K3

PEM fuel cells research activities at Ciemat

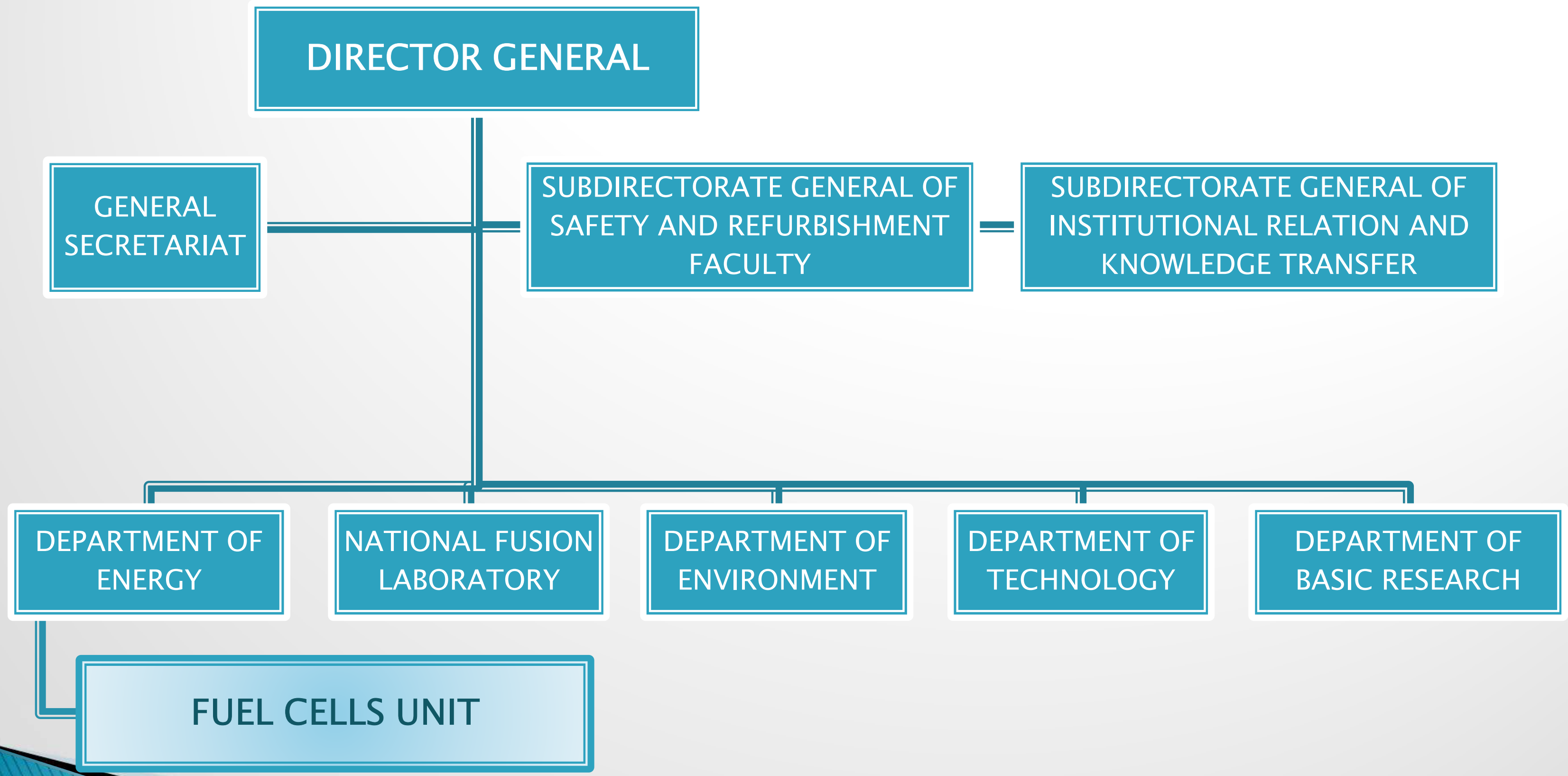
Paloma Ferreira Aparicio

6th De Nora R&D Symposium Agenda
Milan, September 27, 2017

Outline

Ciemat

Ciemat's organizational structure



Renewable energies and energy savings

CIEMAT is working on the following lines:

- Photovoltaic solar energy
- Solar thermal energy
- Aplications of solar radiation
- Wind power
- Bioenergy
- Marine power generation
- Energy efficiency
- Other technologies: energy storage, fuel cells and Geographic Information Technologies (GITs) for integrating renewable energies

The fuel cell research at Ciemat

Fuel cells Unit

Low Temperature FCs

High Temperature FCs

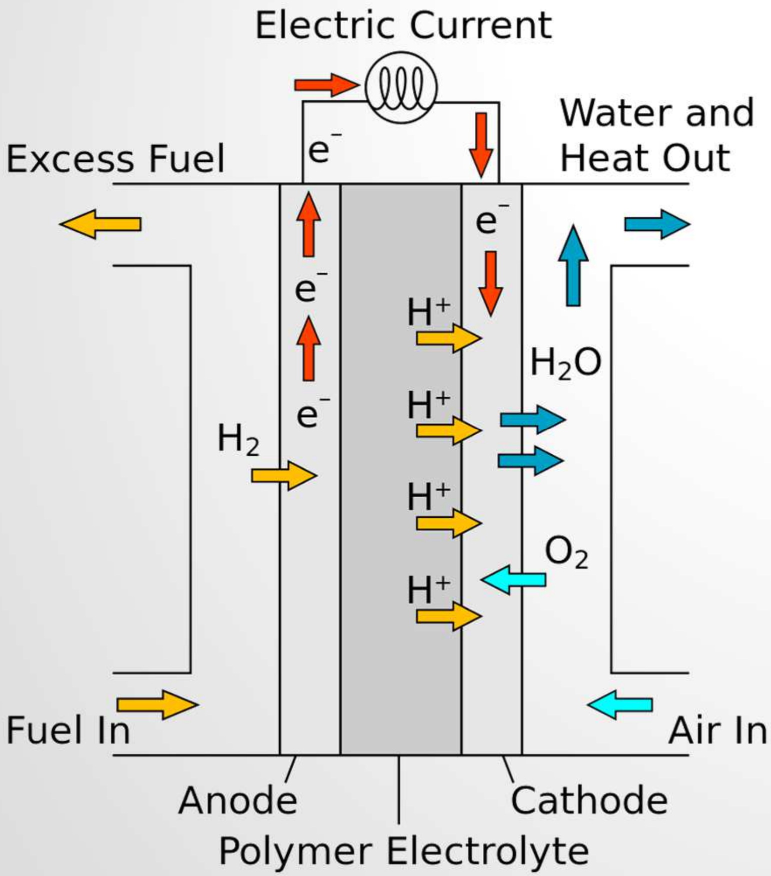
FC systems and integration

H$_2$-operated fuel cells with Nafion Proton Exchange Membranes

Our research team: the PEMFC group

Antonio M. Chaparro	Mª Antonia Folgado Martínez	Julio J. Conde López	Alba María Fernández Sotillo	Marco Antonio Galarza Díaz	Paloma Ferreira Aparicio
• Senior Researcher	• Senior Researcher	• PhD student	• PhD student	• Technician	• Senior Researcher

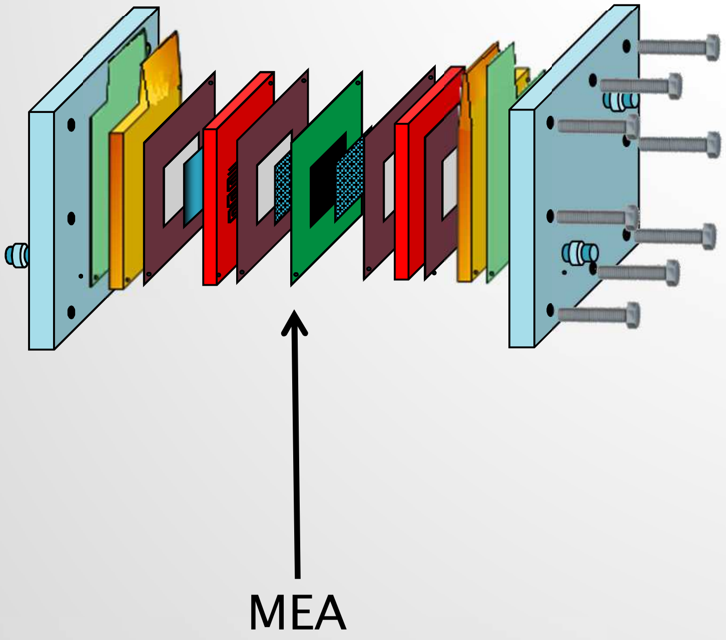
H_2-PEM Fuel Cells



Stack

Single cell

H_2-Single PEM Fuel Cell



Components:

- Endplates
- Fasteners
- Insulators
- Current collectors
- Gaskets
- Flow-field plates
- Membrane-electrode assembly (MEA):
  - electrodes (catalytic layer (CL),
  - microporous layer (MPL),
  - gas difussion layer (GDL),
  - proton exchange membrane (PEM)

Research activities in PEMFC

Electrocatalysts	Synthesis, characterization, activity tests.
Catalytic layers	Catalytic inks preparation, and deposition on gas diffusion subtrates or on polymer membranes.
Ink deposition techniques	Thin film preparation for catalytic layers and coatings for other components.
Membrane-electrode assemblies	Evaluation of MEAs in single fuel cells and in stacks.
H_2 -PEMFCs and stacks	Air-breathing fuel cells: design, fabrication, evaluation od cells and characterization of materials and components.

Ciemat

Synthesis of electrocatalysts

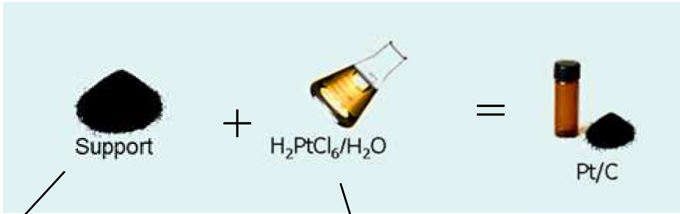
Electrocatalysts

Catalytic layers

Ink deposition techniques

Membrane-electrode assemblies

Cells & stacks



Highy surface area
Good electrical conductivity
High chemical stability

Formation of small and well dispersed Pt particles

High activity for H_2 oxidation, for O_2 reduction
High chemical stability

Electrocatalyst synthesis procedures

Electrocatalysts

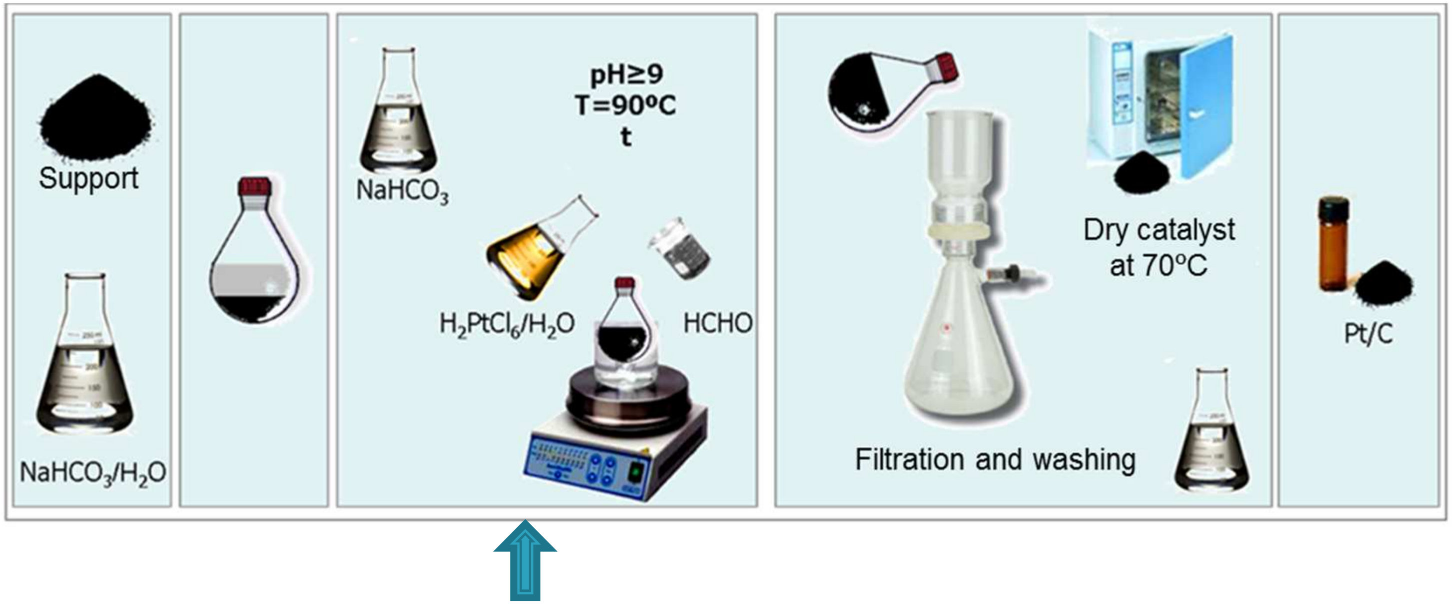
Catalytic layers

Ink deposition techniques

Membrane-electrode assemblies

Cells & stacks

Precipitation-reduction method



The duration of this step is key for particle size control

Pt(20%)/Vulcan XC72:
synthesis procedure and characterization

Electrocatalysts

Catalytic layers

Ink deposition techniques

Membrane-electrode assemblies

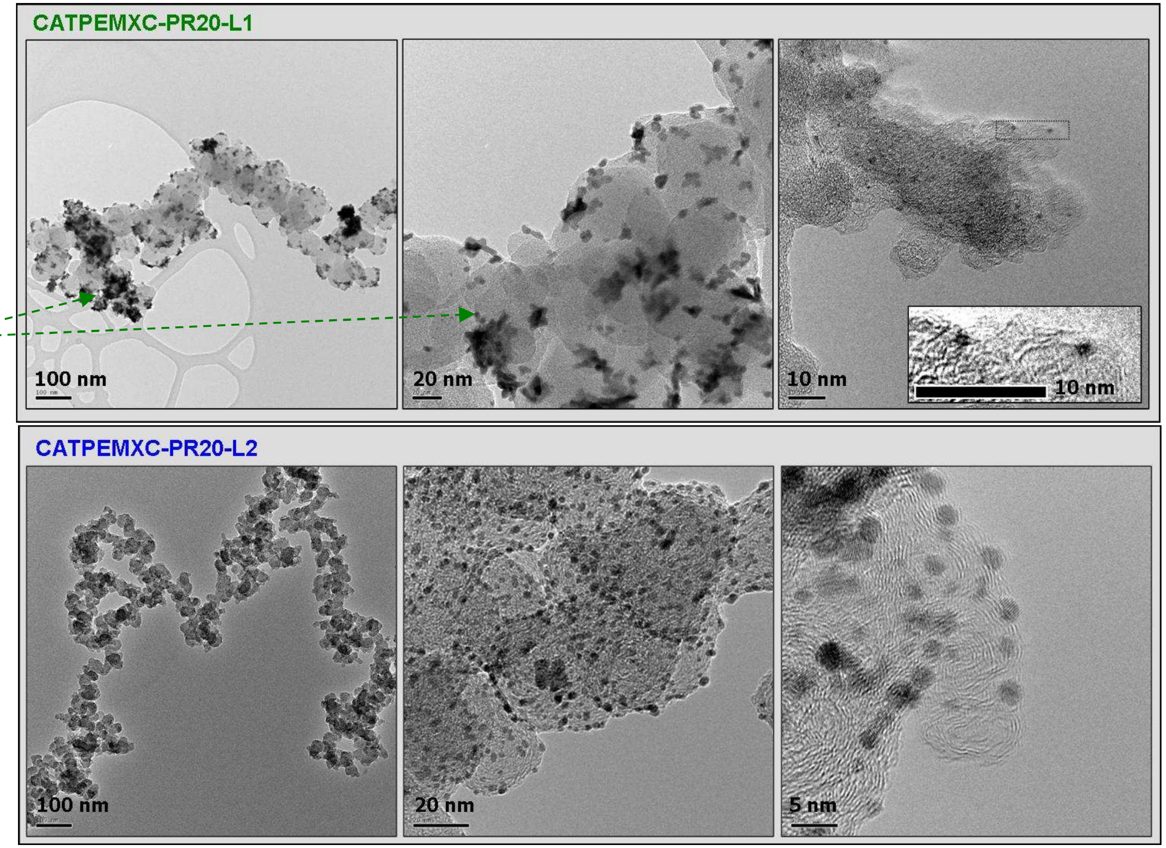
Cells & stacks

TEM

Long step (30 min)

