Forcing water distribution inside a PEM fuel cell by asymmetric MEAs with hydrophobic catalyst layers

***Julio J. Conde**, M. Antonia Folgado,*
Paloma Ferreira-Aparicio, Antonio M. Chaparro

Departamento de energía, CIEMAT
Av. Complutense 40, 28040 Madrid, Spain

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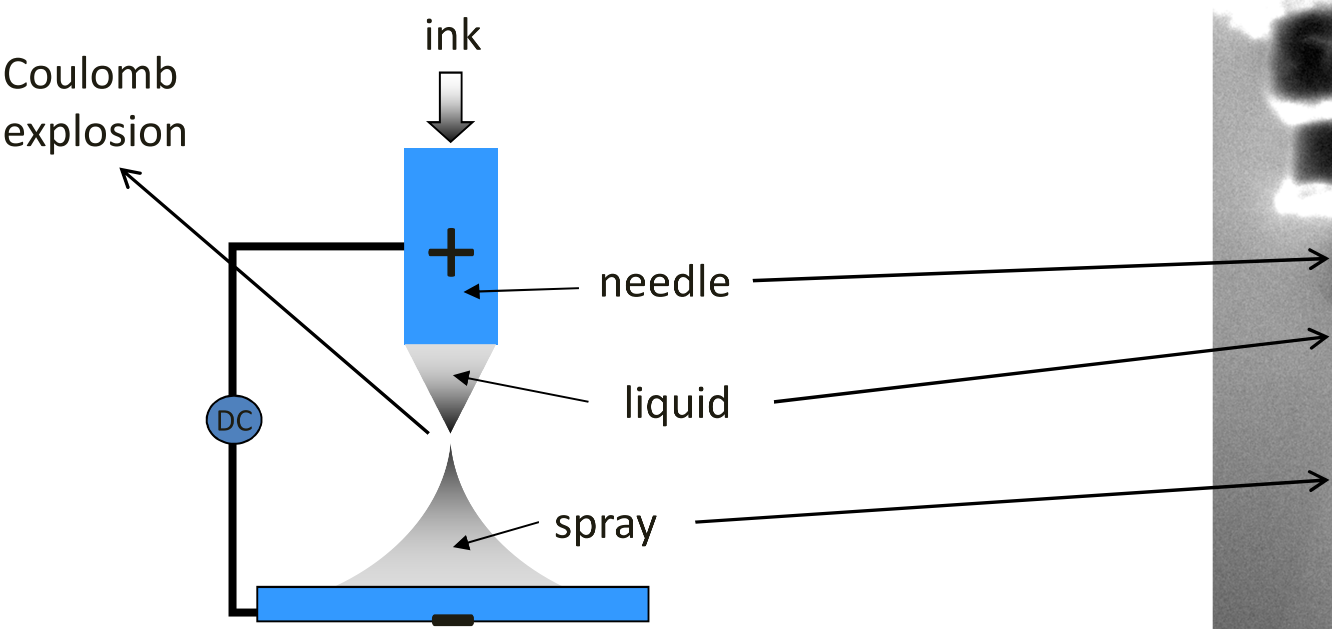
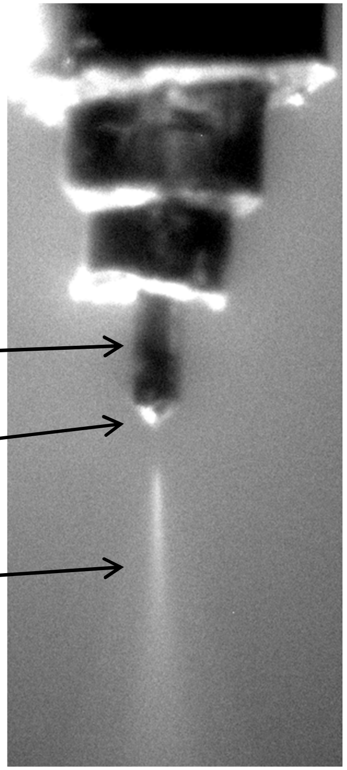
ELECTROSPRAY COATING





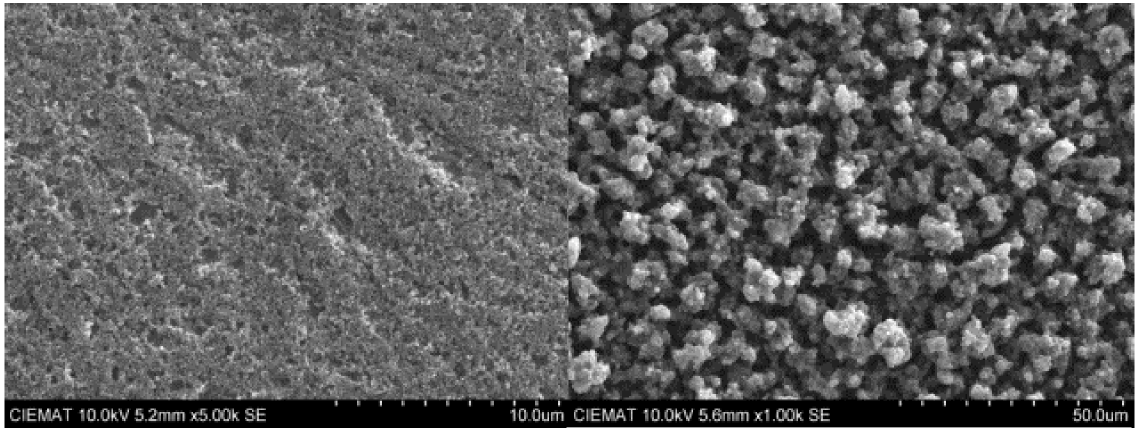
Electrospray is based on the application of a great potential between a metallic needle and a conductive substrate to the produce electrochemical ionization of the catalytic ink, creating a deposition process governed by the electrostatic interaction.

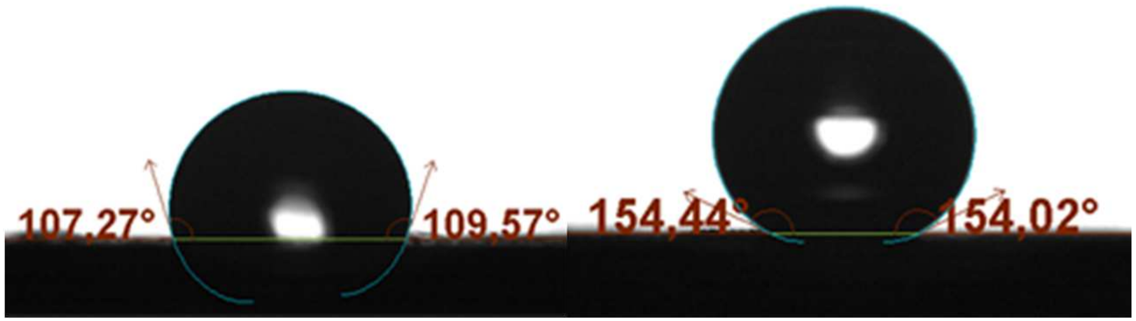
Electrospray parameters	
Ink	Pt/C + Nafion
DC potential	7000 - 12000 kV
Needle-substrate distance	2,5 - 4,0 cm
Capillary diameter	150 µm
Ink flow	0.20 - 0.40 mL h^{-1}
Substrate temperature	25 - 50 ^{o}C

