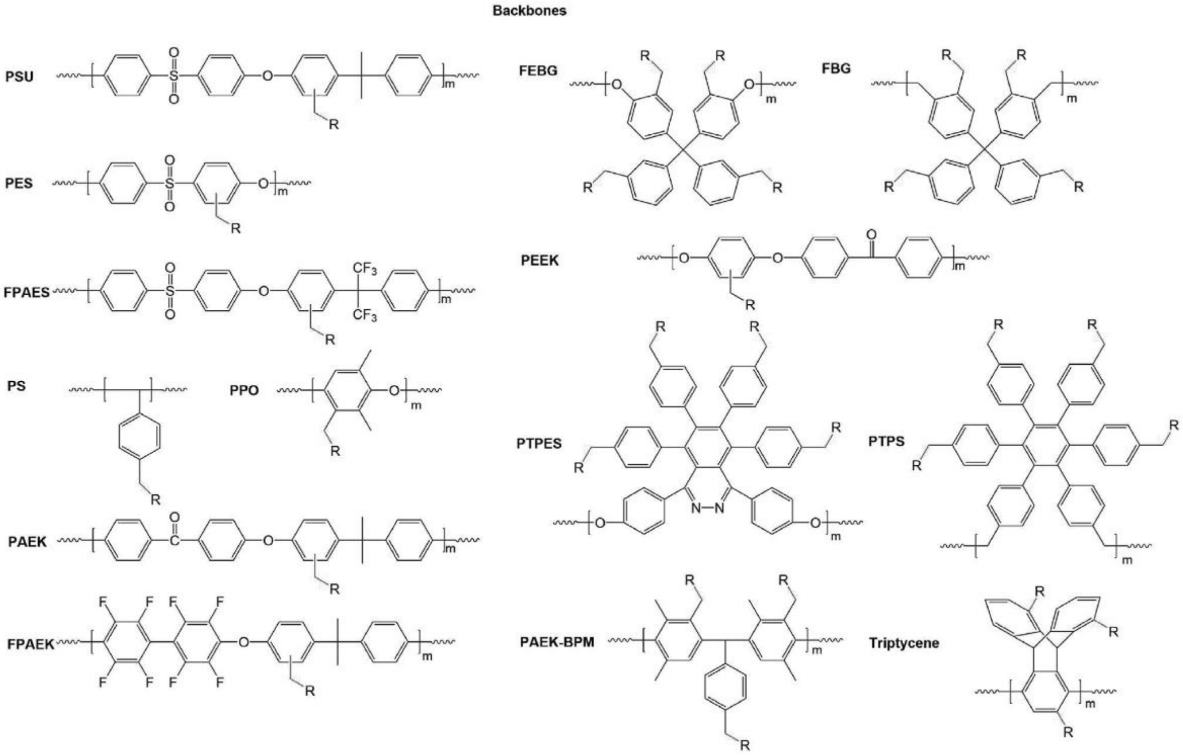
AEMFC – THE ELECTROLYTE

The research on materials suitable to be used as AEM is still open, oriented to study either the capabilities of novel functional groups either to explore approaches to be used to prevent occurrence of Hofman elimination reaction.

In parallel, also backbone formulation is still under investigation in terms of optimising both conduction properties and chemical resistance.

