UNIVERSITÀ DEGLI STUDI DI TRIESTE

Dipartimento di Ingegneria e Architettura

FUEL CELL TECHNOLOGIES

– PART 1 –

PROTON EXCHANGE MEMBRANE FUEL CELLS

Prof. Marco Bogar

A.A. 2023-2024

OUTLINE

1. Proton Exchange Membrane Fuel Cells - Composition
2. Proton Exchange Membrane Fuel Cells - Operation

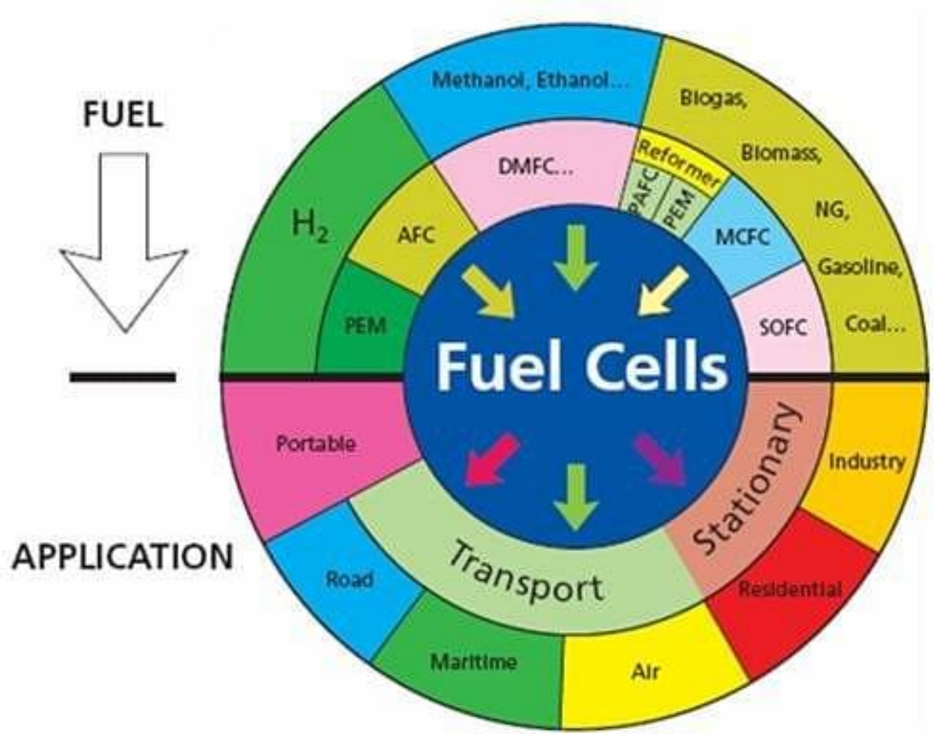
BIBLIOGRAPHY

Reference	Paragraph/Pages
Fuel Cell Systems Explained, Andrew L. Dicks, David A. J. Rand, (2018), Wiley	Ch. 4
Fuel Cell Engines, Mench M. M., (2008), Wiley	Ch. 6.2

Insights	
R1	Grandi M., et al., Recent advancements in high performance polymer electrolyte fuel cell electrode fabrication – Novel materials and manufacturing processes, Journal of Power Sources, 562, (2023), 232734; DOI: https://doi.org/10.1016/j.jpowsour.2023.232734
R2	Lee F.C. et al., Alternative architectures and materials for PEMFC gas diffusion layers: A review and outlook, Renewable and Sustainable Energy Reviews 166 (2022) 112640; DOI: https://doi.org/10.1016/j.rser.2022.112640
R3	Xu Z. et al., Towards mass applications: A review on the challenges and developments in metallic bipolar plates for PEMFC, Progress in Natural Science: Materials International, 30, 6, (2020), 815-824; DOI: https://doi.org/10.1016/j.pnsc.2020.10.015
R4	Humidification strategy for polymer electrolyte membrane fuel cells – A review, Chang Y. et al., Applied Energy, 230, 15 (2018), 643-662; DOI: https://doi.org/10.1016/j.apenergy.2018.08.125

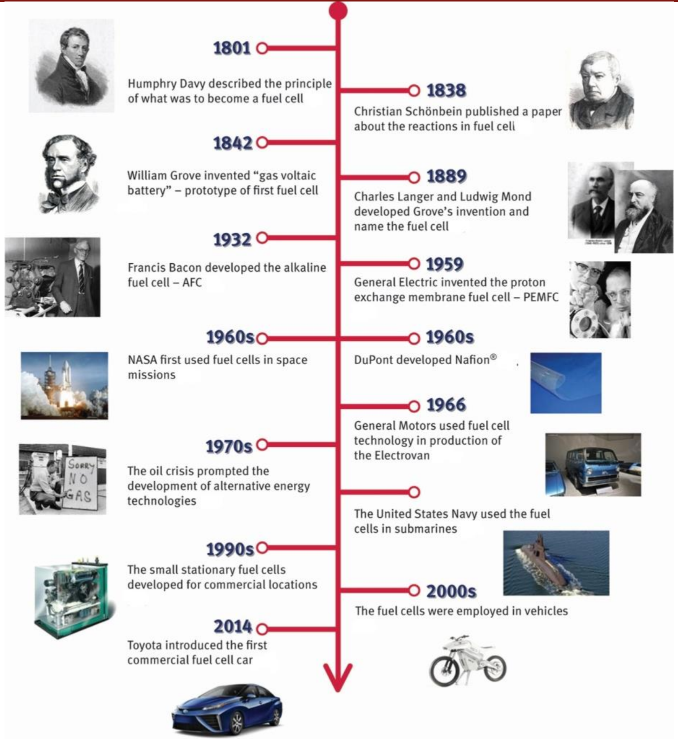
1. PROTON EXCHANGE MEMBRANE FUEL CELLS – COMPOSITION

INTRODUCTION



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

INTRODUCTION



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

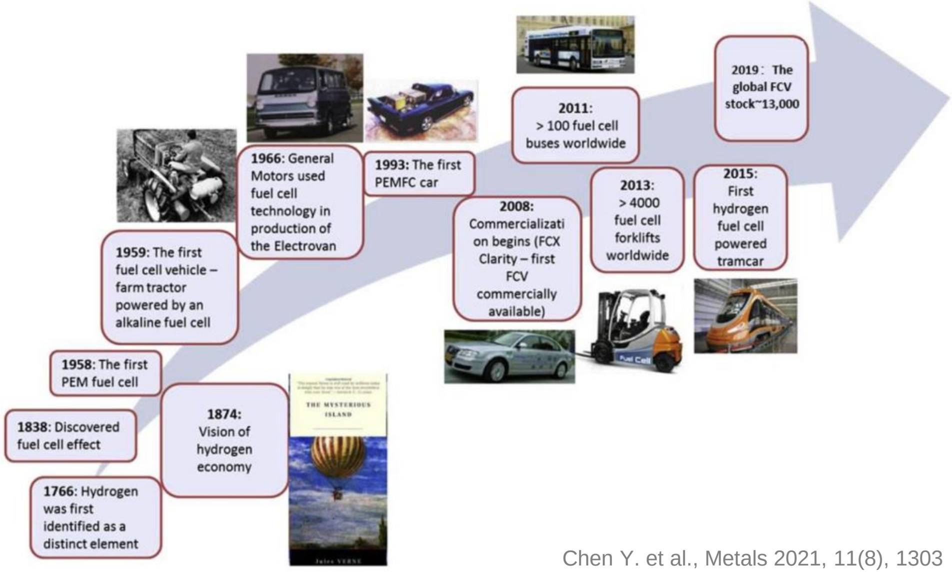
The United States Navy used the fuel cells in submarines

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



1766: Hydrogen was first identified as a distinct element

1838: Discovered fuel cell effect

1874: Vision of hydrogen economy

1958: The first PEM fuel cell

1959: The first fuel cell vehicle – farm tractor powered by an alkaline fuel cell

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

1993: The first PEMFC car

2008: Commercialization begins (FCX Clarity – first FCV commercially available)

2011: > 100 fuel cell buses worldwide

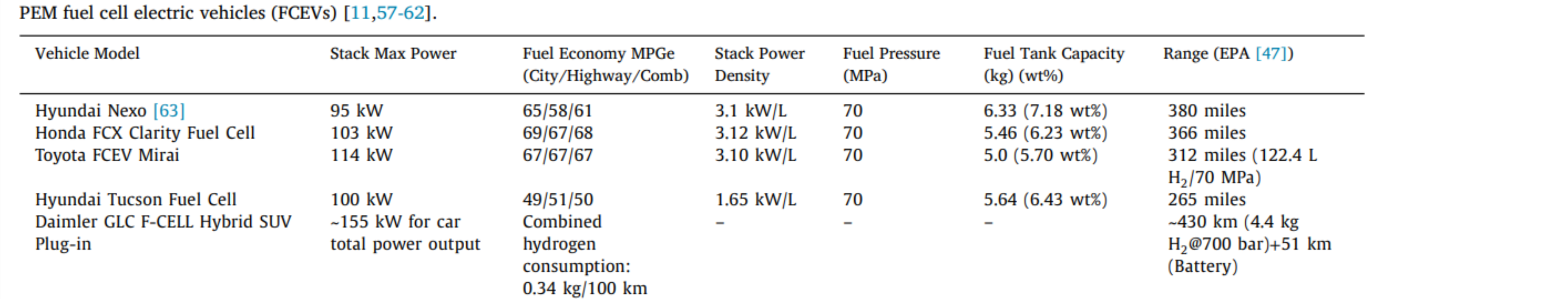
2013: > 4000 fuel cell forklifts worldwide

2015: First hydrogen fuel cell powered tramcar

2019: The global FCV stock~13,000

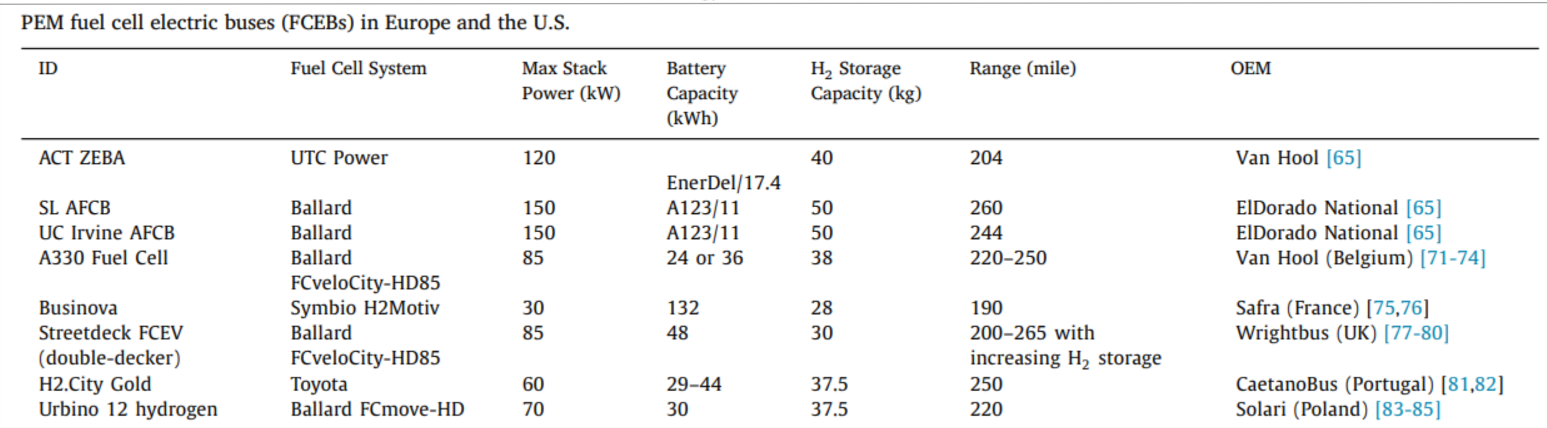
Chen Y. et al., Metals 2021, 11(8), 1303

INTRODUCTION



PEM fuel cell electric vehicles (FCEVs) [11,57-62].

Vehicle Model	Stack Max Power	Fuel Economy MPGe (City/Highway/Comb)	Stack Power Density	Fuel Pressure (MPa)	Fuel Tank Capacity (kg) (wt%)	Range (EPA [47])
Hyundai Nexo [63]	95 kW	65/58/61	3.1 kW/L	70	6.33 (7.18 wt%)	380 miles
Honda FCX Clarity Fuel Cell	103 kW	69/67/68	3.12 kW/L	70	5.46 (6.23 wt%)	366 miles
Toyota FCEV Mirai	114 kW	67/67/67	3.10 kW/L	70	5.0 (5.70 wt%)	312 miles (122.4 L H_2/70 MPa)
Hyundai Tucson Fuel Cell	100 kW	49/51/50	1.65 kW/L	70	5.64 (6.43 wt%)	265 miles
Daimler GLC F-CELL Hybrid SUV Plug-in	~155 kW for car total power output	Combined hydrogen consumption: 0.34 kg/100 km	–	–	–	~430 km (4.4 kg H_2@700 bar)+51 km (Battery)



PEM fuel cell electric buses (FCEBs) in Europe and the U.S.

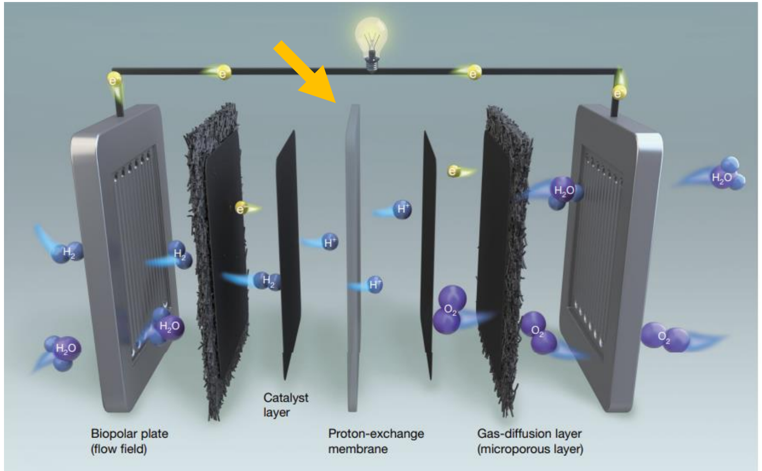
ID	Fuel Cell System	Max Stack Power (kW)	Battery Capacity (kWh)	H_2 Storage Capacity (kg)	Range (mile)	OEM
ACT ZEBA	UTC Power	120	EnerDel/17.4	40	204	Van Hool [65]
SL AFCB	Ballard	150	A123/11	50	260	ElDorado National [65]
UC Irvine AFCB	Ballard	150	A123/11	50	244	ElDorado National [65]
A330 Fuel Cell	Ballard FCveloCity-HD85	85	24 or 36	38	220–250	Van Hool (Belgium) [71-74]
Businova	Symbio H2Motiv	30	132	28	190	Safra (France) [75,76]
Streetdeck FCEV (double-decker)	Ballard FCveloCity-HD85	85	48	30	200–265 with increasing H_2 storage	Wrightbus (UK) [77-80]
H2.City Gold	Toyota	60	29–44	37.5	250	CaetanoBus (Portugal) [81,82]
Urbino 12 hydrogen	Ballard FCmove-HD	70	30	37.5	220	Solari (Poland) [83-85]

Wang Y. et al., Energy and AI, 1, (2020), 100014

MAIN FEATURES

The main features characterizing a PEMFC are:

- A solid electrolyte, able to sustain current conduction in the order of 1 A cm^{-2}
- Electrodes able to operate with low catalyst loadings (cathode: about 0.125 – 0.250 mg cm^{-2}, anode: < 0.1 mg cm^{-2}) showing the best specific power (W kg^{-1}) and area-specific power density (W cm^{-2}) of any other fuel cell type.
- They operate at low temperature and are currently considered for portable, transportation, and small stationary applications.



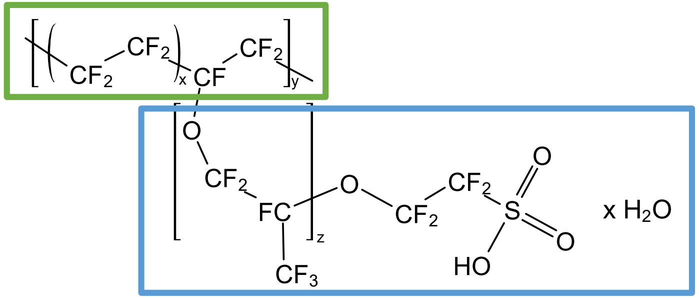
Jiao K. et al., Nature, 595, (2021), 361–369

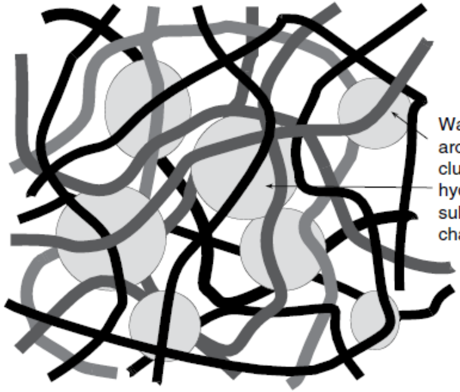
Anode (HOR): $2H_2 \rightarrow 4H^+ + 4e^-$

Cathode (ORR): $O_2 + 4e^- + 4H^+ \rightarrow H_2O$

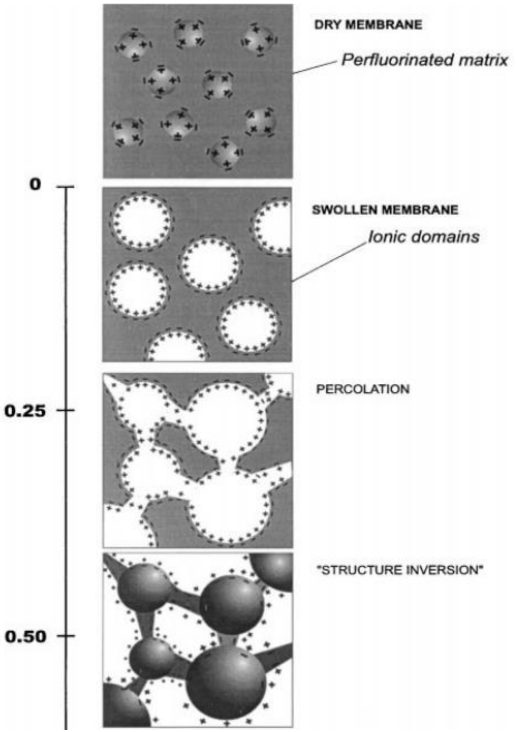
Overall: $2H_2 + O_2 \rightarrow H_2O$

PEMFC – THE ELECTROLYTE





Water collects around the clusters of hydrophylic sulfonate side-chains

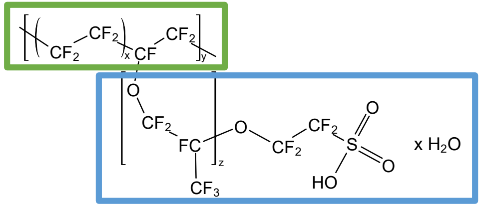


Gebel G., Polymer, 41, 15, (2000), 5829-5838

The most used material as electrolyte is Nafion, a particular type of perfluorinated sulfonic acid (PFSA). In Nafion, the strength of the bonds formed between fluorine and carbon atoms makes the PTFE backbone exceptionally resistant to chemical attacks. Ion conductivity is then guaranteed by terminating the PTFE backbone with sulfonic acid groups (SO_3H). The presence of the SO_3^- ion, together with the accompanying H^+ ions makes the termination parts hydrophilic, contrasting the hydrophobic nature of the polymeric backbone. Hydrophilic clusters are then involved in promoting water absorption and improving ionic conduction.

PEMFC – THE ELECTROLYTE

The number of tetrafluoroethylene groups per polymer chain (k) is used for providing a classification method for each Nafion type. In fact, each formulation is described via the so-called **Equivalent Weight** (EW) of the ionomeric membrane:



$$EW = 100k + MW_{side-chain}$$

Ionic conductivity

Water uptake and swelling

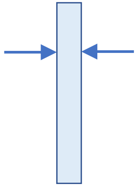
EW
(Backbone-to-side-chain ratio)

Durability

Reactant solubility

For fuel cells, the maximum ionic conductivity of Nafion with EW ranging from 800 to 1200 g/eq. is used.

In parallel to EW, **membrane thickness** (usually ≥ 50 μm) is used to define the properties of the electrolyte.



