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NEW APPROACHES FOR THE CHARACTERIZATION OF POROUS ELECTRODES DEVOTED TO OXYGEN REDUCTION

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NEW APPROACHES FOR THE CHARACTERIZATION OF POROUS ELECTRODES DEVOTED TO OXYGEN REDUCTION

I - INTRODUCTION

Platinum is the reference electrocatalyst in PEMFC

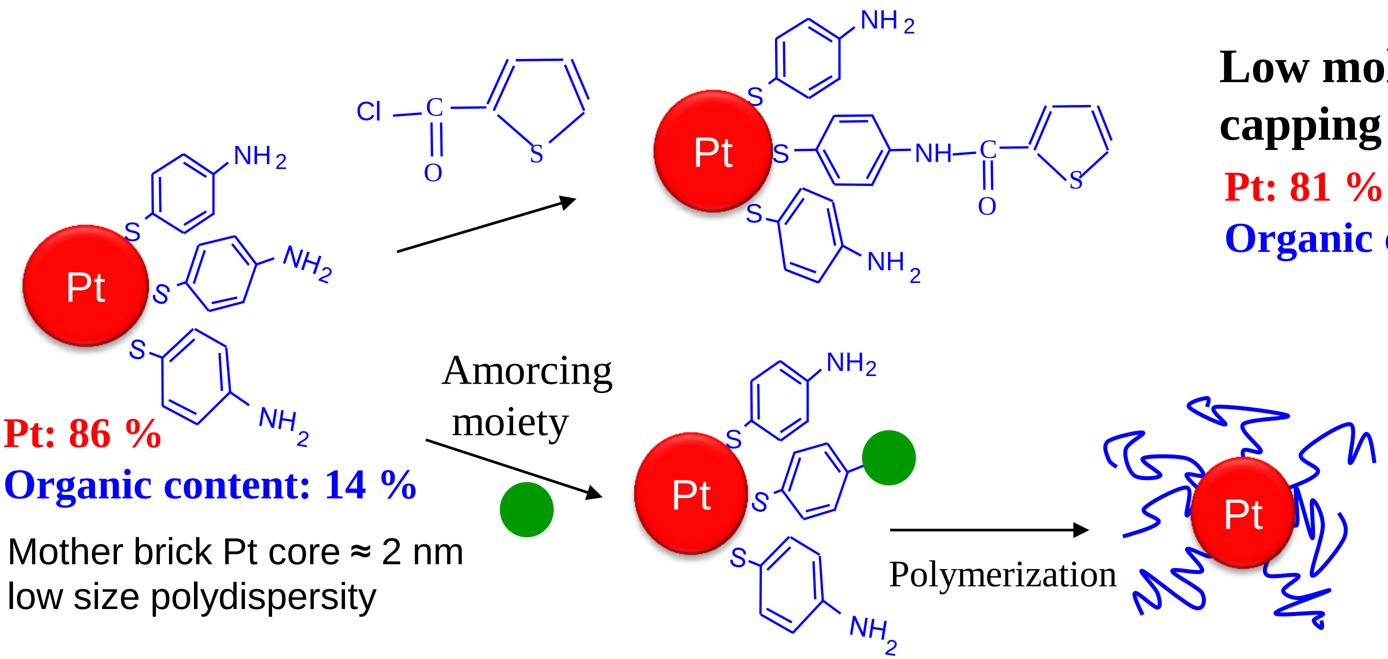
Key challenge (among other) for significant development of PEMFC :

→ Decrease the platinum loading in the electrodes
(necessitates porous electrodes with controlled loading to be prepared)

→ Development of non platinum based electrocatalysts

II – Platinum Organically Grafted Electrocatalyst feature

→ Different kind of organically grafted nanoparticles obtained from the same ”mother brick”



Pt: 86 %
Organic content: 14 %

Mother brick Pt core ≈ 2 nm
low size polydispersity

Low molecular weight organic capping (Pt content dominates)
Pt: 81 %
Organic content: 19 %

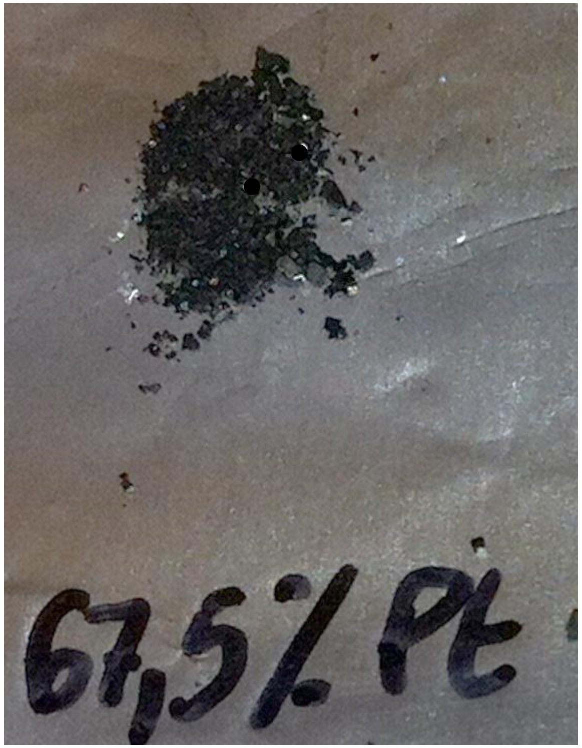
High molecular weight organic capping
(Organic content dominates)
Pt: 15 %
Organic content: 85%

