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DE ESPAÑA

MINISTERIO
DE ECONOMÍA
Y COMPETITIVIDAD

Ciemat

Centro de Investigaciones
Energéticas, Medioambientales
y Tecnológicas

Tailoring electrosprayed carbon layers

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EUROPEAN
FUEL CELL FORUM

A0704

Outline

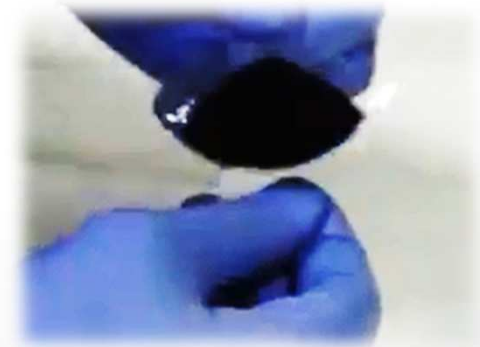
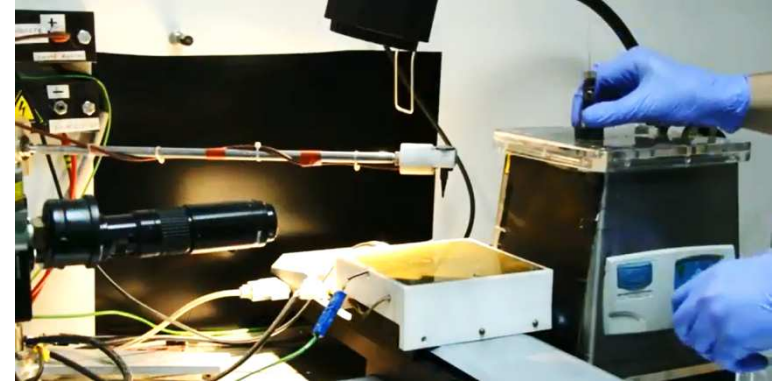
- The electrospray process applied to FC technology
- Main objective of the study
- Our approach
- Results and conclusions

Electrospray application to fuel cell technology

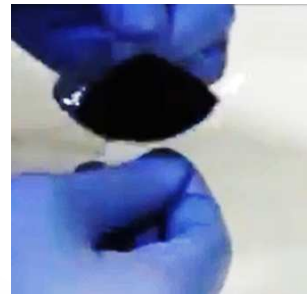
Colloidal inks: deposition of particles for nanostructures

Usually applied to produce catalytic layers or gas diffusion layers.

More recently, it has been applied to produce superhydrophobic protective coatings.

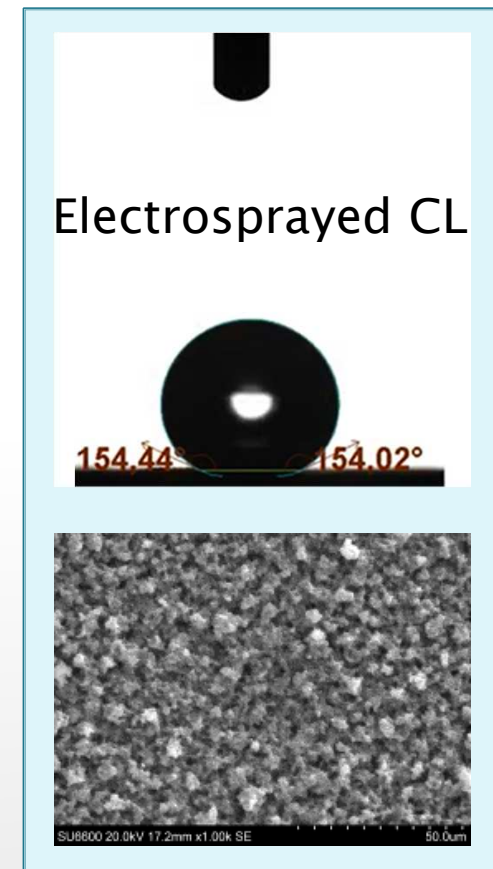


Electrosprayed CB/Nafion colloidal inks: particularities and properties.



- Hydrophobicity +

- Porosity +



Fractal-like structure

Main objective of the study:

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

- Which are the main factors influencing the electrospray process on Nafion/CB inks?
- Is there any relationship between the microstructure of electrosprayed layers, the ink composition, and the electrospraying conditions?
- Is the CB–Nafion interaction relevant for the electrosprayed layers?

Our approach

Analyses of Nafion solutions by mass spectrometry dosed by electrospray ionization (ESI-MS).

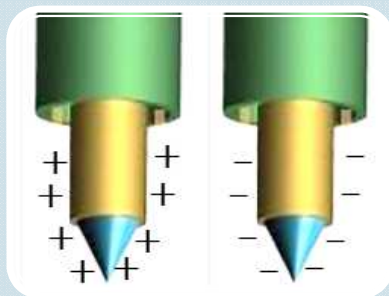
Analysis of films prepared by ESI of **CB-Nafion** inks under different conditions.

Film characterization by:

- SEM
- Tensiometry (Water contact angle)
- TG/MS
- XPS

The electrospray ionization process for Nafion solutions.

ESI-MS technique:



Ionization mode:
Positive
Negative



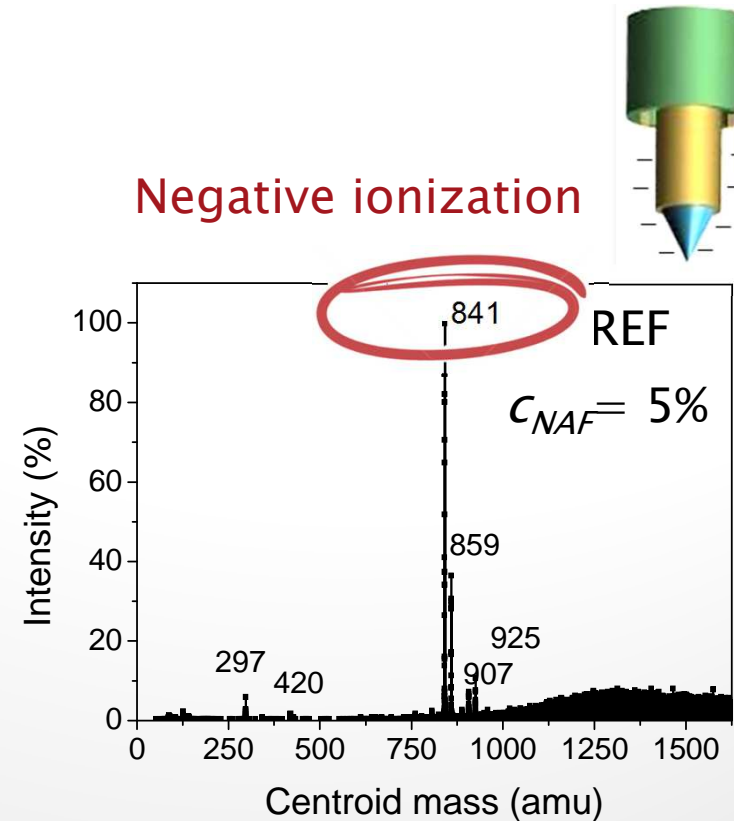
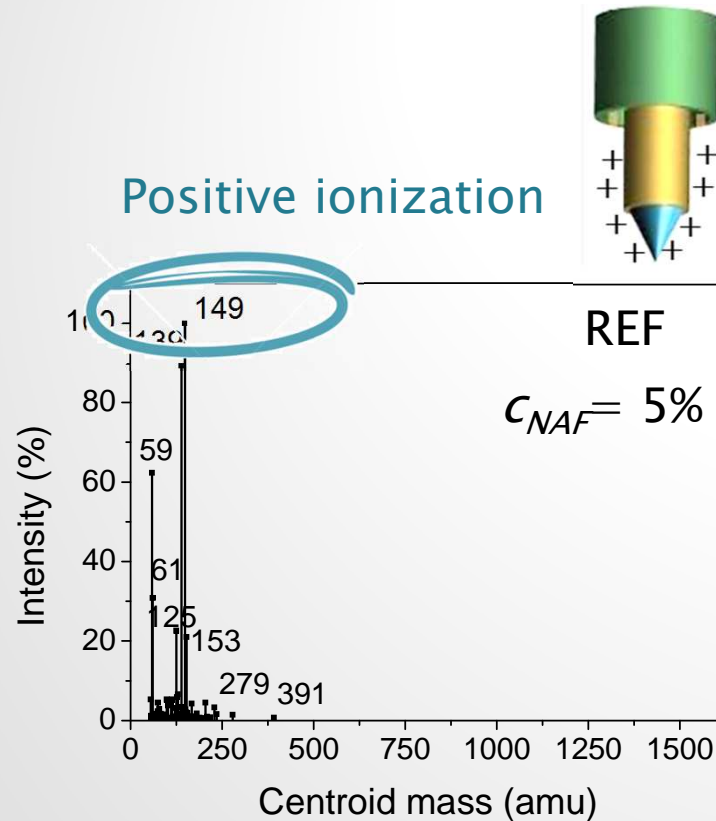
Solvent:
Isopropyl alcohol
Water
Acetone



[Nafion]
1% wt.
2% wt.
4% wt.

Ionization mode

Nafion EW=1000



Very different fragmentation pattern is found for the “as-received” Nafion solution under positive and negative ionization modes

Effect of solvents:

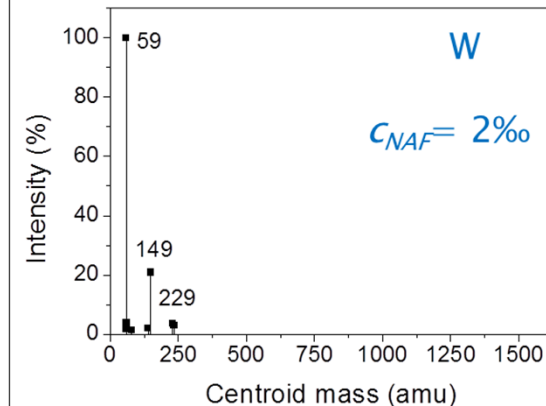
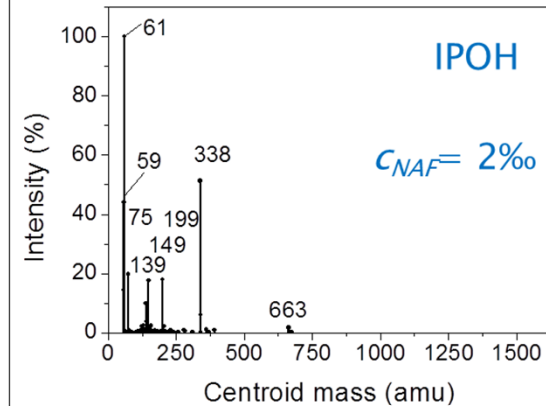
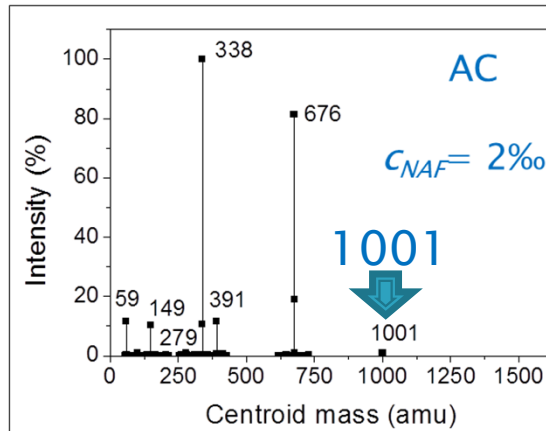


Isopropyl alcohol (IPOH)
Acetone (AC)
Water (W)