Advantages of electrospray deposition

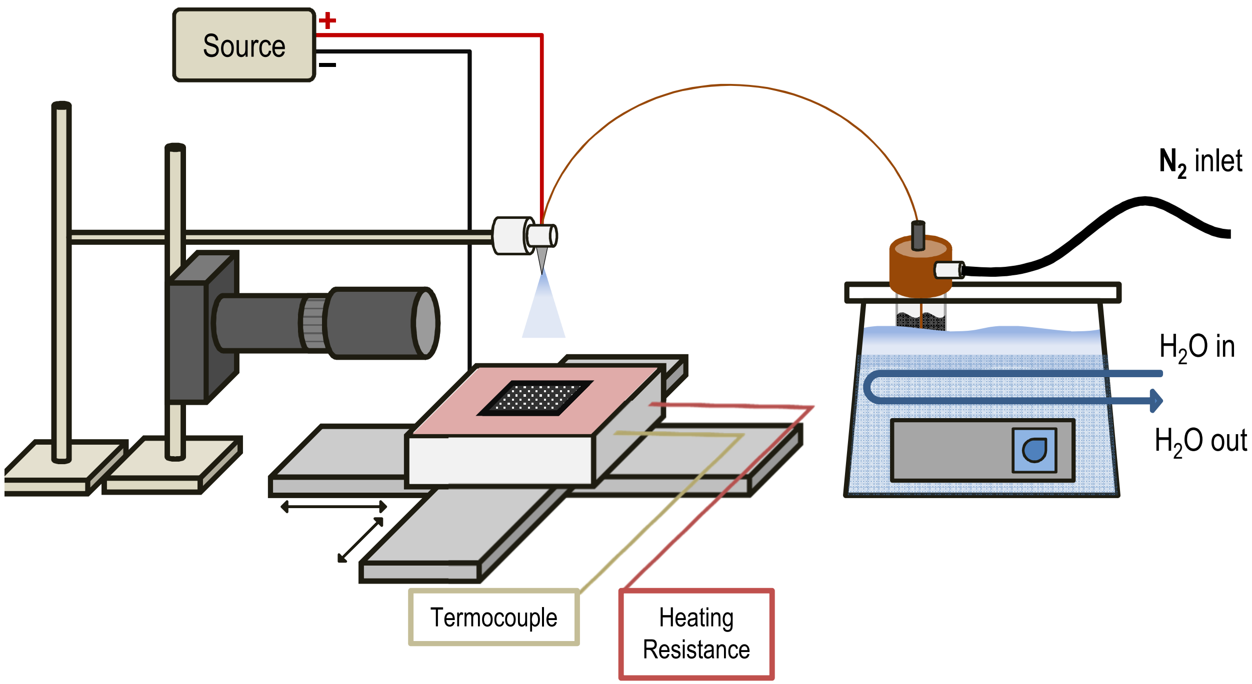
- **Better catalyst utilization**: Catalyst particles are electrically attracted towards the charged substrate
- **Advanced microstructure**: Increased macroporosity and hydrophobicity vs standard methods
- **Allow the use of complex substrates**: Electrostatic interactions of the particles with the substrate permits using non-planar substrates

AIRBRUSH | ELECTROSPRAY



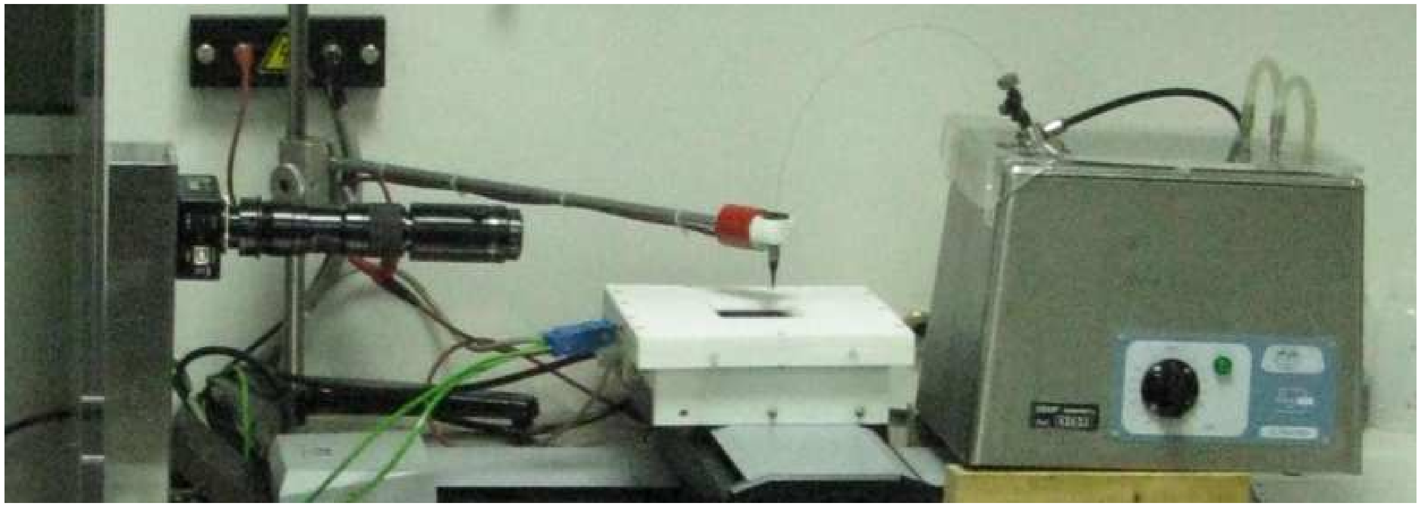


ELECTROSPRAY COATING



SETUP FEATURES

- Flux in the capillary controlled by nitrogen pressure
- Temperature controlled sonicated ink during the process
- Heated base with a precision XY axis
- Continuous control of the process with a camera