Aggregation of small particles

Short step (15 min)



The control of duration of the precipitation-reduction step in the synthesis is the key for obtaining well dispersed particles and reducing the average Pt particle size

Pt(20%)/Vulcan XC72: characterization

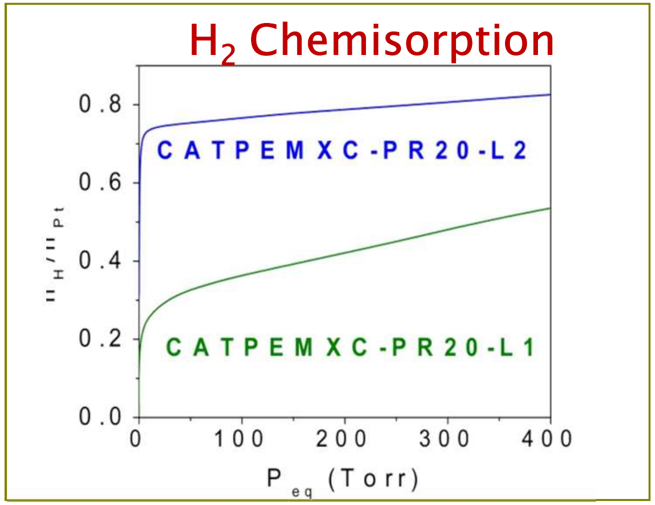
Electrocatalysts

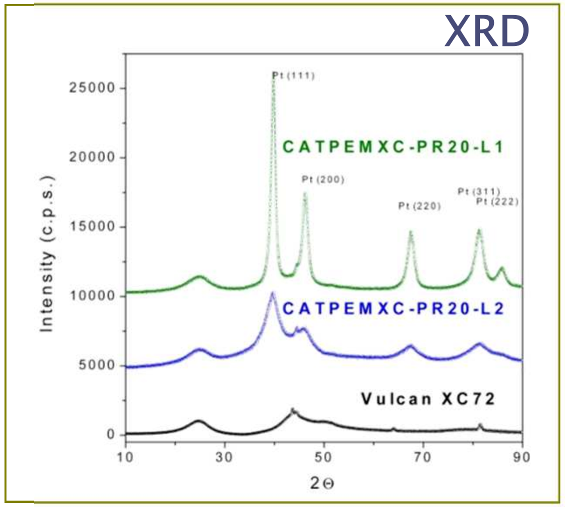
Catalytic layers

Ink deposition techniques

Membrane-electrode assemblies

Cells & stacks





XRD technique overvalue largest particles

Catalyst	H_2 chemisorption d (nm)	H_2 chemisorption A (m^2/g_{Pt})	XRD d (nm)	XRD A (m^2/g_{Pt})
L1	4,0 ± 0,4	70 ± 7	6,5 ± 0,2	43 ± 2
L2	1,5 ± 0,1	182 ± 18	3,0 ± 0,2	93 ± 7

Better agreement with statistical TEM measurements

TPO: A uselful characterization tool
Catalyzed oxygen diffusion from Pt particles

Electrocatalysts

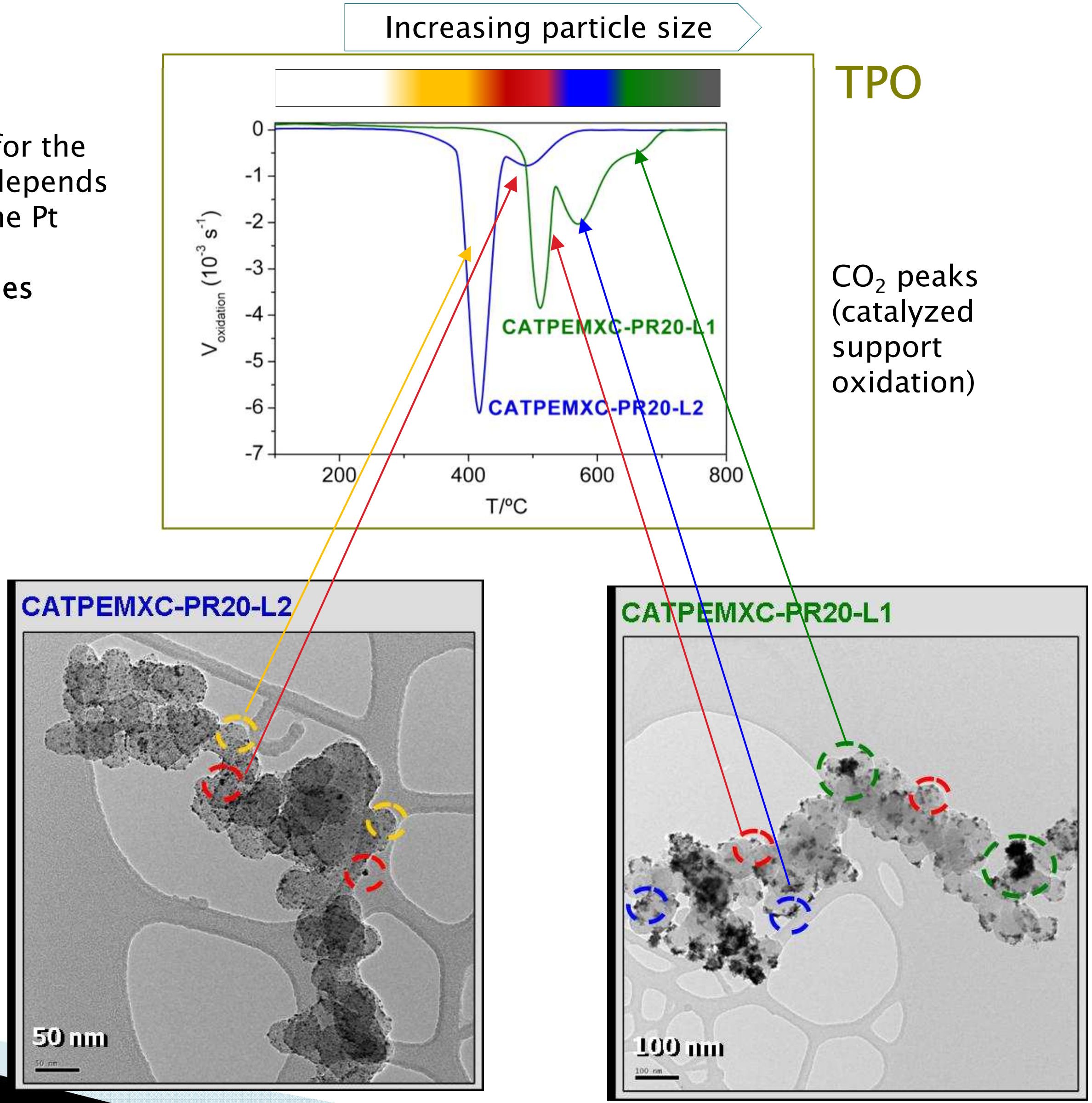
Catalytic layers

Ink deposition techniques

Membrane–electrode assemblies

Cells & stacks

The temperature for the support oxidation depends on the size of the Pt aggregates:
smaller particles reduce T_{ox}



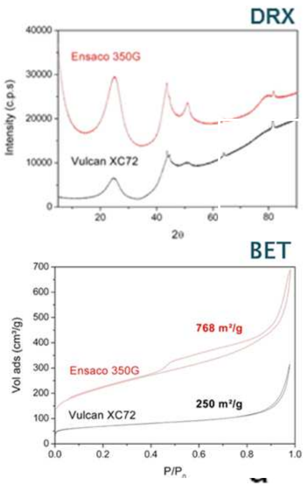
TPO

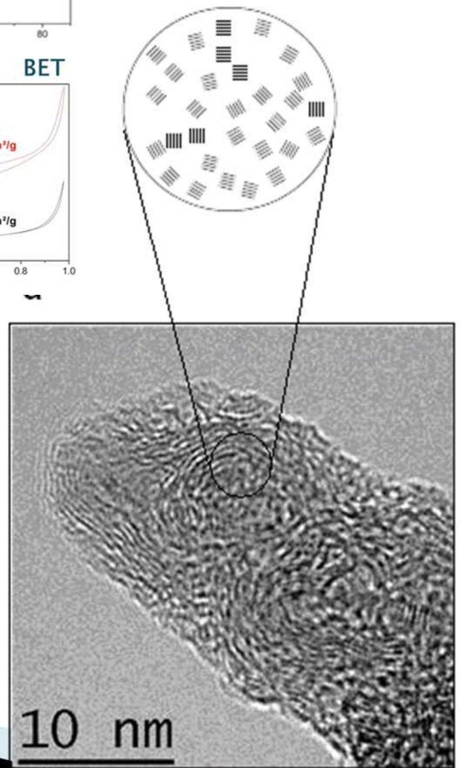
CO_2 peaks (catalyzed support oxidation)

Types of carbon supports

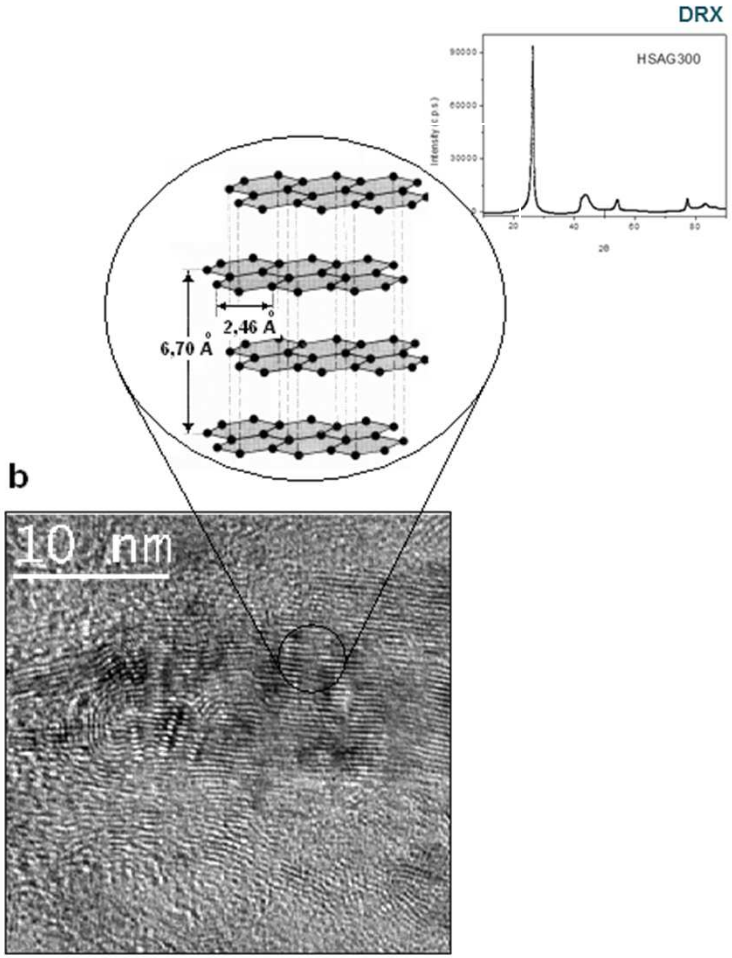
- Electrocatalysts
- Catalytic layers
- Ink deposition techniques
- Membrane-electrode assemblies
- Cells & stacks

- **Carbon Blacks**
  Vulcan XC72 (Cabot Corp.)
  Ensaco 350G (Timcal, Imerys)





- **Graphites**
  HSAG300 (Timcal, Imerys)