PEMFC – THE ELECTROLYTE

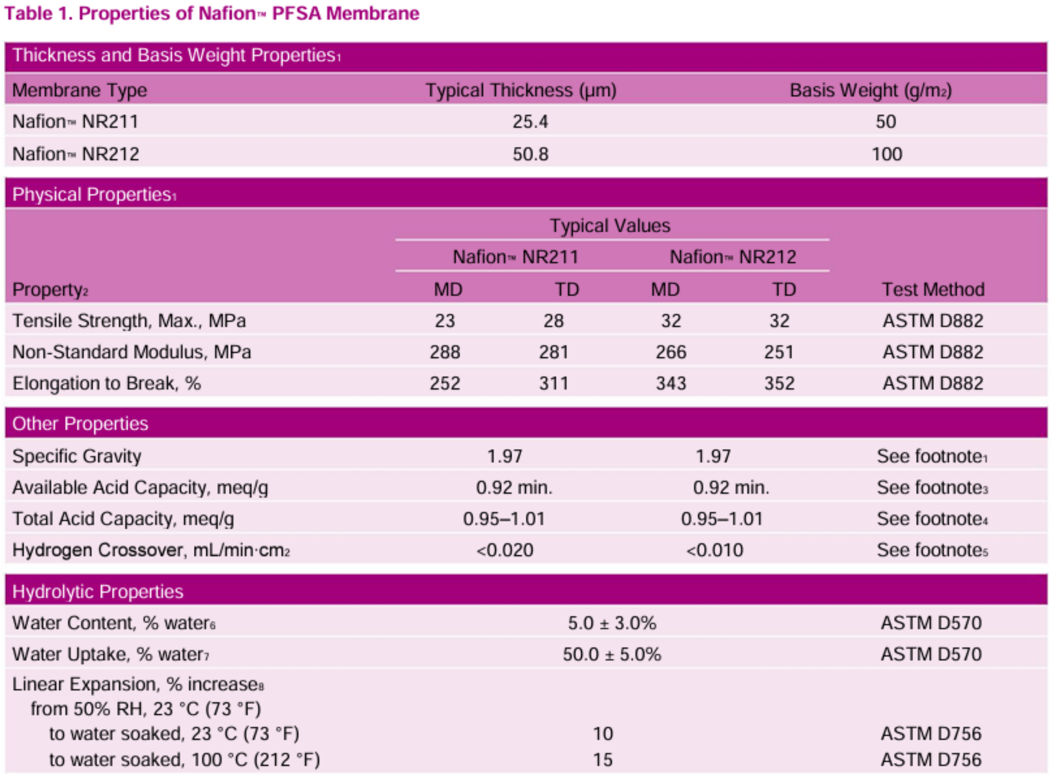


Table 1. Properties of Nafion™ PFSA Membrane

Thickness and Basis Weight Properties[1]		
Membrane Type	Typical Thickness (µm)	Basis Weight (g/m$_2$)
Nafion™ NR211	25.4	50
Nafion™ NR212	50.8	100

Physical Properties[1]					
	Typical Values				
	Nafion™ NR211		Nafion™ NR212		
Property[2]	MD	TD	MD	TD	Test Method
Tensile Strength, Max., MPa	23	28	32	32	ASTM D882
Non-Standard Modulus, MPa	288	281	266	251	ASTM D882
Elongation to Break, %	252	311	343	352	ASTM D882

Other Properties			
Specific Gravity	1.97	1.97	See footnote[1]
Available Acid Capacity, meq/g	0.92 min.	0.92 min.	See footnote[3]
Total Acid Capacity, meq/g	0.95–1.01	0.95–1.01	See footnote[4]
Hydrogen Crossover, mL/min·cm$_2$	<0.020	<0.010	See footnote[5]

Hydrolytic Properties		
Water Content, % water[6]	5.0 ± 3.0%	ASTM D570
Water Uptake, % water[7]	50.0 ± 5.0%	ASTM D570
Linear Expansion, % increase[8]		
from 50% RH, 23 °C (73 °F)		
to water soaked, 23 °C (73 °F)	10	ASTM D756
to water soaked, 100 °C (212 °F)	15	ASTM D756

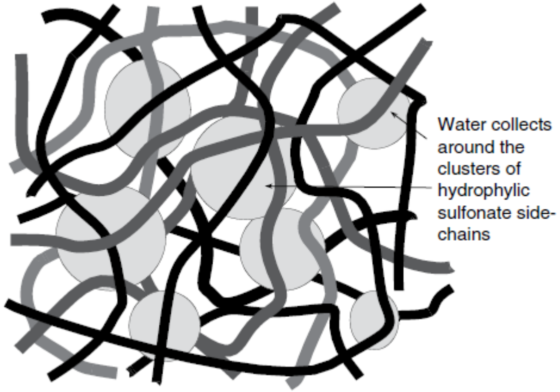
https://www.nafion.com/en/products/sulfonic-membranes

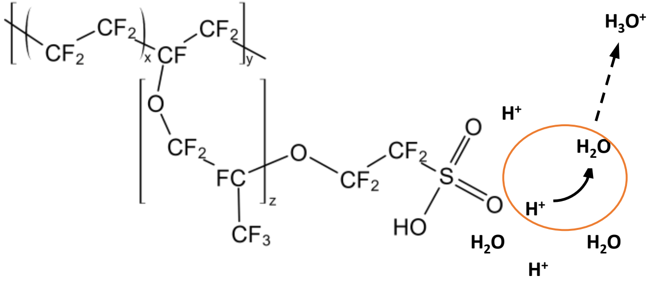
PEMFC – THE ELECTROLYTE – IONIC CONDUCTIVITY

The hydrophilic regions around the clusters of sulfonated side-chains in Nafion and other PFSAs can lead to the absorption of large quantities of water.

Within these hydrated regions, the H^+ ions are weakly attracted to the sulphonic acid groups (SO_3^-) and are therefore mobile; in these regions, a diluted acid is thus created, where hydronium ions (H_3O^+) are formed.

Dry perflourinated ionomers are almost completely non-conductive, so PEFCs typically operate with humidified reactant flow to boost conductivity and reduce ohmic losses.

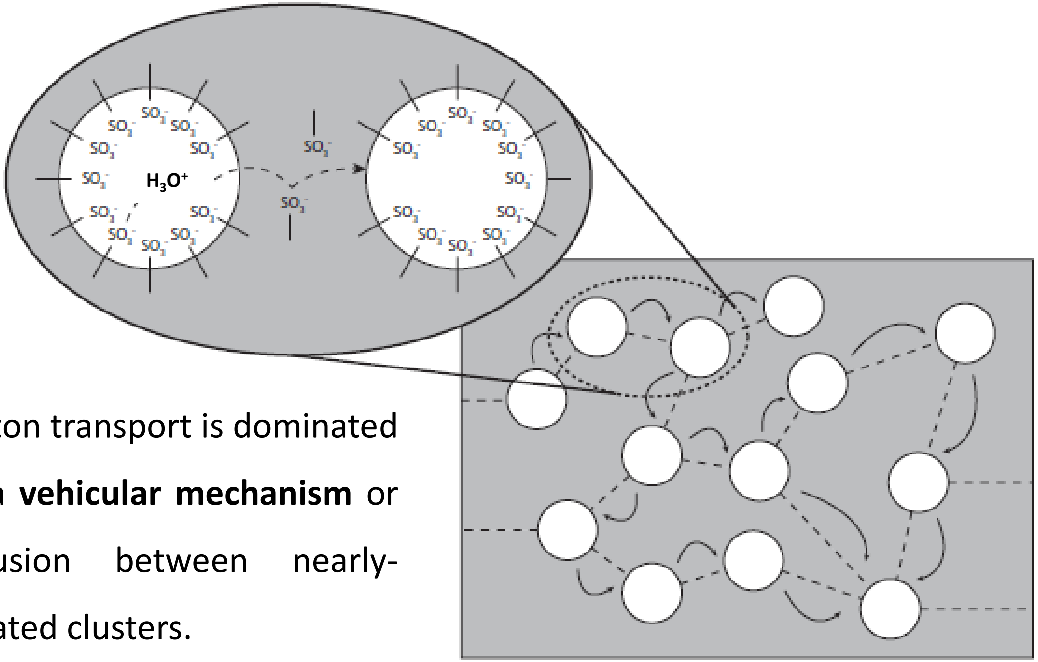




PEMFC – THE ELECTROLYTE – IONIC CONDUCTIVITY

Low water content

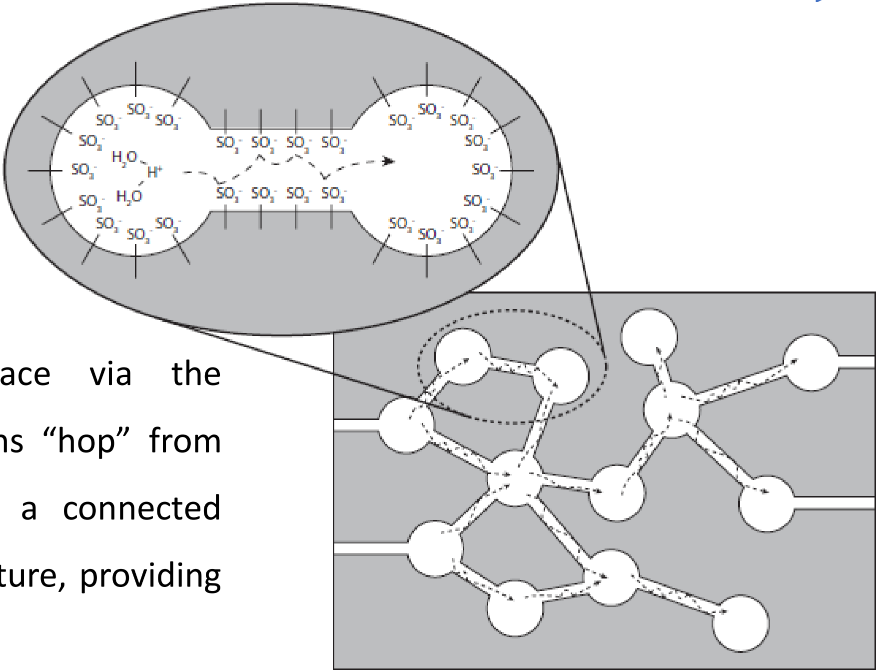
High water content



Proton transport is dominated by a **vehicular mechanism** or diffusion between nearly-isolated clusters.

PEMFC – THE ELECTROLYTE – IONIC CONDUCTIVITY

Low water content High water content



Proton transport takes place via the **Grotthuss mechanism**: protons “hop” from one H_3O^+ to another along a connected pathway in the ionomer structure, providing high proton conductivity.

PEMFC – THE ELECTROLYTE – PFSA MEMBRANES

Nafion and other perfluorosulfonic acids (PFSA) ionomers are characterized by the following features:

- Resistant to chemical attack and stable in both oxidizing and reducing environments.
- Mechanically strong, on account of the durable PTFE backbone, and so can be made into very thin films, down to 50 μm.
- Suitable for operating in acidic environment.
- Able to absorb large quantities of water.
- Good proton conductors when well hydrated, to allow H^+ ions to move quite freely within the material.

PEMFC – THE ELECTROLYTE – PFSA MEMBRANES

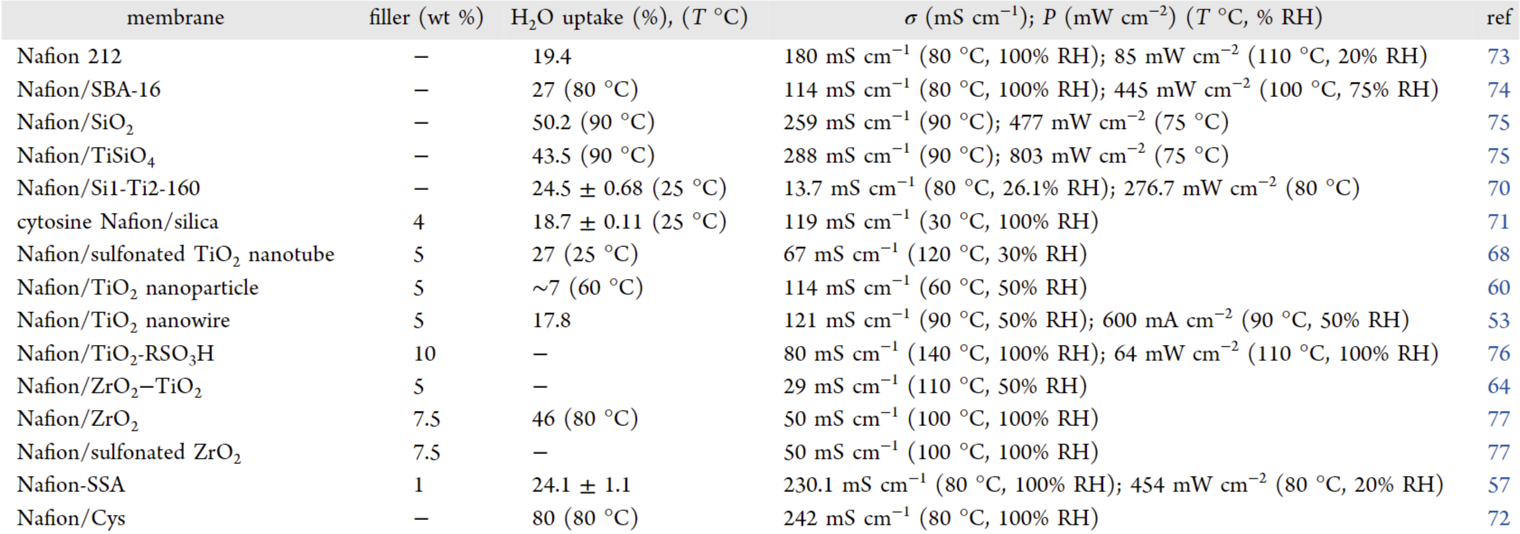
Conversely, PFSA membranes suffer from two major disadvantages:

- high cost, due to the inherent expense of the fluorination step in the synthesis of the ionomer
- inability to operate above about 80°C at atmospheric pressure due to evaporation of water from the membrane (glass transition temperature is around 120-130°C).
- Issues in relation to sustainability, due to the presence of fluorine.

PEMFC – THE ELECTROLYTE – PFSA MEMBRANES

In this framework, several strategies have been explored for improving PFSA characteristics, such as:

- Add inorganic fillers (such as ZrO_2, TiO_2, or SiO_2), with the aim of improving: proton conductivity, the ability to retain water molecules, and with the aim of extending to upper temperatures the operational range of PFSA membranes. Issues: filler concentration cannot exceed some threshold values otherwise proton conductivity is reduced.



membrane	filler (wt %)	H_2O uptake (%), (T °C)	σ (mS cm^{-1}); P (mW cm^{-2}) (T °C, % RH)	ref
Nafion 212	–	19.4	180 mS cm^{-1} (80 °C, 100% RH); 85 mW cm^{-2} (110 °C, 20% RH)	73
Nafion/SBA-16	–	27 (80 °C)	114 mS cm^{-1} (80 °C, 100% RH); 445 mW cm^{-2} (100 °C, 75% RH)	74
Nafion/SiO_2	–	50.2 (90 °C)	259 mS cm^{-1} (90 °C); 477 mW cm^{-2} (75 °C)	75
Nafion/$TiSiO_4$	–	43.5 (90 °C)	288 mS cm^{-1} (90 °C); 803 mW cm^{-2} (75 °C)	75
Nafion/Si1-Ti2-160	–	24.5 ± 0.68 (25 °C)	13.7 mS cm^{-1} (80 °C, 26.1% RH); 276.7 mW cm^{-2} (80 °C)	70
cytosine Nafion/silica	4	18.7 ± 0.11 (25 °C)	119 mS cm^{-1} (30 °C, 100% RH)	71
Nafion/sulfonated TiO_2 nanotube	5	27 (25 °C)	67 mS cm^{-1} (120 °C, 30% RH)	68
Nafion/TiO_2 nanoparticle	5	~7 (60 °C)	114 mS cm^{-1} (60 °C, 50% RH)	60
Nafion/TiO_2 nanowire	5	17.8	121 mS cm^{-1} (90 °C, 50% RH); 600 mA cm^{-2} (90 °C, 50% RH)	53
Nafion/TiO_2-RSO_3H	10	–	80 mS cm^{-1} (140 °C, 100% RH); 64 mW cm^{-2} (110 °C, 100% RH)	76
Nafion/ZrO_2–TiO_2	5	–	29 mS cm^{-1} (110 °C, 50% RH)	64
Nafion/ZrO_2	7.5	46 (80 °C)	50 mS cm^{-1} (100 °C, 100% RH)	77
Nafion/sulfonated ZrO_2	7.5	–	50 mS cm^{-1} (100 °C, 100% RH)	77
Nafion-SSA	1	24.1 ± 1.1	230.1 mS cm^{-1} (80 °C, 100% RH); 454 mW cm^{-2} (80 °C, 20% RH)	57
Nafion/Cys	–	80 (80 °C)	242 mS cm^{-1} (80 °C, 100% RH)	72

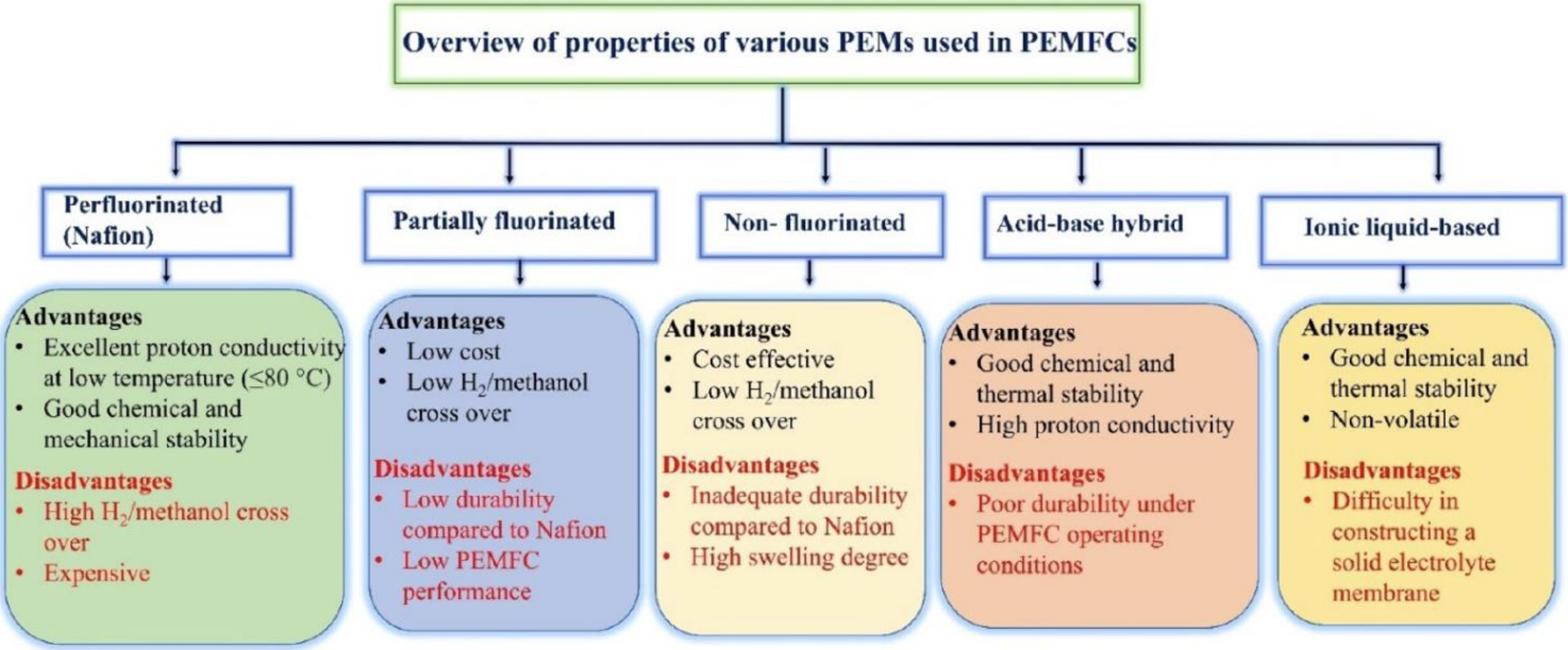
Javed A. et al., ACS Applied Materials & Interfaces, 15, 25, (2023), 29655-31102

PEMFC – THE ELECTROLYTE – PFSA MEMBRANES

- Use carbon-based nanofillers (such as carbon nanotubes or functionalized graphene oxide), to form long range-ion conductivity channels.
- As an alternative to fluorinated PFSA, the use of nonfluorinated polymers (such as the sulfonated polyether ether ketone, SPEEK) have been investigated. The interest in this extent is related to the possibilities to operate at high temperatures (above 100 °C), where nonfluorinated polymer membranes are already used (such as the Polybenzimidazole, PBI, characterized by high melting point, above 600 °C). and allowing to operate a High-Temperature PEMFC within the range 150 – 180 °C.

  Such class of materials is characterized by poor proton conduction, which is increased by doping the polymer with strong acids.

PEMFC – THE ELECTROLYTE – PFSA MEMBRANES



Overview of properties of various PEMs used in PEMFCs

Perfluorinated (Nafion)

Advantages
- Excellent proton conductivity at low temperature (≤80 °C)
- Good chemical and mechanical stability

Disadvantages
- High H_2/methanol cross over
- Expensive

Partially fluorinated

Advantages
- Low cost
- Low H_2/methanol cross over

Disadvantages
- Low durability compared to Nafion
- Low PEMFC performance

Non- fluorinated

Advantages
- Cost effective
- Low H_2/methanol cross over

Disadvantages
- Inadequate durability compared to Nafion
- High swelling degree

Acid-base hybrid

Advantages
- Good chemical and thermal stability
- High proton conductivity

Disadvantages
- Poor durability under PEMFC operating conditions

Ionic liquid-based

Advantages
- Good chemical and thermal stability
- Non-volatile

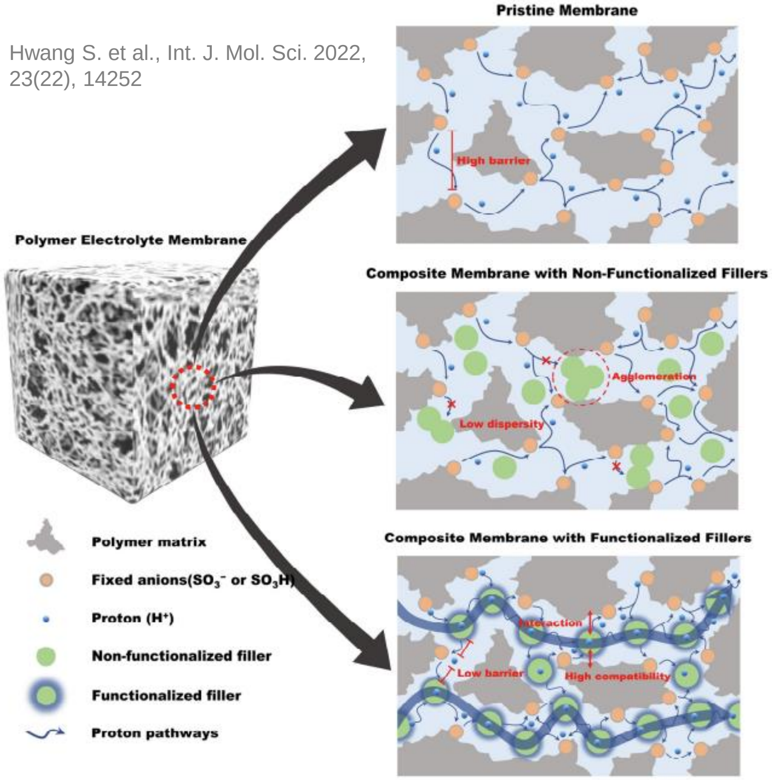
Disadvantages
- Difficulty in constructing a solid electrolyte membrane

Javed A. et al., ACS Applied Materials & Interfaces, 15, 25, (2023), 29655-31102

PEMFC – THE ELECTROLYTE – PFSA MEMBRANES

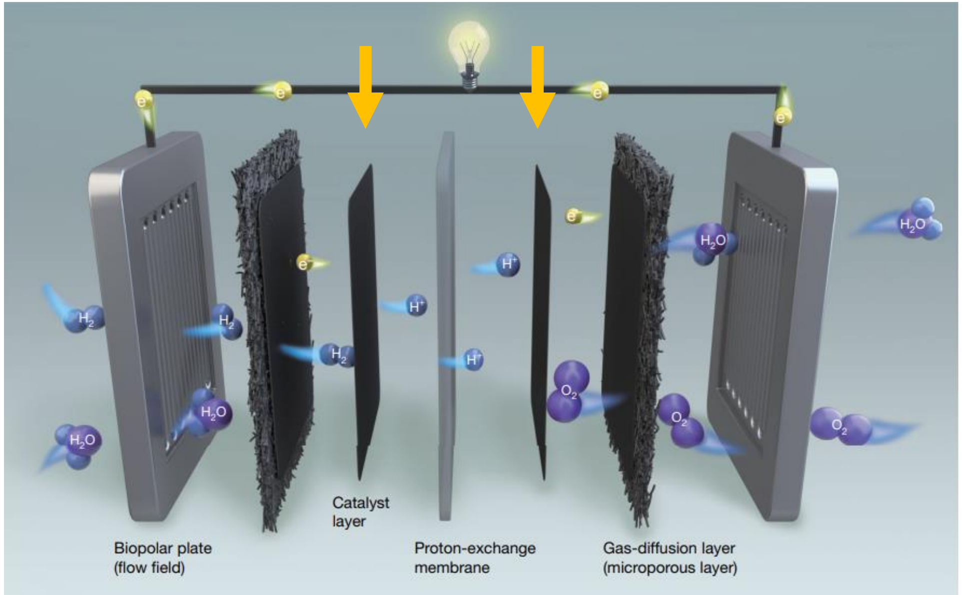
Most of the difficulties relating to the creation of effective functionalized PFSA membranes, are related to the formation of agglomerated domains of the functional groups or dopants, due to the low compatibility between the non-functionalized composites and the polymer matrix, leading to an impairment of mechanical strength, chemical stability and proton conductivity.