WATER TRANSPORT IN PEMFC

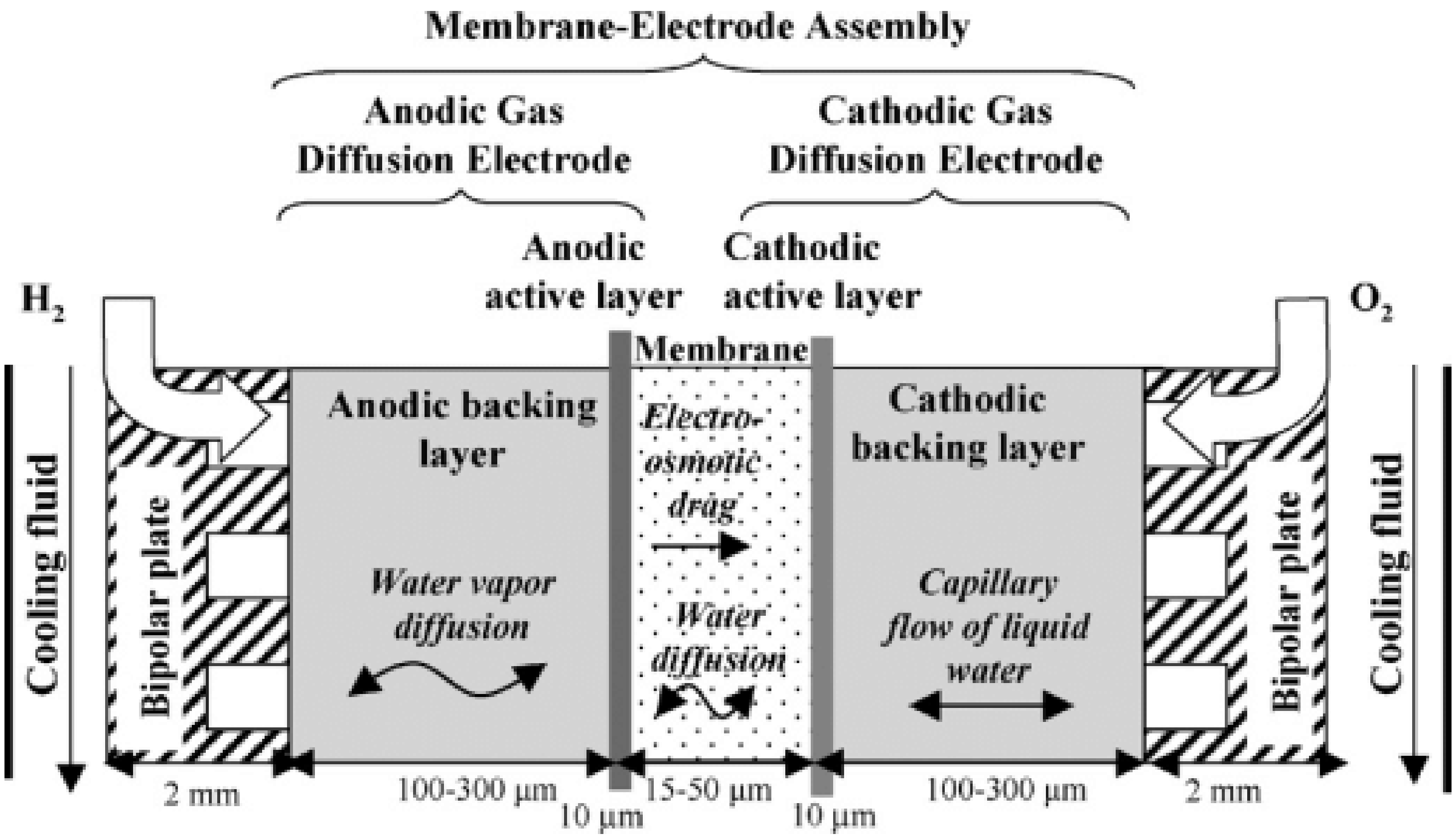
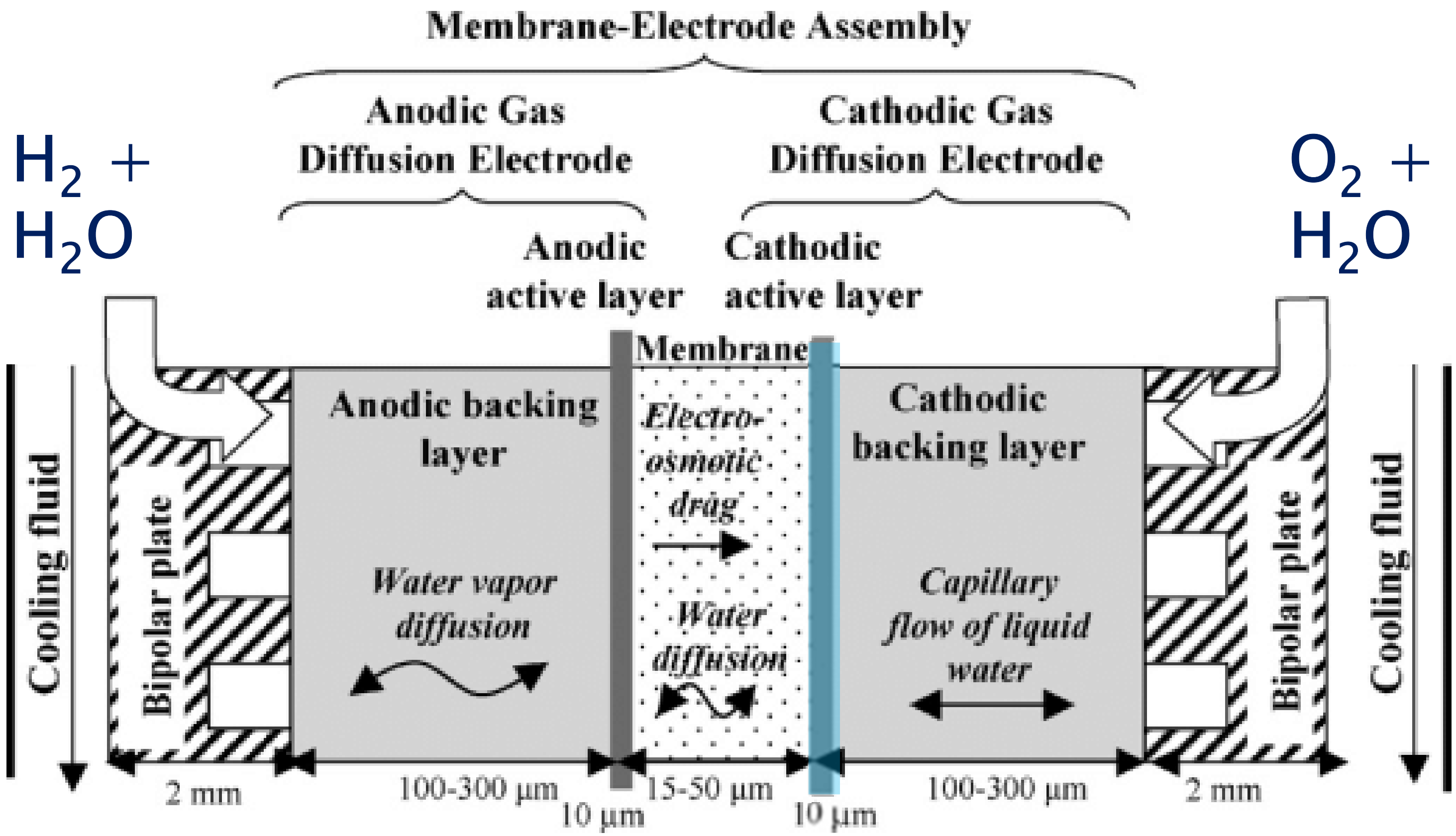