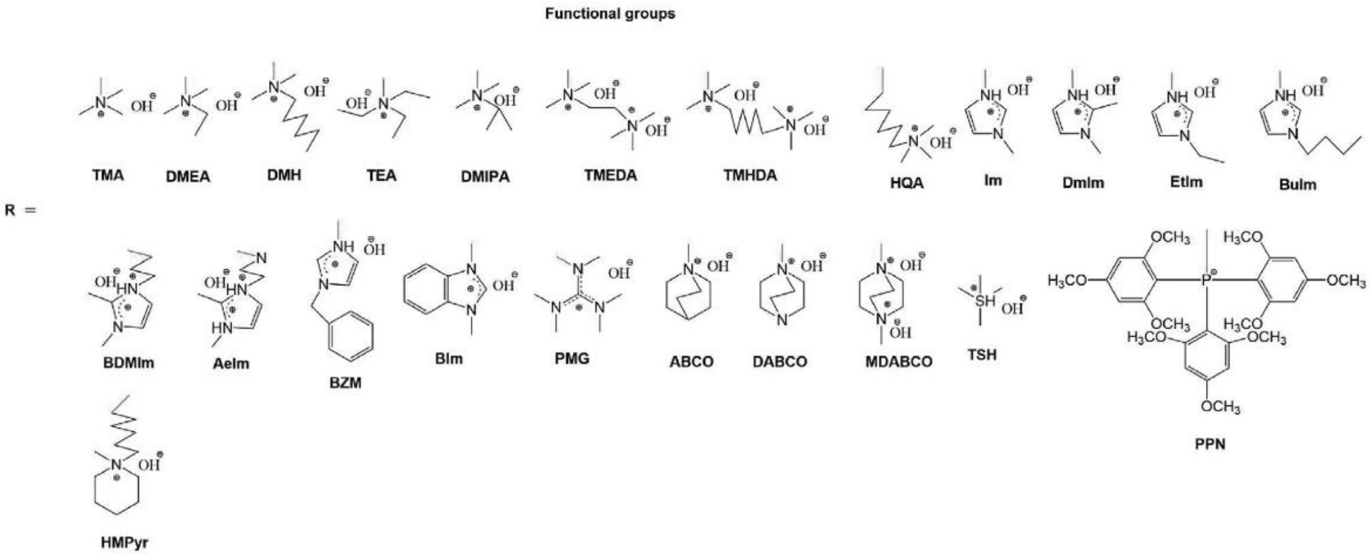


AEMFC – THE ELECTROLYTE



Feng Z. et al., International Journal of Hydrogen Energy, 48, (2023), 25830-25858

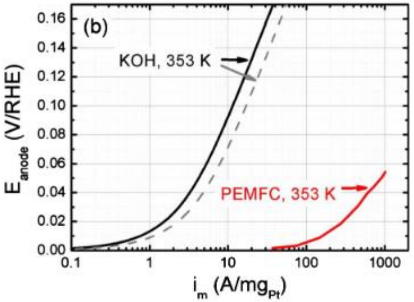
AEMFC – THE ELECTROLYTE



Feng Z. et al., International Journal of Hydrogen Energy, 48, (2023), 25830-25858

AEMFC – THE ELECTRODES

As HOR reaction evolves differently in alkaline media, Pt is characterised by worse performances for the HOR with respect in acidic media (exchange current density is lower of about two orders of magnitude). This outcome could be reconducted to several phenomena (still under investigation), such as: higher hydrogen binding energy to catalyst surface, temporary adsorption to the surface of ion-pair-water-complexes. To date, some approaches have been tried to reduce such efficiency loss, as changing catalyst morphology from catalyst nanoparticles to more elongated ones (such as nanotubes), with the aim of acting on reducing binding energy with the introduction of other metals, or by adding Pd or oxophilic elements, which were found useful to help sustaining oxygen diffusion on the catalyst surface (thus by using bifunctional catalyst).



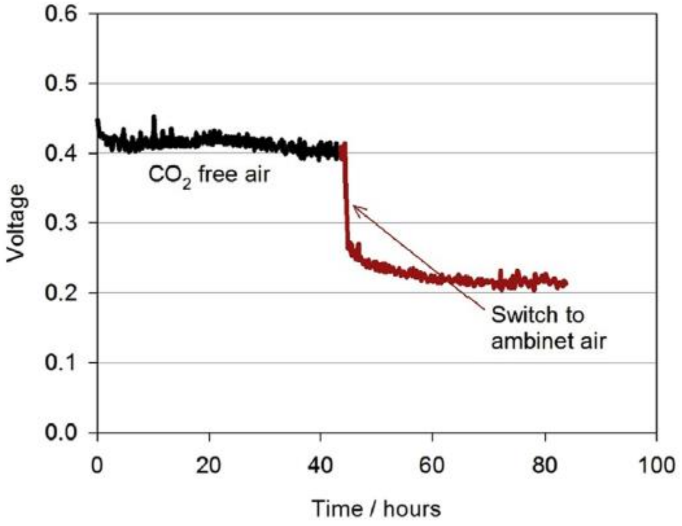
Sheng W. et al., Journal of The Electrochemical Society, 157, 11, (2010), B1529-B1536

As platinum-group-free metals Ni (and its combination with Pd) was found being valuable alternatives to Pt.