Research is trying to mitigate these drawbacks by designing composite materials with the aim of enhancing PEM properties by improving the configuration of the interface.



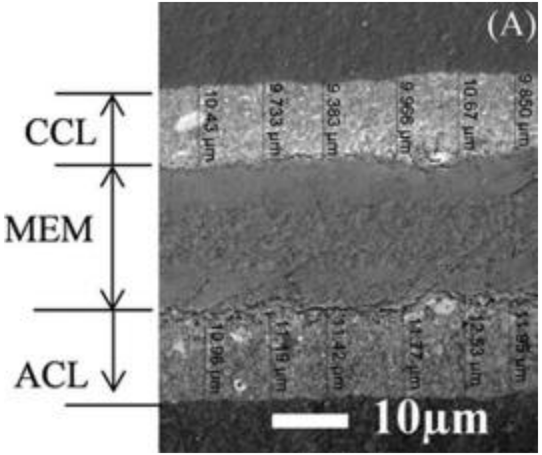
Hwang S. et al., Int. J. Mol. Sci. 2022, 23(22), 14252

PEMFC – THE ELECTRODES

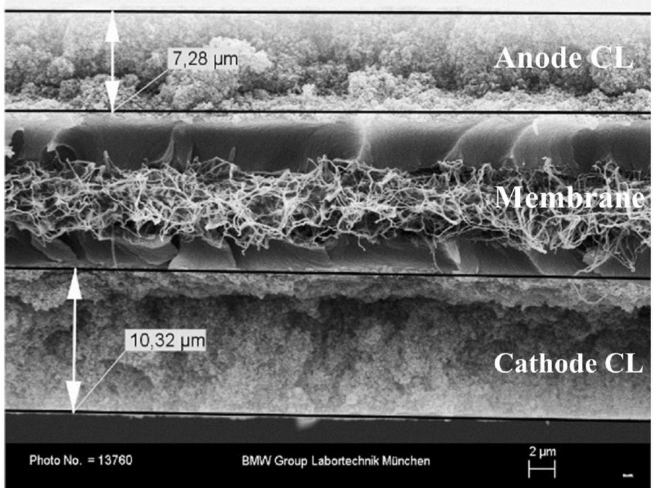


Jiao K. et al., Nature, 595, (2021), 361–369

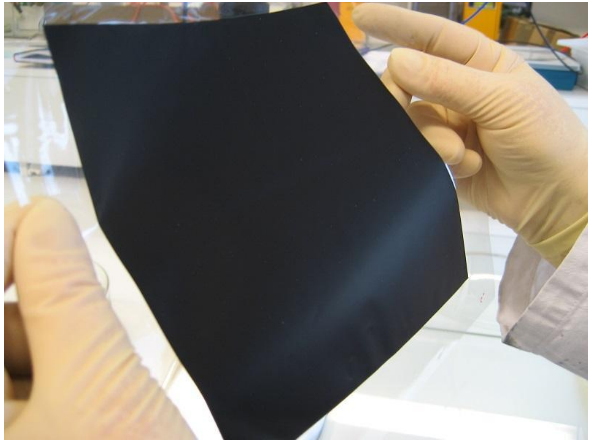
PEMFC – THE CATALYST COATED MEMBRANE



Banas C. J. et al., Journal of The Electrochemical Society, 165, 6, (2018), F3015-F3023



Obermaier M. et al., Scientific reports, 8, *(2018), 4933*



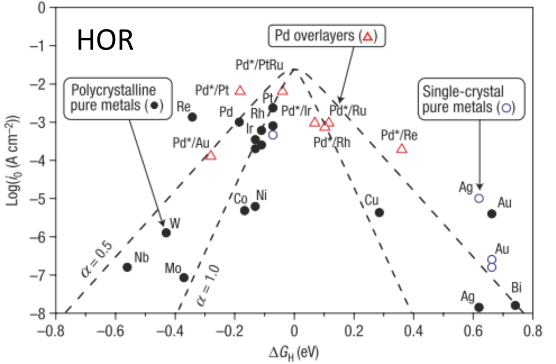
https://www.europages.de/Catalyst-Coated-Membrane-CCM-MEA/HIAT-GGMBH/cpid-5550346.html

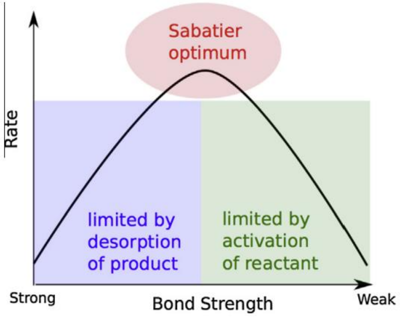
PEMFC – THE ELECTRODES

Historically, Pt has been always used as catalyst material. For comparing the material performances for each specific reaction, the Sabatier principle is used to build the so-called Volcano plots.

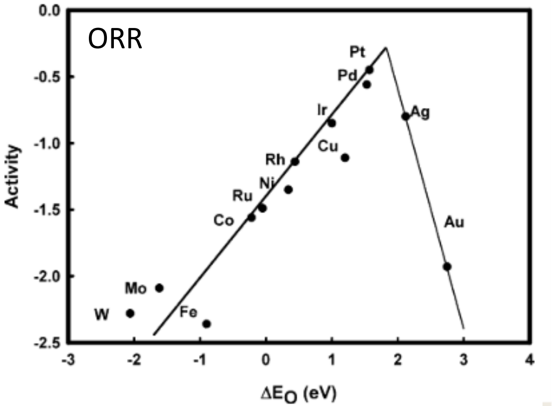
The Sabatier principle is a qualitative criterion stating that the best catalysts should bind atoms and molecules with an intermediate strength: catalyst-reactant bond strength should not be too weak and it should be able to activate the reactants, and not be too strong to limit products desorption. This leads to a volcano-type relationship between activity and bond strength.

Greely J., Nature Materials, 5, (2006), 909–913





Medford A.J. et al., Journal of Catalysis, 328, (2015), 36-4

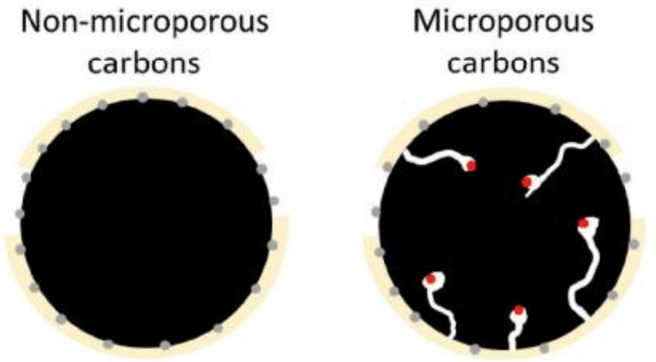


Nørskov J.K. et al., Phys. Chem. B, 108, 46, (2004), 17886–17892

PEMFC – THE ELECTRODES

The catalyst layer is composed by a set nanoparticles dispersed onto a carbon-made support. The most common support materials belong to the class of the amorphous carbon materials, and the most well-known are commercialized under the name Vulcan XC72, Acetylene black and Ketjen black.

They are the optimal materials for their high electrical conductivity and decent corrosion resistance. Support materials are usually characterized by their specific surface areas (m^2/g).

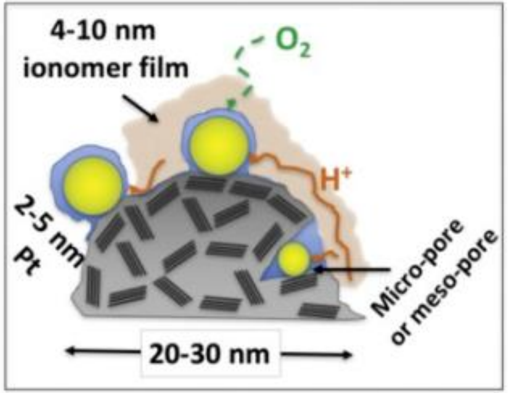


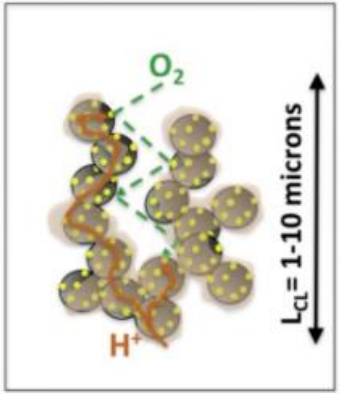
Grandi M. et al., Journal of Power Sources, 562, 1 (2023), 232734

PEMFC – THE ELECTRODES

Catalyst layers are formed starting from a solution containing a volatile solvent, the dispersed catalyst nanoparticles, the carbon support, and a small ionomer percentage. In this way, during solvent evaporation, an ionomer film is formed overlapping catalyst nanoparticles. Once the solvent is evaporated, the remaining ionomer acts as a “glue” reinforcing the catalyst adhesion to the substrate and promoting both proton diffusion towards the reaction sites and diffusion channels for the formed water to be expelled from the electrode.

This ink can be deposited in two different ways, being sprayed either on the electrolyte or onto the Microporous Layer, a dedicated layer created onto the Gas Diffusion Layers.



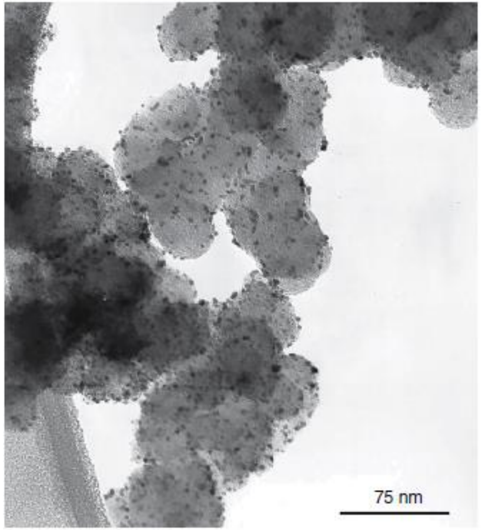


Poojary S. et al., Molecules 2020, 25(15), 3387

PEMFC – THE ELECTRODES

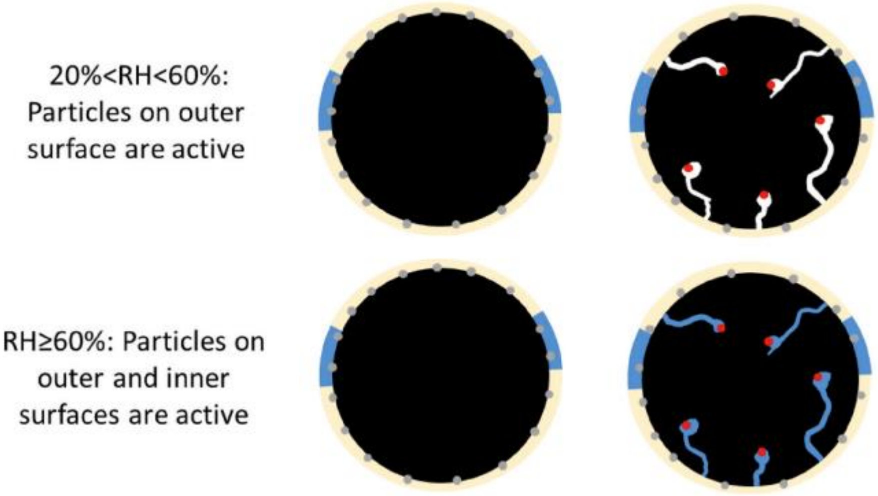
Among the two methods, depositing catalyst on the electrolyte is preferred because when deposited on the GDL, additional cleaning and processing methods (hot-pressing the MEA) are needed.

The loading of Pt is different for the electrodes; on the anode electrode is usually around 50 / 25 µg cm^{-2}, while on the cathode electrode improvements are still expected; on commercial Toyota Mirai, the catalyst loading at the cathode was equal to 0.3 mg cm^{-2}, but the DOE set as a target to reach the 0.1 mg cm^{-2} for the 2025 and research is still carried out in this framework, overall concerning the needs to satisfy also stability requirements.



PEMFC – THE ELECTRODES

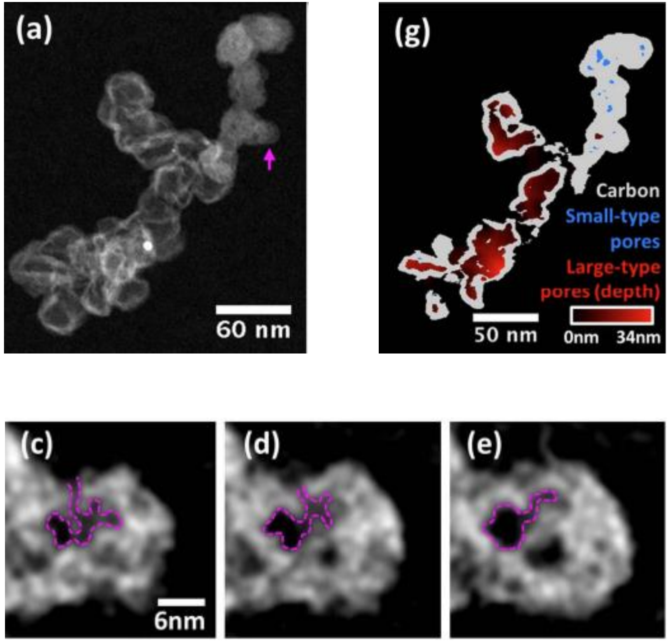
The pore structure significantly influences how the ionomer covers the metal particles and at which humidification level the particles are in electrolyte contact.



20%<RH<60%: Particles on outer surface are active

RH≥60%: Particles on outer and inner surfaces are active

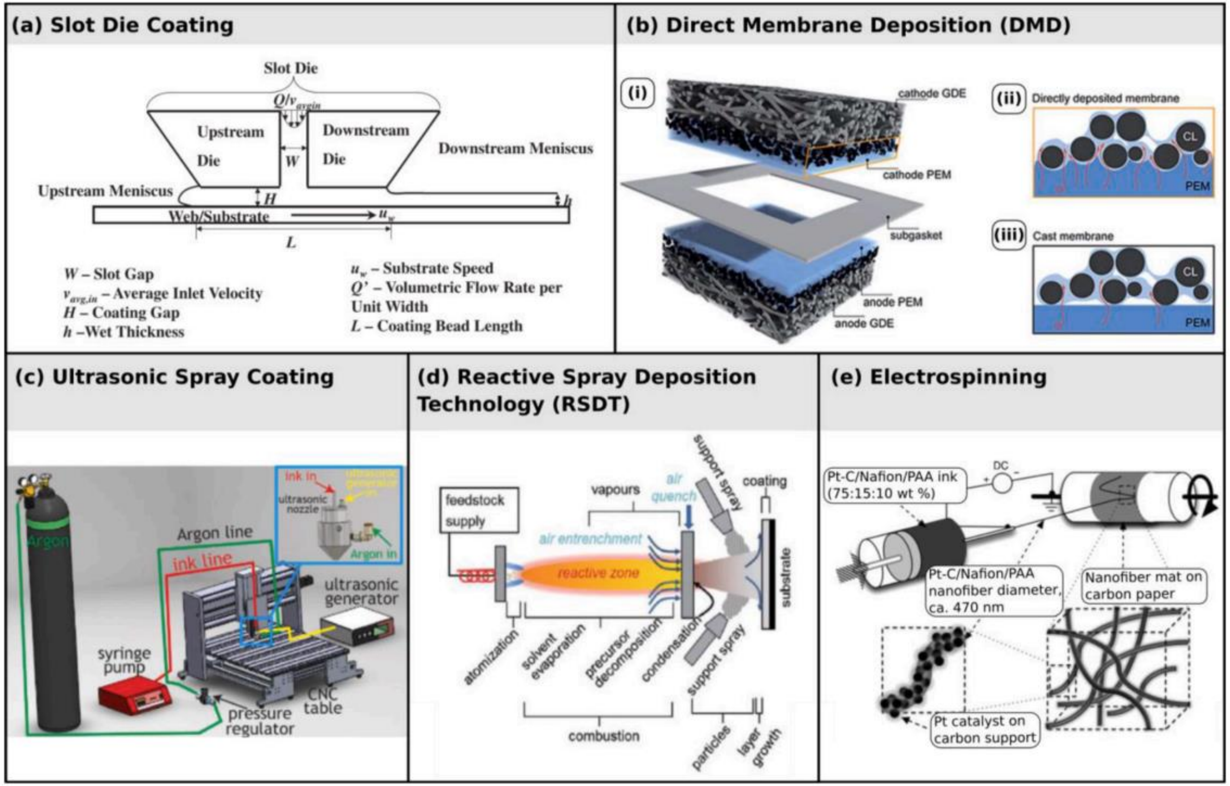
Grandi M. et al., Journal of Power Sources, 562, 1 (2023), 232734



Padgett E. et al., J. Electrochem. Soc. 165, (2018), F173

PEMFC – THE ELECTRODES – FABRICATION TECHNIQUES

R.1



Grandi M. et al., Journal of Power Sources, 562, 1 (2023), 232734

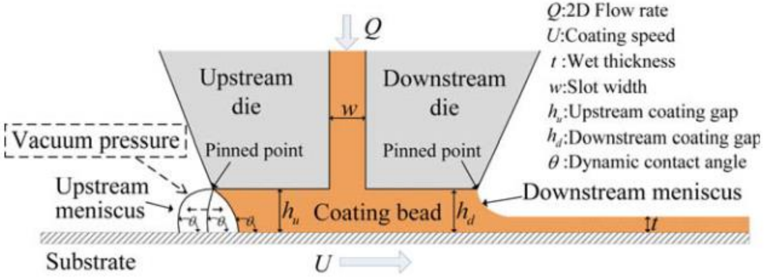
PEMFC – THE ELECTRODES – FABRICATION TECHNIQUES

Die Coating

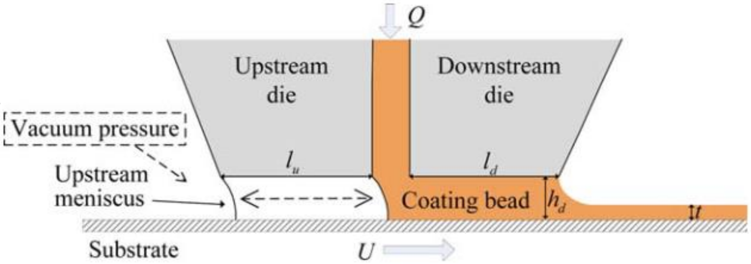
Commonly used for thin film production. It works by moving a substrate beneath the slot die through which a liquid ink or ionomer is pumped. Since this method can be easily integrated into industrial roll-to-roll extrusion systems, it is largely considered to be the most promising large scale MEA fabrication method because of its high scalability.

It allows to produce thin films ranging from 10 nm to few hundreds of µm up to 2 m/s; the substrate can be heated to reduce drying times.

It can be used for depositing the ionomer onto a gas diffusion electrode, or for depositing both the electrolytic and catalyst layers.