Image: A. Turhan et al. (2008) Journal of Power Sources 180, 773-783

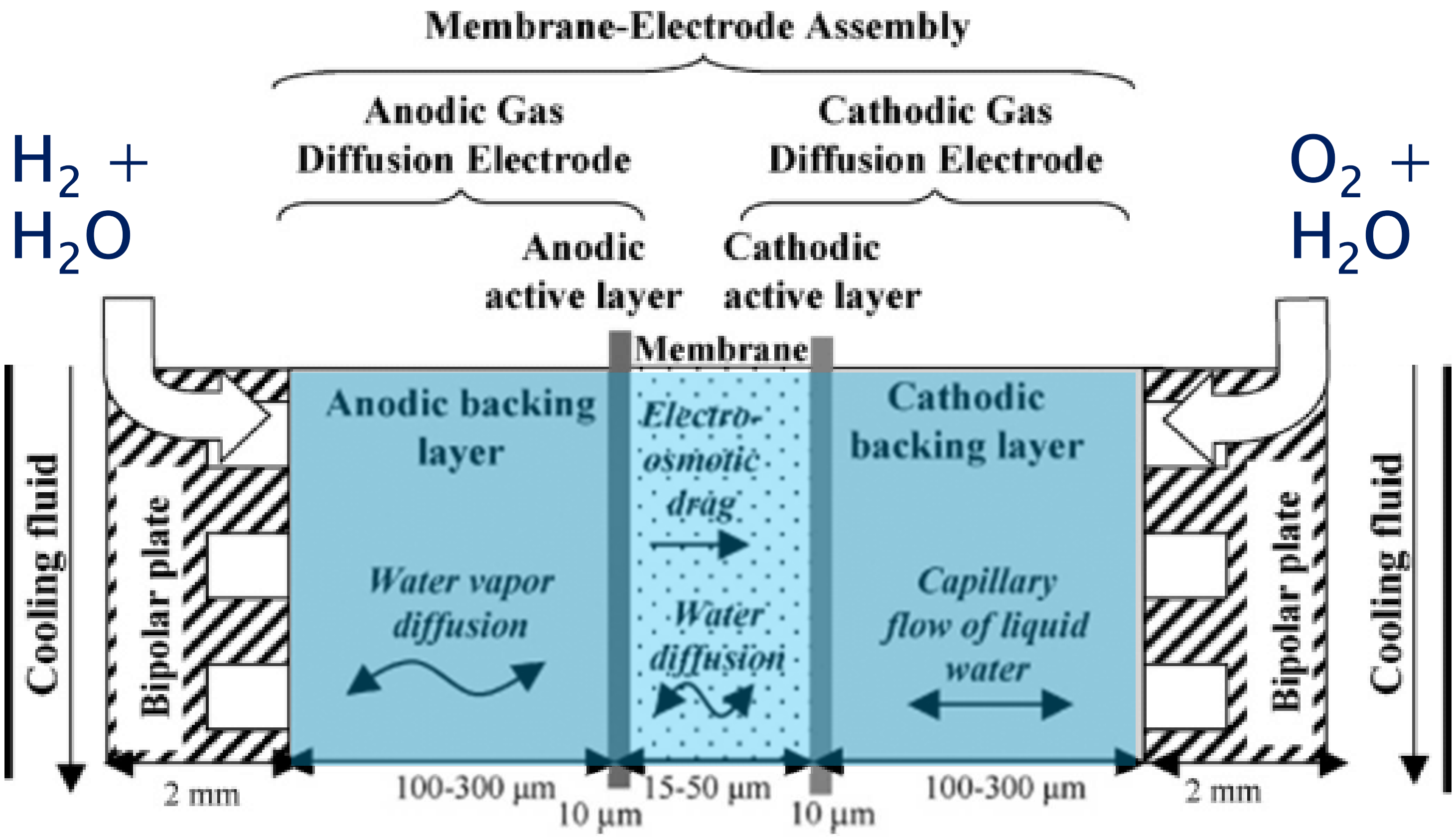
WATER TRANSPORT IN PEMFC



Water is introduced with the feed gases and also generated in the ORR reaction!

Image: A. Turhan et al. (2008) Journal of Power Sources 180, 773-783

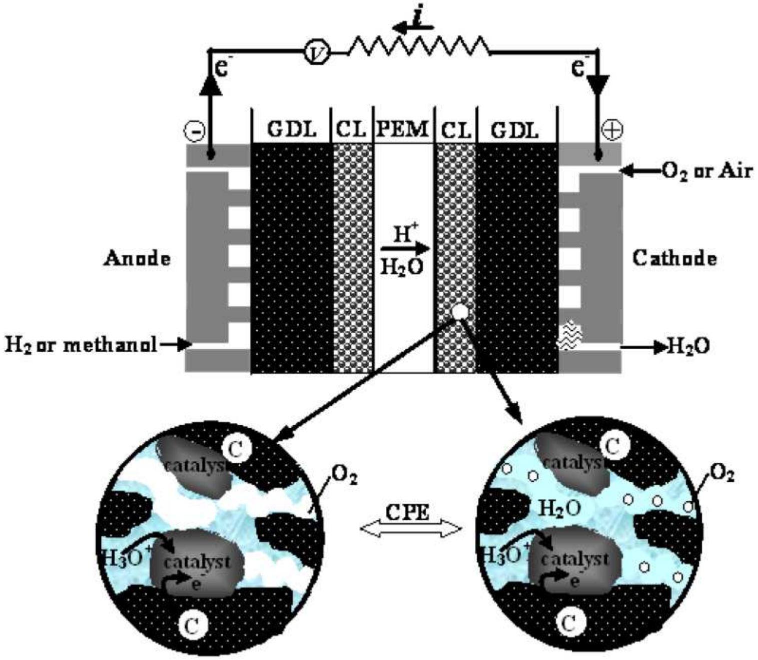
WATER TRANSPORT IN PEMFC



And then distributed following the different transport mechanisms

Image: A. Turhan et al. (2008) Journal of Power Sources 180, 773-783

WATER TRANSPORT IN PEMFC



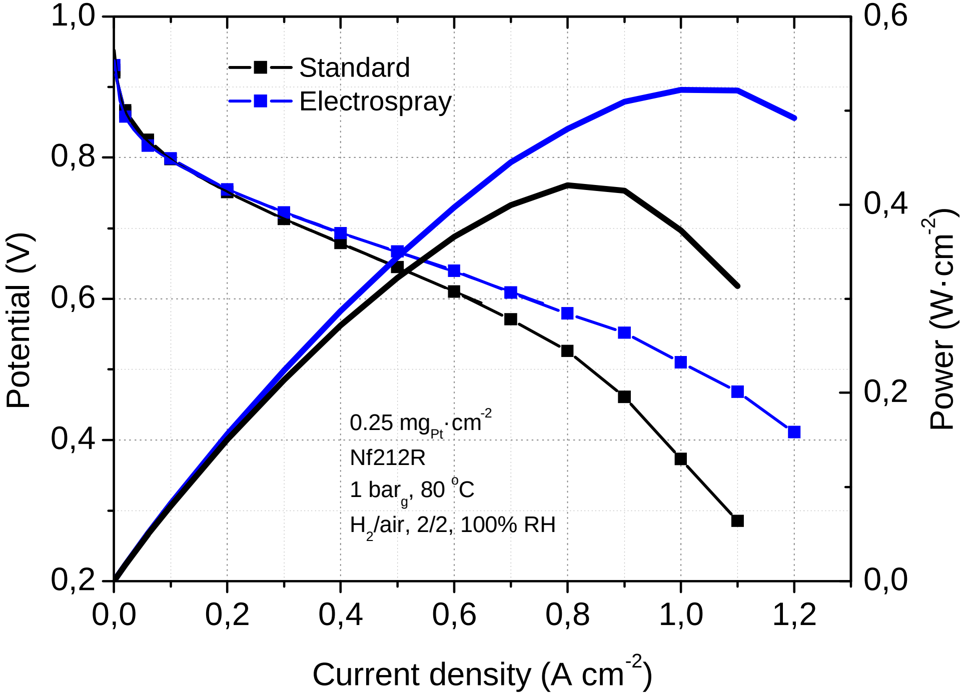
Water management is <u>crucial</u> to maximize the performance of PEM fuel cells

Water produced in the cathode side can cause problems in gas mass transfer and reduce the performance

In the event that flooding occurs, it causes irreversible damage to the fuel cell

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

ELECTROSPRAY CLs IN PEM FUEL CELLS



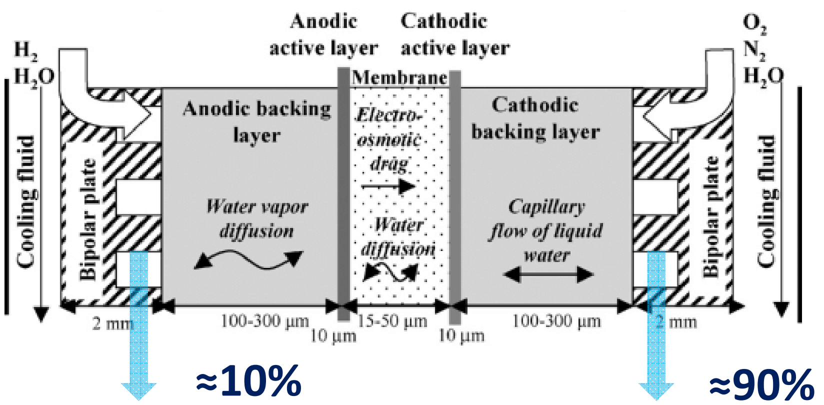
CELL PERFORMANCE

- Previous experiments* showed a better performance (20%) of electrosprayed catalyst layer in the cathodic side
- This effect was attributed to a better water distribution between the cathodic and the anodic side