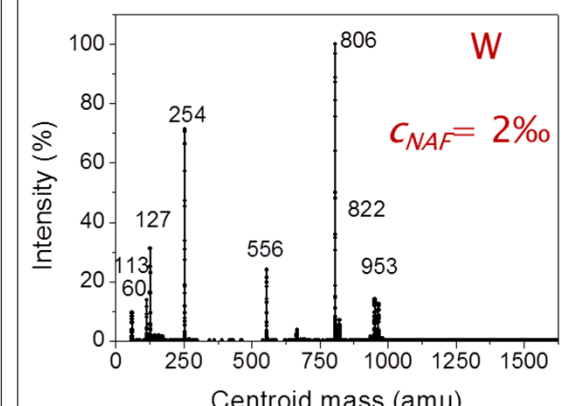
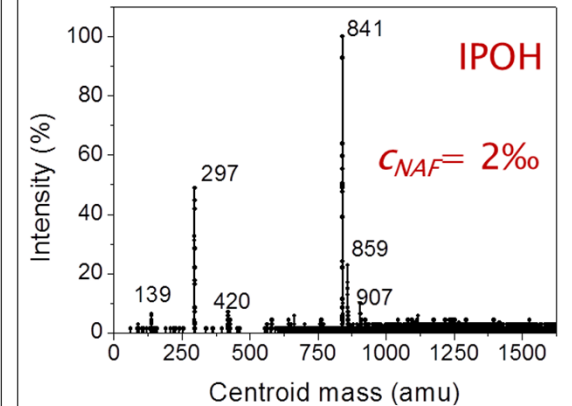
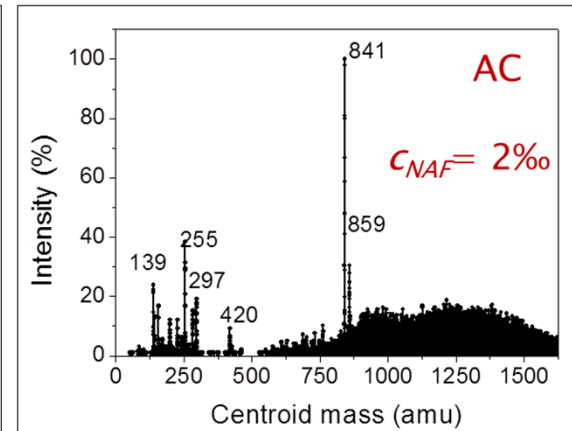
Larger fragments are obtained for:

AC > IPOH > W

Positive ionization



Negative ionization

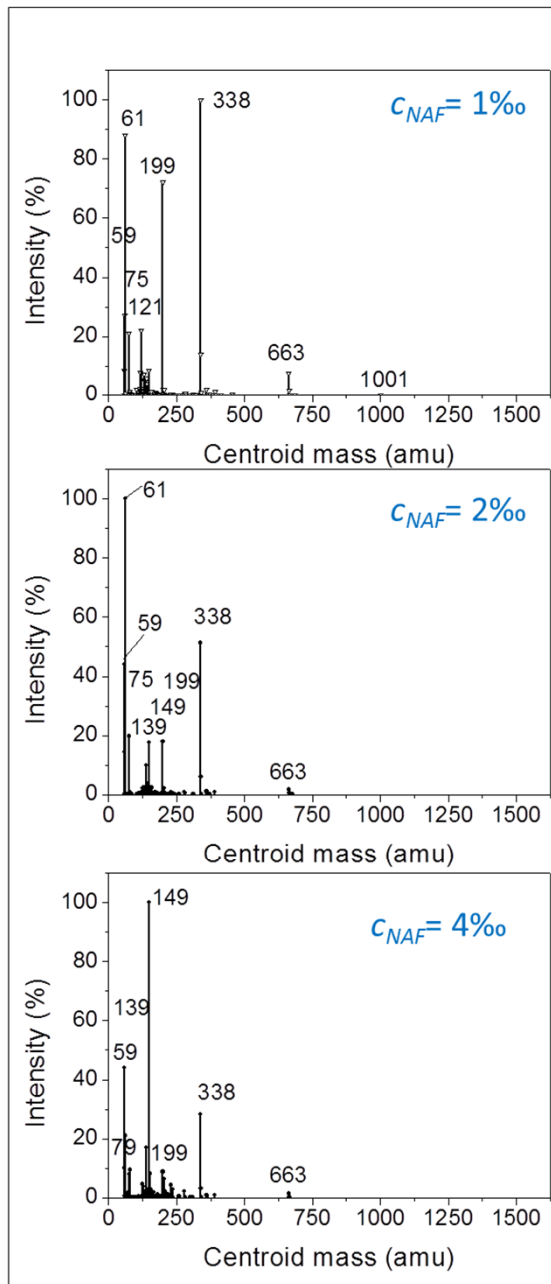


Concentration effect

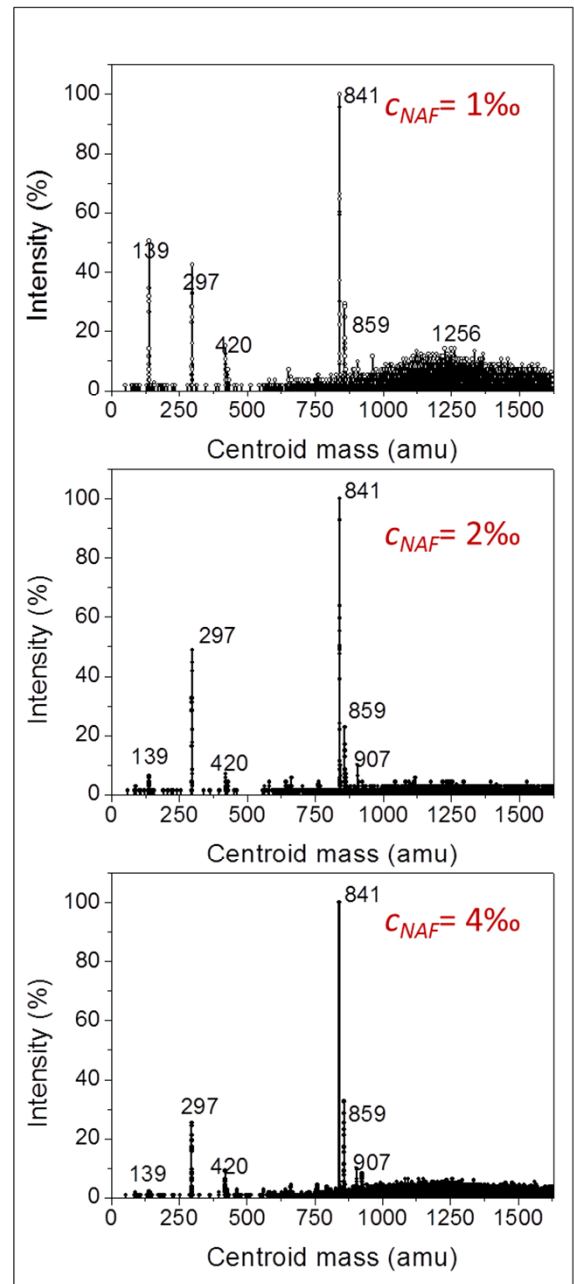


By increasing concentration, higher fragmentation is favored under positive ionization

Positive ionization (IPOH)

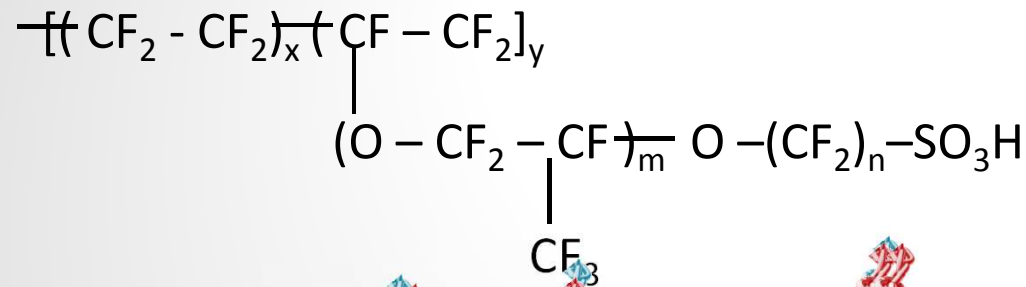


Negative ionization (IPOH)



The electrospray process for Nafion solutions.