Upstream meniscus pinned



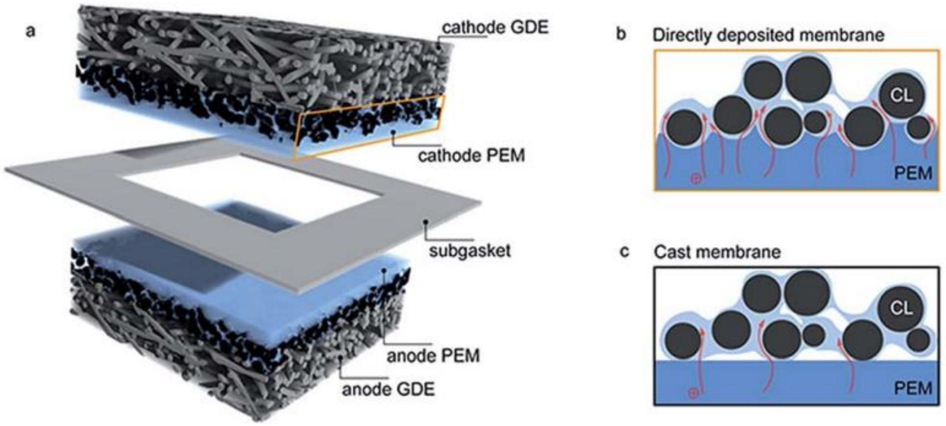
Upstream meniscus free

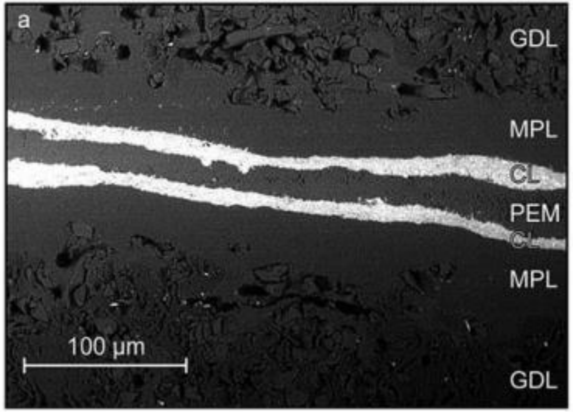
Ding X. et al., 62, 7, (2016), 2508-2524

PEMFC – THE ELECTRODES – FABRICATION TECHNIQUES

Direct MEA deposition

The PEM is directly deposited onto the catalyst layers of gas diffusion electrode. The layer stack is then directly sealed with a thin PTFE sub-gasket preventing fuel crossover. Such approach is used for enhancing proton conductivity to the reaction sites and to reduce membrane resistance. Ionomer deposition can be performed via inkjet printing, or also for screen-printing or spry-coating, thus sustainable for industrial upscale.





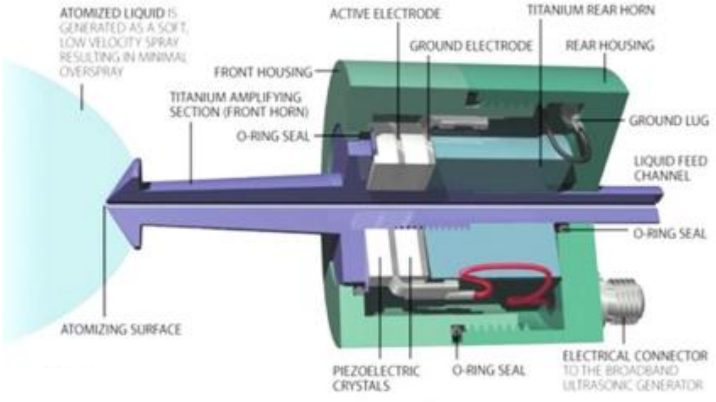
Klingele M. et al., J. Mater. Chem. A, 3, (2015), 11239-11245

PEMFC – THE ELECTRODES – FABRICATION TECHNIQUES

R.1

Ultrasonic spray coating

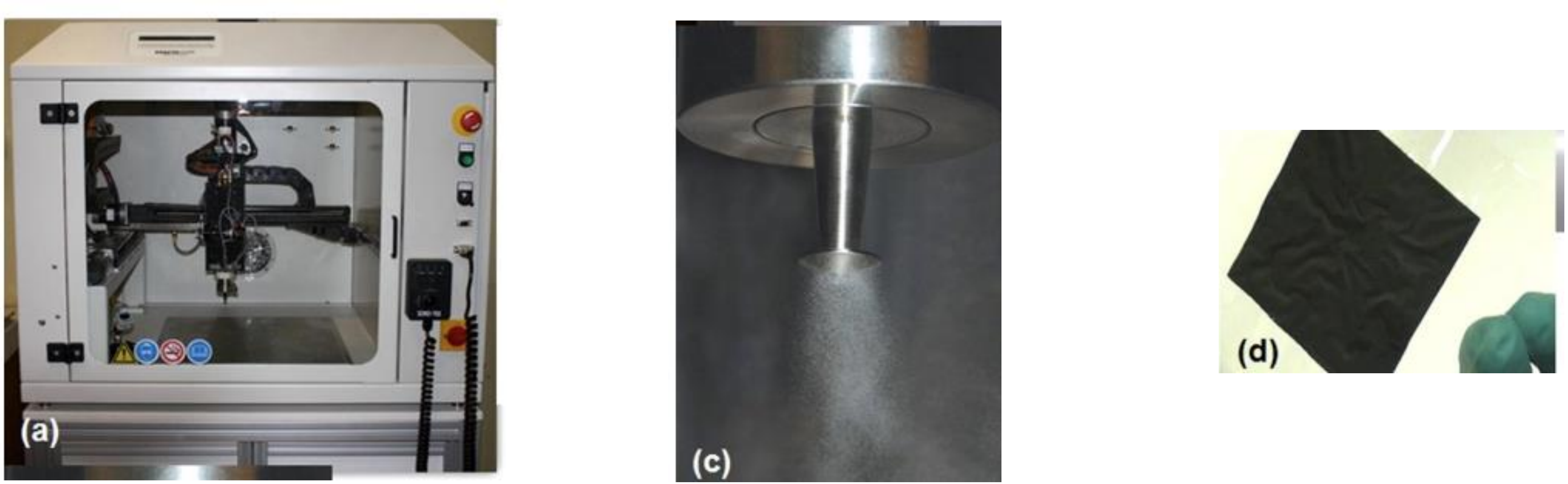
An ultrasonic nozzle incorporated into a spray gun. The catalyst ink is pumped through the vibrating nozzle where it is dispersed into a fine mist (preventing particle cauterization). An inert gas (i.e. argon) is used as medium.



Millington B. et al., Journal of Power Sources, 196, 20, (2011), 8500-8508

PEMFC – THE ELECTRODES – FABRICATION TECHNIQUES

The main advantage of such a technique relies in the high reproducibility of the manufacturing system and in the homogeneity of the thickness of the deposited layer.



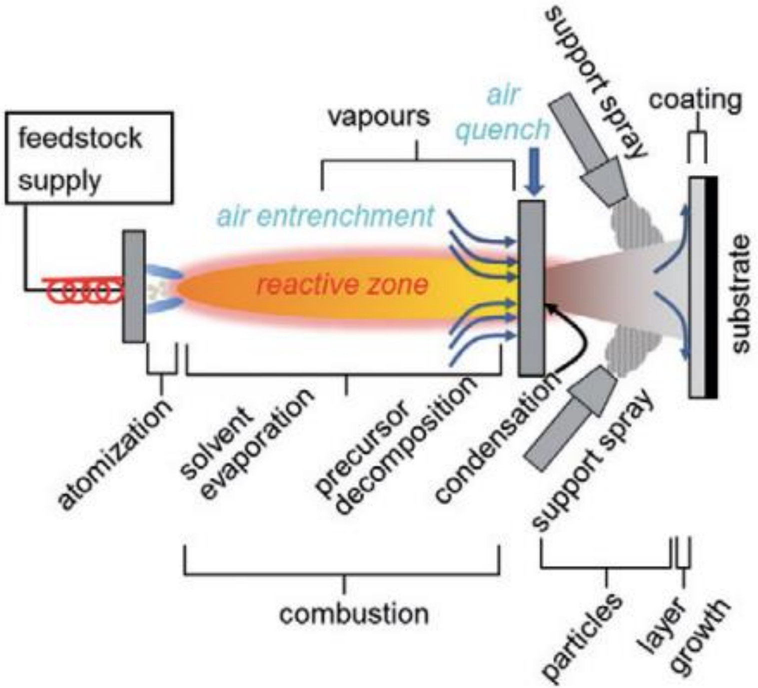
Millington B. et al., Journal of Power Sources, 196, 20, (2011), 8500-8508

PEMFC – THE ELECTRODES – FABRICATION TECHNIQUES

R.1

Reactive spray deposition

It is a promising method for reducing MEA production costs, because all of the steps related to catalyst fabrication and deposition are harmonized into one processing step: small particles of catalyst material, are shot out of a nozzle in the form of a gas flame, where they are instantly cooled into atom-sized solids and sprayed onto the fuel cell membrane in a carefully calibrated fine layer. The flame-based dispersion of the catalyst material allows it to bond to the membrane quickly, eliminating several binding and drying steps

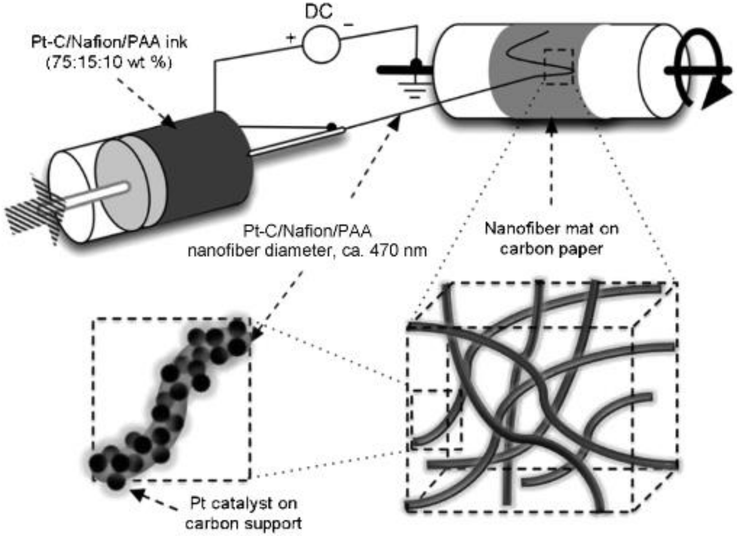


Maric R., Fuel Cells Bulletin, 2012, 4, (2012), 15

PEMFC – THE ELECTRODES – FABRICATION TECHNIQUES

Electrospinning

It is a well-established method to produce nanometer sized fibers with a given diameter. A solution (suspension or melt of the envisaged material) is subsequently pumped through a syringe with an inner needle diameter of a few micrometers. An electric field is generated by applying a high voltage between the needle and the counter electrode, tearing the droplet at the needle tip into fibrous form as it accelerates towards the counter electrode in a nanometer-sized jet.



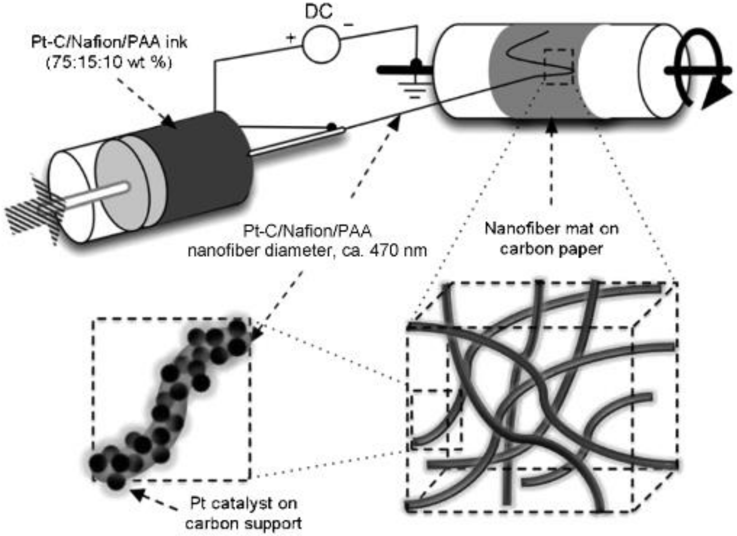
Zhang W., et al., ChemSusChem, 4, 12, (2011), 1753-1757

PEMFC – THE ELECTRODES – FABRICATION TECHNIQUES

R.1

However, the jet does not travel in a linear motion on its path towards the counter electrode, yet it bends in a complicated but not random spiraling trajectory. This phenomenon can be predicted theoretically and controlled experimentally and thus a wide variety of different nanofiber architectures can be fabricated.

the electrospinning ink requires an additional carrier polymer. This needs to be added to give the dispersion enough stability to endure the electrospinning process

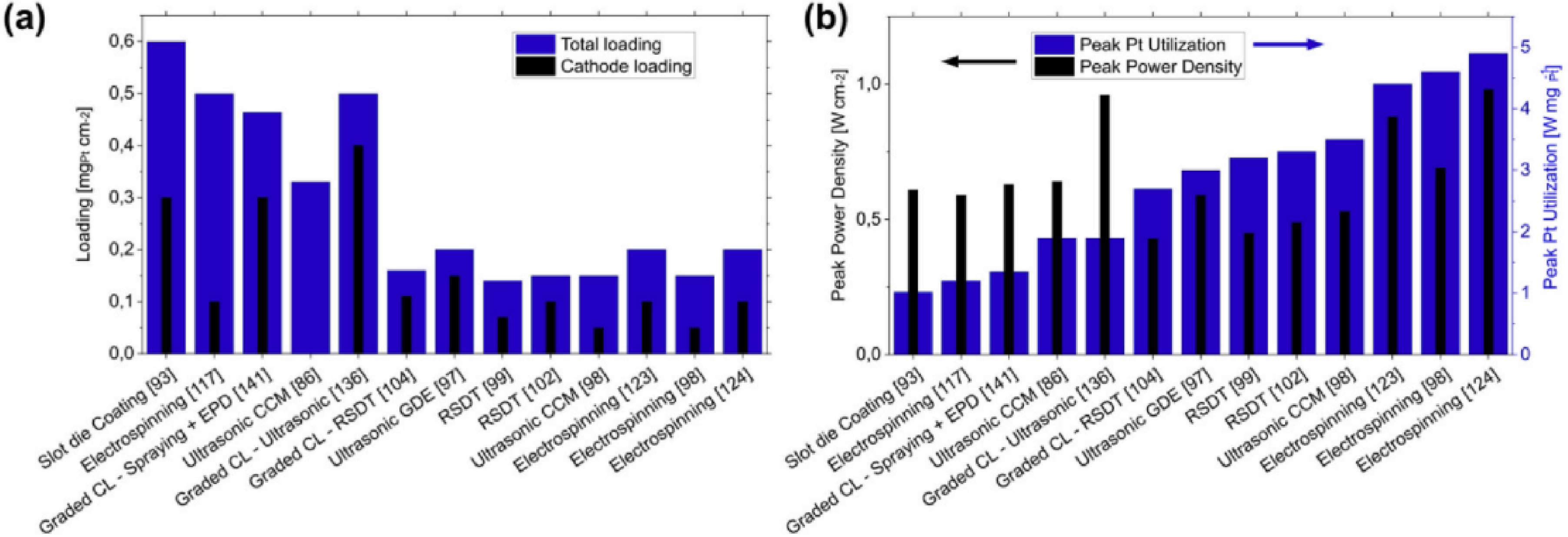


Zhang W., et al., ChemSusChem, 4, 12, (2011), 1753-1757

PEMFC – THE ELECTRODES – FABRICATION TECHNIQUES

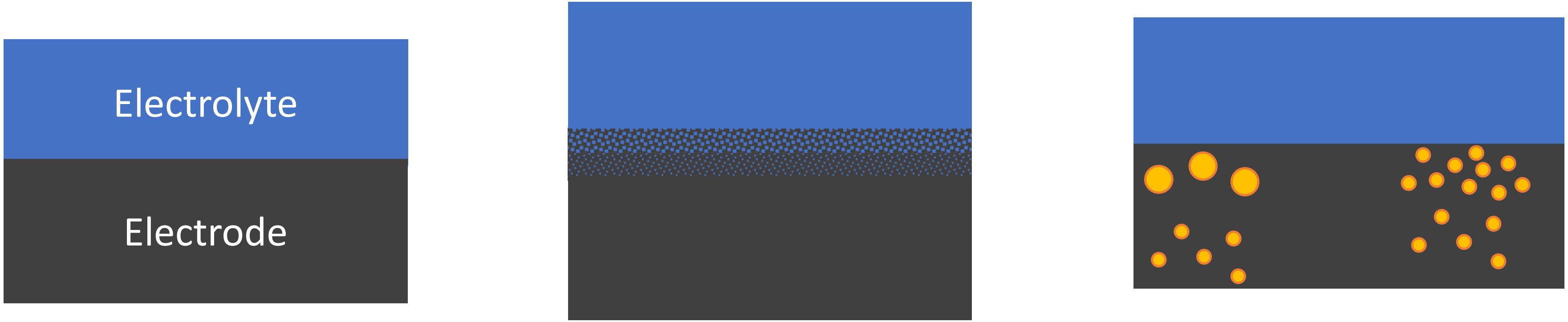
R.1

Both reactive spray deposition, electrospinning and ultrasonic spray coating can all achieve total loadings at or even below 0.2 mgPt cm^{-2}, while maintaining high peak power densities.

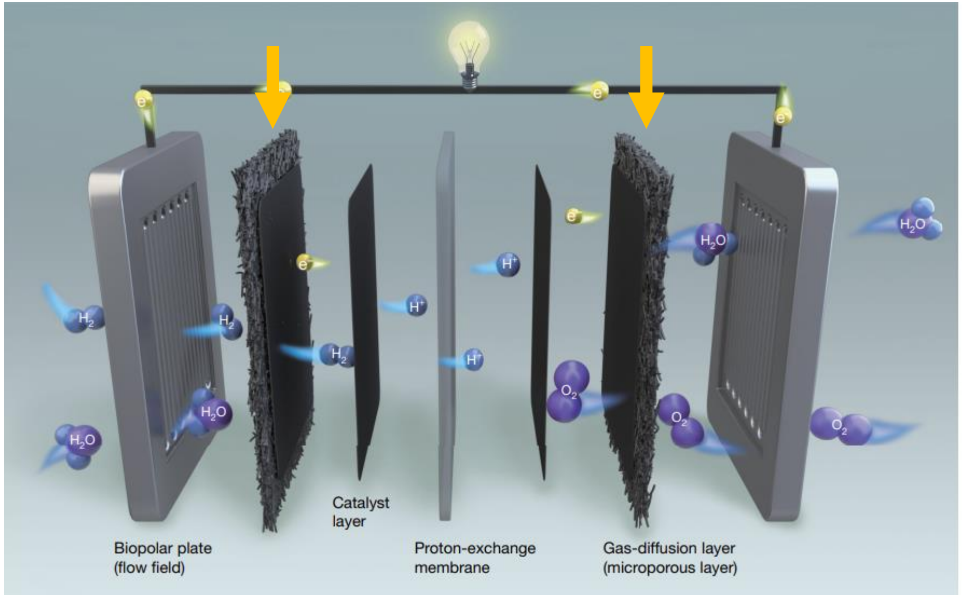


PEMFC – THE ELECTRODES – GRADED CATALYST

Graded catalyst layers have been thought as a possible solution to overcome the issues related to the unequal reaction rates and degradation degrees within the catalyst layers.



PEMFC – THE GAS DIFFUSION LAYER



Jiao K. et al., Nature, 595, (2021), 361–369

PEMFC – THE GAS DIFFUSION LAYER

The GDL (also known as Diffusion Media, or Porous Transport Layer) is the outermost layer of the MEA, it is made by a porous, conductive material (usually carbon fibers), arranged in form of carbon paper or carbon cloth, with a typical thickness of 100 ÷ 400 µm.

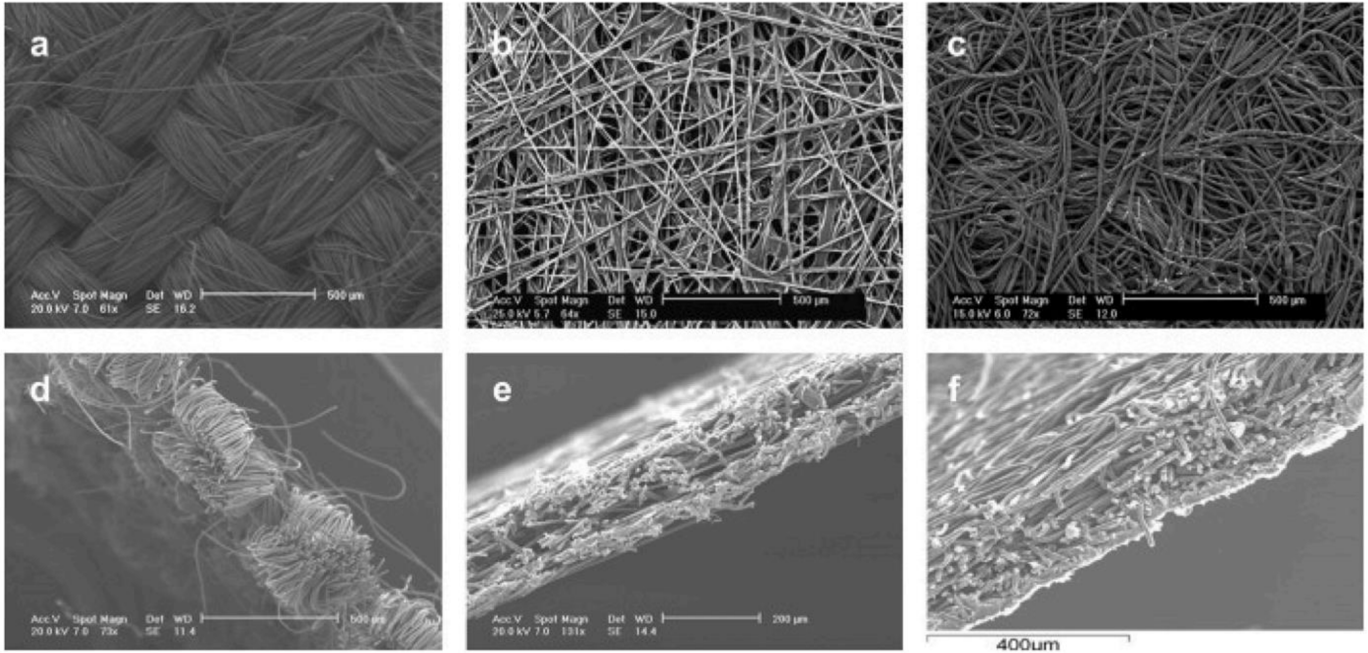
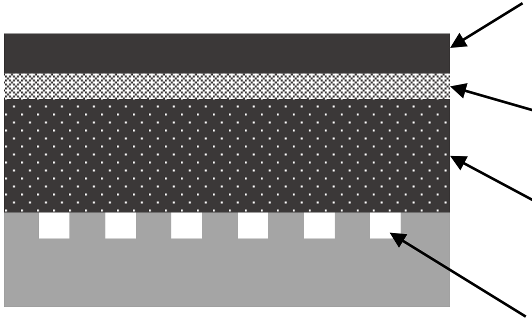


Fig. 1. SEM images the surfaces (top row) and cross-sections (bottom row) of: (a, d) carbon cloth (Ballard 1071HCB); (b, e) carbon paper (Toray H-060); and (c,f) carbon felt (Freudenberg C2). Reproduced with permission from Elsevier [12].