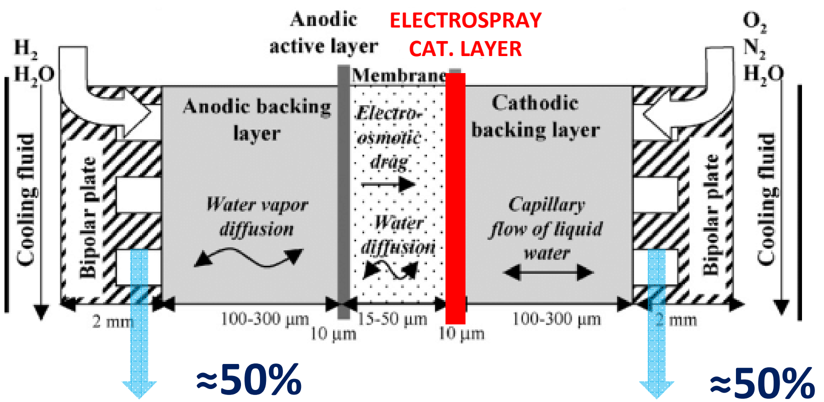
***See: A.M. Chaparro et al. J.Power Sources 325 (2016) 609-619**

ELECTROSPRAY CLs IN PEM FUEL CELLS

CONVENTIONAL PEMFC



ELECTROSPRAYED CATHODE



TOTAL WATER DISTRIBUTION

- Previous experiments* showed a the modification of the water distribution of the cell
- In certain conditions, electrospray in cathodic CL can push a extra 40% of the cell water to the anode

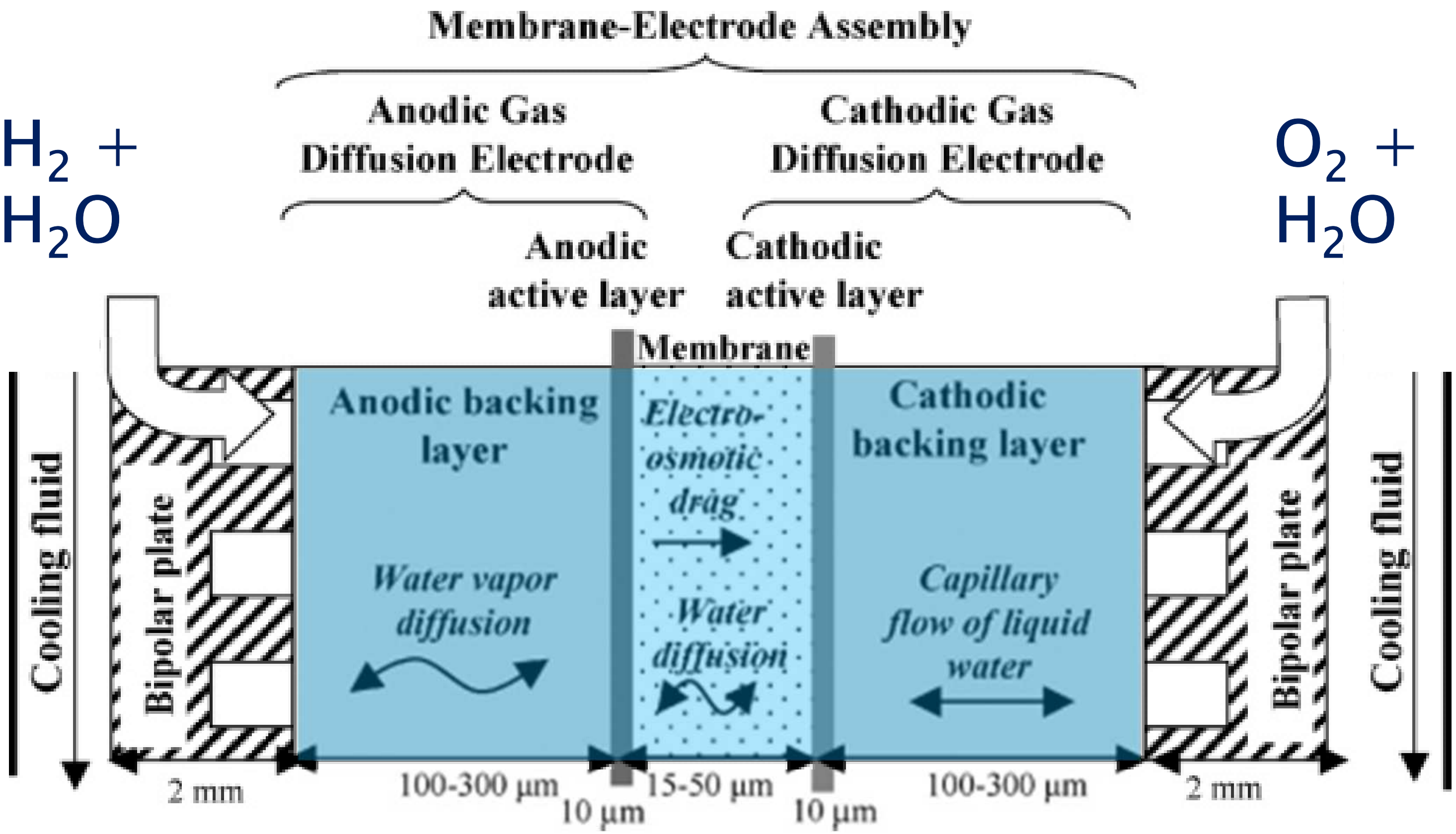
***See**: **M.A. Folgado et al. Fuel Cells (2018) published online**

OBJECTIVES

- Study of the behavior of electrosprayed catalyst layers in the cathodic side of the MEA
- Knowing that electrosprayed layers change the water distribution inside a PEM fuel cell, the objective is to control the distribution according to the applications of the cell.
- Study the influence of the thickness of hydrophobic and hydrophilic catalyst layers inside PEM fuel cells