Properties of supports

Electrocatalysts

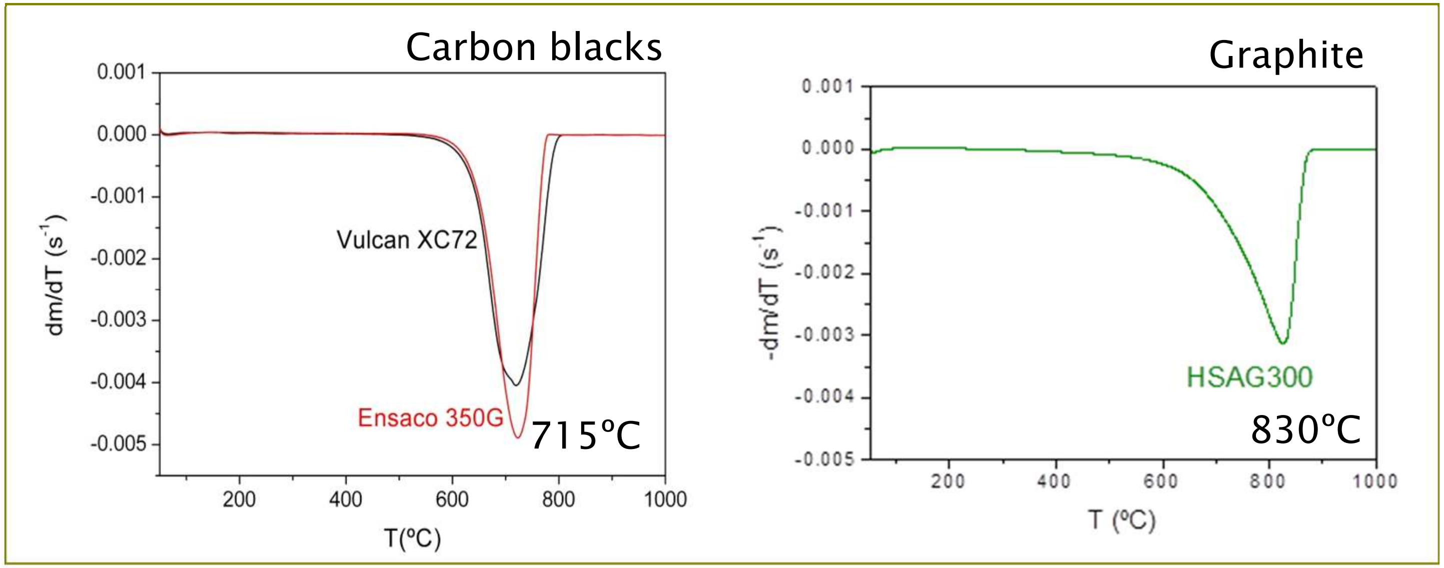
Catalytic layers

Ink deposition techniques

Membrane-electrode assemblies

Cells & stacks

TGA (N_2/O_2) – Temperature programmed oxidation

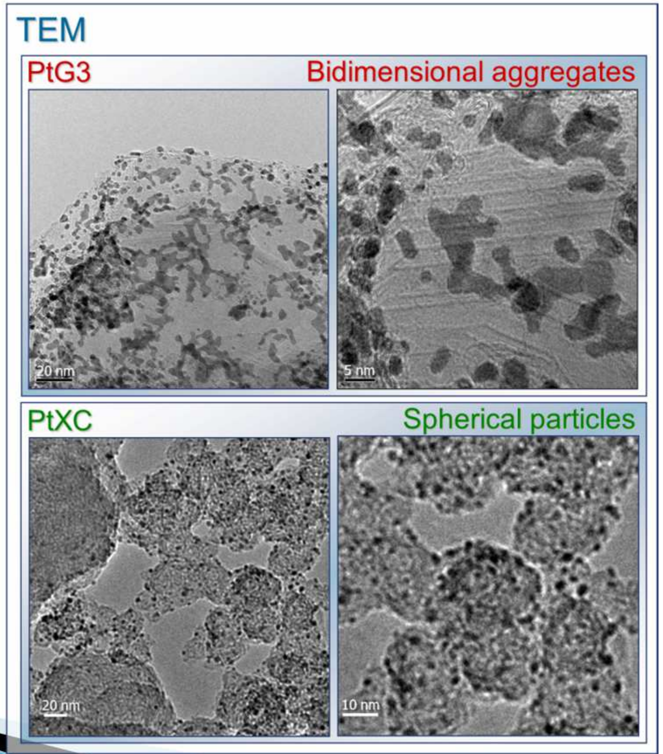


Graphites are more stable against corrosion than CBs

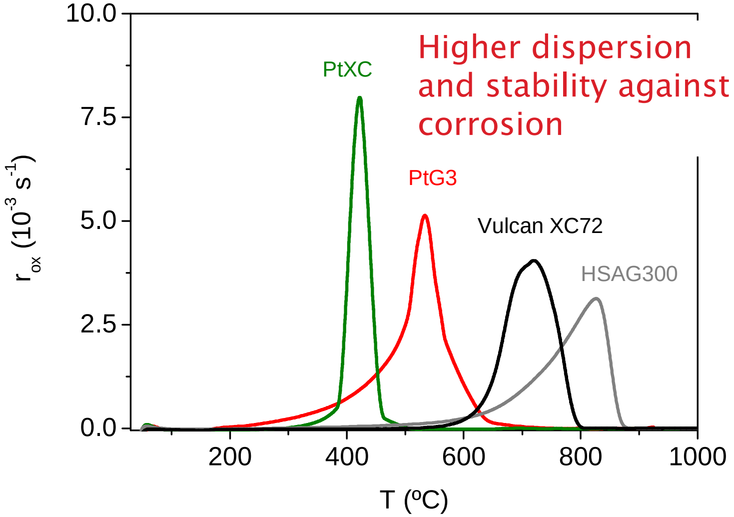
HSAG vs CB supported catalysts

Catalyst properties synthesized by the precipitation-reduction method.

Catalyst	Pt (%)	d_{DRX} [5] (nm)	A_{DRX} (m^2/g_{Pt})	H/Pt quim	A_{quim} (m^2/g_{Pt})
PtG3 (HSAG)	15,0	**2,5 ± 0,2**	111 ± 9	0,95	**234 ± 23**
PtXC (CB)	14,1	**2,4 ± 0,5**	116 ± 25	0,33	**82 ± 8**



TGA (N_2/O_2) - TPO




Journal of Power Sources 192 (2009) 57–62

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

High surface area graphite as alternative support for proton exchange membrane fuel cell catalysts

P. Ferreira-Aparicio[a,*], M.A. Folgado[a], L. Daza[a,b]

PEMFC electrodes

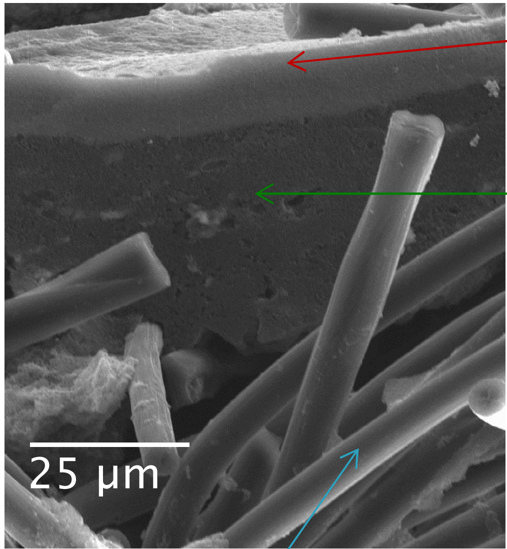
Electrocatalysts

Catalytic layers

Ink deposition techniques

Membrane-electrode assemblies

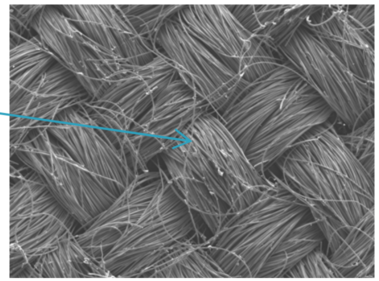
Cells & stacks



Catalytic layer (CL)

Microporous layers (MPL)

Gas diffusion layer (GDL)



Catalytic layers

Electrocatalysts

Catalytic layers

Ink deposition techniques

Membrane-electrode assemblies

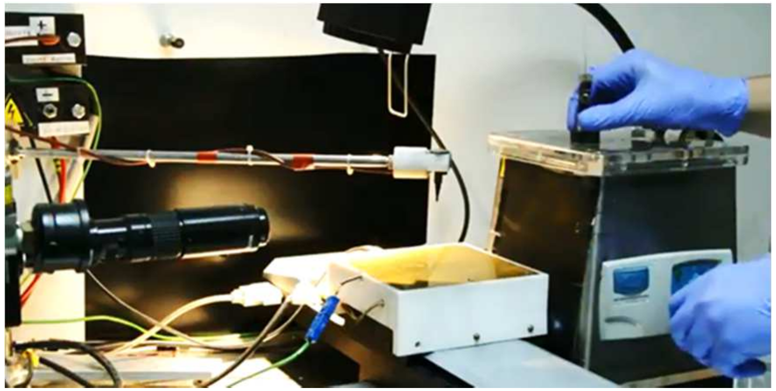
Cells & stacks

Electrocatalyst + ionomer = Catalyst Ink
(Nafion)

Deposition procedures for catalyst layers

Aerography

Electrospray



The electrospray technique for carbon inks

Electrocatalysts

Catalytic layers

Ink deposition techniques

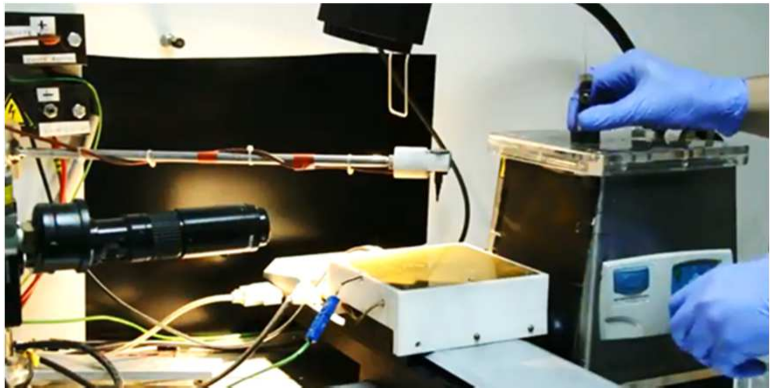
Membrane-electrode assemblies

Cells & stacks

Colloidal inks: deposition of particles for nanostructures

Usually applied to produce catalytic layers or
gas diffusion layers.

More recently, we are applying this technique to produce
superhydrophobic protective coatings.



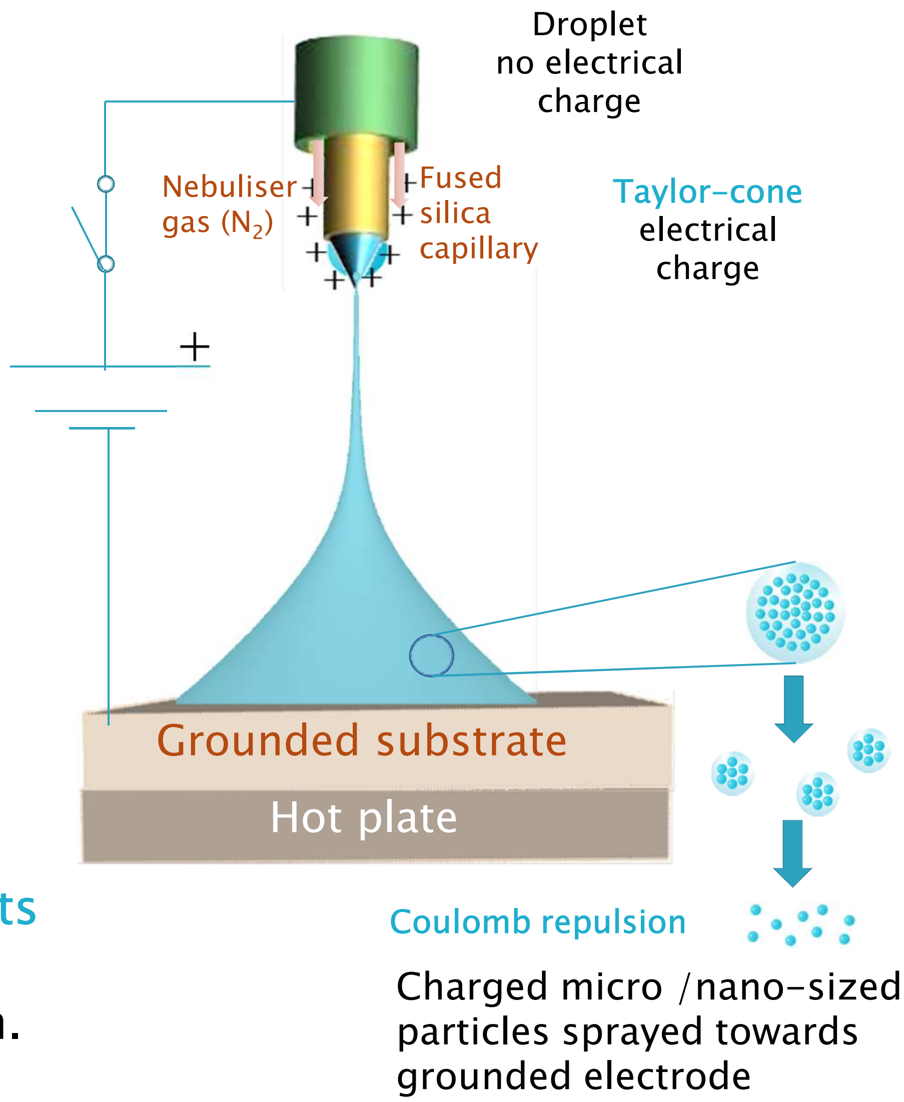
Ciemat

The electrospray process

High voltage application to disperse a liquid supplied through an emitter.

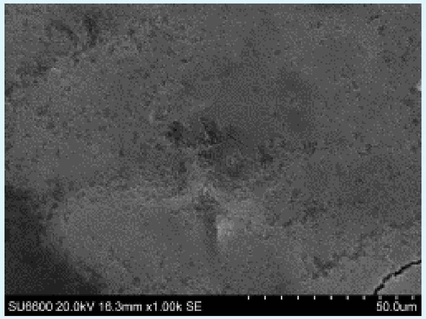
The liquid reaching the emitter tip forms a Taylor cone. A liquid jet is emitted through its apex.

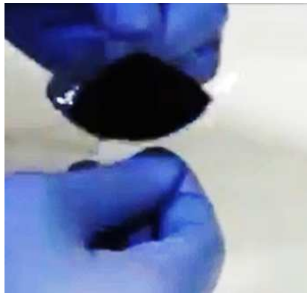
Small and highly charged liquid droplets are radially dispersed by Coulomb repulsion.



Ciemat

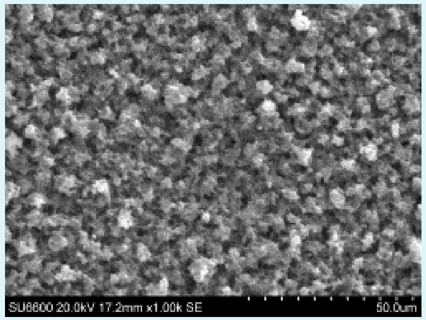
Electrosprayed CB/Nafion colloidal inks: particularities and properties.





− Hydrophobicity+

− Porosity +



Fractal-like structure

Ciemat

The electrospray process for CB/Nafion colloidal inks :

Electrocatalysts

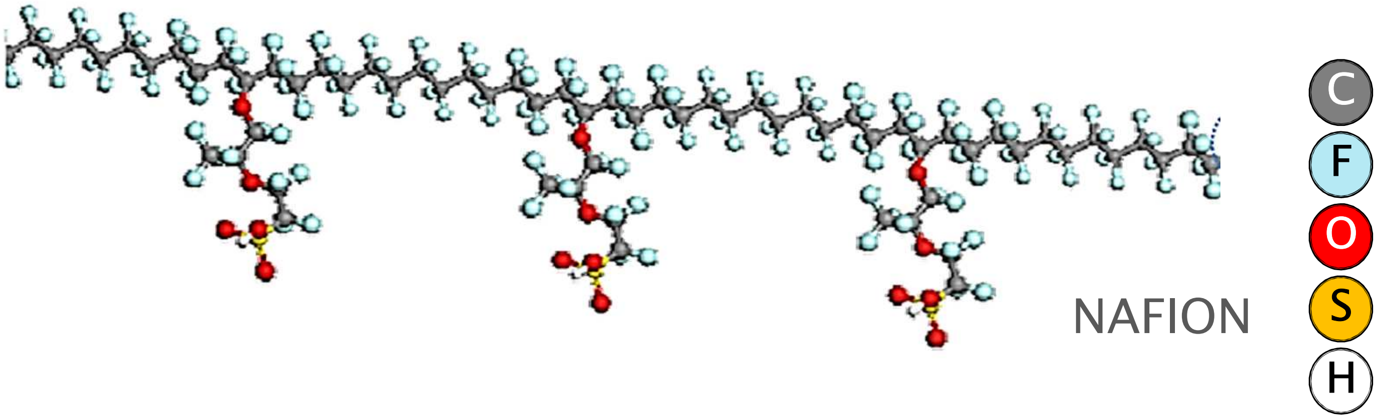
Catalytic layers

Ink deposition techniques

Membrane-electrode assemblies

Cells & stacks

Deeper knowledge on factors affecting the structure of electrosprayed layers to tailor their properties.



- Which is the effect of the electrospray ionization on the Nafion solutions?
- Is the CB-Nafion interaction relevant for the electrosprayed layers?