Lee F.C., et al., Renewable and Sustainable Energy Reviews, 166, (2022), 112640

PEMFC – THE GAS DIFFUSION LAYER – THE MICROPOROUS LAYER

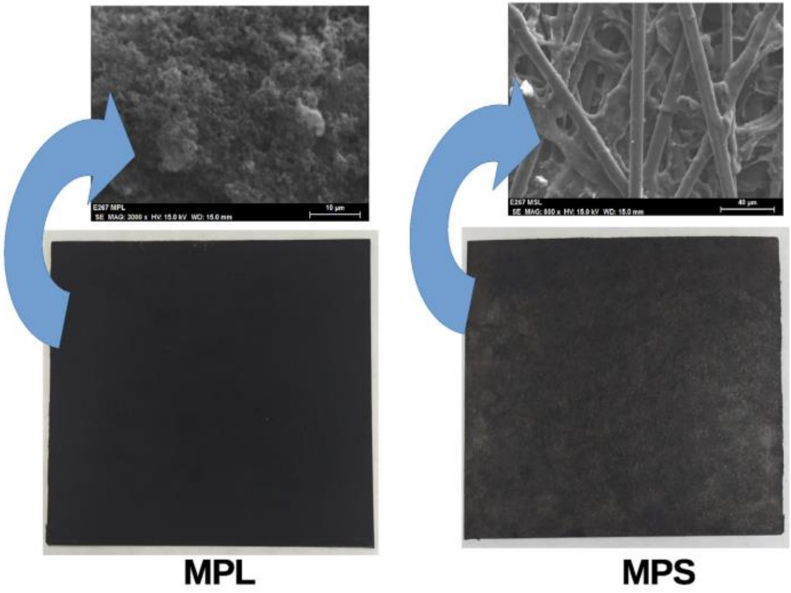


Catalyst layer

Micro Porous Layer
(Carbon black/PTFE mix)

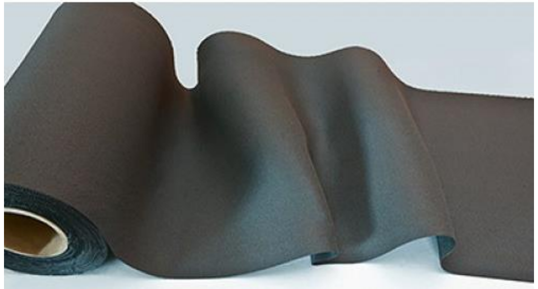
Micro Porous Substrate
(Carbon paper / cloth)

Flow channel

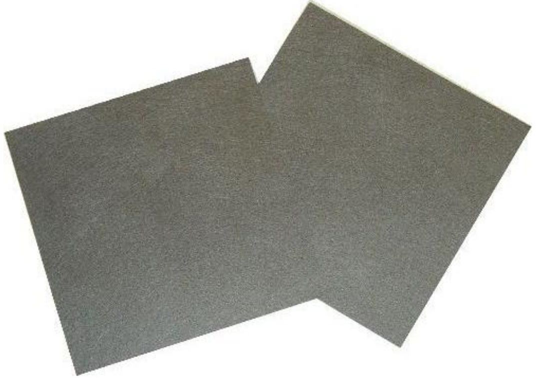


Navarro A.J., et al., International journal of hydrogen energy, 47, (2022), 7990-7999

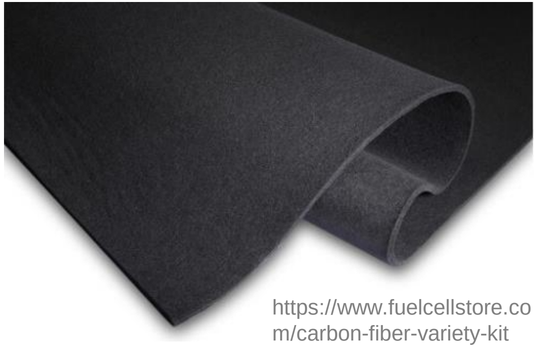
PEMFC – THE GAS DIFFUSION LAYER



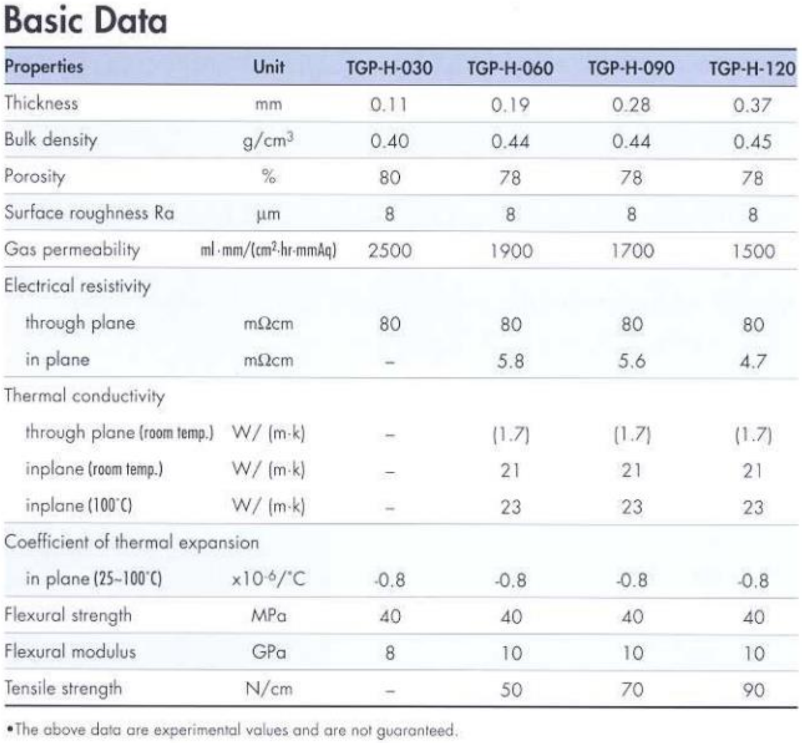
https://www.fuelcellstore.com/avcarb-1071-hcb?search=gas%20diffusion%20layer&page=3



https://www.fuelcellstore.com/toray-carbon-paper-030?search=gas%20diffusion%20layer&page=4



https://www.fuelcellstore.com/carbon-fiber-variety-kit



Basic Data

Properties	Unit	TGP-H-030	TGP-H-060	TGP-H-090	TGP-H-120
Thickness	mm	0.11	0.19	0.28	0.37
Bulk density	g/cm^3	0.40	0.44	0.44	0.45
Porosity	%	80	78	78	78
Surface roughness Ra	μm	8	8	8	8
Gas permeability	ml·mm/(cm^2·hr·mmAq)	2500	1900	1700	1500
Electrical resistivity					
through plane	mΩcm	80	80	80	80
in plane	mΩcm	–	5.8	5.6	4.7
Thermal conductivity					
through plane (room temp.)	W/(m·k)	–	(1.7)	(1.7)	(1.7)
inplane (room temp.)	W/(m·k)	–	21	21	21
inplane (100°C)	W/(m·k)	–	23	23	23
Coefficient of thermal expansion					
in plane (25~100°C)	x10^{-6}/°C	-0.8	-0.8	-0.8	-0.8
Flexural strength	MPa	40	40	40	40
Flexural modulus	GPa	8	10	10	10
Tensile strength	N/cm	–	50	70	90

•The above data are experimental values and are not guaranteed.

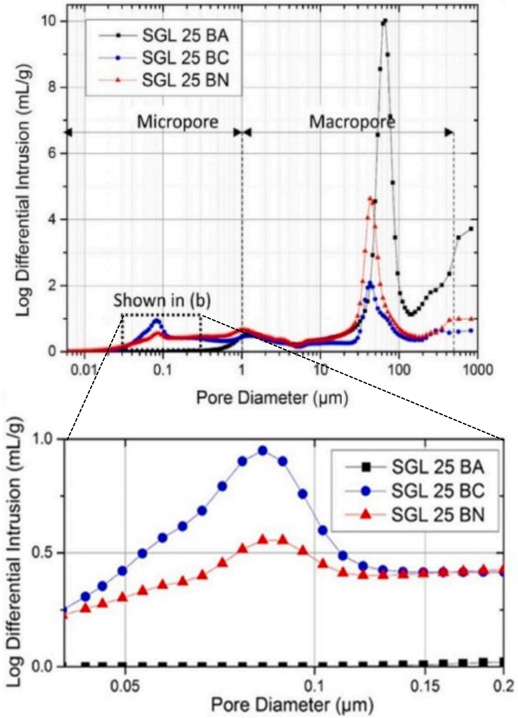
PEMFC – THE GAS DIFFUSION LAYER – POROSITY

R.2

Pore size distribution is commonly measured via Mercury Intrusion Porosimetry: based on the premise that a non-wetting liquid (or having a contact angle, θ, greater than 90°C) is going to only intrude the porous capillaries under pressure, by means of the Washburn equation, linking θ, surface tension (γ), pressure (P), and pore size (d):

$$P = -\frac{4\gamma \cos\theta}{d}$$

The pore size distribution can be retrieved throughout the volume intruded at each pressure increment.



Lee F.C. et al., Renewable and Sustainable Energy Reviews 166 (2022) 112640

PEMFC – THE GAS DIFFUSION LAYER

Porosity (pore size distribution) and tortuosity

Hydrophobicity

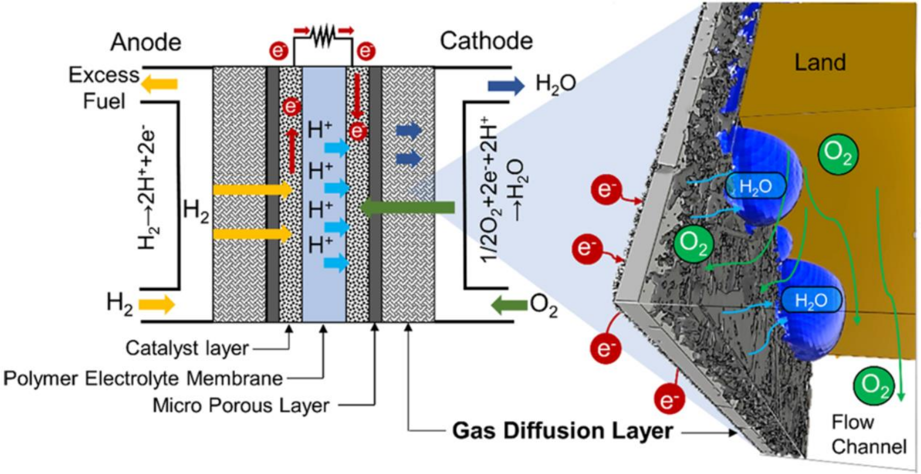
Electrical and thermal conductivities

Stiffness and chemical stability

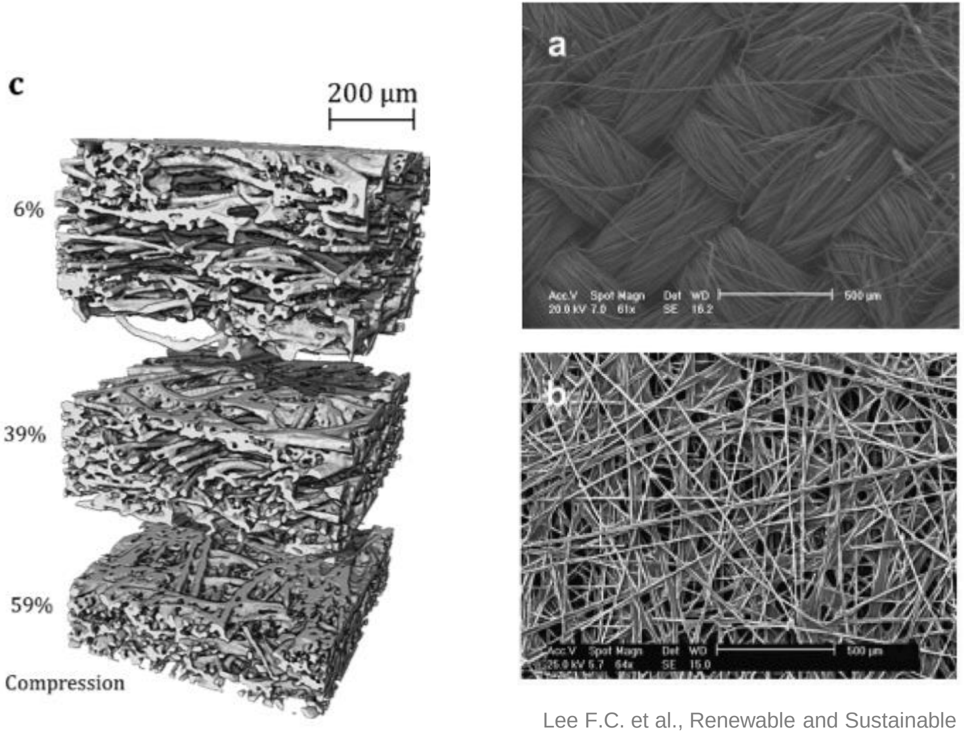
Property	**Function**
Pore size distribution and gas permeability	Transport of reactant gases
Hydrophobic and hydrophilic	Facilitate water management
Electrical conductivity	Transports electrons within the fuel cell
Thermal conductivity	Transport heat out of the fuel cell
Surface energy and pore size distribution	Transport humidity
Surface stability, purity, and high corrosion resistant	Corrosion stability
High compressibility and bending stiffness	Through plane resistance (GDL-BPP-GDL sandwich)

PEMFC – THE GAS DIFFUSION LAYERS – COMPRESSION

To guarantee proper compression, changes in the degree of GDL mechanical compression is usually allowed to range between 10% and 30%



Satjaritanun P. et al., Acc. Mater. Res. 2022, 3, 4, 416–425



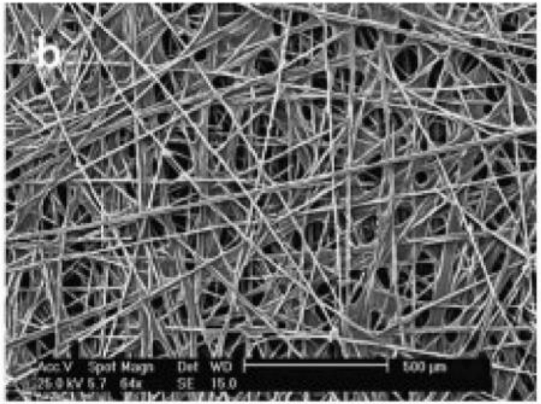
Lee F.C. et al., Renewable and Sustainable Energy Reviews 166 (2022) 112640

PEMFC – THE GAS DIFFUSION LAYER – POROSITY

GDL porosity is essential in regulating the mass transport to/from the catalyst layer.

High porosity provides a higher reduction of water saturation and improves the value of the limiting current density, it can conversely cause a decrease in the through-plane electronic conductivity, thus reducing the mechanical behavior of the GDL.

Moreover, it was found as pore-size distribution at the Micro Porous Layer level affects mass transport more than the total porosity.

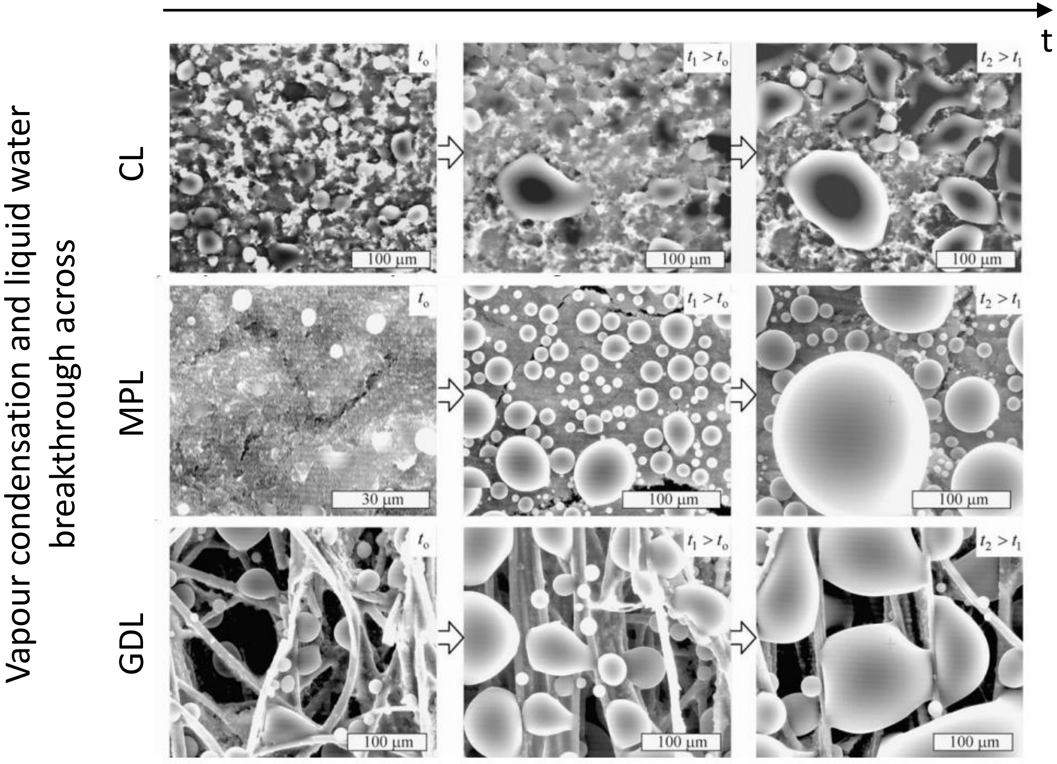


Lee F.C. et al., Renewable and Sustainable Energy Reviews 166 (2022) 112640

PEMFC – THE GAS DIFFUSION LAYER – THE WATER MANAGEMENT

In order to effectively enhance water transport, GDLs need to be adequately hydrophobic.

In fact, during water condensation in the fuel cell, water flow is achieved via capillary pressure that is influenced by the hydrophobic level of the membranes and pore radius. It was proven that the hydrophobic nature of materials determines the extent of water management within the fuel cell



Ji M., Wei Z., Energies 2009, 2(4), 1057-1106

PEMFC – THE GAS DIFFUSION LAYER – THE WATER MANAGEMENT

Hydrophobicity is achieved by adding hydrophobic agents to the carbon backbone. As hydrophobic agents the most commonly used are polytetrafluoroethylene (PTFE) or fluorinated ethylene propylene (FEP).

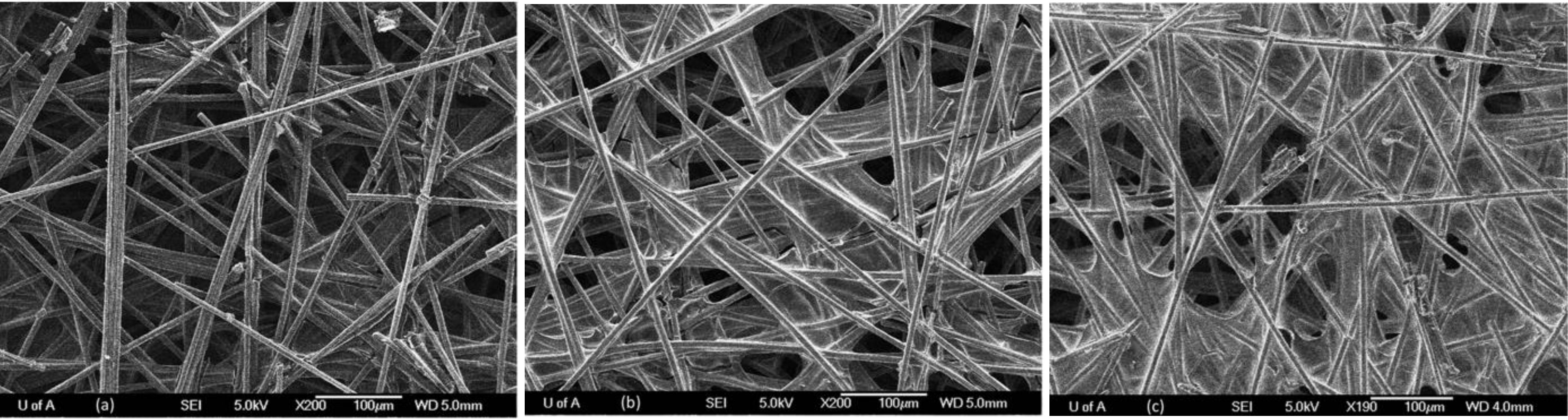
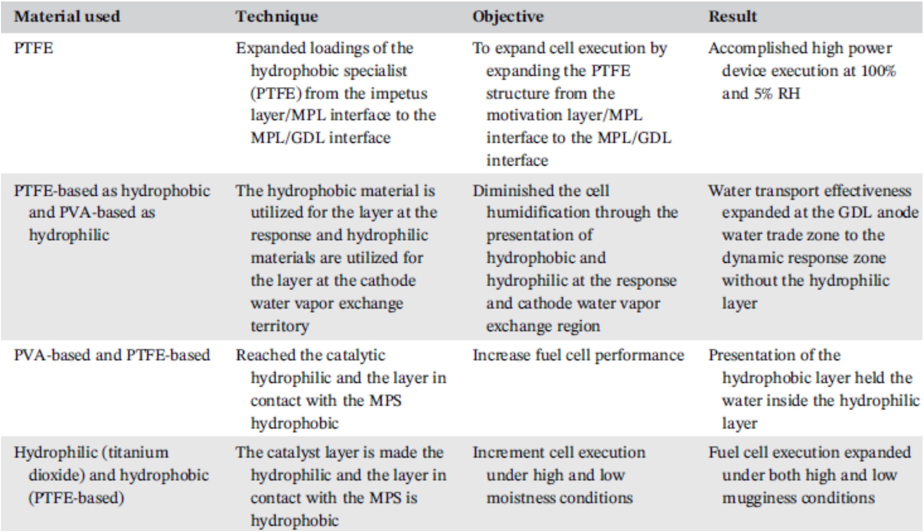