EXPERIMENTAL

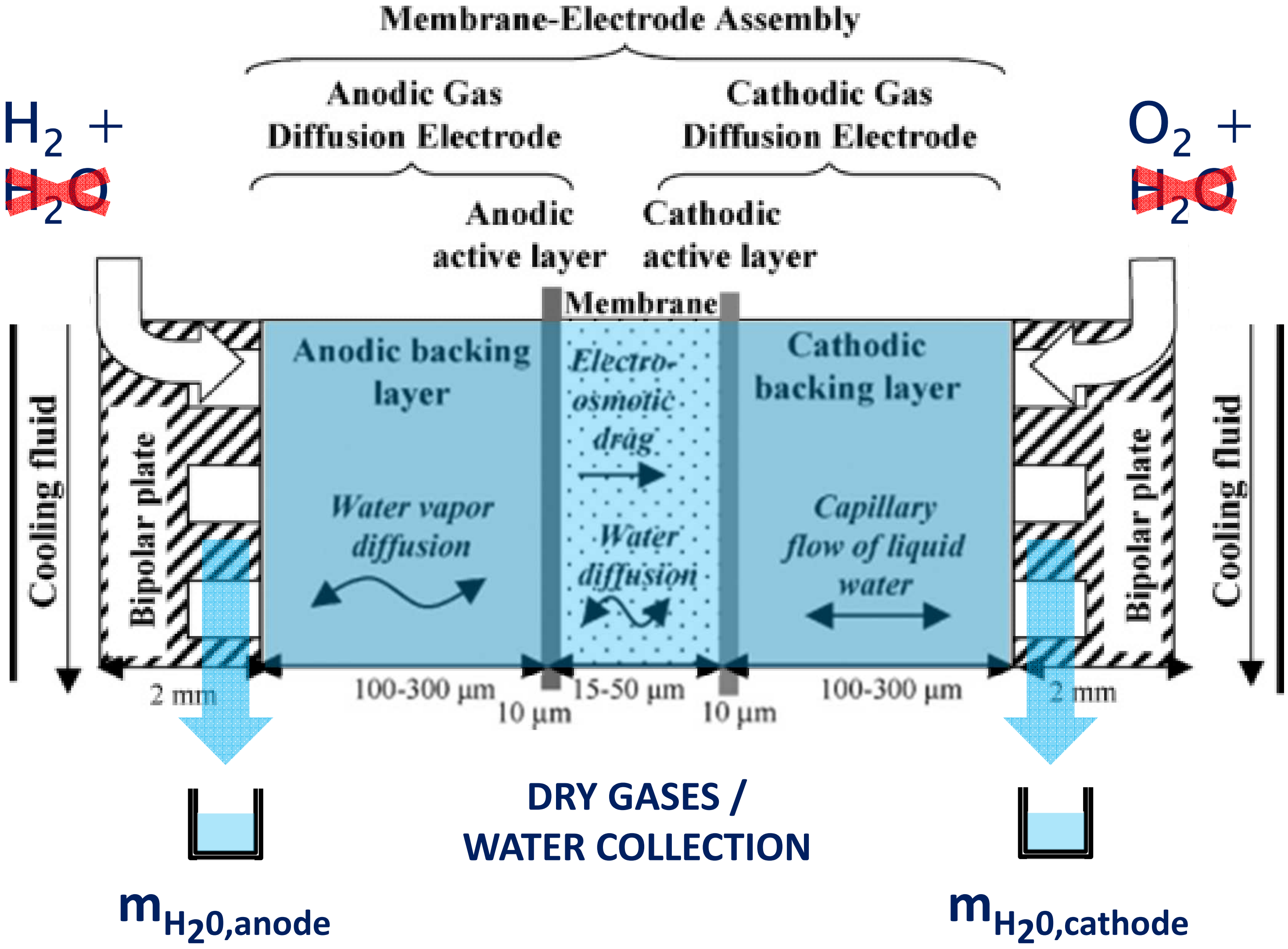
H_2 +
H_2O



O_2 +
H_2O

ACTIVATION WITH HUMIDIFIED GASES

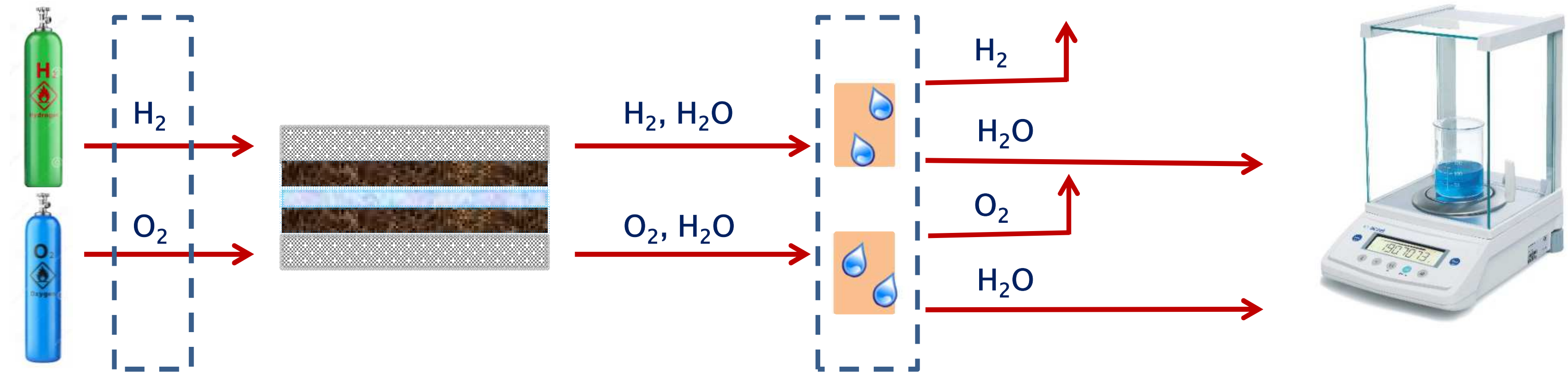
EXPERIMENTAL



EXPERIMENTAL CONDITIONS

INLET: Dry gases

OUTLET: Peltier condensers



Measurement procedure:

1- MEA activation @ 80ºC/100% RH

2- Gas inlet/outlet drying @ 80ºC/0% RH

3- Water collection experiments:
- Self-humidification: 80ºC/0% RH
- Constant gas feed stoichiometry →1.5/1.5 H_2/O_2

Water collection

- Refrigerated with Peltier cells @ 5ºC
- Water collection vs Faraday law > 90% efficiency
- Water recoveries from anode (w_a) and anode (w_c) given in percentages of the nominal faradaic production:

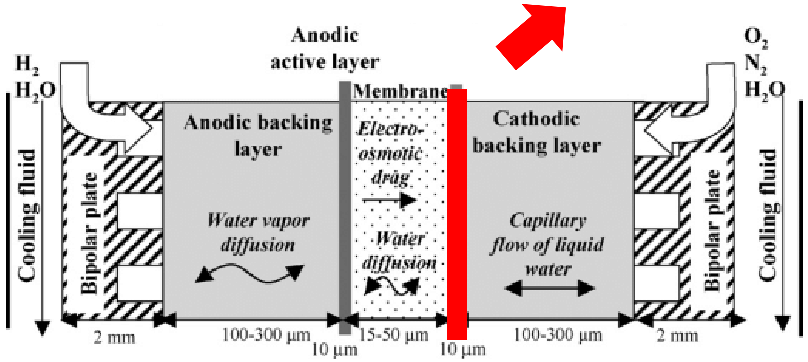
$$w_i = 100 \cdot m_{H_2O} \frac{z \cdot F}{I \cdot t \cdot M_{H_2O}}$$

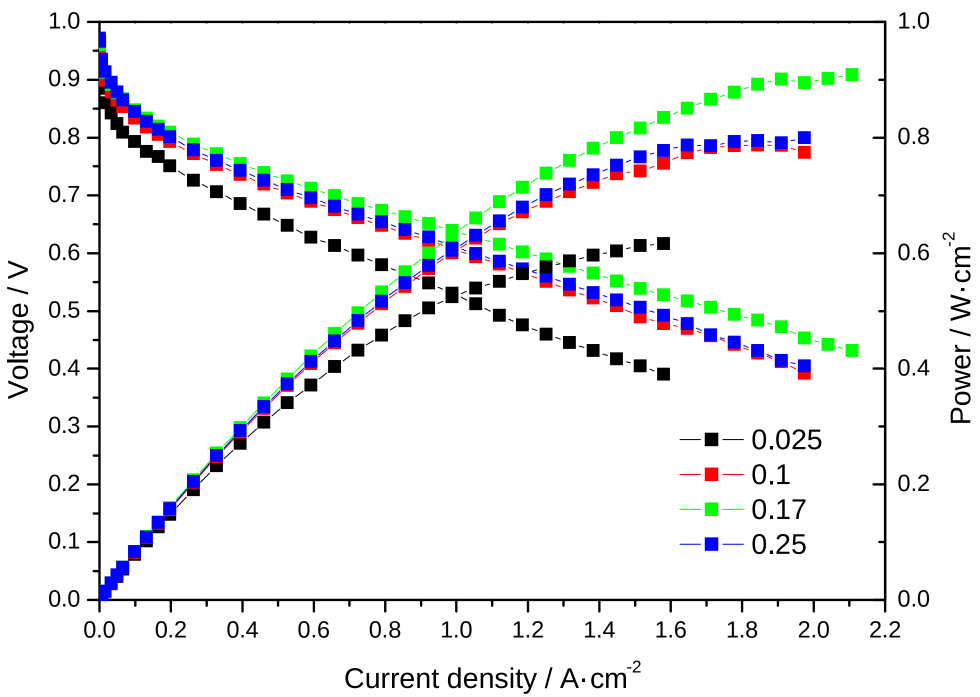
RESULTS

VARIATION OF THE THICKNESS OF THE ELECTROSPRATED CL

Effect of ELECTROSPRAYED cathode catalyst (Pt/C) LOADING

- ELCCM38 – 0.025 mg·cm^{-2} Pt
- ELCCM39 – 0.10 mg·cm^{-2} Pt
- ELCCM40 – 0.17 mg·cm^{-2} Pt
- ELCCM41 – 0.25 mg·cm^{-2} Pt