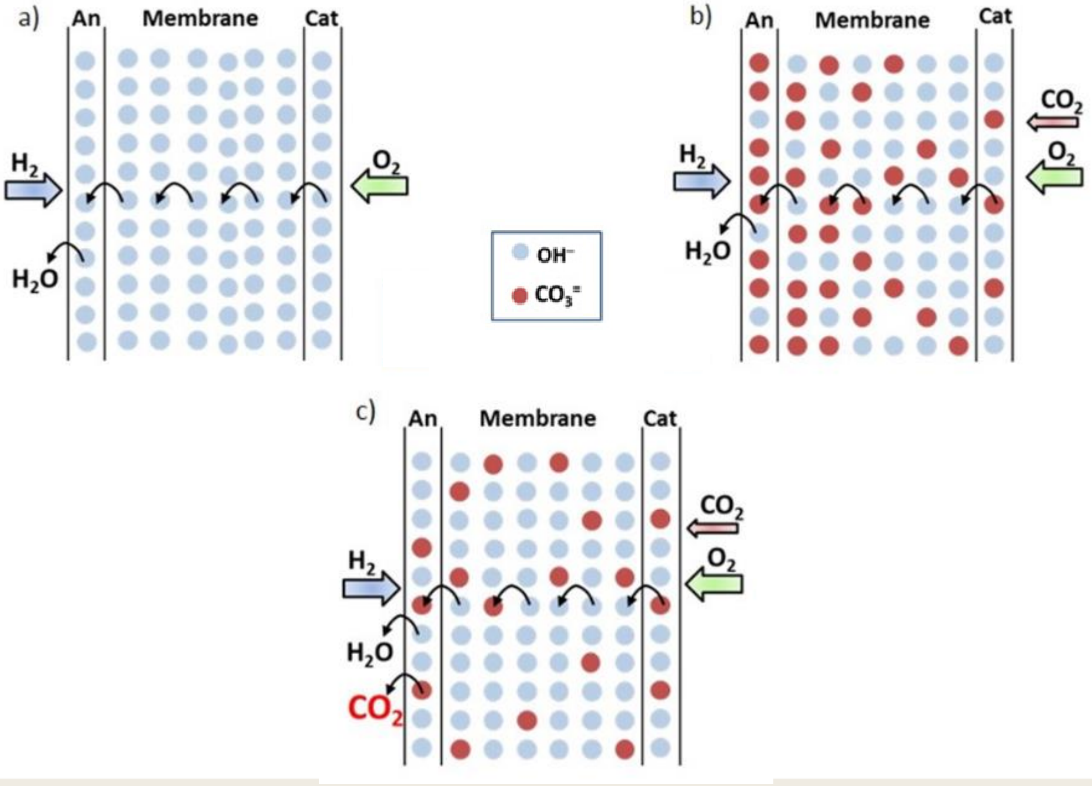
AEMFC – THE ELECTRODES

As ORR catalyst materials metals non belonging to the Pt group can be used, and this fact is the main factor driving interest in AEM technology, due to the benefits in terms of costs reduction for the catalyst layer. In this framework the best element which was found is Ag, characterized by an efficiency of about 10% with respect Pt, but also a cost per produced power which for Ag about the 7% of the Pt reference.

AEMFC – IMMUNITY TO CO_2



$$\Delta V \propto \log([OH^-]_{anode})$$



AEMFC – WATER MANAGEMENT

For AEMFC water management is more complex, as they are operating in a more water-rich environment. In fact:

1. For every couple of electrons retrieved by the HOR, a couple of water molecules are produced:

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

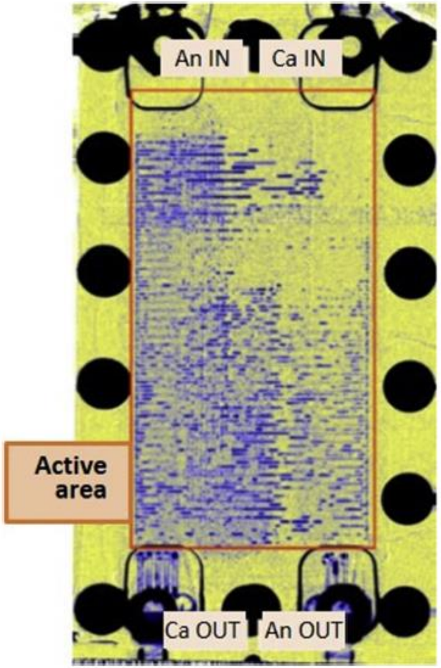
while for each couple of electrons consumed by the ORR, only one water molecule is consumed:

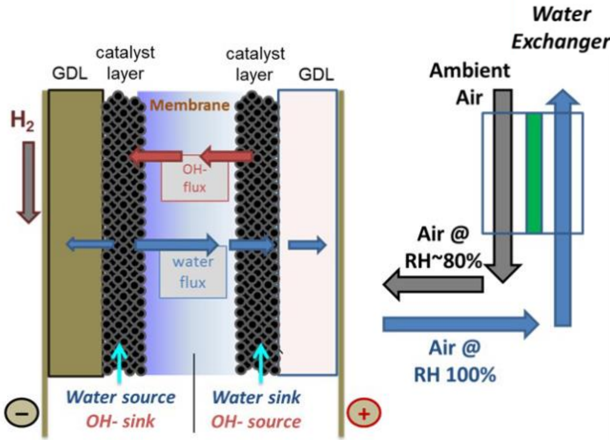
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

and cathode is more prone to dry out

AEMFC – WATER MANAGEMENT

2. In addition, being the cathode supplied by air, and that oxygen fraction in air is equal to about 20%, stoichiometry in air needs to be higher than for anode. Higher flow rates, further hindering proper cathode hydration. This issue is particularly marked when dealing with fuel cell stacks and/or cells with large active areas. Without changes to, for example, the flow field's design, the membrane water permeability, and/or the stack cooling mode, such a local dry out in the AEMFC cathode would be expected and may become increasingly severe with increasing cell operation temperature (in the picture cell was run at 60°C).

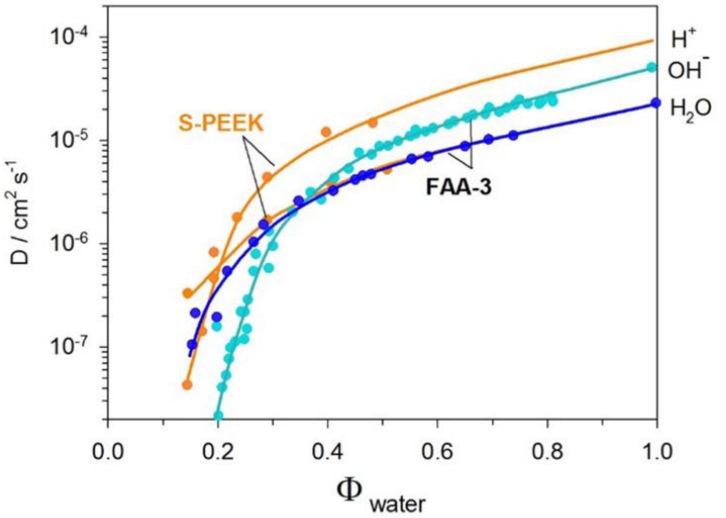




AEMFC – WATER MANAGEMENT

3. Anion exchange membranes need higher hydration levels that proton exchange ones to produce the phase separation required to sustain hydroxide transport. This might lead to anode flooding, leading to limitations in mass gas transport, and consequent loss of performances. In this extent, tuning the hydrophobicity of both electrodes and GDL is of fundamental importance to improve fuel cell performances.

The performance drop is much more severe in AEM than in PEM technology.



A better water distribution within the MEA can be achieved by increasing the water flux from the anode to the cathode across the membrane at some given cell current and providing an additional route for water transport from the anode to the cathode.

AEMFC – WATER MANAGEMENT

A better water distribution within the MEA can be achieved:

1. by increasing the water flux from the anode to the cathode across the membrane at some given cell current
2. and by providing an additional route for water transport from the anode to the cathode.

The first strategy would require thinner membranes: currently membrane thickness is about 30 µm. Ideally, thickness should be lowered to 10 µm or below.

The second one would requires system design modifications, able to transport water molecules from the anode exhaust to the cathode inlet and / or allowing water building up in the anode flow field.

AEMFC - SUMMARY

AEM represents a promising technology, overall because it can use PGM-free catalysts materials for the cathode electrode and because of its invulnerability to CO_2 poisoning. Nonetheless several improvements still need to be carried out in almost all of the fuel cell compartments:

- Anion exchange membrane stability to chemical degradation and to high temperature operation (above 80 °C) still needs to be improved. If possible membrane thickness should be diminished to improve water management capabilities. Chemistry of the membrane should be also tuned to improve hydroxide conductivity.
- Being able to maintain catalysts stability and reducing anode PGM loading below (100 µg cm^{-2}) or replace it with PGM-free catalyst would allow to obtain cost-competitive stacks.

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