Positive ionization



Negative ionization

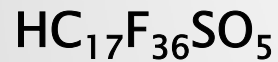
m=1

n=2

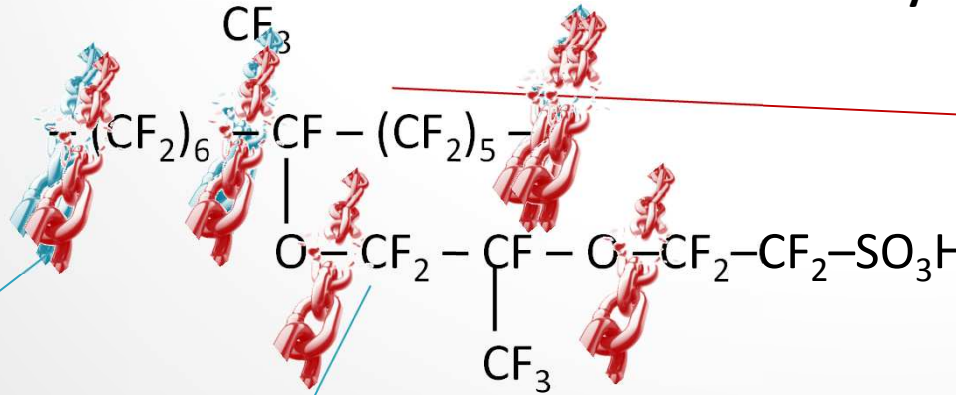
x=5

y=1

EW=1000



1001 Da



$m/z \text{ (B)} = 297$



$m/z \text{ (A)} = 338$



$m/z \text{ (B)} = 664$

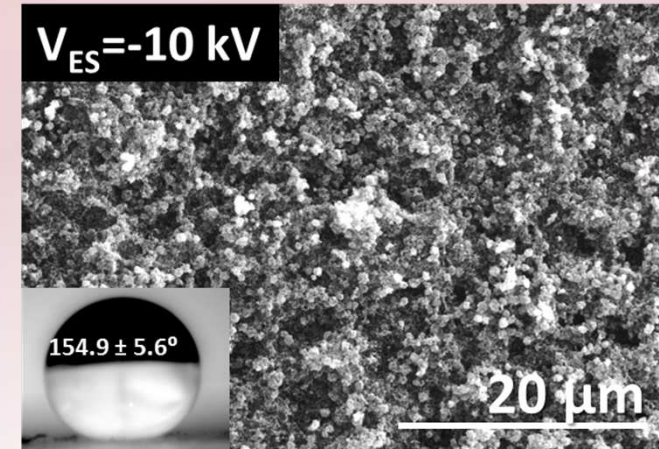
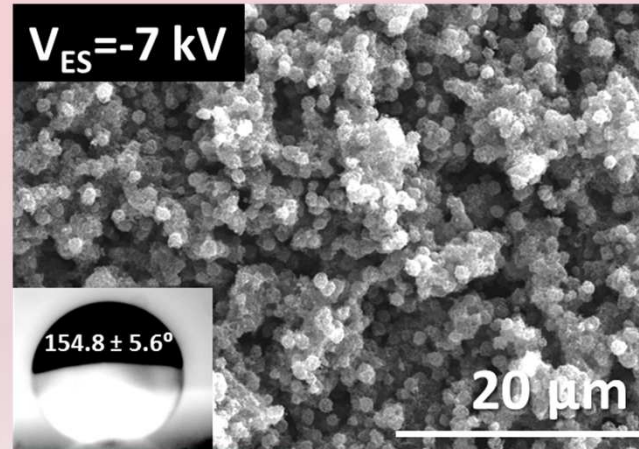


$m/z \text{ (A)} = 841$

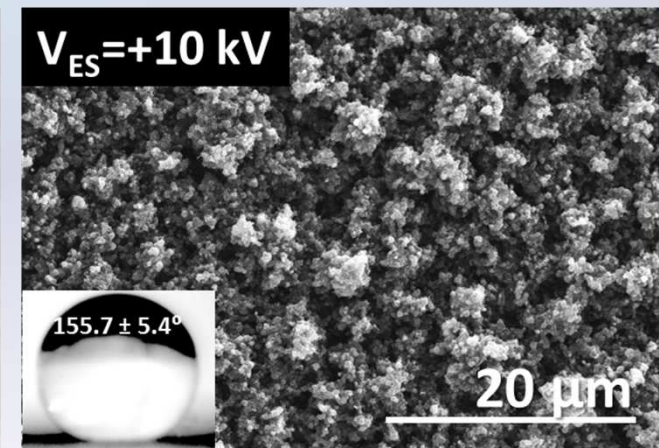
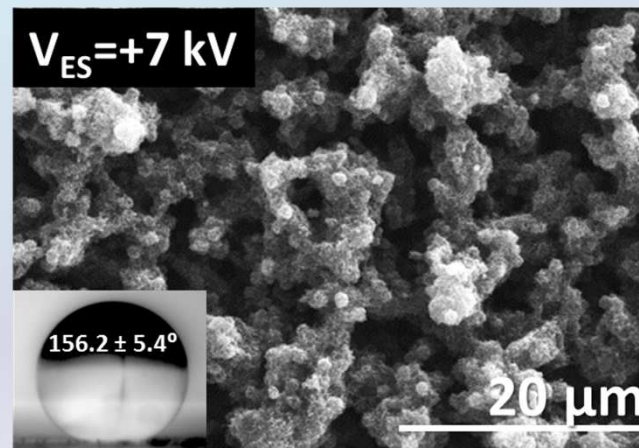