MEA elements

- ANODE: commercial electrode (FCETC, 0.30 mg Pt/cm^2, Pt/C 40%, ionom. 30%)

- MEMBRANE: Nafion NR212

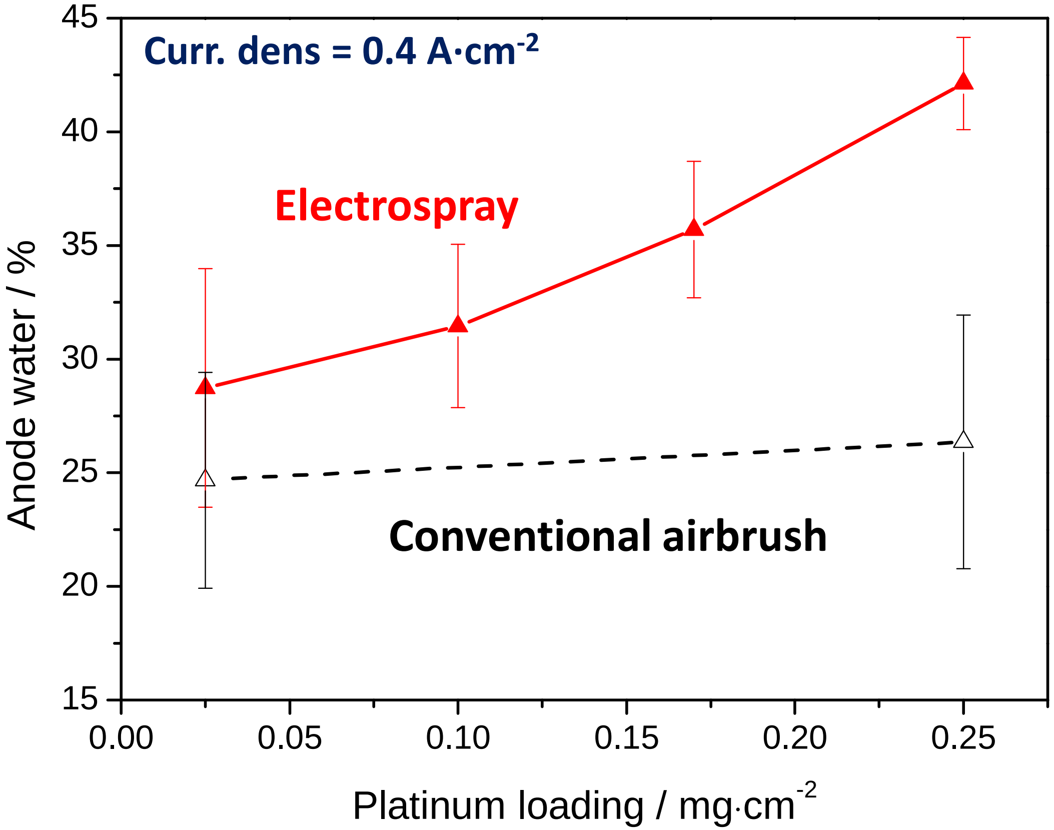
-CATHODE: Electrosprayed layers (Pt/C 20%) and GDL ELAT E-TEK LT1200W

-Electrode area: 15.2 cm^2

The optimum platinum loading is 0.17 mgcm^{-2} Pt due to better Ri(dc).

RESULTS

Water recovered in the anode recovered in the anode at medium and low current densities is found to be controlled by the thickness of the layer and can be modified between 10–15%



The thickness effect in <u>hydrophilic airbrushed layers</u> seems to not affect the water distribution at all

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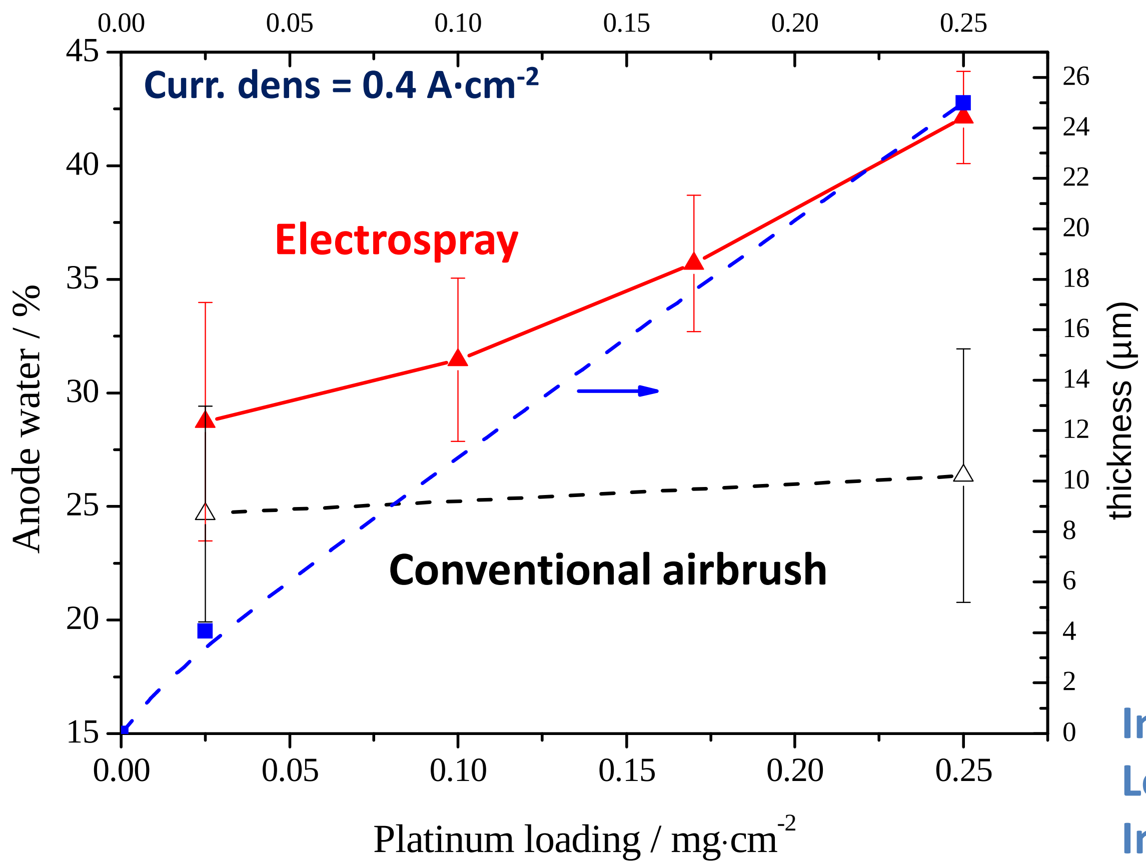


The thickness effect in <u>hydrophilic airbrushed layers</u> seems to not affect the water distribution at all