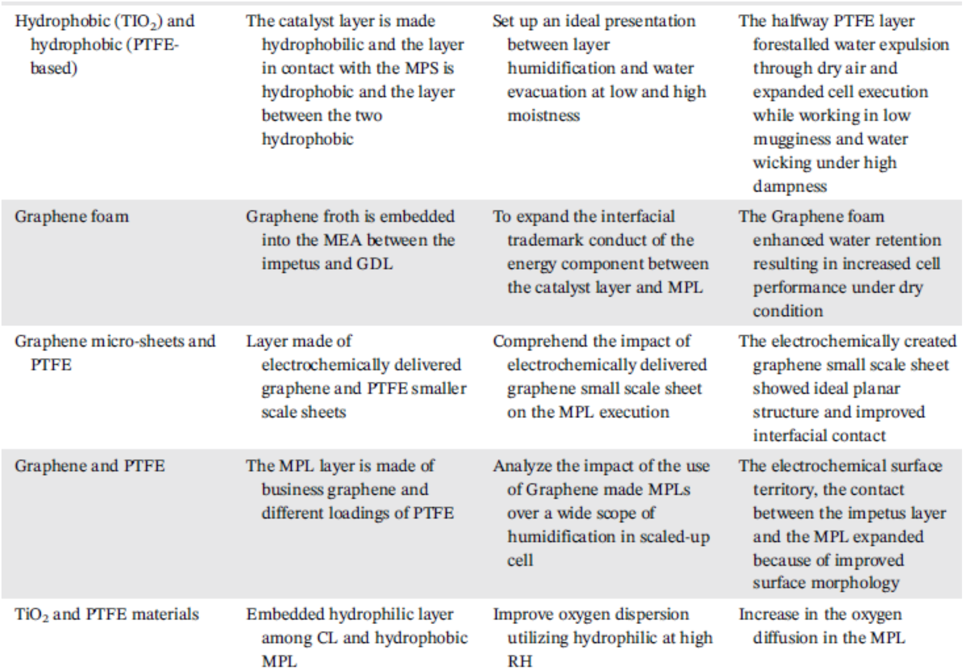
Figure 2. Top views of GDLs showing a decrease in pore size for increased PTFE loading and the difference between the PTFE for the Toray and SGL GDL. (a) Untreated Toray GDL; (b) 5% PTFE Toray GDL; (c) 10% PTFE Toray GDL;

Carrigy N.B., et al., J. Electrochem. Soc. 160 (2013) F81

PEMFC – THE GAS DIFFUSION LAYER – THE WATER MANAGEMENT



Material used	Technique	Objective	Result
PTFE	Expanded loadings of the hydrophobic specialist (PTFE) from the impetus layer/MPL interface to the MPL/GDL interface	To expand cell execution by expanding the PTFE structure from the motivation layer/MPL interface to the MPL/GDL interface	Accomplished high power device execution at 100% and 5% RH
PTFE-based as hydrophobic and PVA-based as hydrophilic	The hydrophobic material is utilized for the layer at the response and hydrophilic materials are utilized for the layer at the cathode water vapor exchange territory	Diminished the cell humidification through the presentation of hydrophobic and hydrophilic at the response and cathode water vapor exchange region	Water transport effectiveness expanded at the GDL anode water trade zone to the dynamic response zone without the hydrophilic layer
PVA-based and PTFE-based	Reached the catalytic hydrophilic and the layer in contact with the MPS hydrophobic	Increase fuel cell performance	Presentation of the hydrophobic layer held the water inside the hydrophilic layer
Hydrophilic (titanium dioxide) and hydrophobic (PTFE-based)	The catalyst layer is made the hydrophilic and the layer in contact with the MPS is hydrophobic	Increment cell execution under high and low moistness conditions	Fuel cell execution expanded under both high and low mugginess conditions



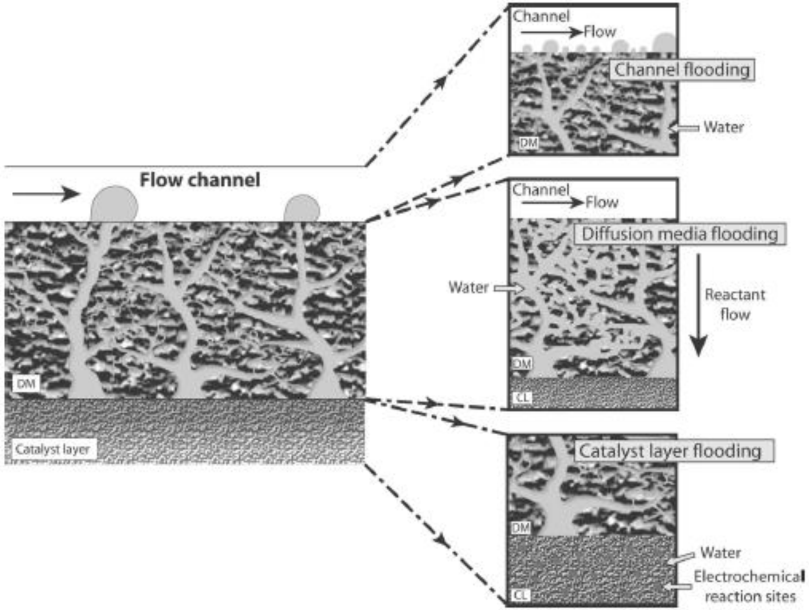
Hydrophobic (TIO_2) and hydrophobic (PTFE-based)	The catalyst layer is made hydrophobilic and the layer in contact with the MPS is hydrophobic and the layer between the two hydrophobic	Set up an ideal presentation between layer humidification and water evacuation at low and high moistness	The halfway PTFE layer forestalled water expulsion through dry air and expanded cell execution while working in low mugginess and water wicking under high dampness
Graphene foam	Graphene froth is embedded into the MEA between the impetus and GDL	To expand the interfacial trademark conduct of the energy component between the catalyst layer and MPL	The Graphene foam enhanced water retention resulting in increased cell performance under dry condition
Graphene micro-sheets and PTFE	Layer made of electrochemically delivered graphene and PTFE smaller scale sheets	Comprehend the impact of electrochemically delivered graphene small scale sheet on the MPL execution	The electrochemically created graphene small scale sheet showed ideal planar structure and improved interfacial contact
Graphene and PTFE	The MPL layer is made of business graphene and different loadings of PTFE	Analyze the impact of the use of Graphene made MPLs over a wide scope of humidification in scaled-up cell	The electrochemical surface territory, the contact between the impetus layer and the MPL expanded because of improved surface morphology
TiO_2 and PTFE materials	Embedded hydrophilic layer among CL and hydrophobic MPL	Improve oxygen dispersion utilizing hydrophilic at high RH	Increase in the oxygen diffusion in the MPL

Okonkwo P.C., Otor C. Int J Energy Res. 2021;45:3780–3800.

PEMFC – HYDRATION AND WATER MANAGEMENT

The main problems related to hydration and water management in PEMFCs relies to the need of optimizing the operating conditions in order to:

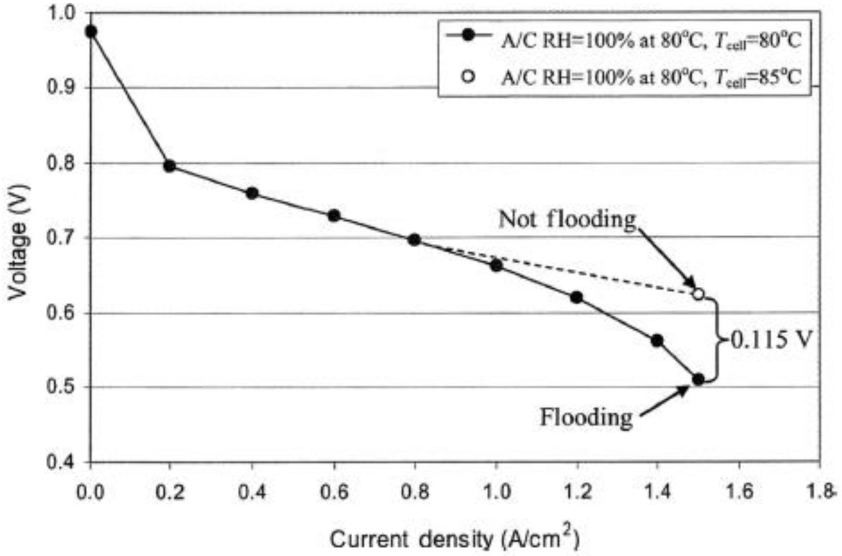
- keep the electrolyte hydrated to increase proton conductivity
- prevent water flooding in order to avoid the clogging of the reaction sites.



PEMFC – HYDRATION AND WATER MANAGEMENT

- prevent anodic dry out and/or fast withdrawal of water from the fuel cell which would increase ohmic resistance (and lead to development of cracks).

Ideally, the water produced by the fuel cell should keep the electrolyte hydrated, and the flow of the oxidant at the cathode would be supposed to promote the removal of the water in excess.

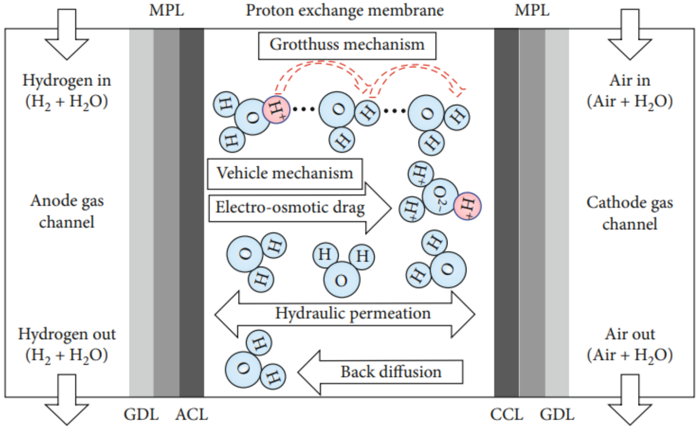


PEMFC – HYDRATION AND THE WATER MANAGEMENT

Water management is, most probably, the most important issue to deal with when designing GDLs. To highlight the weight of water transport across the MEA, the HOR and ORR reactions can be expresses considering humidified H_2:

$$2H_2 + 4nH_2O \rightarrow 4H^+ \cdot nH_2O + 4e^-$$

$$O_2 + 4H^+ \cdot nH_2O + 4e^- \rightarrow (n+2)H_2O$$



Wang G. et al., International Journal of Energy, (2023), 1138198

Thus, when current flows, cations flowing towards the cathode transport with themselves also water molecules via electro-osmotic drag.

This fact induces the formation of a hydration-gradient inducing water back diffusion across the ionomer, and a possible presence of excess of water at the cathode.

Electroosmotic drag is relevant as it can lead to anode dry out even though the cathode is hydrated relying upon the gas humidification and temperature. Also to reduce the intensity of this process, water needs to be effectively drained from the cathode.

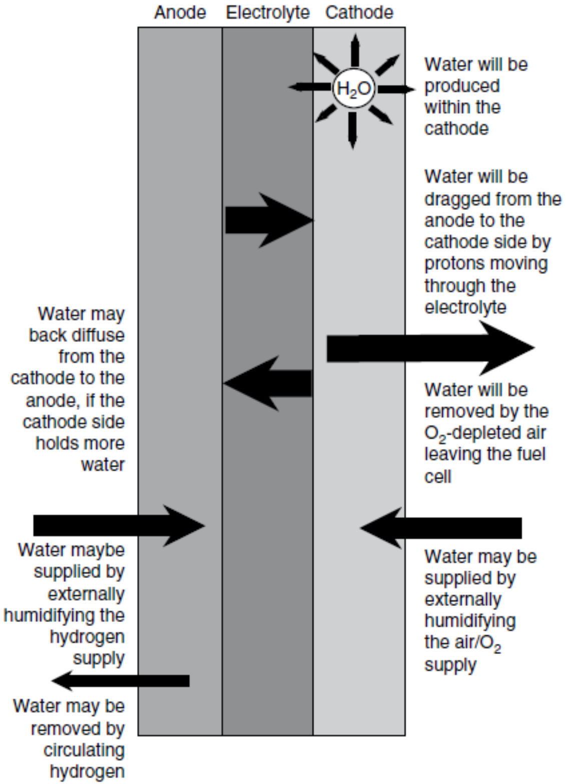
PEMFC – HYDRATION AND WATER MANAGEMENT

Electro-osmotic drag is quantified as per each H^+ ion moving from the negative to the positive electrode between 1 and 2.5 water molecules are conveyed. This means that, especially at high current densities, the negative side of the electrolyte can become easily dried out, even if the positive side is well hydrated.

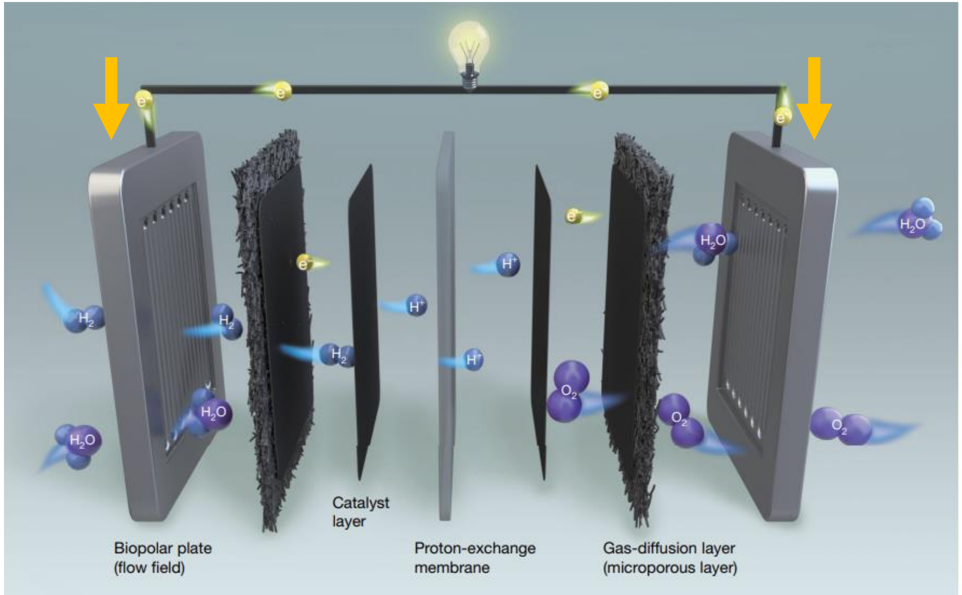
When running PEMFCs at cell temperatures above about 60°C, the air will always dry out the electrodes faster than water is produced.

External hydration is thus needed to humidifying the gas(es) before entering the fuel cell.

Counter-intuitively, by adding by-product to the reactants, it is in this way possible to greatly improve the fuel cell performances.



PEMFC – THE BIPOLAR PLATES



Jiao K. et al., Nature, 595, (2021), 361–369

PEMFC – THE BIPOLAR PLATES

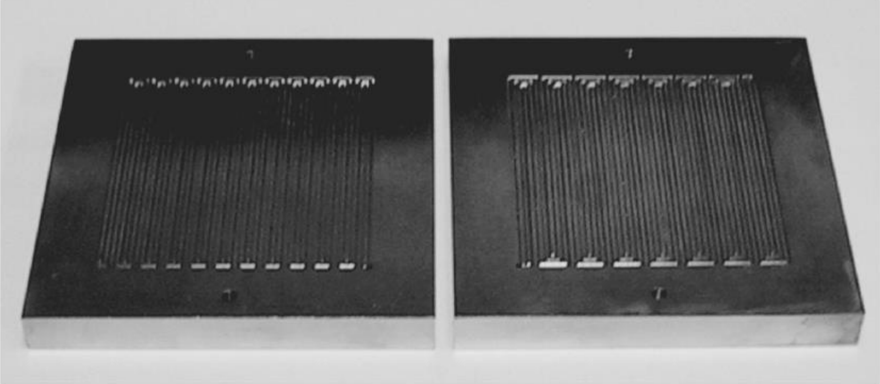
The bipolar plates are the components of the fuel cell hosting:

- the electrical connectors for the electrical circuit
- the flow field, to homogenously distribute gases on the surface of the MEA
- host the heating/cooling system

Their optimum design is essential overall in stack assembly.

Bipolar plates need to be characterized by:

- Good electrical conductivity (>100 S cm^{-1})
- High thermal conductivity (> 20 W m^{-1} K^{-1})
- High resistance to chemical attack and corrosion.
- High mechanical stability, especially under compression (flexural strength >25 MPa)
- Low gas permeability ($<10^{-5}$ Pa L s^{-1} cm^{-2})
- Low density, in order to minimize both weight and volume of the cell/stack



Hydrogen and fuel cells
Prof. Marco Bogar

PEMFC – THE BIPOLAR PLATES

Material	Advantages	Drawbacks	Application
Graphite	• High electrical and thermal conductivities • Very low density	• t_{PLATE} ~ few mm to guarantee mechanical stability • Machining graphite is time consuming • Graphite is brittle	Laboratory testing
Metal based (Stainelss steels, Ti or Al alloys)	• High electrical and thermal conductivities • Easily machinable	• High density • Prone to be corroded on the long term	Industrial standard

PEMFC – THE BIPOLAR PLATES

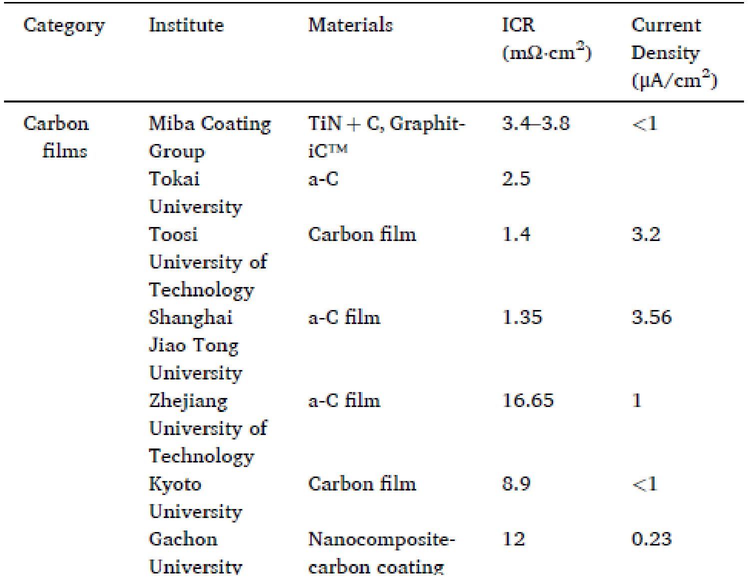
- Stainless steel bipolar plates are cheaper than titanium-based ones, nonetheless, the harsh environment (humid, warm, subjected to the development of high potentials during the start-up/shut-down stages) in which PEMFCs operate, can lead to the release of Fe contaminants (Fe^{3+}, Fe^{2+}, Cu^{2+}, leading to the poisoning of the MEA), and to the growth of passivation layers on bare metals (increasing the interfacial resistance between the plate and the GDL).

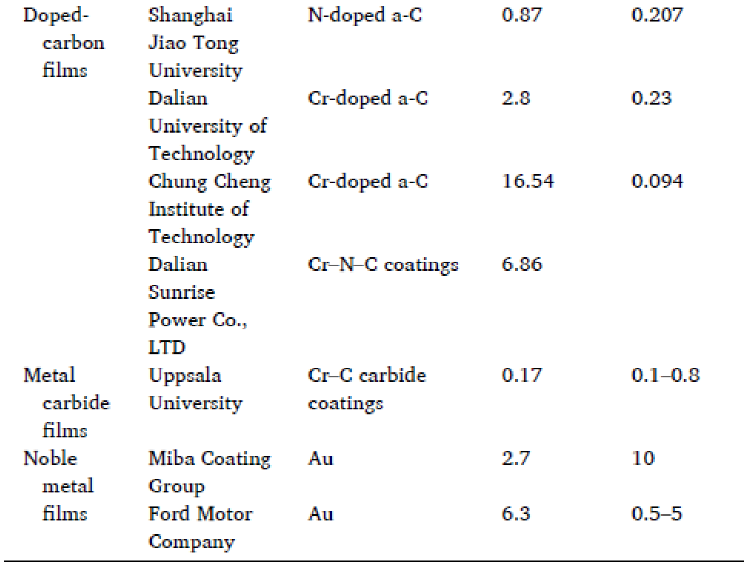
- To increase the chemical stability of the bipolar plates, two approaches are commonly followed:
  - Protect the plate surface with a coating increasing the chemical stability of the surface
  - Develop a novel non-coated material with strong corrosion resistance: in this extent, solutions employing stainless steels with high Cr content and Ti-alloys (as an example Toyota Mirai uses Ti-alloys bipolar plates allowing to guarantee the 5000 h of life time, but they are more expensive than stainless steel ones).