Ciemat

The electrospray ionization process for Nafion solutions: ESI-MS technique

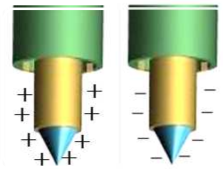
Electrocatalysts

Catalytic layers

Ink deposition techniques

Membrane-electrode assemblies

Cells & stacks



Ionization mode

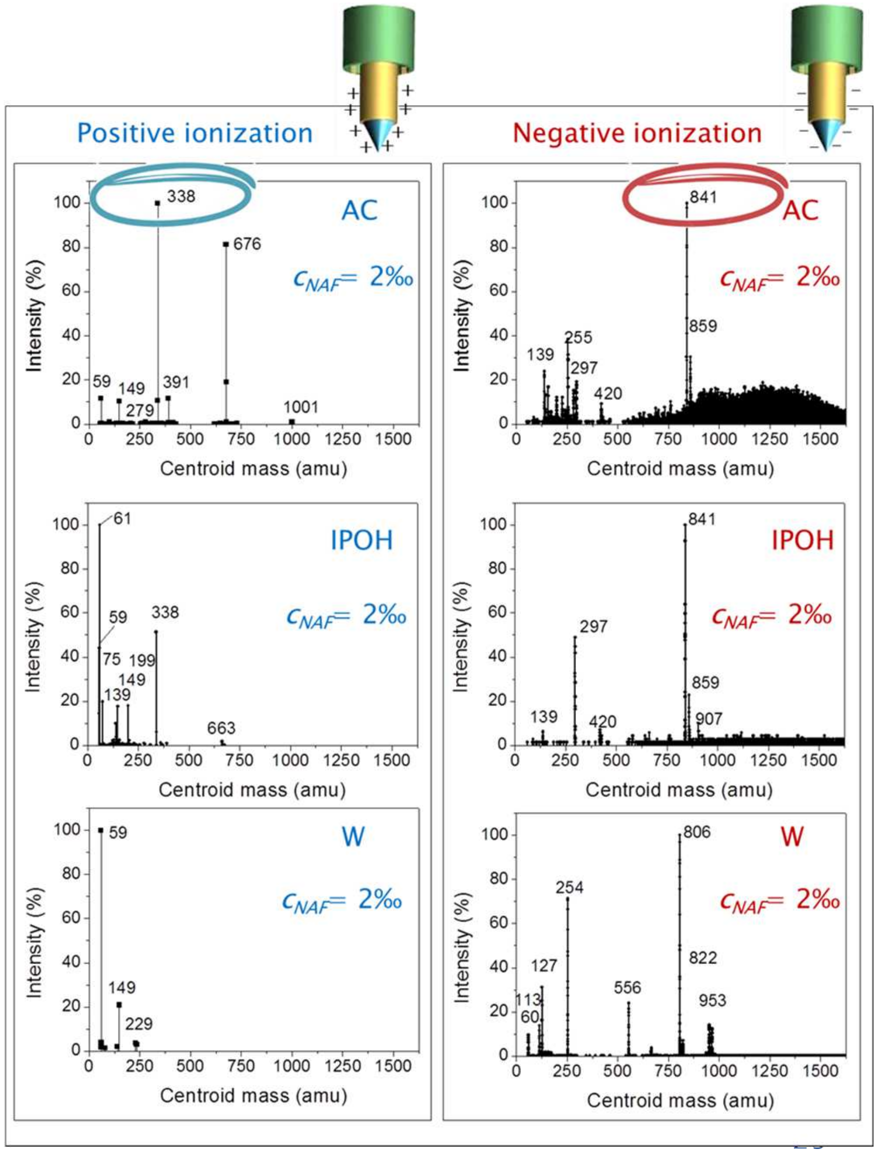
Solvent

Isopropyl alcohol (**IPOH**)
Acetone (**AC**)
Water (**W**)

Larger fragments are obtained for:

AC > IPOH > W

Under negative ionization mode



The electrospray process for Nafion solutions.

Electrocatalysts

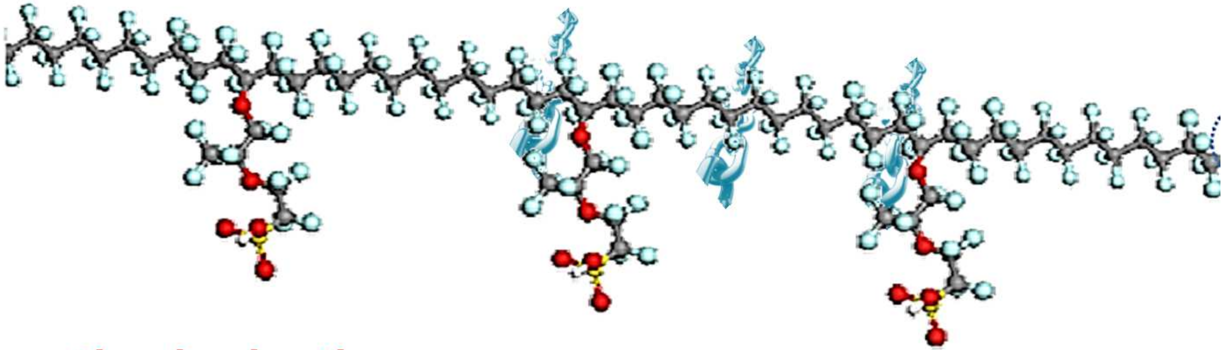
Catalytic layers

Ink deposition techniques

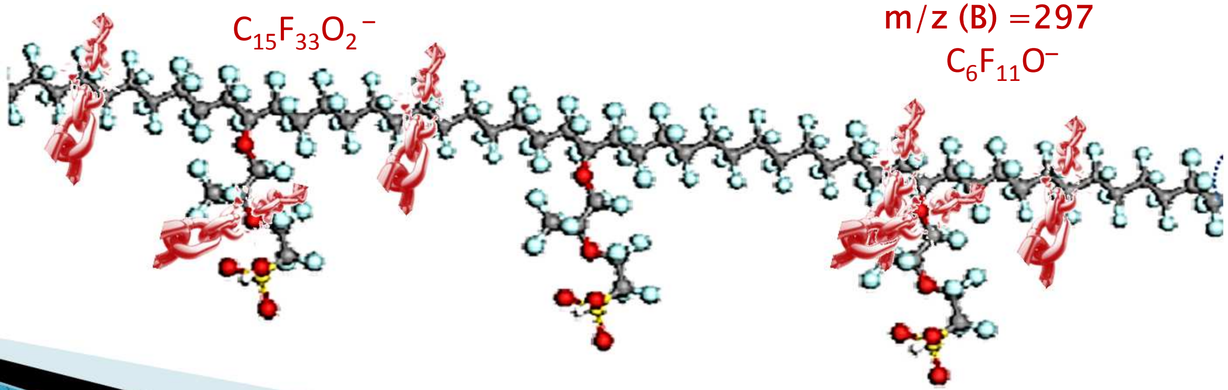
Membrane-electrode assemblies

Cells & stacks

Positive ionization

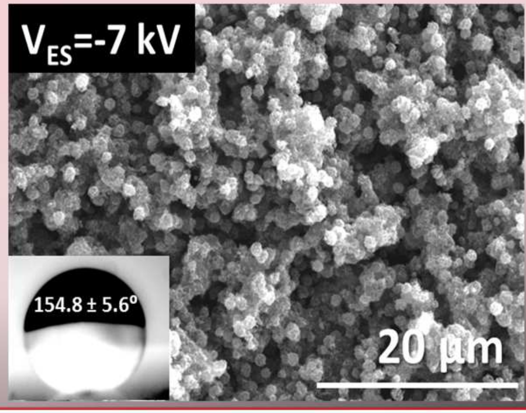


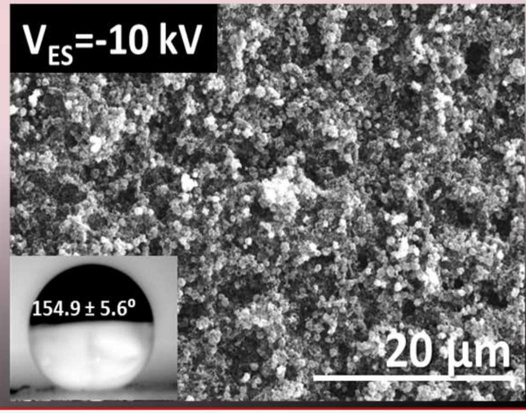
Negative ionization



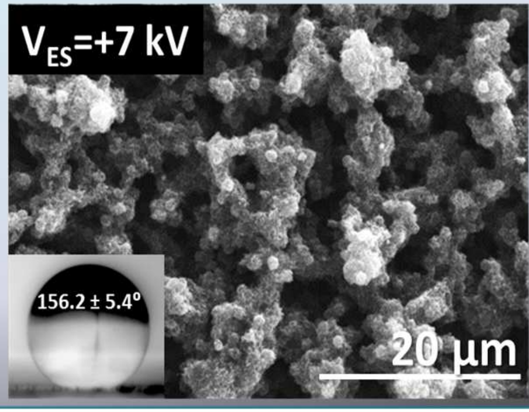
Ionization of CB-Nafion inks:
applied voltage & ionization mode

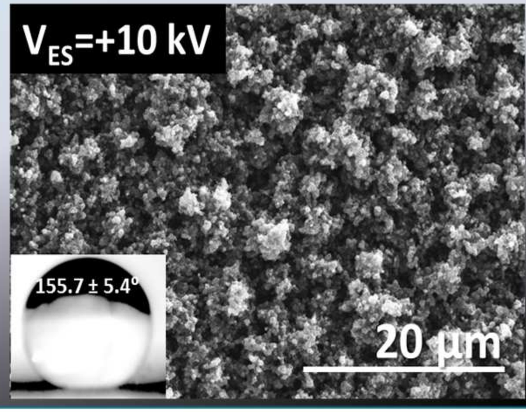
Negative Ionization





Positive ionization





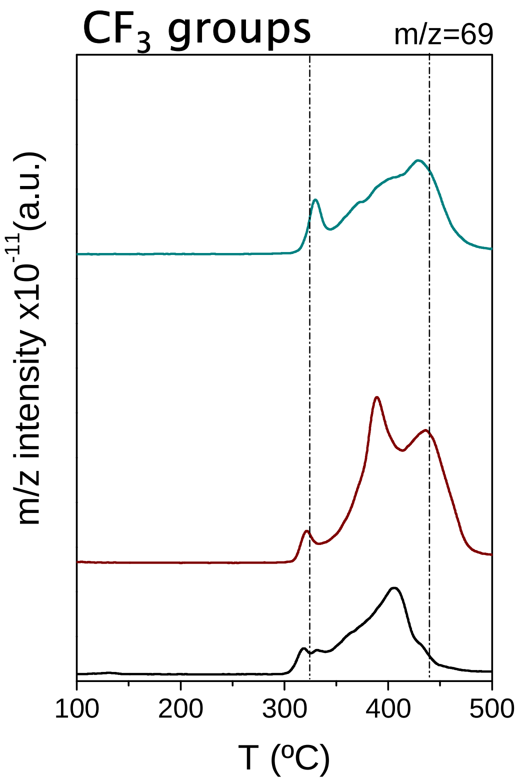
Superhydrophobic films

Ciemat

Interaction of Nafion – CB:

TG/MS – Nafion thermal decomposition under N_2

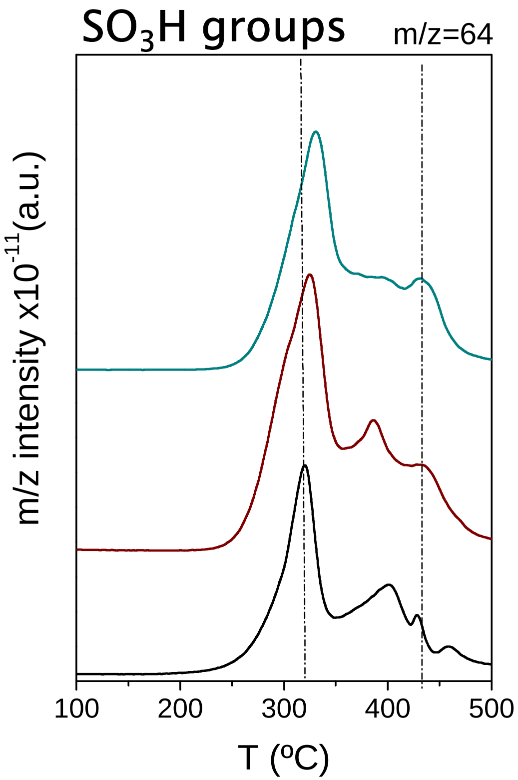
Nafion ionomer



Positive ionization

Negative ionization

No ionization



Interaction of Nafion – CB:

TG/MS – Nafion thermal decomposition under N_2

Electrocatalysts

Catalytic layers

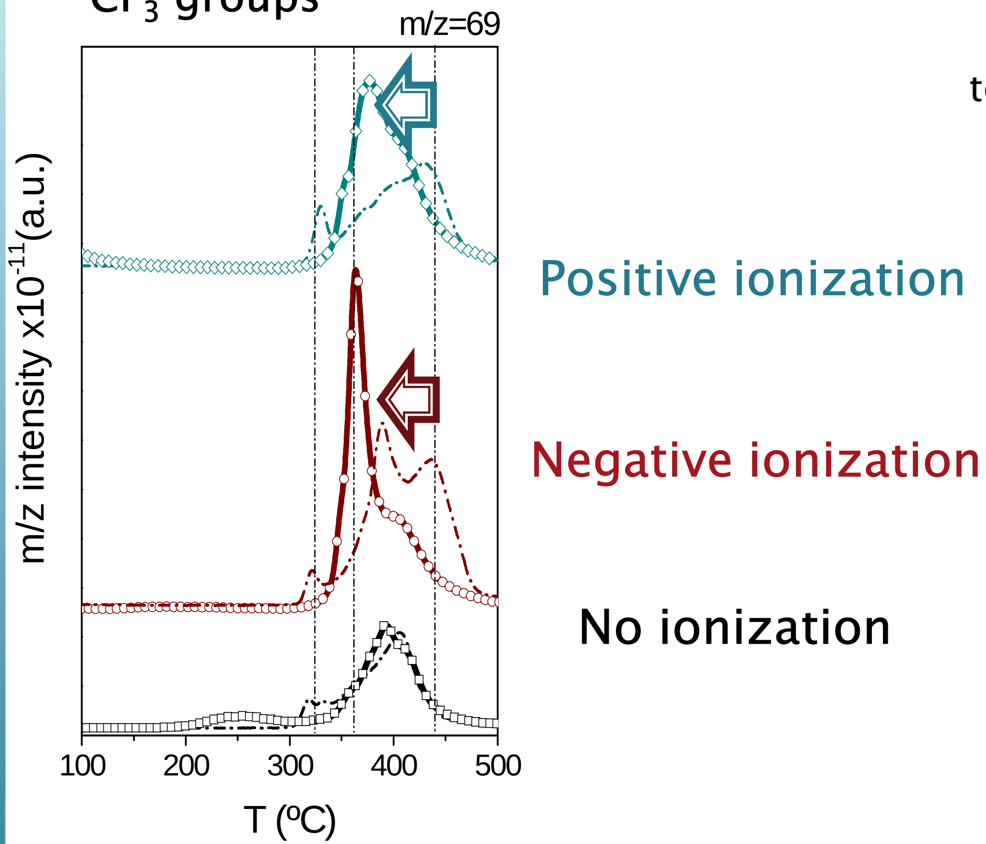
Ink deposition techniques

Membrane-electrode assemblies

Cells & stacks

Nafion vs Nafion-CB

CF_3 groups



The fluorinated chains decompose at lower temperatures in the presence of CB when applying ESI

Electrocatalysts

Catalytic layers

Ink deposition techniques

Membrane-electrode assemblies

Cells & stacks

Interaction of Nafion – CB:

TG/MS – Nafion thermal decomposition under N_2

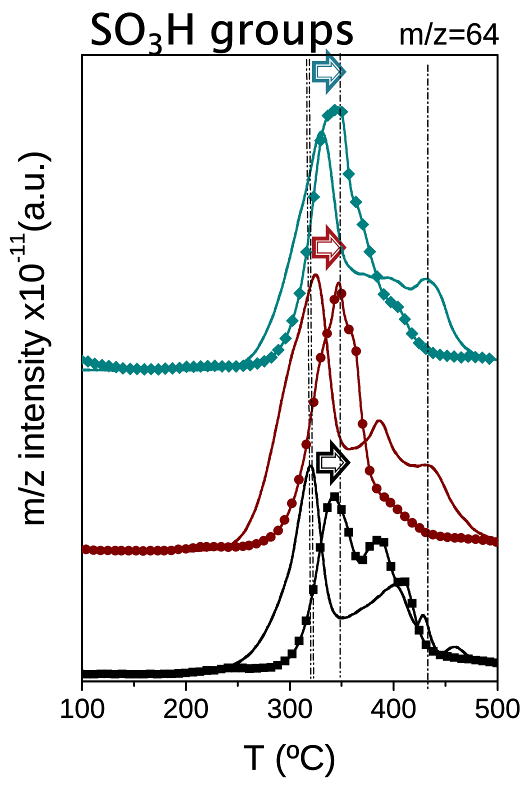
Nafion vs Nafion-CB

The most labile **sulfonic groups** are always stabilized in the presence of CB, even when no ionization is applied