Ionization of inks: applied voltage & CB-Nafion film microstructure

Negative
ionization



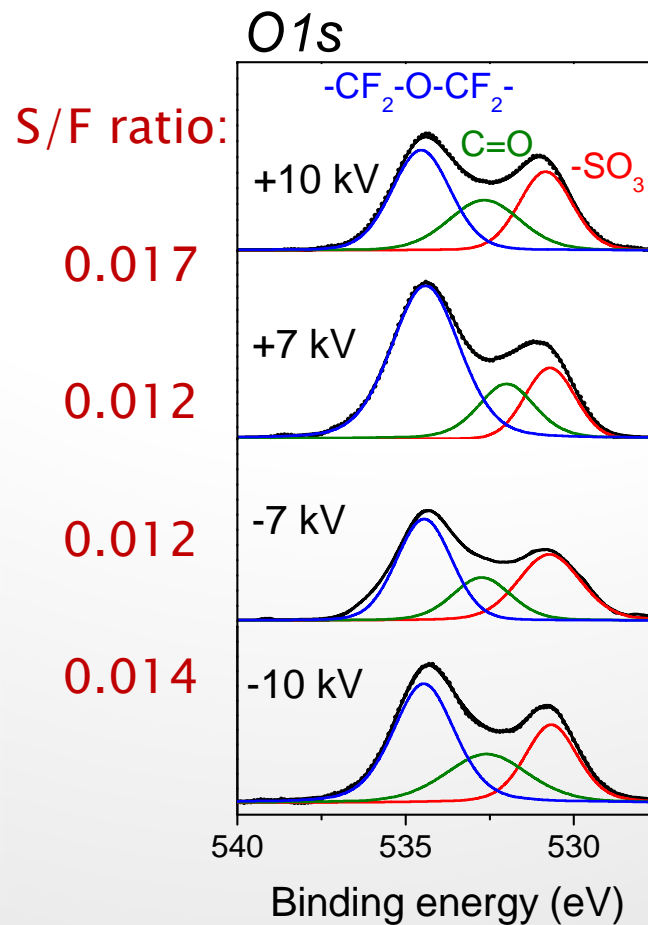
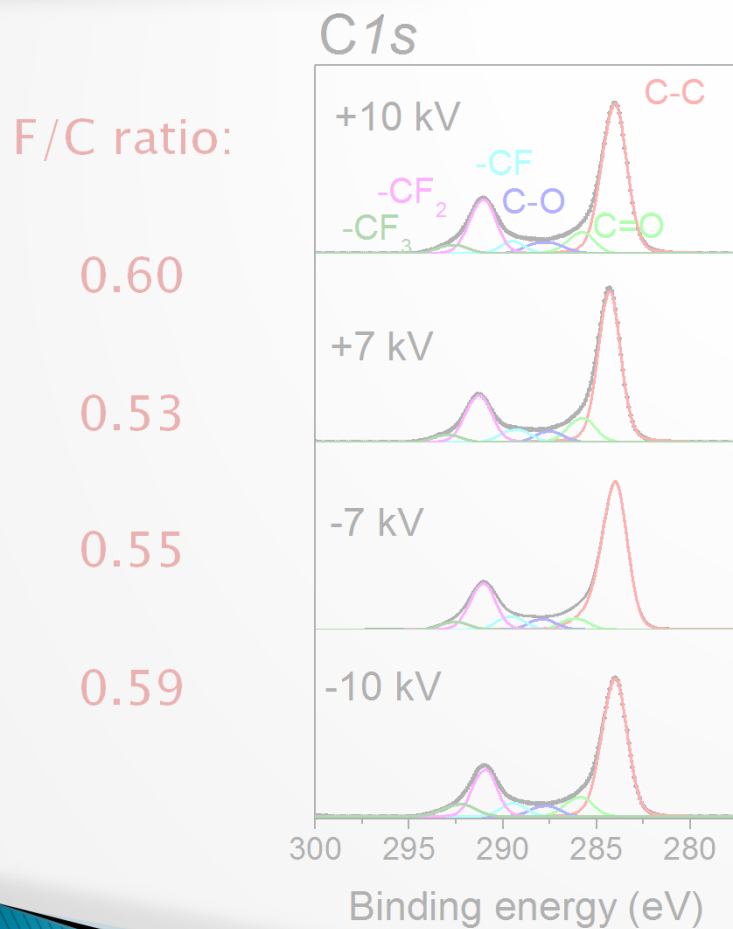
Positive
ionization