PEMFC – THE BIPOLAR PLATES

R.3

Recent materials used as coatings on metallic bipolar plates





Category	Institute	Materials	ICR (mΩ·cm^2)	Current Density (μA/cm^2)
Carbon films	Miba Coating Group	TiN + C, Graphit-iC™	3.4–3.8	<1
	Tokai University	a-C	2.5	
	Toosi University of Technology	Carbon film	1.4	3.2
	Shanghai Jiao Tong University	a-C film	1.35	3.56
	Zhejiang University of Technology	a-C film	16.65	1
	Kyoto University	Carbon film	8.9	<1
	Gachon University	Nanocomposite-carbon coating	12	0.23
Doped-carbon films	Shanghai Jiao Tong University	N-doped a-C	0.87	0.207
	Dalian University of Technology	Cr-doped a-C	2.8	0.23
	Chung Cheng Institute of Technology	Cr-doped a-C	16.54	0.094
	Dalian Sunrise Power Co., LTD	Cr–N–C coatings	6.86	
Metal carbide films	Uppsala University	Cr–C carbide coatings	0.17	0.1–0.8
Noble metal films	Miba Coating Group	Au	2.7	10
	Ford Motor Company	Au	6.3	0.5–5

low cost and good performance

Outstanding chemical stability

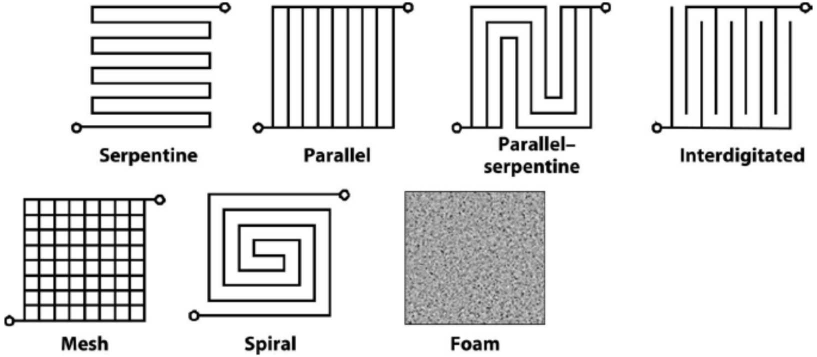
PEMFCS – THE FLOW FIELD

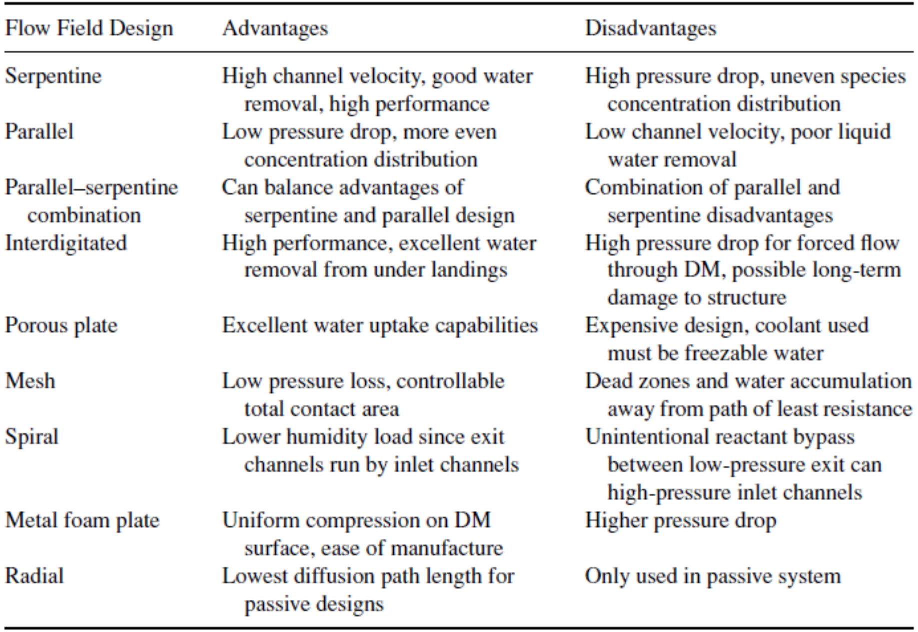
In order to operate at best, gases have to be uniformly distributed over the two surfaces of the MEA. The flow field is machined in the cover plates at this aim.

Ideally, the flow field should be characterized by:

- Excellent mass transport of the reactants to and products from the catalyst layer with a proper water balance to achieve a moist electrolyte with minimal flooding of the GDL and channels under a wide range of operating conditions.
- Excellent electron transport to and from the catalyst layers.
- Adequate heat transport to the coolant channels.
- Low pressure drop from inlet to exit.
- Low cost of manufacture.
- Compact design.

PEMFCS – THE FLOW FIELD

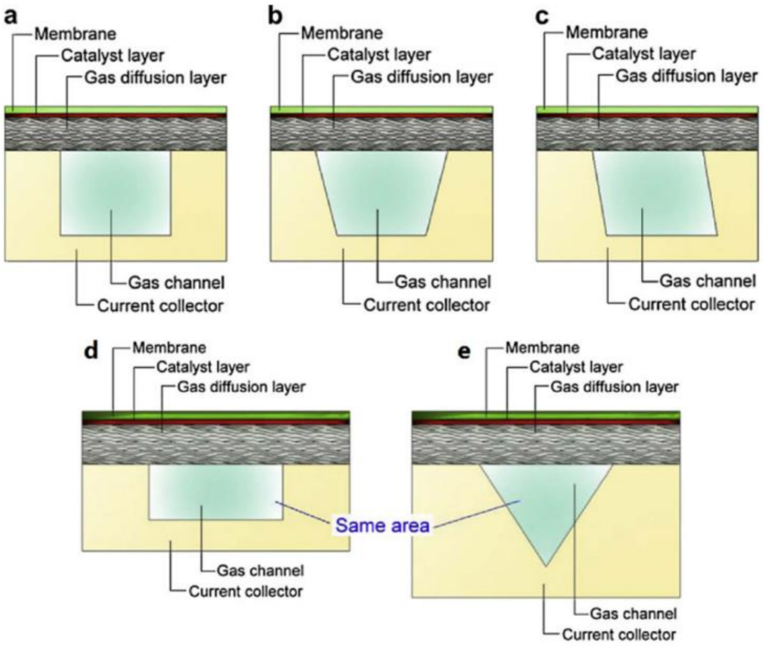




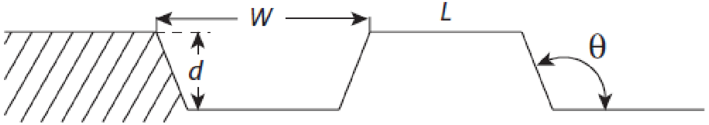
Flow Field Design	Advantages	Disadvantages
Serpentine	High channel velocity, good water removal, high performance	High pressure drop, uneven species concentration distribution
Parallel	Low pressure drop, more even concentration distribution	Low channel velocity, poor liquid water removal
Parallel–serpentine combination	Can balance advantages of serpentine and parallel design	Combination of parallel and serpentine disadvantages
Interdigitated	High performance, excellent water removal from under landings	High pressure drop for forced flow through DM, possible long-term damage to structure
Porous plate	Excellent water uptake capabilities	Expensive design, coolant used must be freezable water
Mesh	Low pressure loss, controllable total contact area	Dead zones and water accumulation away from path of least resistance
Spiral	Lower humidity load since exit channels run by inlet channels	Unintentional reactant bypass between low-pressure exit can high-pressure inlet channels
Metal foam plate	Uniform compression on DM surface, ease of manufacture	Higher pressure drop
Radial	Lowest diffusion path length for passive designs	Only used in passive system

The serpentine pattern is preferred by most PEMFC manufacturers, offering a good compromise between the issues of pressure drop and water removal. To avoid big pressure drops due to large number of turns in the flow path, multiple parallel serpentines can be machined.

PEMFC – THE FLOW FIELD



Wang Y. et al., Energies 2023, 16, 4207



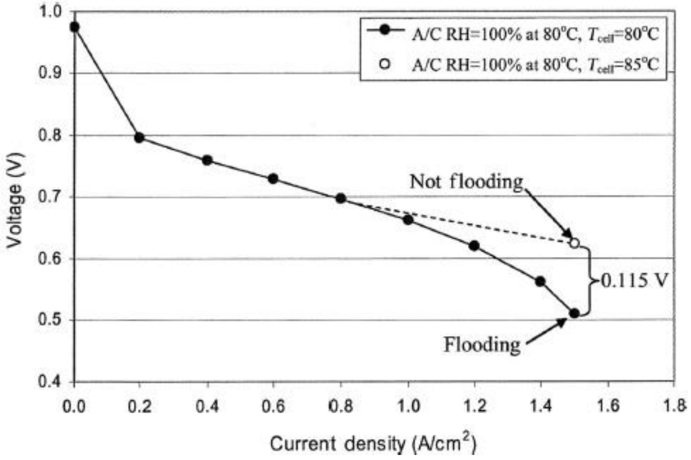
L = land width (typically 0.2–2.5 mm)
W = channel width (typically 0.5–2.5 mm)
θ = draft angle (typically 0–15°)
d = depth (typically 0.5–2.5 mm)
$W:L$ (typically 3:1–1:1)

2. PROTON EXCHANGE MEMBRANE FUEL CELLS – OPERATION

PEMFC OPERATION – HUMIDIFICATION AND WATER BALANCE

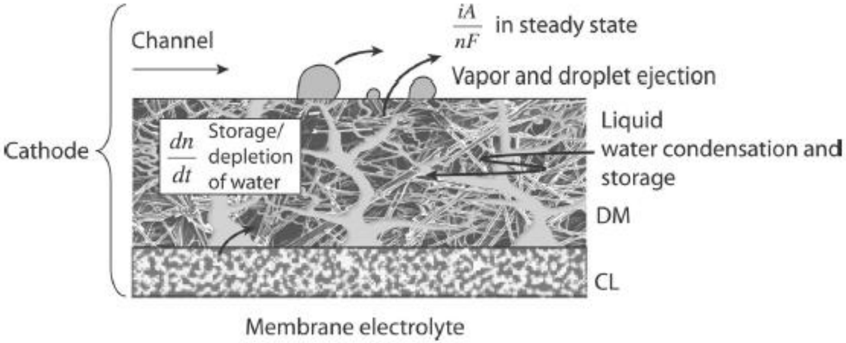
Water balance can be defined as the area of expertise in which the interactions among fuel cell operating regime is investigated and optimised in function of moist and water creation (in example, a question mark in fuel cell investigation addresses to the physical state in which water is produced: liquid or gaseous?).

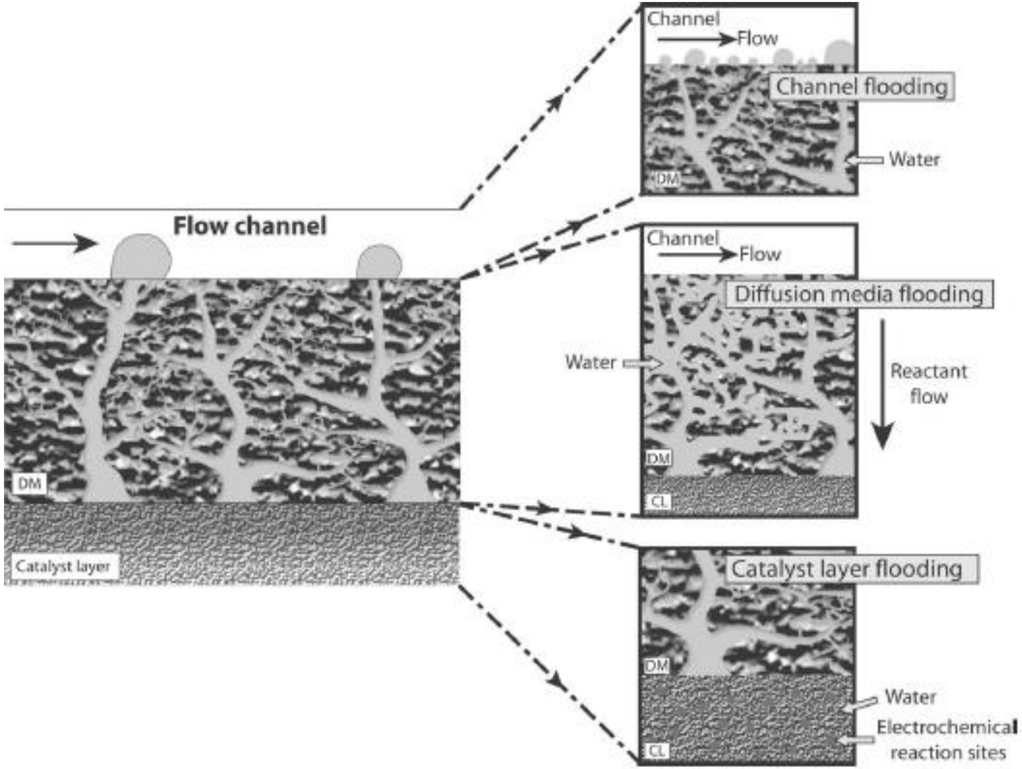
Water balance is fundamental because it allows to improve fuel cell performances: in example, a flooded fuel cell will be subjected to tighter boundaries in diffusion-related limitations, while a too dry MEA will not be able to sustain sufficient ionic conductivity.



PEMFC – THE GAS DIFFUSION LAYER – THE WATER MANAGEMENT

Water flooding can either affect channel, GDL, and/or the catalyst layer.



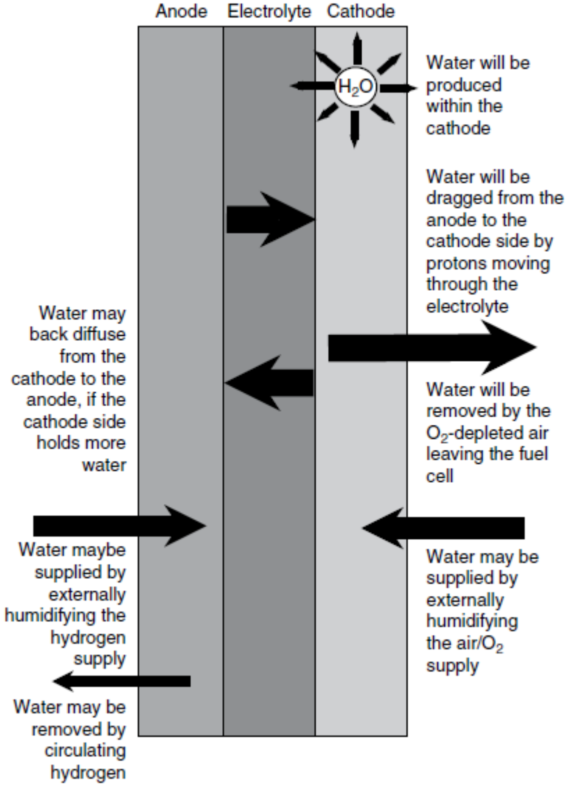


PEMFC OPERATION – HUMIDIFICATION AND WATER BALANCE

From previous sections it was shown as hydration of the MEA is required in order to sustain satisfying proton conductivity across the electrolyte. At the same time, the water content within the cell must be limited in order to prevent flooding of the MEA with consequent reduction of FC performances.

Such a balance is complicated to be reached and managed due to the opposite constraints which are needed to be satisfied. The gas flown is usually set with an excess of stoichiometry in order to remove the excess of produced water. In this way, uniform proton conductivity throughout the whole cell should be achieved, but local conditions might be quite different from ideality due to:

- uneven water distribution
- drying effects due to temperature and/or to the electro-osmotic drag
- reduction of produced current which makes air flow drying the MEA
- saturation of the gas flow at the outlet which makes the gas unable to drain the excess of produced water



PEMFC OPERATION – HUMIDIFICATION AND WATER BALANCE

Fortunately, the dependence among the phenomena involved are predictable and controllable. In this extent, water management is a crucial aspect to be dealt with in PEMFCs.

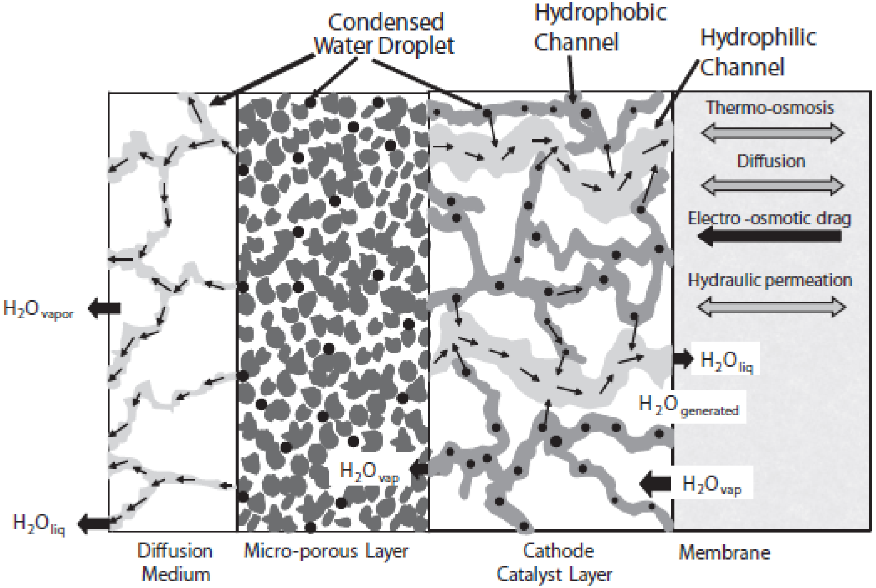
The interest in correctly managing the water management is also due to the fact that a poor water management in PEMFCs leads to:

- Internal stresses within the electrolyte, related to uneven swelling of the membrane, invoking physical stresses and degradation of the electrolyte and catalyst layers.
- Contamination through water-soluble ionic species, such as accumulation of calcium, iron oxides, copper magnesium and other metals.
- Enhanced risk damage related to freeze-out, producing permanent damage to the MEA. It is essential to purge any excess water from the PEMFC to prevent such an occurrence.

PEMFC OPERATION – HUMIDIFICATION AND WATER BALANCE

Local water balance

Despite water balance has macroscopic effects on the fuel cell operation, this phenomenon develops locally inside the MEA. Within the MEA, water transport can occur via four different phenomena: diffusion, electro-osmotic drag, hydraulic permeability, and thermo-osmosis



PEMFC OPERATION – HUMIDIFICATION AND WATER BALANCE

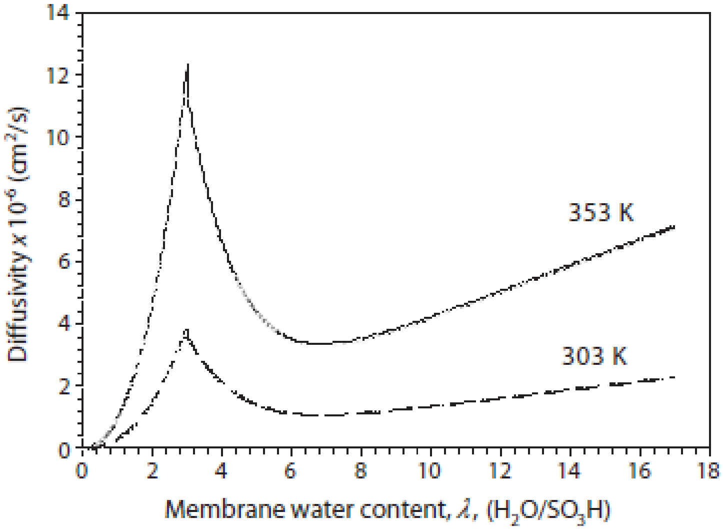
Diffusion

Diffusion takes place along a concentration gradient. As already seen before it can be modelled according to the Fick's law:

$$\dot{n}_w = -D_w \frac{dC_w^m}{dx}$$

Where D_w is the water diffusivity in the ionomer layer, which is dependant on the water content within the membrane:

$$\lambda = N_{H_2O}/N_{SO_3H}$$



PEMFC OPERATION – HUMIDIFICATION AND WATER BALANCE

Hydraulic permeability

Hydraulic permeation through the membrane occurs as a result of a pressure difference between the anode and cathode.

$$\dot{n}_{w,c} = \frac{k k_r}{\mu l} \Delta P_{ca}$$

Where k and k_r are the effective and relative permeabilities of the membrane, μ is the viscosity, and l the membrane thickness. Water transport takes place due to the gradient pressure. While gas pressure difference is usually null among the two electrodes, some capillary pressure gradient can establish within the MEA forcing liquid water movement.

Temperature and heat-flux driven flow

Mainly due to capillary forces, water flows from the hotter side towards the colder one. This effect can be mainly show up during start-up or shut-down conditions, when larger temperature gradients are present. During normal operation, phase change (vapour/liquid) makes this phenomenon overlap with electro-osmotic drag.

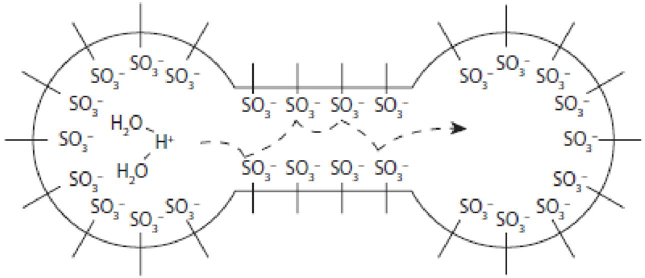
PEMFC OPERATION – HUMIDIFICATION AND WATER BALANCE

Electro-osmotic drag

Cations moving towards the cathode by means of the Grotthuss and vehicular mechanisms are surrounded by polar water molecules, which are drag towards the cathode side. The ratio of water flux can be estimated by means of the Faraday ‘s law:

$$\dot{n}_{w,c} = n_d \frac{iA}{F}$$

Where n_d is the number of water molecules per proton (drag coefficient), which was determined ranging from 1 to 5 depending on gas stoichiometry and cell operative conditions.



PEMFC OPERATION – HUMIDIFICATION AND WATER BALANCE

Dry air is mainly composed by N_2 (78% mol), O_2 (21% mol), and Ar and other gases (CO_2, H_2, H_2O, He, … 1% mol).

Humidity is defined as the concentration of water vapour present in the air. While absolute humidity (AH) defines such a concentration value with respect a volume of the air/water mixture ($AH = m_w/m_{dry\_air}$), in order to take also into account of the effects of the temperature, relative humidity (RH) needs to be considered.

In fact, RH is defined as the ratio of the partial pressure of water vapour in the air to the saturation vapour pressure of water at the same temperature:

$$RH = \frac{p_w}{p_{w,sat}}100$$

It expresses how much water vapour is present in the air with respect the water vapour that air could potentially contain at a given temperature.

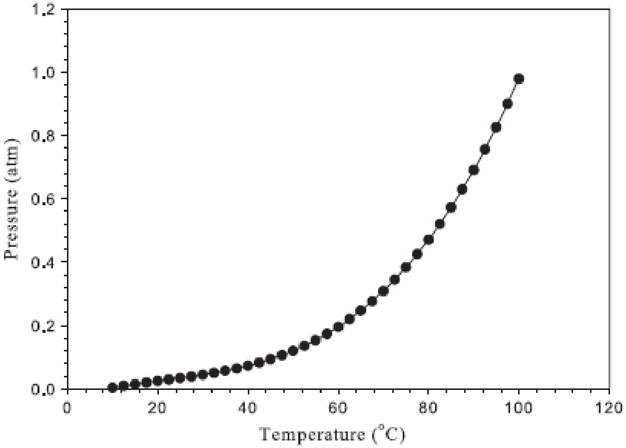


Figure 3.12 Saturation pressure versus temperature for water.