Positive ionization

Negative ionization

No ionization



Electrocatalysts

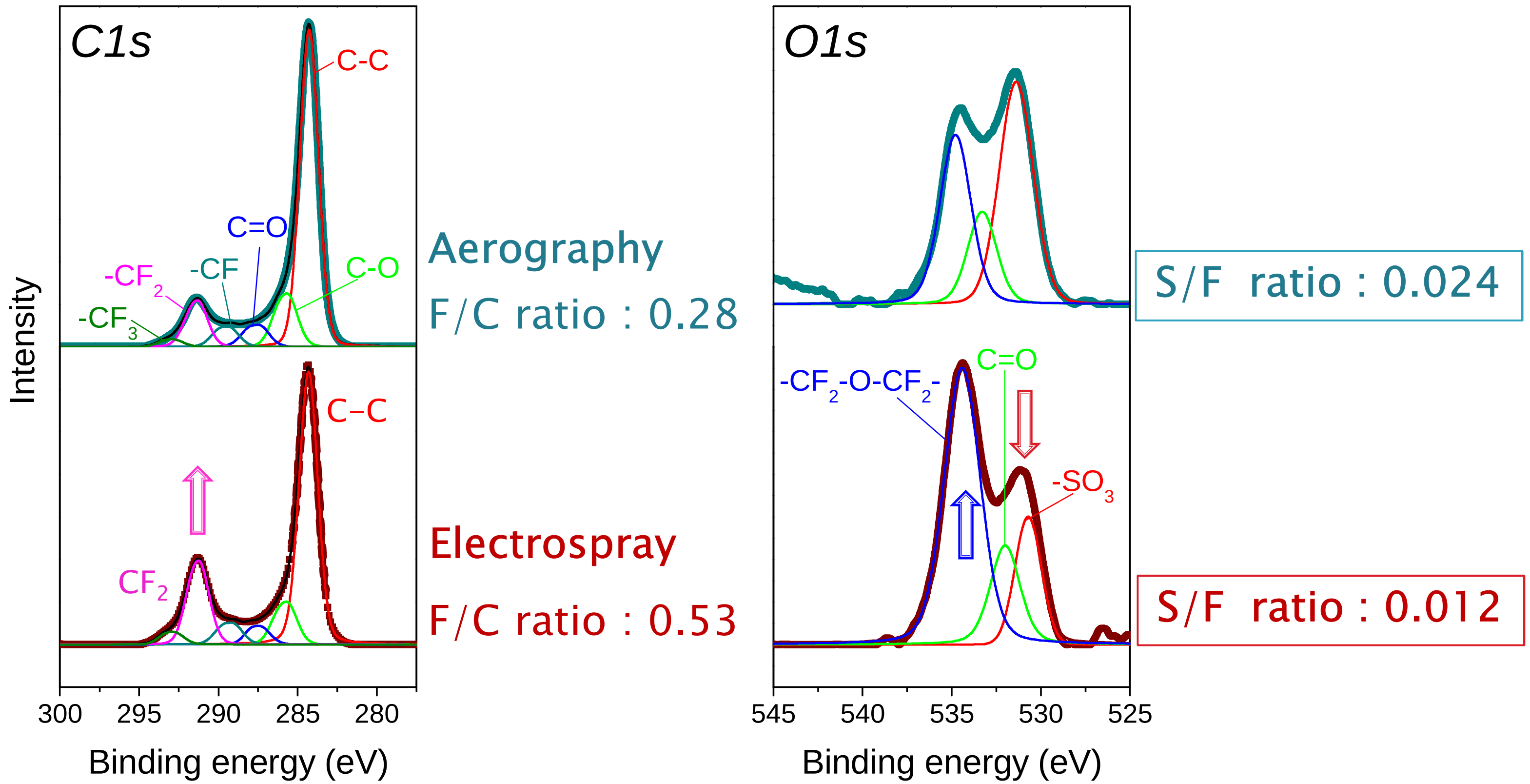
Catalytic layers

Ink deposition techniques

Membrane-electrode assemblies

Cells & stacks

XPS analysis of CB-Nafion films



Perfluorinated chains are better distributed on the CB surface in ES samples

A higher proportion of ether groups as compared to sulfonic groups is always found for ES samples

Ciemat

Proposed model for ES CB-Nafion films

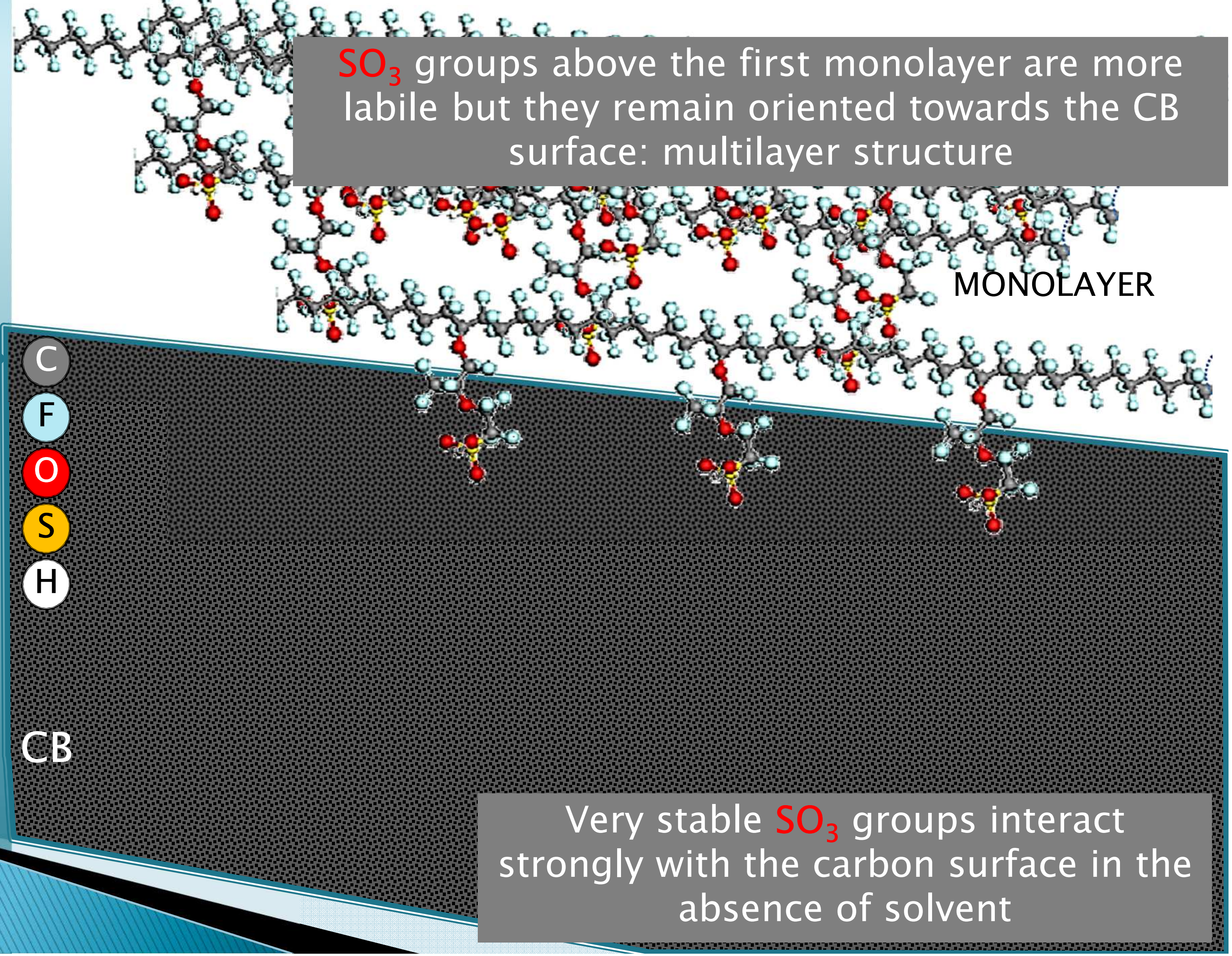
Electrocatalysts

Catalytic layers

Ink deposition techniques

Membrane-electrode assemblies

Cells & stacks



SO_3 groups above the first monolayer are more labile but they remain oriented towards the CB surface: multilayer structure

Very stable SO_3 groups interact strongly with the carbon surface in the absence of solvent

Electrocatalysts

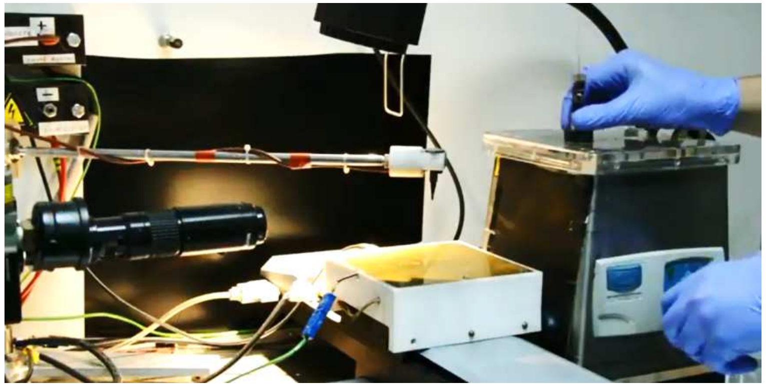
Catalytic layers

Ink deposition techniques

Membrane-electrode assemblies

Cells & stacks

Electrospray application to fuel cell technology



Property of interest: superhydrophobicity

New focus of research:

application of electrosprayed films to produce superhydrophobic protective coatings on metals.