Superhydrophobic films

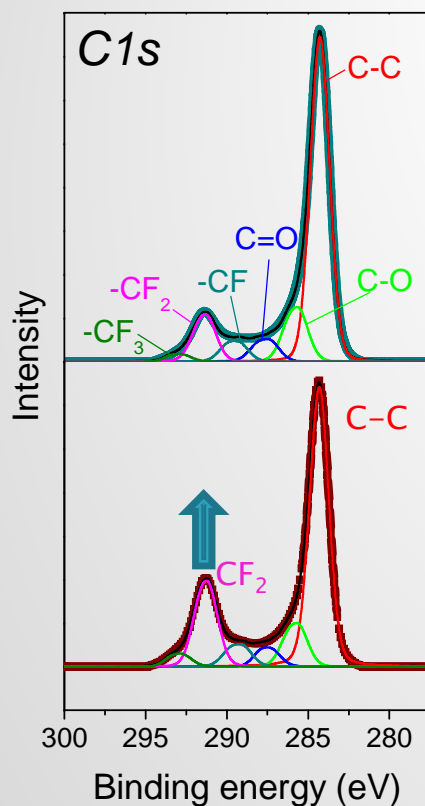
XPS analysis of ES CB-Nafion films

20wt% Nafion on CB



XPS analysis of CB-Nafion films

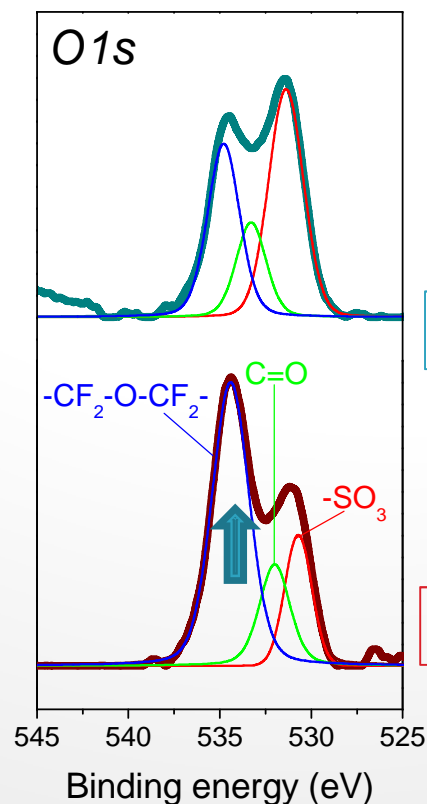
20wt% Nafion on CB



Aerography
F/C ratio : 0.28

Electro spray 7 kV
F/C ratio : 0.53

Perfluorinated chains are better distributed on the CB surface



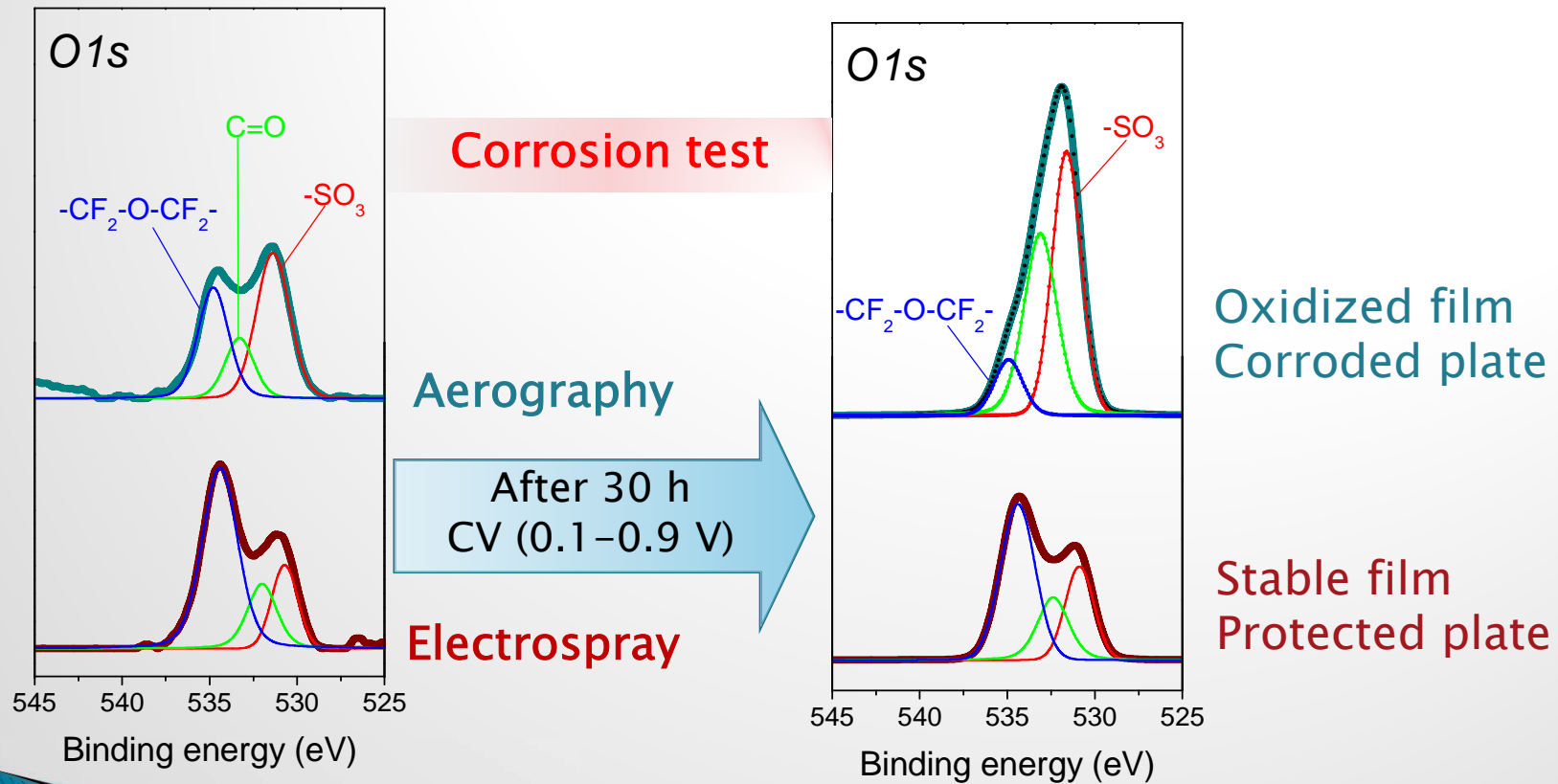
A higher proportion of ether groups as compared to sulfonic groups is always found for ES samples

S/F ratio : 0.024

S/F ratio : 0.012

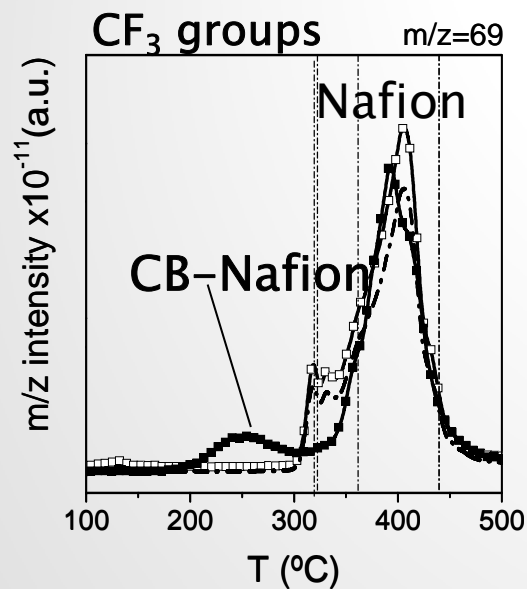
XPS analysis: protection against corrosion of CB–Nafion films

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



TG/MS – Nafion thermal decomposition

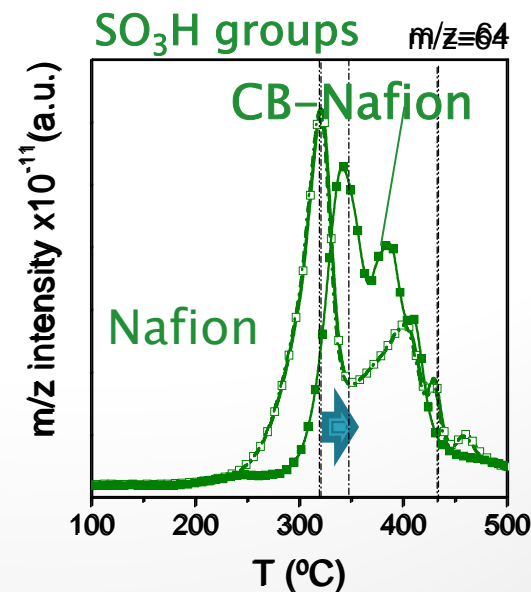
Self-supported Nafion vs CB-supported Nafion