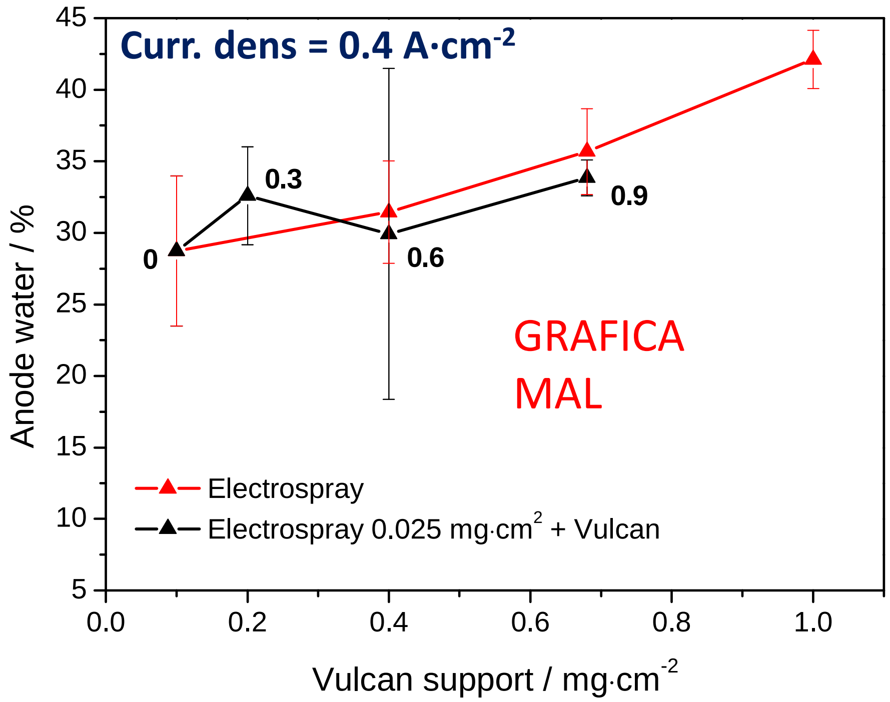
In order to test that this effect is only caused by the thickness of the hydrophobic layer, a <u>constant platinum loading</u> is going to be tested with <u>additional carbon support</u>

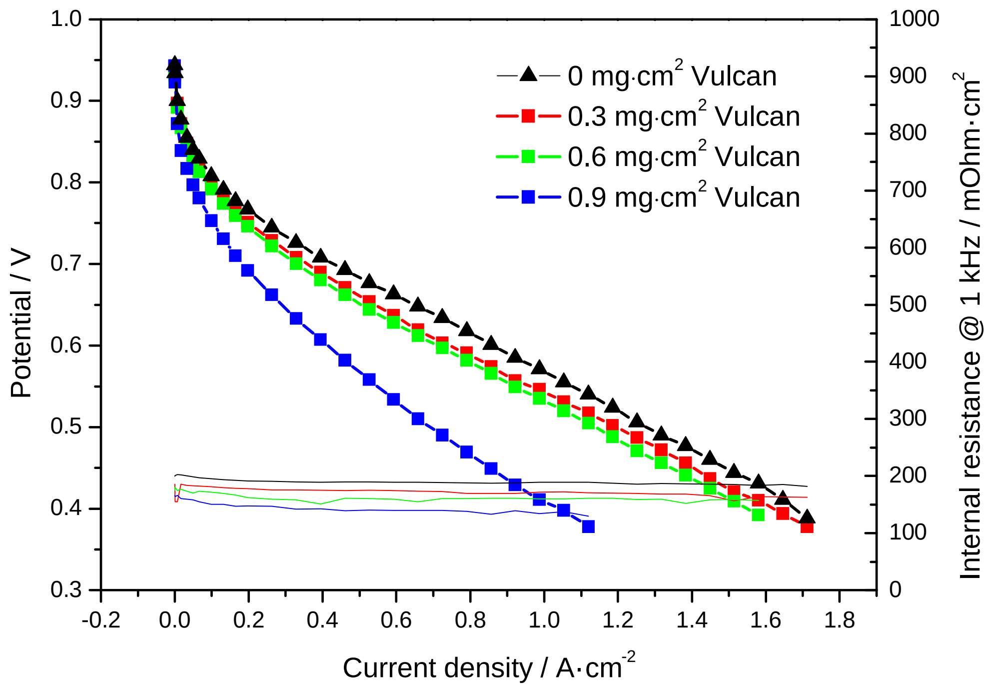
Incluyendo los espesores obtenidos
Los espesores son algo irregulares p
Incluir un dato sobre la dispersión d

RESULTS

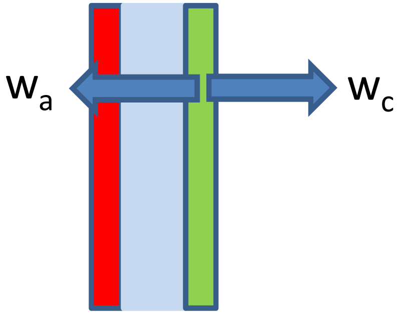
CONSTANT PLATINUM LOADINGS and ADDED Vulcan support

- ELCCM38 – 0.025 mg·cm^{-2} Pt
- ELCCM42 – 0.025 mg·cm^{-2} Pt + 0.1 mg·cm^{-2} Vulcan (Simulating 0.05 mg·cm^{-2} Pt)
- ELCCM47 – 0.025 mg·cm^{-2} Pt + 0.3 mg·cm^{-2} Vulcan (Simulating 0.10 mg·cm^{-2} Pt)
- ELCCM48 – 0.025 mg·cm^{-2} Pt + 0.6 mg·cm^{-2} Vulcan (Simulating 0.17 mg·cm^{-2} Pt)





DISCUSSION



The ratio of water collected from anode and cathode is proportional to the ratio of their hydraulic conductivities and inversely proportional to the water path lengths. In cathode, the catalyst layer length (L_{CL}) can be made explicit:

$$\frac{w_a}{w_c} = A + \frac{k_a L_{CL}}{k_c L_a} \longrightarrow w_a = 100\,\frac{A + \frac{k_a L_{CL}}{k_c L_a}}{1 + A + \frac{k_a L_{CL}}{k_c L_a}}$$

A simple relation can be inferred for $w_a = f(L_{CL})$

$$w_a = 100\,\frac{\mathrm{A} + \mathrm{B} \cdot \mathrm{L}_{CL}}{1 + \mathrm{A} + \mathrm{B} \cdot \mathrm{L}_{CL}}$$

A = w_a/w_c for L_{CL}=0 (should be independent of catalyst layer type)
B = ka/(kcLa) = cte/kc (should depend on catalyst layer type)

B parameter could be used to determine ratios of the hydraulic conductivity among different catalyst layer types:
k_{ES}/k_{AE}

Currently optimizing thickness measurement!

CONCLUSIONS

1- It is demonstrated that the thickness of electrosprayed catalyst layer determines water distribution inside a fuel cell, to a higher degree that other deposition methods (airbrush)

This opens a possibility of a PASSIVE CONTROL of water distribution inside a PEM fuel cell

- The fraction of recovered anode water depends of the hydrophobicity of the catalyst layer (CL)
- It is believed that the thickness of the electrosprayed layers have a great effect in the hydraulic conductivity

2 - The addition of extra carbon support in a certain quantity, seems to not accept cell performance

ACKNOWLEDGMENTS

Ministry of Economy and Competitiveness for financial support under contract E-LIG-E (ENE 2015-70417-P).

For more information, visit:

http://projects.ciemat.es/web/elige
(Project website)

http://rdgroups.ciemat.es/web/pilascomb
(Fuel Cell unit website)