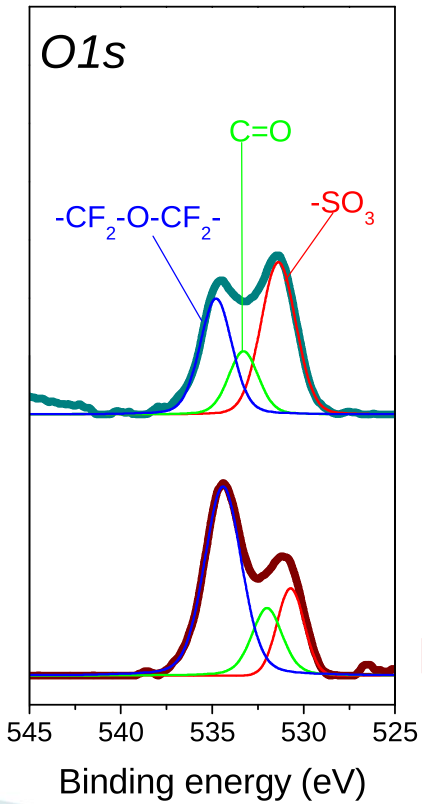
Ciemat

XPS analysis:
protection against corrosion of CB-Nafion films

SS plate covered with a thin film of 20wt% Nafion-CB

Corrosion test

Before

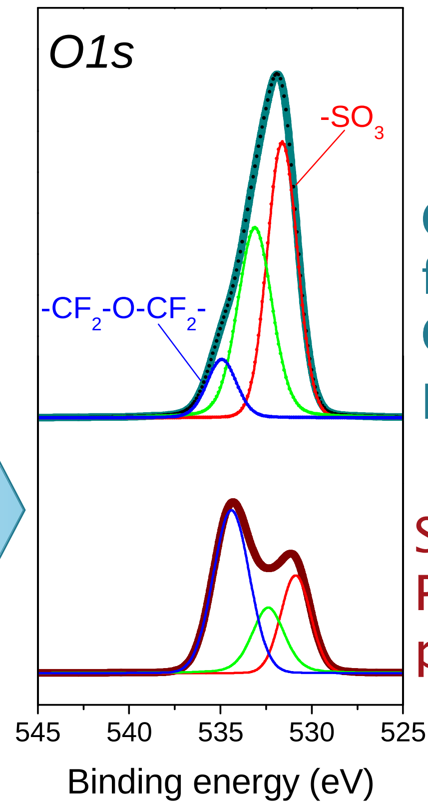


Aerography

Continuous CV (0.1-0.9 V) for 30 h

Electrospray

After corrosion test



Oxidized film Corroded plate

Stable film Protected plate

Membrane-electrode assemblies

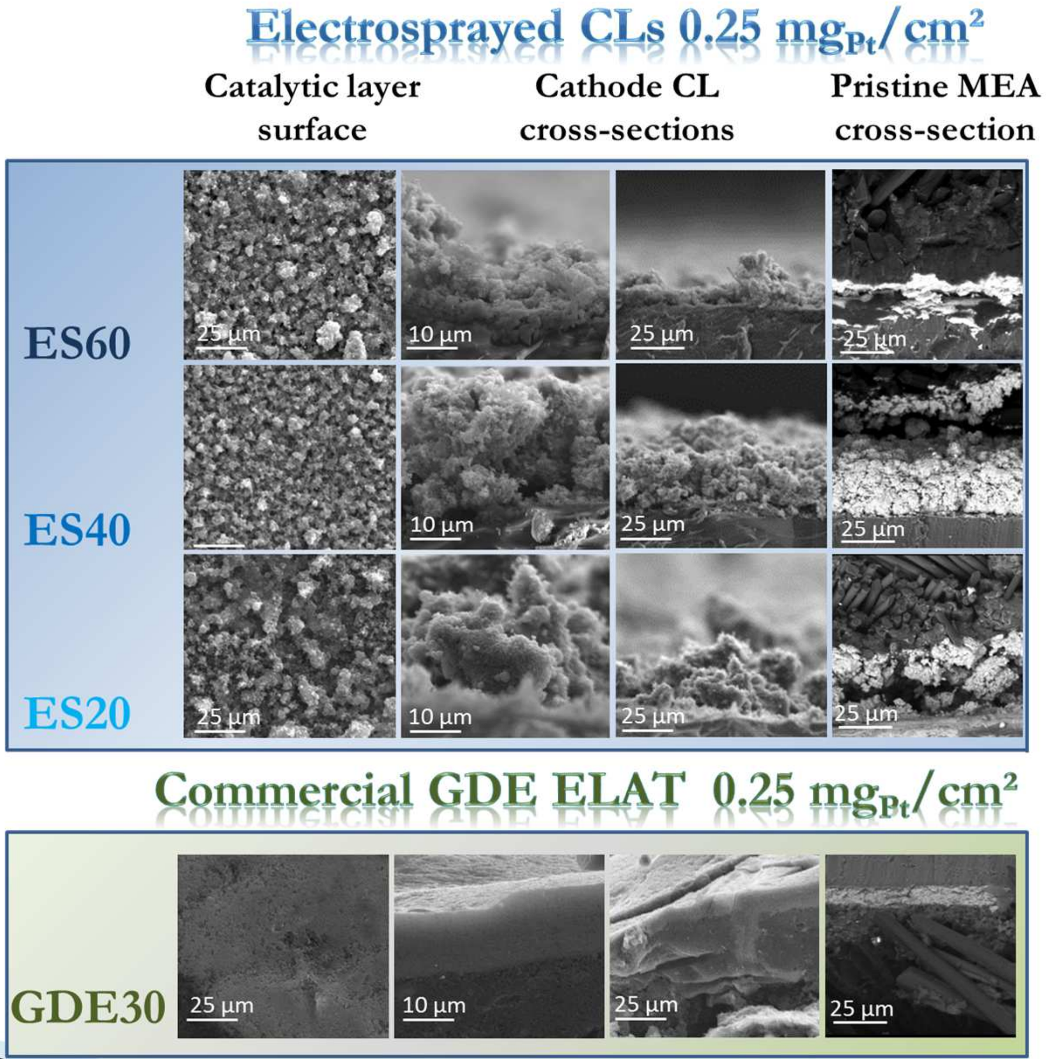
Electrocatalysts

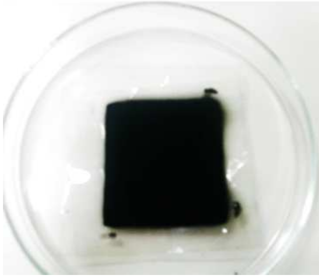
Catalytic layers

Ink deposition techniques

Membrane-electrode assemblies

Cells & stacks





Membrane-electrode assemblies

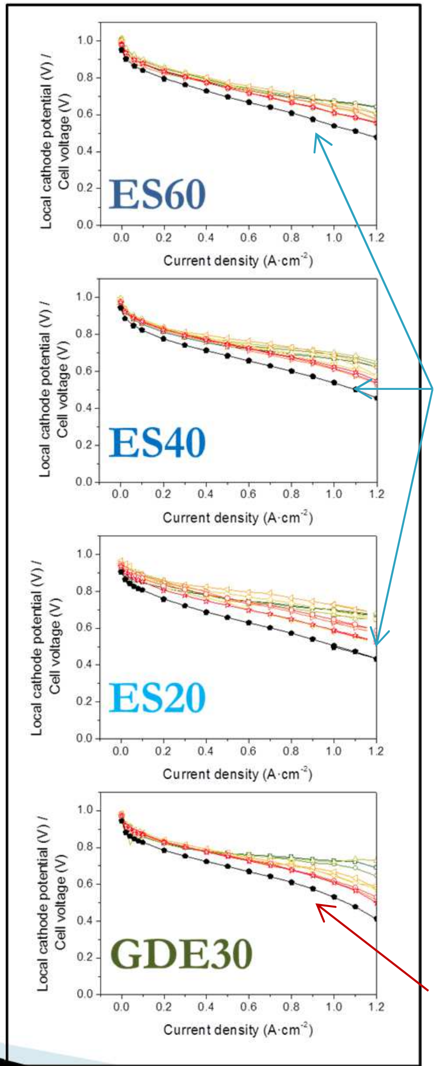
Electrocatalysts

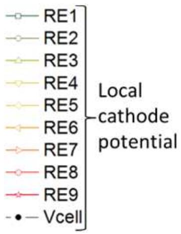
Catalytic layers

Ink deposition techniques

Membrane-electrode assemblies

Cells & stacks



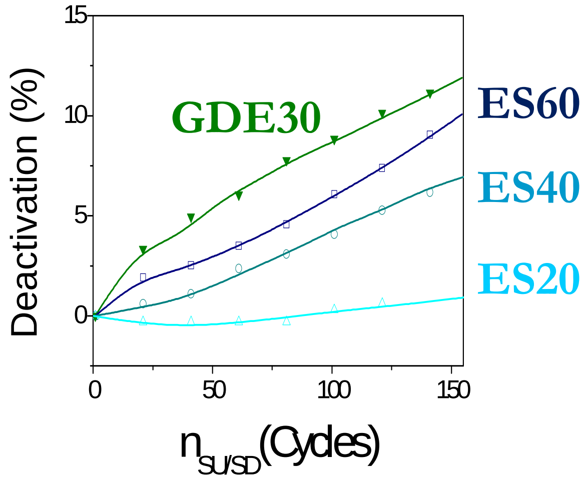


Improved mass transport for ES-CLs

Mass transport limitation at the cathode outlet at high current densities

Accelerated stress tests by start-up/shut-down of the cells

Cell performance degradation vs $[Pt]_{CL}$



Lower degradation rate for ES-CLs

PEMFCs stacks assembly

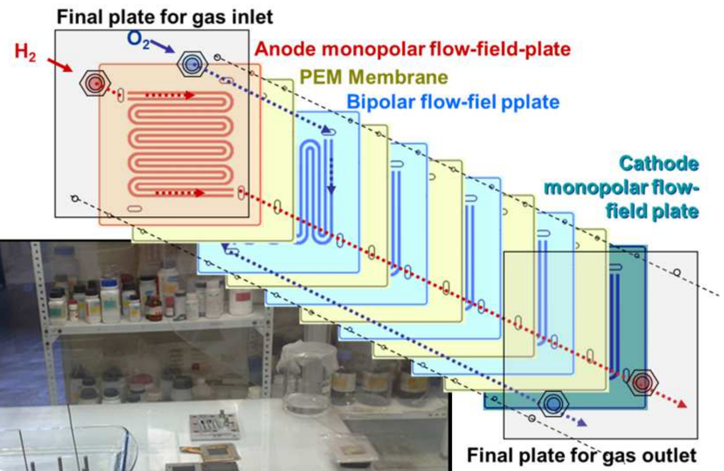
Electrocatalysts

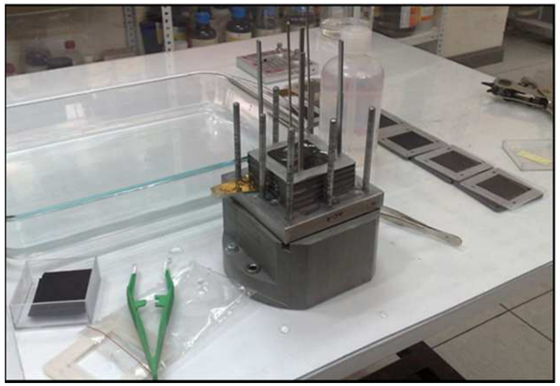
Catalytic layers

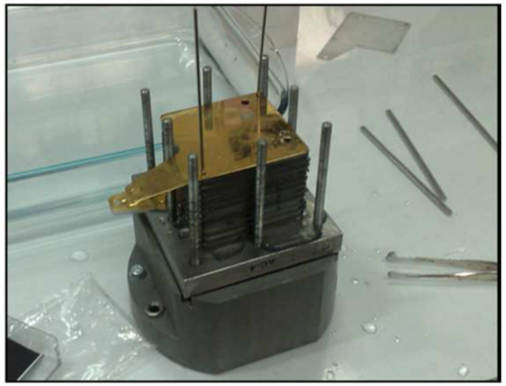
Ink deposition techniques

Membrane-electrode assemblies

Cells & stacks







PEMFC stack tests

Electrocatalysts

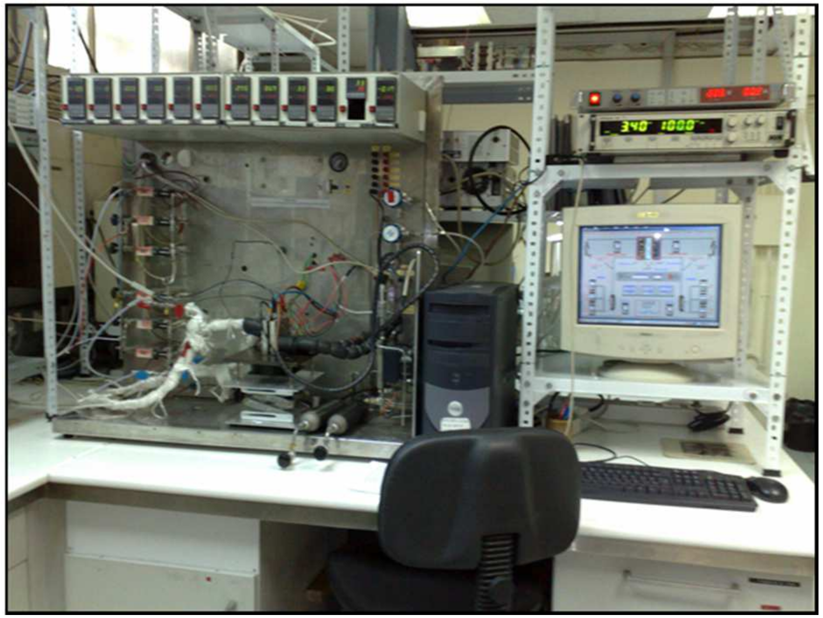
Catalytic layers

Ink deposition techniques

Membrane-electrode assemblies

Cells & stacks

- PEMFC bench for performance evaluation of cells and stacks following standard protocols.



New designs for PEMFCs

Electrocatalysts

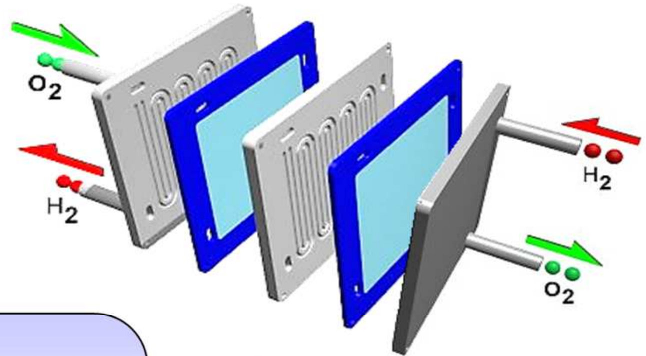
Catalytic layers

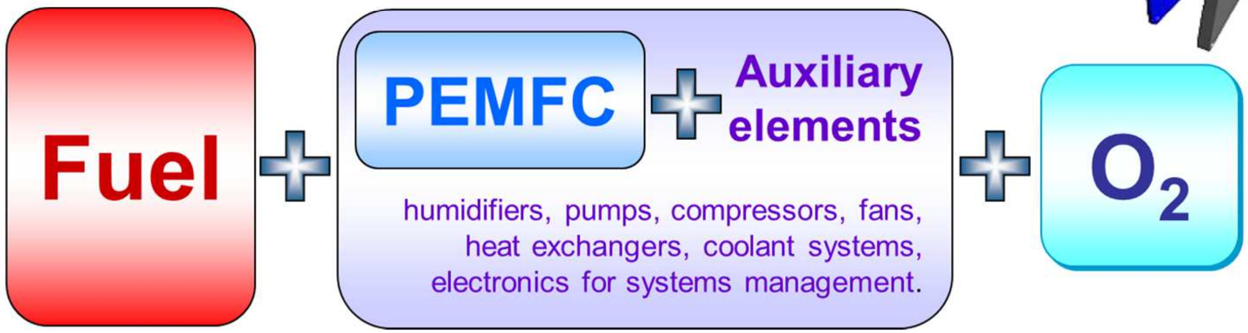
Ink deposition techniques

Membrane-electrode assemblies

Cells & stacks

- Fuel cells are apparently simple devices.





- They need many auxiliary elements to obtain high performance.

New designs for PEMFCs

Electrocatalysts

Catalytic layers

Ink deposition techniques

Membrane-electrode assemblies

Cells & stacks

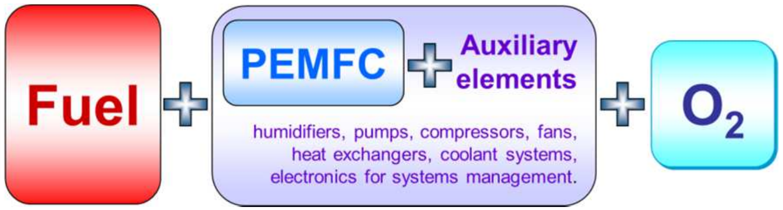
Conventional PEMFC systems:

- Very complex
- Very heavy
- Very voluminous

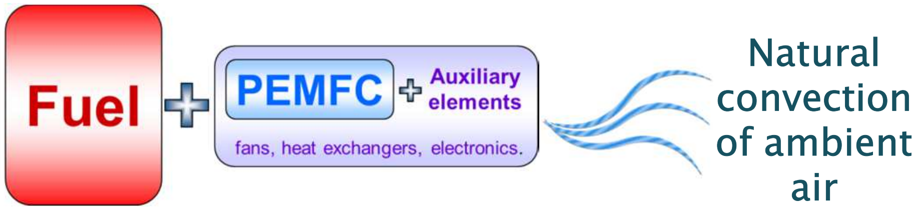
Ciemat

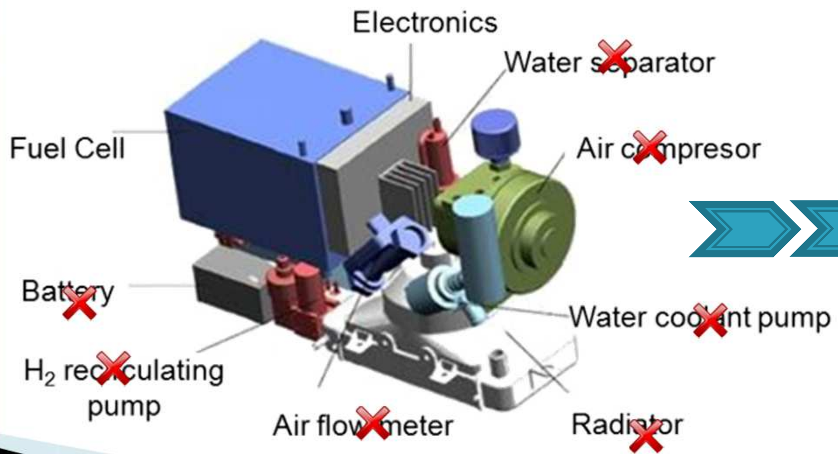
Increasing energy density in PEMFCs

- Fuel cells towards miniaturization



- Passive systems will yield lower performance but higher energy density

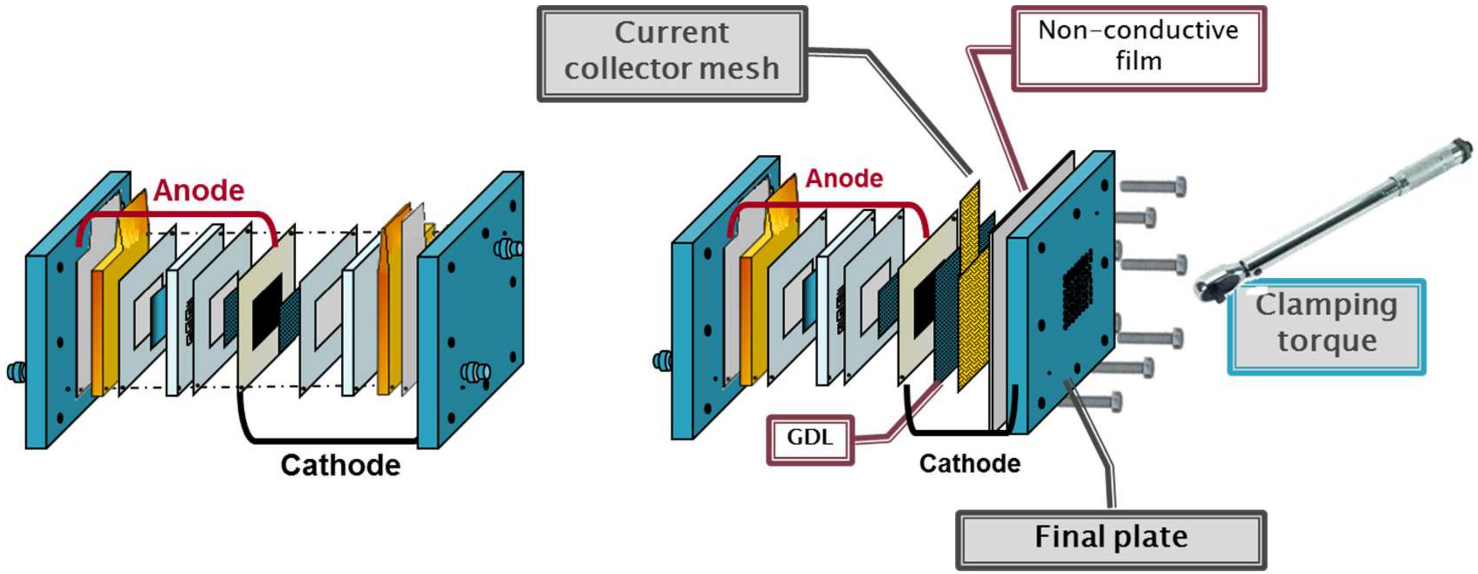




Open cathode architecture

- Electrocatalysts
- Catalytic layers
- Ink deposition techniques
- Membrane-electrode assemblies
- **Cells & stacks**

Progressive modification of the concept of a conventional PEMFC.