Aerography
(no ionization)

Perfluorinated chains
←

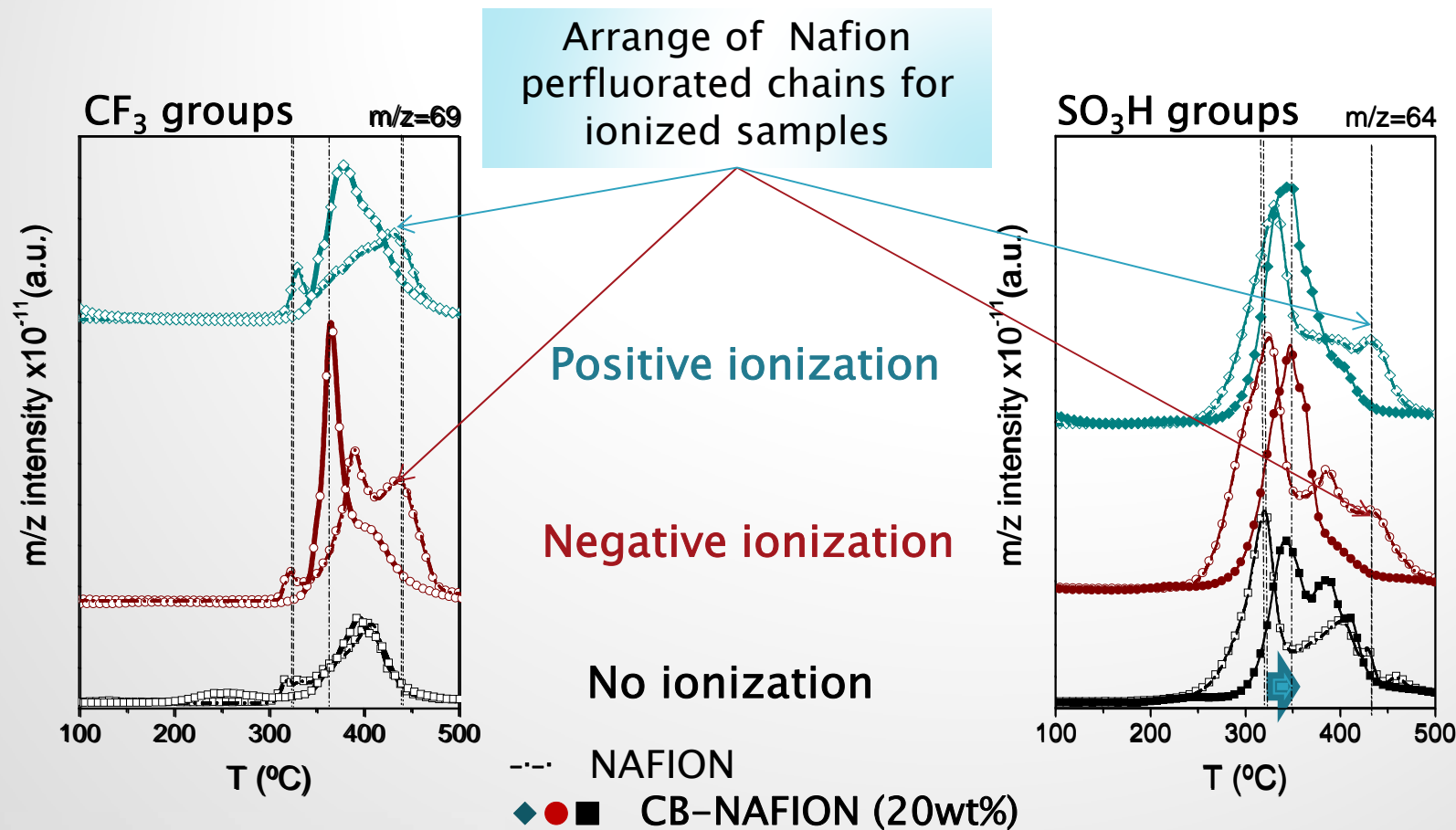
Sulfonic groups
→



The most labile sulfonic groups are stabilized in the presence of CB.