PEMFC OPERATION – HUMIDIFICATION AND WATER BALANCE

Usually measuring humidity is difficult (overall for high RH values), thus, as a marker for the state of hydration of the MEA is represented by measuring the RH at the exit of the cathode electrode, which can be estimated via:

$$RH_{out} = \frac{p_w}{p_{out}} = \frac{\dot{n}_w}{\dot{n}_w + \dot{n}_{O_2} + \dot{n}_x}$$

Here, the rate of produced water can be related to the fuel cell operational conditions by means of the Faraday's law:

$$\dot{n}_w = \frac{I}{4F} = \frac{P_e}{2FV_C}$$

the rate of oxygen present at the output (thus non reacted) can be quantified as:

$$\dot{n}_{O_2} = (\lambda - 1)\frac{P_e}{4FV_C}$$

while the rate of the other gases present at the output becomes non-negligible mainly when air is used as an oxidant. In such conditions, being $\frac{c_{N_2}}{c_{O_2}} = \frac{0.78}{0.21} = 3.72$: $\dot{n}_x = 3.72\frac{P_e}{4FV_C} = 3.72\,\dot{n}_{O_2}$

PEMFC OPERATION – HUMIDIFICATION AND WATER BALANCE

and:

$$RH_{c,output} = \frac{p_w}{p_{out}} = \frac{0.42}{\lambda + 0.21}$$

In this equation the relation among stoichiometry and relative humidity is highlighted. In particular, RH can be increased: by lowering the stoichiometry, by lowering the temperature, or by increasing the operating pressures. However, the first two options lead to a reduction in FC performances, while the third approach requires supplementary equipment to be added at the setup.

PEMFC OPERATION – WATER BALANCE

It worth to remember as fuel cells operate dynamically, “swinging” among three regimes, which can be identified by relating the law of mass conservation (at constant volume) with the Faraday’s law:

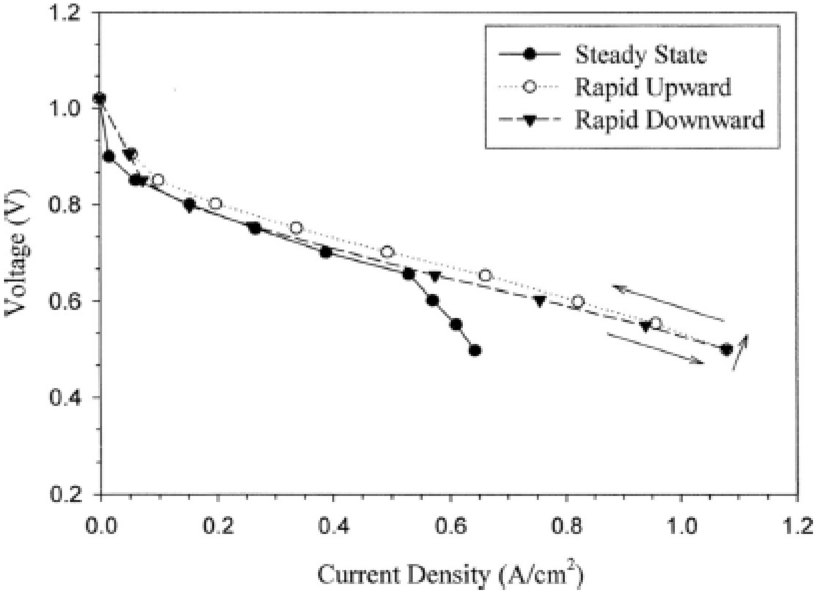
$$\left.\frac{dm}{dt}\right|_{CV} = (\dot{m}_{in} - \dot{m}_{out})_{w,a} + (\dot{m}_{in} - \dot{m}_{out})_{w,c} = \frac{I(t)}{2F}$$

1. $\left.\frac{\mathrm{dm}}{\mathrm{dt}}\right|_{\mathrm{CV}} > 0$ water is keeping to accumulate int the MEA and in the channels. If not removed, channels are going to be flooded.
2. $\left.\frac{dm}{dt}\right|_{CV} < 0$ water is being depleted and the MEA could start soon to dry out with time.
3. $\left.\frac{dm}{dt}\right|_{CV} = 0$ the fuel cell is correctly hydrated: not flooded, nor drying. In these conditions steady state balance is reached.

Usually the cell operates slightly varying between these three operational modes: the equilibrium is usually reached for a constant value of current ant load variations, require an adjustment in FC operations.

PEMFC OPERATION – WATER BALANCE

A final consideration needs to be made at the time scale at which water balance processes take place: in fact, as already introduced, water balance adjustments involve water transport across different areas of the fuel cell: the flow field, the GDL, and the CCM. It is clear as adjustments of the liquid-phase balance take place on much longer timescales than adjustments related to gas-phase mass balance.

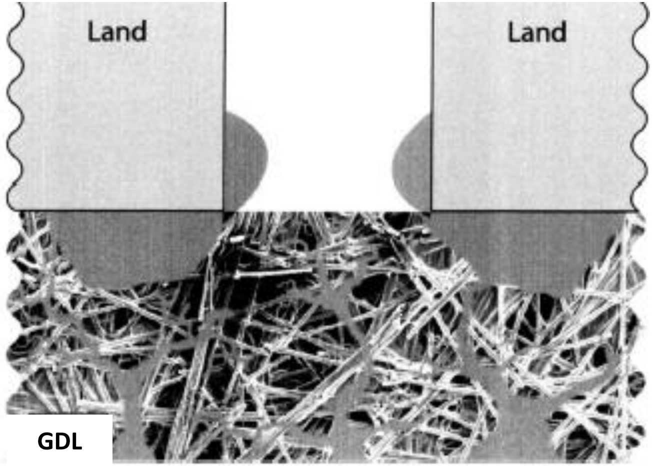


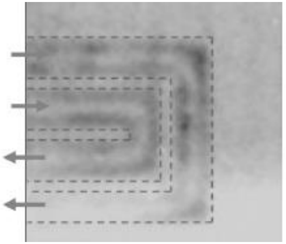
PEMFC OPERATION – WATER MANAGEMENT

Nonetheless water transport is very specific to the instantaneous fuel cell conditions, some aspects can be generalized.

In fact, flow field lands have been recognized as points in which water condensation is promoted, even in drier operating regimes. In fact, heat transfer in lands in much more efficient than in the interstitial space formed in the grooves. This fact was extensively studied by means of neutron-based investigation techniques (late part of the course).

Proper water removal under the lands is thus mandatory to avoid water flooding. To promote water removal, PTFE additives are usually added to the GDL.

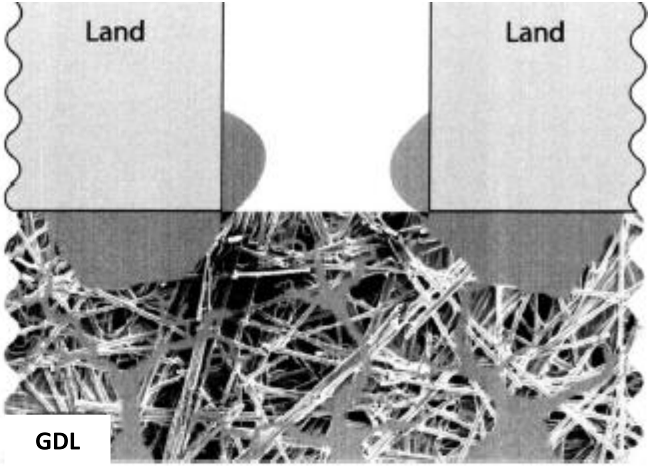


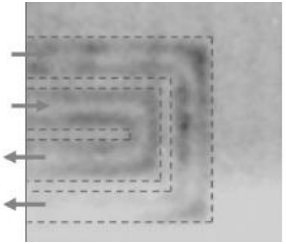


PEMFC OPERATION – WATER MANAGEMENT

In this extent, hydrophobic agents added to the GDL are used to increase the capillary water pressure and promote water movement towards more hydrophilic locations and/or areas characterized by a lower degree of liquid saturation.

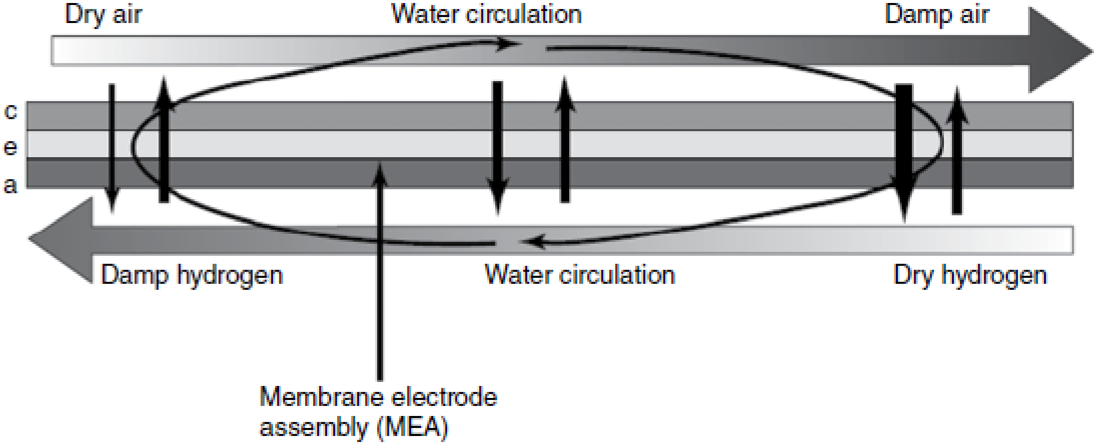
To enhance water movement, hydrophobic regions must coexist with hydrophilic ones: in fact, hydrophobic media provide suction areas for water droplets (from where water can be removed by convection or evaporation). The existence of networked paths driving water diffusion.





PEMFC OPERATION – WATER MANAGEMENT

Thus, the water produced at the cathode can be used to self-hydrate the gases at the inlets, with the aim of keeping the RH in between the 80 and 100%. At lower RH values, the MEA dries out, while at higher RH values, an excess of water is produced, leading to MEA flooding. In both conditions, the PEMFC will operate at limited performances and the risk of occurrence in irreversible degradation phenomena will rise. Self-humidification can be achieved by flowing fuel and oxidant in opposite direction in the cell (counter-current flow of reactant gases).

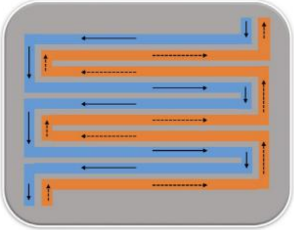


PEMFC OPERATION – INTERNAL HUMIDIFICATION METHODS

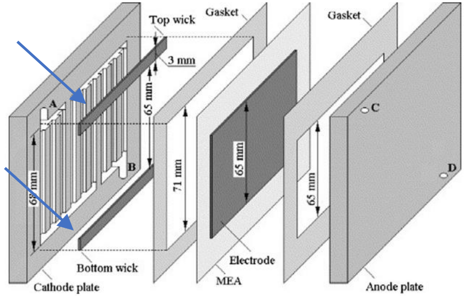
The internal humidification methods aim to maintain the membrane in a hydrated state by changing the internal PEMFC structure or composition without adopting external devices. This objective can be achieved by chemical-based methods, or by physical based ones.

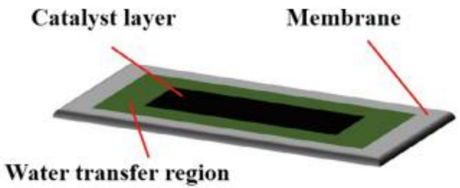
Physical-based methods

They mainly focus on flow field design and investigate the possibility to design special areas within the FC dedicated to water transport. Among the advantages, there is no need for additional equipment and no parasitic energy is consumed. However, proper water management can only be achieved under restricted operating conditions. And also, the humidification performance is less effective than the external humidification methods.



Chang Y. et al., Applied Energy, 230, 15 (2018), 643-662



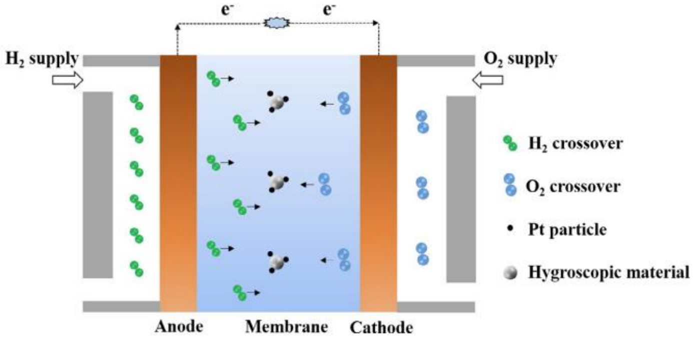


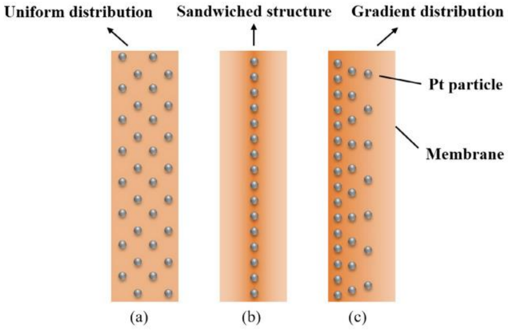
PEMFC OPERATION – INTERNAL HUMIDIFICATION METHODS

Chemical-based methods

Hygroscopic materials (such as TiO_2 or Pt and SiO_2) are added to the membrane in order to improve water retention and back diffusion. Such an approach did not lead to remarkable improvements, mainly due to the difficulty to control the degree of dispersion of additives in the membrane. In this framework different distribution patterns were found to showed more interesting results. Nonetheless such approach has not found an application yet, mainly to the doubts related to the promotion of formulation of unwanted electronic conduction pathways (which would short-circuit the FC), and to the reduction of membrane durability.

Other methods are under investigation in changing the chemistry of the catalyst layer or the GDLs, without remarkable achievements, so far.





Chang Y. et al., Applied Energy, 230, 15 (2018), 643-662

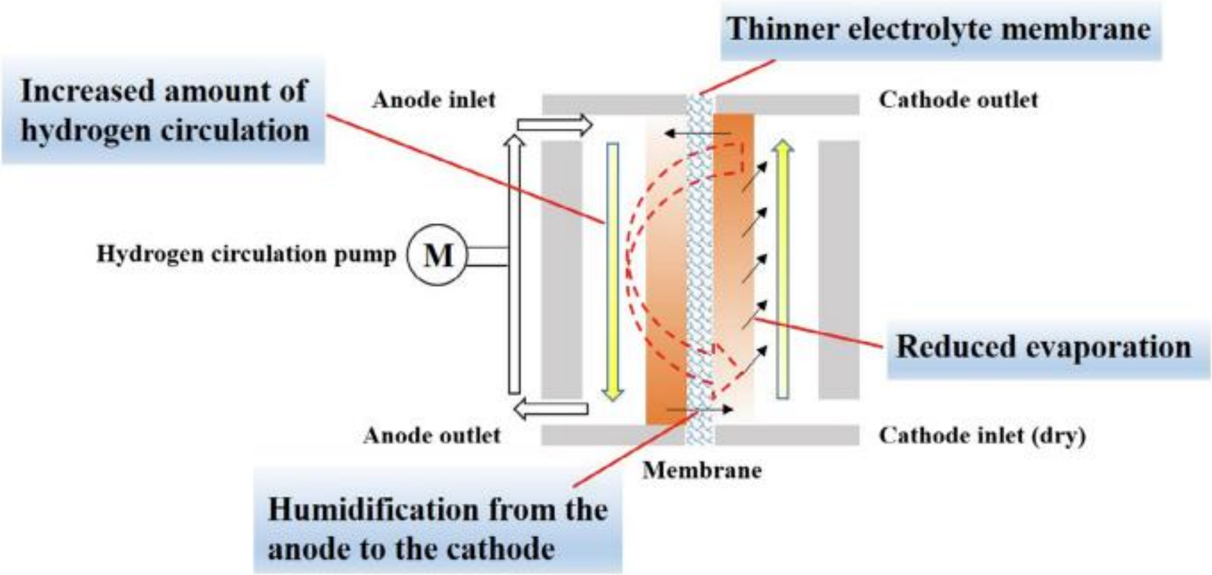
PEMFC OPERATION – INTERNAL HUMIDIFICATION METHODS

In summary, internal humidification methods, allow to reduce at best system volume and weight, being thus attractive for compact applications. However, the physical methods result into complicated design, while the chemical methods are limited by durability and stability. In addition, both methods can only be used for low power or portable PEMFC applications, while for high power devices still needs further optimization.

Internal humidification methods are mostly effective up to 60°C and they start being poor if the FC is wanted to be operated at higher temperatures, or when fuel cell stacks need to be handled. External humidification systems, consisting in devices dedicated to adding water vapour in the gas flow before entering the FC, need here to be used.

PEMFC OPERATION – INTERNAL HUMIDIFICATION METHODS

Nonetheless, they can be used in combination with external methods to improve the overall yields. In example, Toyota Mirai uses a thin membrane for improving the water managements (promoting water back diffusion), in addition with a recirculation pump which is adding damp hydrogen from the anode outlet to the drier fuel at the anode inlet.



Thinner electrolyte membrane

Increased amount of hydrogen circulation

Reduced evaporation

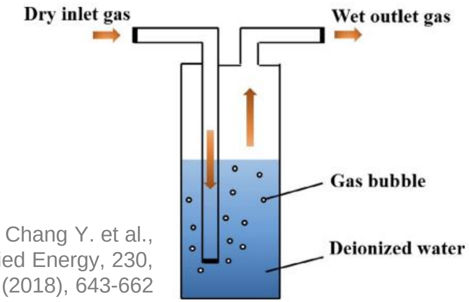
Humidification from the anode to the cathode

Chang Y. et al., Applied Energy, 230, 15 (2018), 643-662

PEMFC OPERATION – EXTERNAL HUMIDIFICATION METHODS

Bubbling

A pipe leads the gas of interest into a confined and temperature-controlled chamber in which deionized water is present. Under the assumption that the dew point of the humidified air is the same as the temperature of the water, the incoming gas, bubbled in the water, transports water molecules while evaporating from the liquid, and is conveyed at the outlet in a humidified state. Such a class of humidifiers have different performances according to the operating temperature and the geometry of both the chamber and the pipes. It is highly suitable for stationary plants, providing good humidity control and can be integrated in a FC system because of the possibility to exploit the heat generated from the FC for pre-heating water and gases. The main disadvantage is related to the pressure loss which is introducing in the system.



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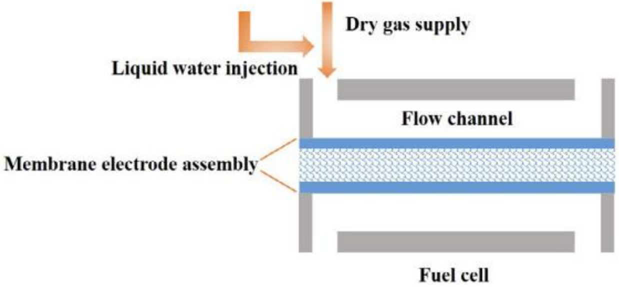
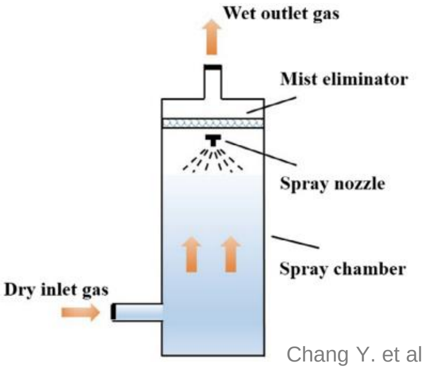
Direct injection



Water droplets are directly injected in the gas flow as a spray. Steam is not used because it would required additional energy for being generated. It allows to precisely tune the amount of water added to the gas and, even if it requires additional instrumentation to be added to the setup and energy to be supplied.

Injector technology is wide mature and is used especially in larger fuel-cell systems. However, particular attention must be done due to the enhanced risk of flooding the MEA with liquid water. A membrane dedicated to mist elimination can be added to the system, in order to reduce the amount of liquid water in the gas flow.

Direct injection is attractive because bringing some advantages: on overall heat management, allowing to recover the heat generated from the FC operation by pre-heating the gases, and because of the liquid water evaporation in the MEA helps in reducing temperature locally.



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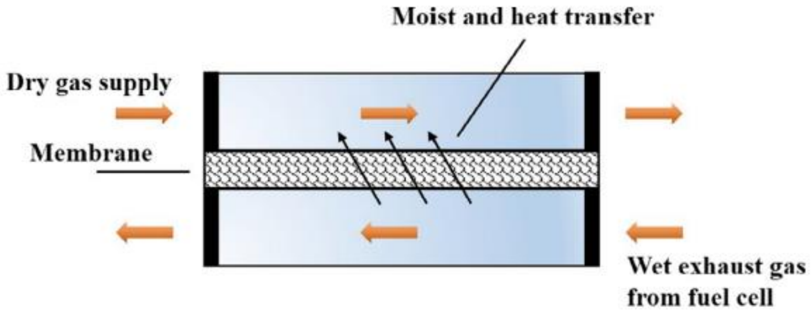
PEMFC OPERATION – EXTERNAL HUMIDIFICATION METHODS

Gas-to-gas membrane humidifier

As already seen during in introduction a membrane (for example made by Nafion) can be used to transfer heat and humidity from FC outlets to inlets.

The real capabilities of this method have still to be explored both in terms of materials (such as new formulations and membrane thickness) as well as in terms of the design of the setup (in terms of exchange area and degree of humidification of gases at the inlets and at the outlets).



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PEMFC OPERATION – EXTERNAL HUMIDIFICATION METHODS

The gas bubbling humidifier method and direct water injection method are commonly used at present because of the advantages such as high humidification performance and easiness of control. They are relatively suitable for stationary applications. However, the additional devices increase the volume and weight of the system, which is not favorable for compact applications such as automobile. New methods of external humidification are under test. Among them, membrane humidifier method is quite attractive due to the simple structure, light weight and good performance which are preferable for automotive applications. However, it should be noticed that the humidification performance is highly dependent on operating parameters such as flow rate, temperature and pressure, which should be considered comprehensively for practical applications.

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