Open cathode architecture

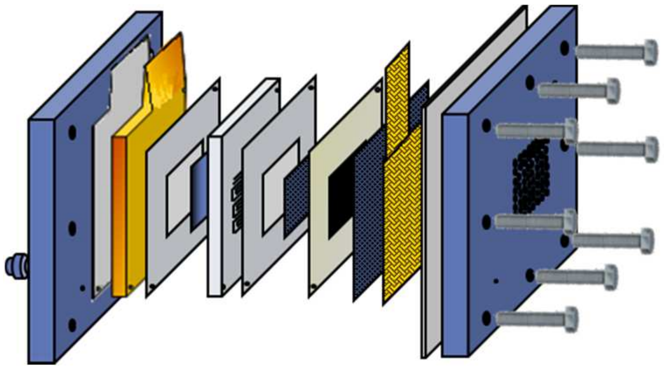
Electrocatalysts

Catalytic layers

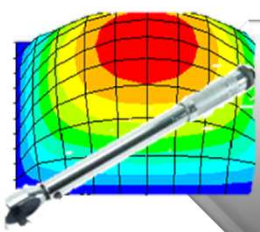
Ink deposition techniques

Membrane-electrode assemblies

Cells & stacks



Cathode plates allowing for air accessibility and water removal

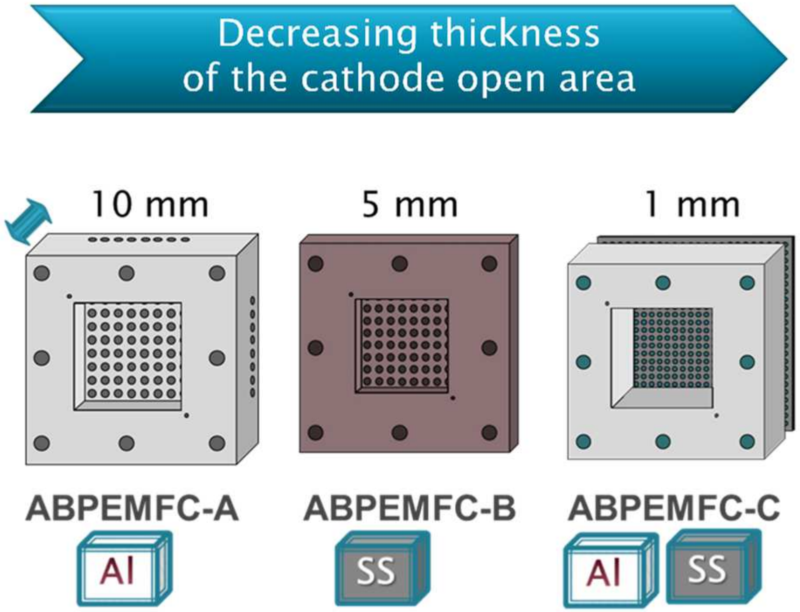


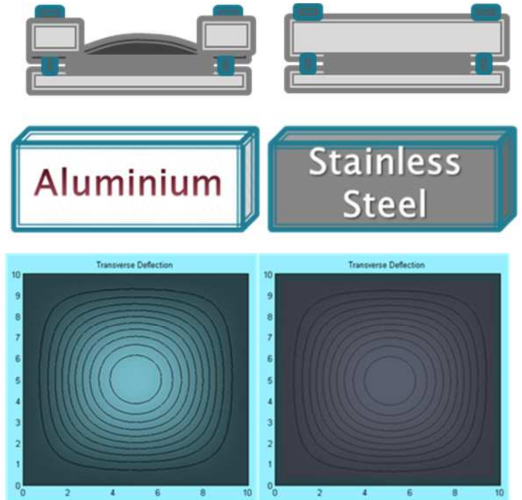
Homogeneous distribution of the clamping pressure

Efficient current collection from the GDE (metal mesh)

Open cathode architecture:
End plate thickness and clamping pressure

Material properties (stiffness, flexural strength)





Transverse deflection
Clamped, Square Isotropic Plate
With a Uniform Pressure Load

Open cathode architecture

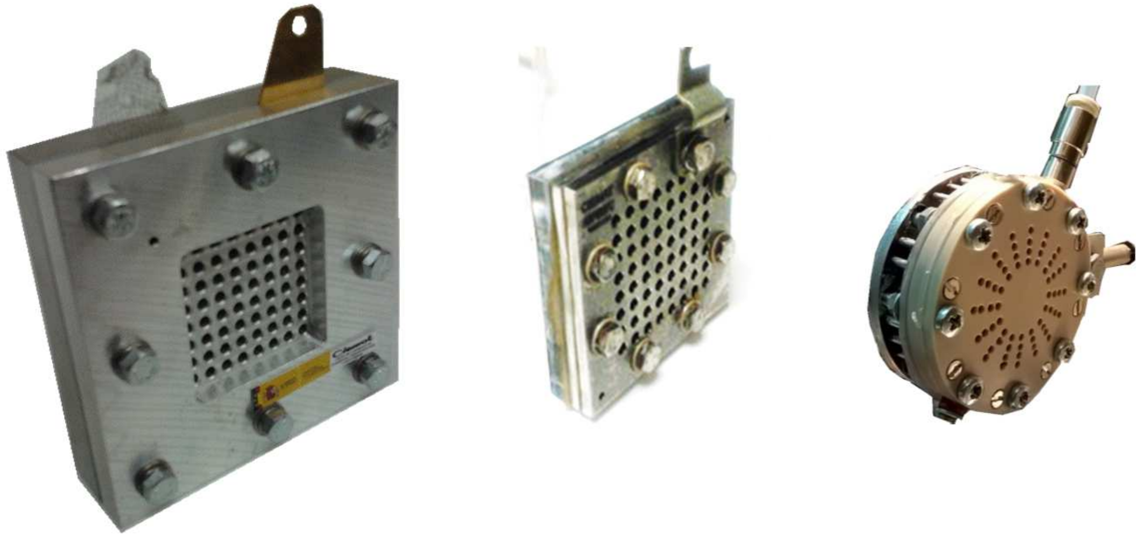
Electrocatalysts

Catalytic layers

Ink deposition techniques

Membrane-electrode assemblies

Cells & stacks



The evolution

Water management in PEMFCs

Electrocatalysts

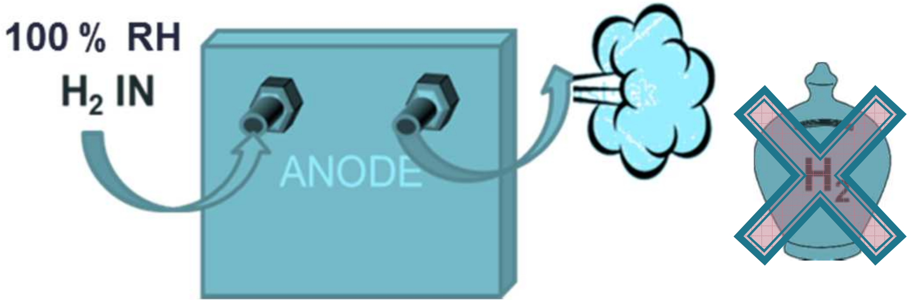
Catalytic layers

Ink deposition techniques

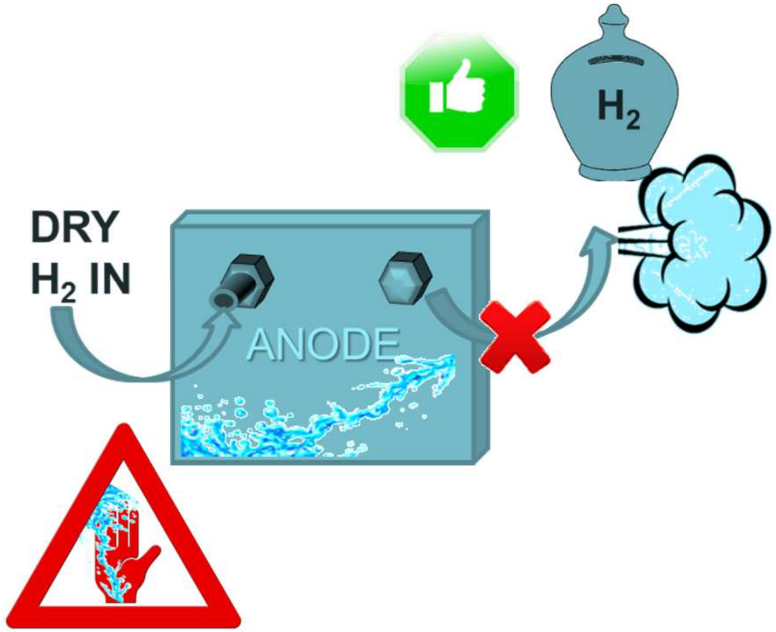
Membrane-electrode assemblies

Cells & stacks

Optimal operation: usually achieved with fully humidified flow-through anode (**FTA**).

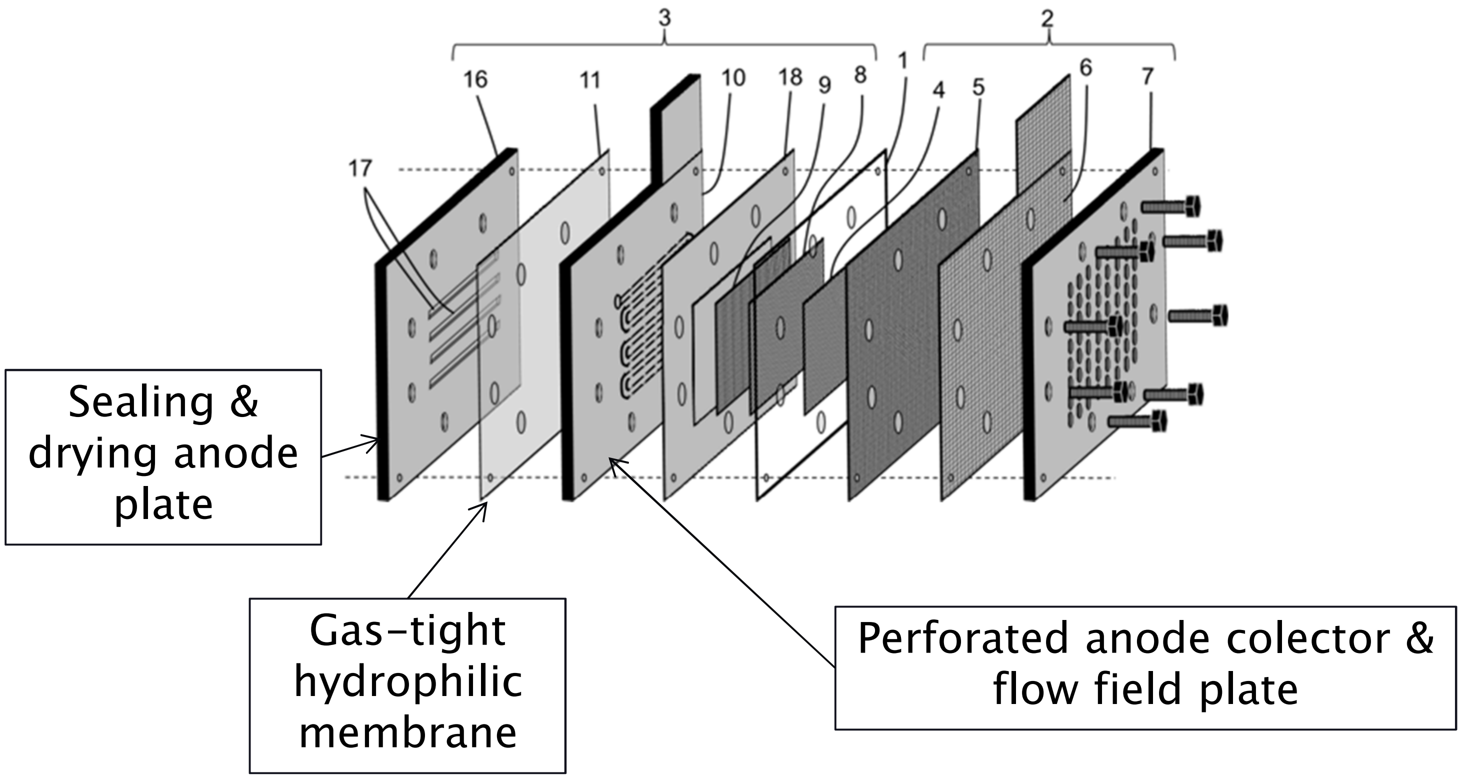


Dead-Ended Anode (**DEA**) mode and natural air convection cathode are preferred for compact FC systems.



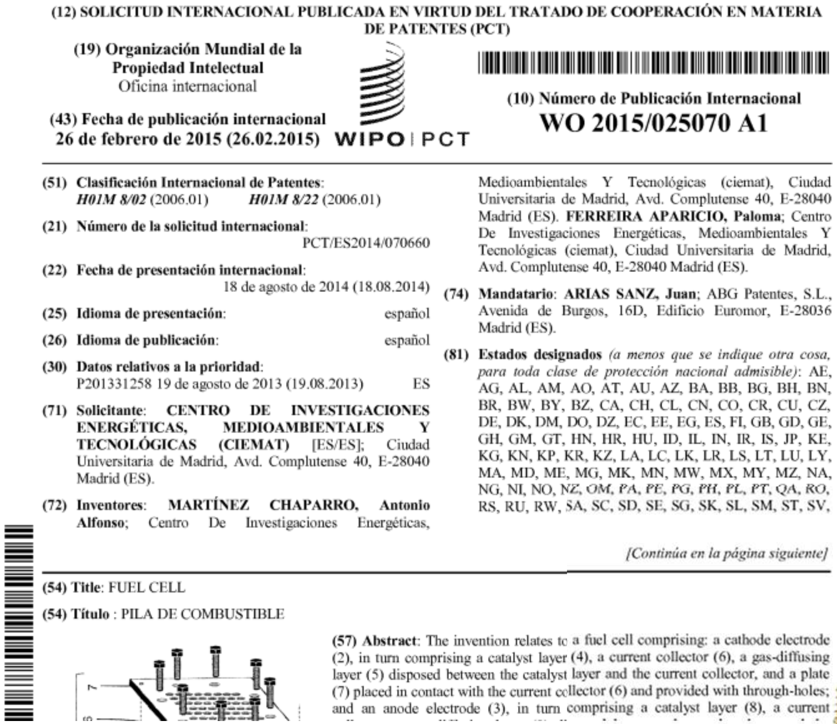
DEA operation mode for PEMFCs

For completely passive air-breathing PEMFCs, water management poses a **big challenge** under DEA operation. This new configuration allows continuous stable performance.



AIR BREATHING FUEL CELL:
A NOVEL HARDWARE CONFIGURATION

- Electrocatalysts
- Catalytic layers
- Ink deposition techniques
- Membrane-electrode assemblies
- **Cells & stacks**



(12) SOLICITUD INTERNACIONAL PUBLICADA EN VIRTUD DEL TRATADO DE COOPERACIÓN EN MATERIA DE PATENTES (PCT)

(19) Organización Mundial de la Propiedad Intelectual
Oficina internacional

(43) Fecha de publicación internacional
26 de febrero de 2015 (26.02.2015)

WIPO | PCT

(10) Número de Publicación Internacional
WO 2015/025070 A1

(51) Clasificación Internacional de Patentes:
H01M 8/02 (2006.01) *H01M 8/22* (2006.01)

(21) Número de la solicitud internacional:
PCT/ES2014/070660

(22) Fecha de presentación internacional:
18 de agosto de 2014 (18.08.2014)

(25) Idioma de presentación: español

(26) Idioma de publicación: español

(30) Datos relativos a la prioridad:
P201331258 19 de agosto de 2013 (19.08.2013) ES

(71) Solicitante: **CENTRO DE INVESTIGACIONES ENERGÉTICAS, MEDIOAMBIENTALES Y TECNOLÓGICAS (CIEMAT)** [ES/ES]; Ciudad Universitaria de Madrid, Avd. Complutense 40, E-28040 Madrid (ES).