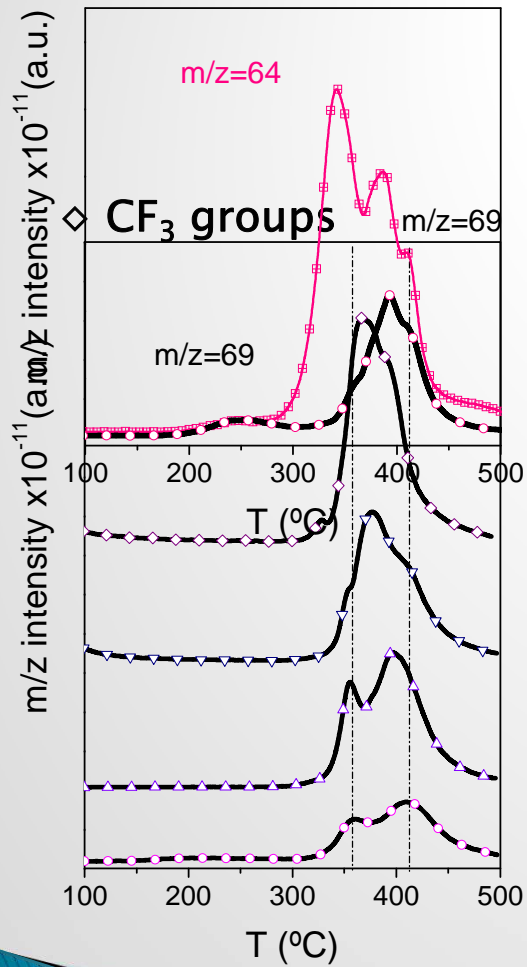
TG/MS – Nafion thermal decomposition

Self-supported Nafion vs CB-supported Nafion



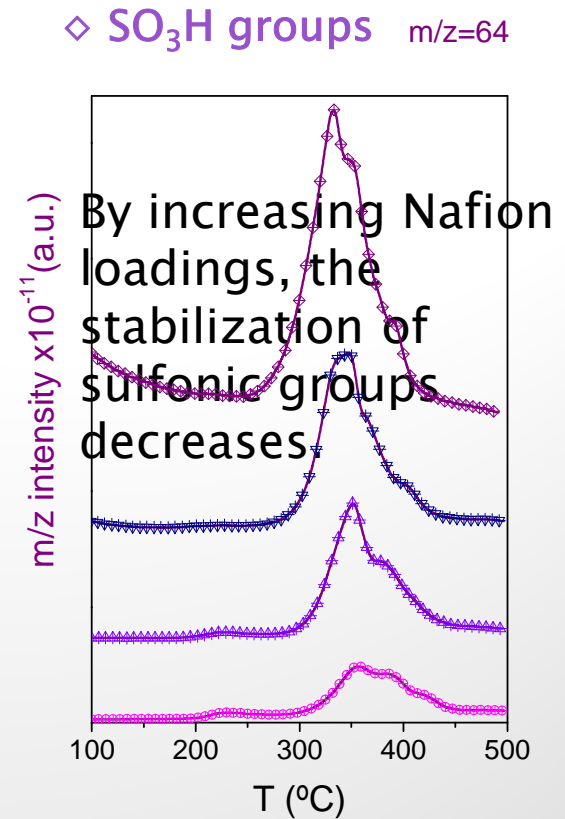
The most labile sulfonic groups are stabilized in the presence of CB, even when no ionization is applied

MS: ES CB-NAFION films (+7 kV) thermal decomposition at increasing Nafion loadings

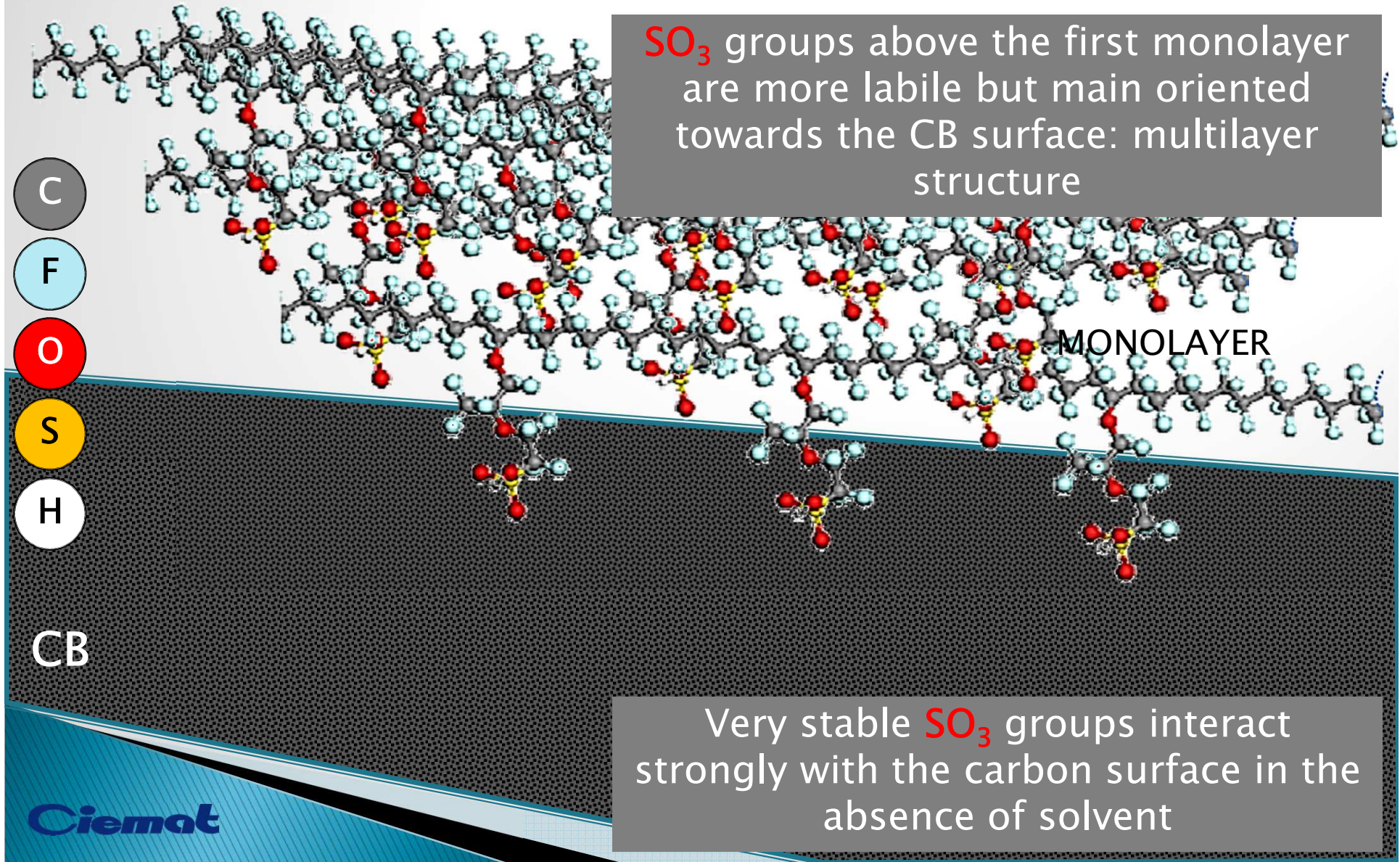


Aerography
20wt% Nafion on CB

40wt% Nafion on CB
20wt% Nafion on CB
10wt% Nafion on CB
5wt% Nafion on CB

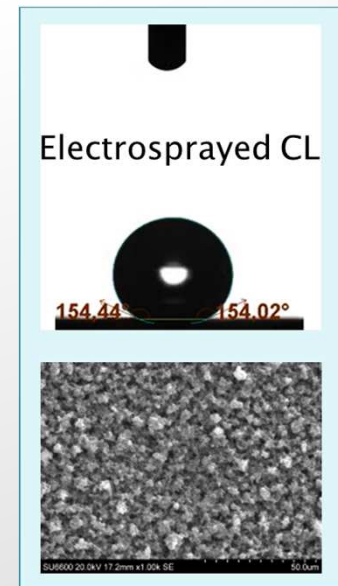


Proposed model for ES CB–Nafion films



Conclusions

- **Electrospray deposition of CB–Nafion inks allows the preparation of fractal-like films of superhydrophobic properties that constitute good protective barriers for metals against corrosion.**
- **Electrospray ionization induces some changes in the PFSA ionomer arrangement, which depend on the solvent, applied voltage, ionomer concentration, and the presence of CB in the ink.**
- **Electrospray always favors the orientation of side chains toward the carbon surface.**
- **Amounts below 20wt% are enough to form a monolayer on Vulcan CB.**





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Tailoring electrosprayed carbon layers

Thank you for your attention!

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