(72) Inventores: **MARTÍNEZ CHAPARRO, Antonio Alfonso**; Centro De Investigaciones Energéticas, Medioambientales Y Tecnológicas (ciemat), Ciudad Universitaria de Madrid, Avd. Complutense 40, E-28040 Madrid (ES). **FERREIRA APARICIO, Paloma**; Centro De Investigaciones Energéticas, Medioambientales Y Tecnológicas (ciemat), Ciudad Universitaria de Madrid, Avd. Complutense 40, E-28040 Madrid (ES).

(74) Mandatario: **ARIAS SANZ, Juan**; ABG Patentes, S.L., Avenida de Burgos, 16D, Edificio Euromor, E-28036 Madrid (ES).

(81) Estados designados *(a menos que se indique otra cosa, para toda clase de protección nacional admisible)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV,

[Continúa en la página siguiente]

(54) Title: FUEL CELL

(54) Título : PILA DE COMBUSTIBLE

(57) **Abstract**: The invention relates tc a fuel cell comprising: a cathode electrode (2), in turn comprising a catalyst layer (4), a current collector (6), a gas-diffusing layer (5) disposed between the catalyst layer and the current collector, and a plate (7) placed in contact with the current cellector (6) and provided with through-holes; and an anode electrode (3), in turn comprising a catalyst layer (8), a current

ES 2466590 A1

10/04/2014

- Completely **passive**.
- Novel anode design for dead-ended operation
- ***Stoichiometric*** $\mathbf{H_2}$ **consumption**.

Electrocatalysts

Catalytic layers

Ink deposition techniques

Membrane-electrode assemblies

Cells & stacks

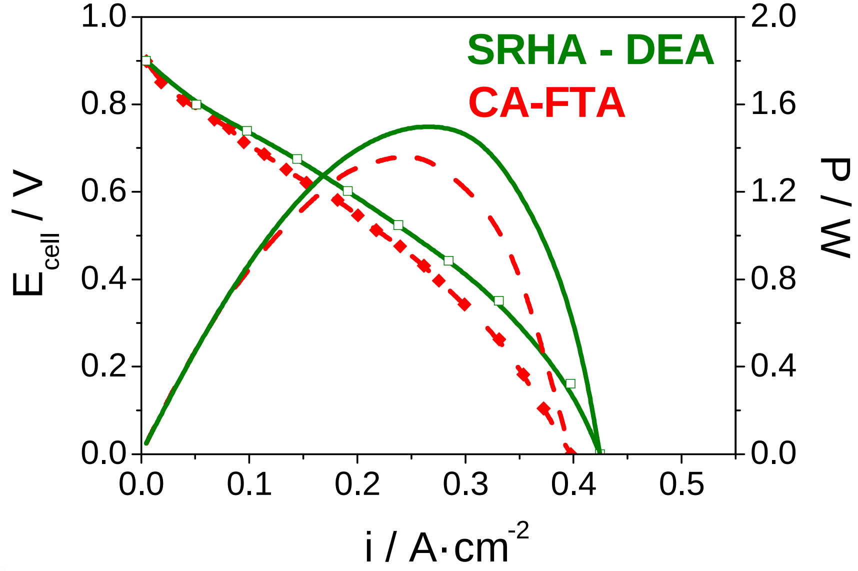
SRHA – DEA vs. CA – FTA

Self-Regulating Humidity Anode under Dead-Ended operation with dry H_2 (SRHA-DEA)

Conventional Anode (CA) operating with flowing – through dry H_2 (CA-FTA)

Climatic chamber conditions:
40% RH
298 K

More efficient water management and improved performance.



Temperature impact – EIS analysis
SRHA–DEA vs CA–FTA

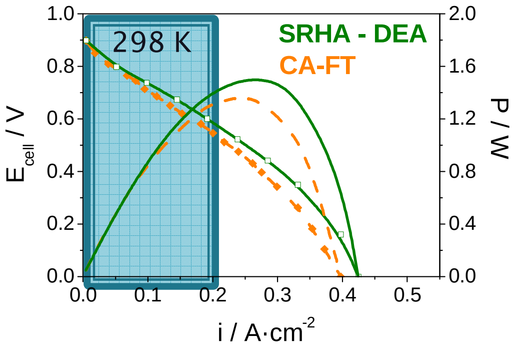
Electrocatalysts

Catalytic layers

Ink deposition techniques

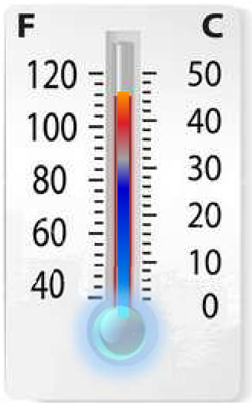
Membrane–electrode assemblies

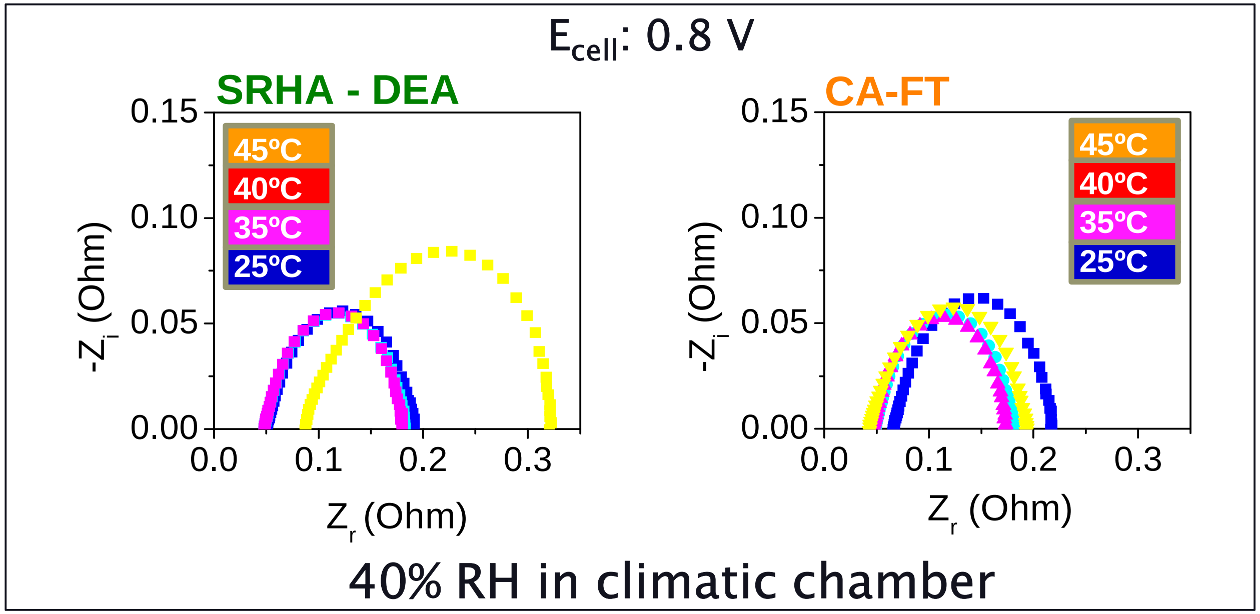
Cells & stacks



i<0.2 A·cm^{-2}: ANODE flooding conditions

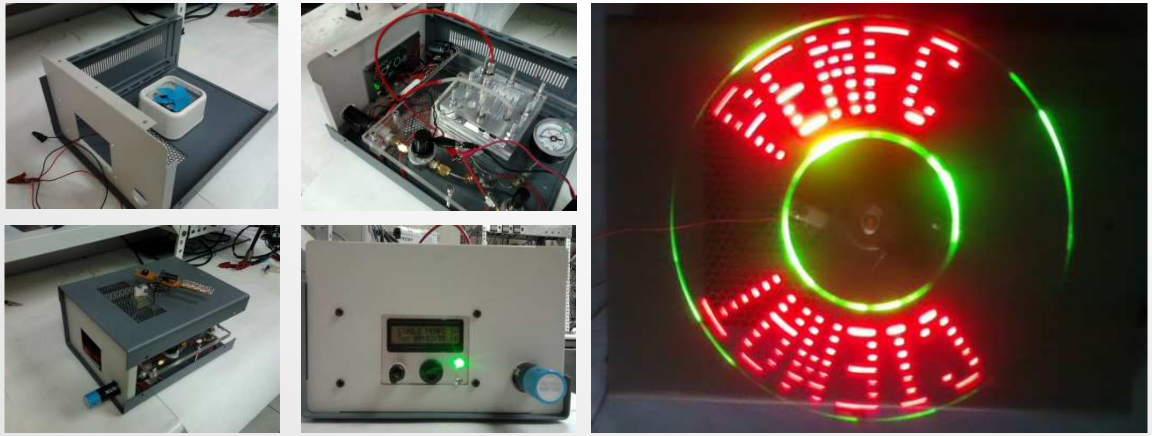
SRHA–DEA performance is less dependent on external temperature than CA–FTA up to 40ºC.





Portable applications

System components and assembly

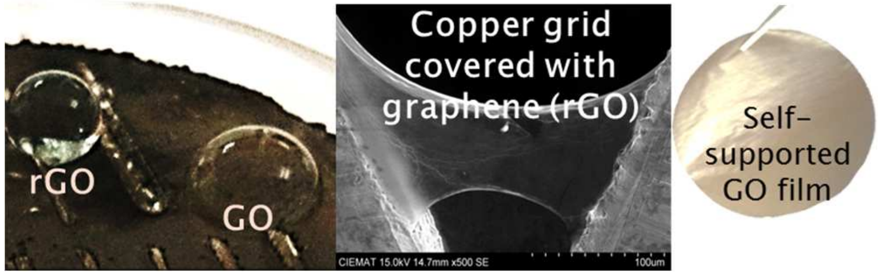


E-LIG-E project (2016-2019)
Efficient and LIGght Energy

- Improving the cell
- Fabricating test planar passive stacks
- Demostrating their operation in portable applications

E-LIG-E: improving the cell

Applications of **reduced graphene oxide (rGO)** and **graphene oxide (GO)** on FC contacts and other surfaces: water management



Applications of **electrosprayed carbon coatings** in contacts and electrodes: corrosion protection and hydrophobicity

Applications of **additive manufacturing** (FDM) to reduce cost, and weight.
Tests with different termoplastic polymers.
3D printed PEMFCs

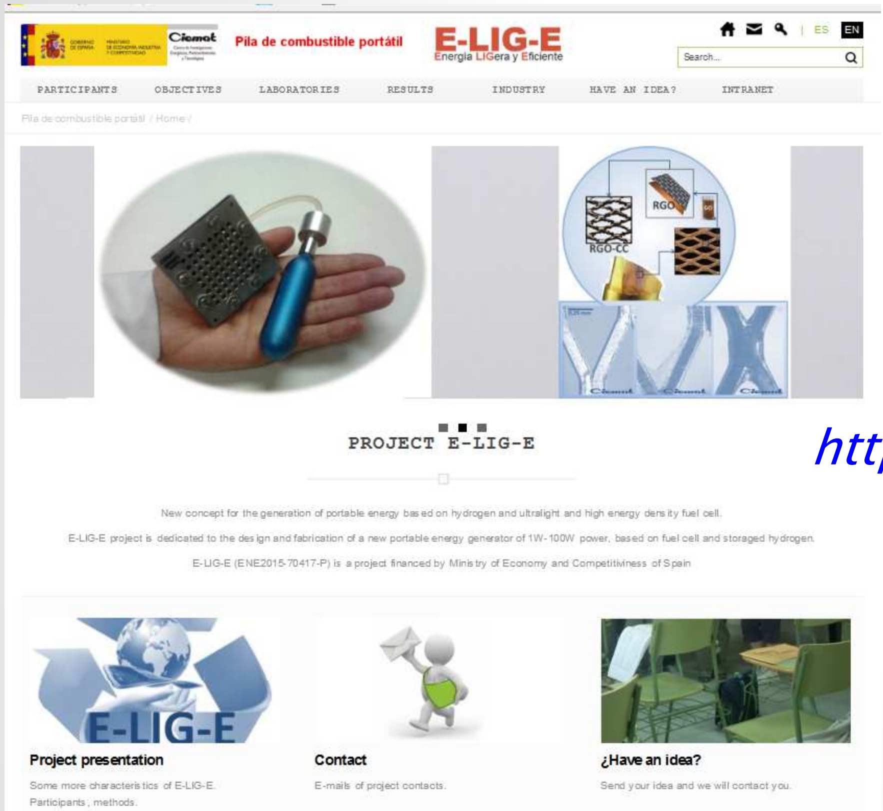
E-LIG-E:
participants from 4 CIEMAT units

- Fuel Cells – PEMFC group
- Microscopy and Surface Analysis
- Electronics
- Energy Systems Analysis

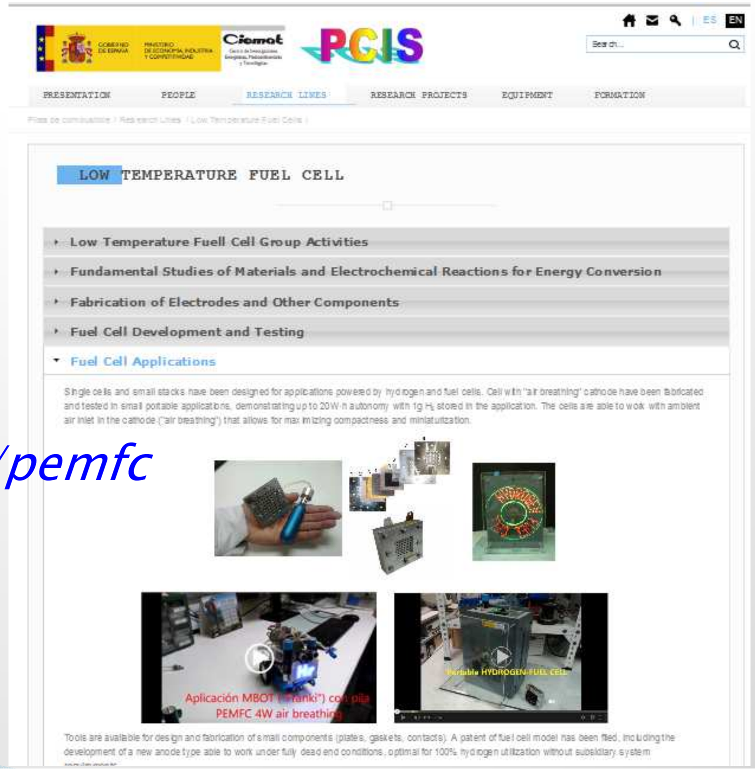
E-LIG-E project (2016-2019)
Efficient and LIGght Energy

Next application:

Zeppelin with 3 motors.
powered by
Ciemat's air breathing
PEMFC stack.



http://projects.ciemat.es/web/elige



http://rdgroups.ciemat.es/web/pilascomb/pemfc

Julio José Conde-López
Alba María Fernández Sotillo
Paloma Ferreira-Aparicio
Antonio Martínez Chaparro
Mª Antonio Folgado Martínez
Marco Antonio Galarza Díaz

Thank You

paloma.ferreira@ciemat.es

+34 91 346 0897

CIEMAT
Avda. Complutense 40.
Madrid. E-28040.

www.ciemat.es

Ciemat