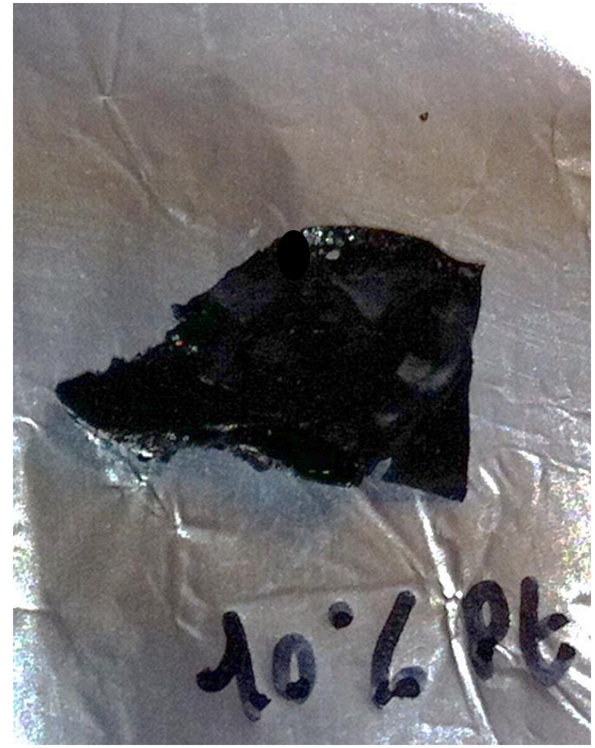
- Gives different kind of powders with well defined feature (few hundreds of mg at laboratory scale)

*H. Perez, J.-P. Pradeau, P.-A. Albouy, and J. Perez-Omil Chem. Mat 11 (12) (**1999**) 3560-3463*
*H. Perez, V. Noël, S. Cavaliere-Jaricot, A. Etcheberry, P-A. Albouy Thin Solid Films 517 (**2008**) 755*
*G. Carrot, F. Gal, C. Cremona, J. Vinas, H. Perez, Langmuir 25 (**2009**), 471*

II - Platinum Organically Grafted Electrocatalyst feature

Different kind of grafted nanoparticles obtained from the ”mother brick”



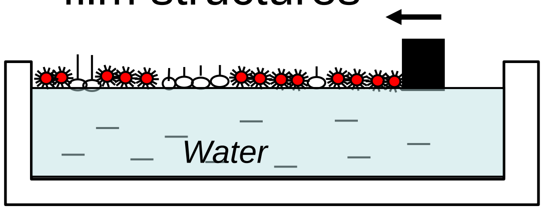


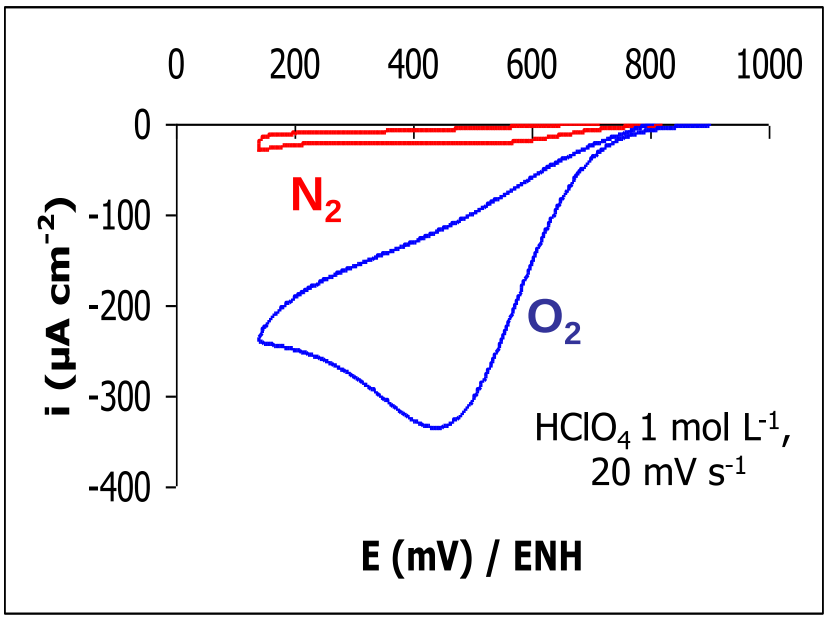
$[C]_{Pt}$ controlled

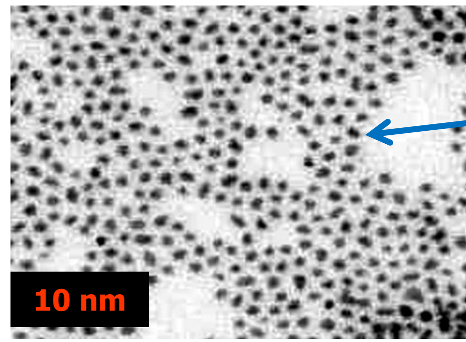
Higly stable solutions with a precisely controlled Pt concentration can be prepared: easy to handle !

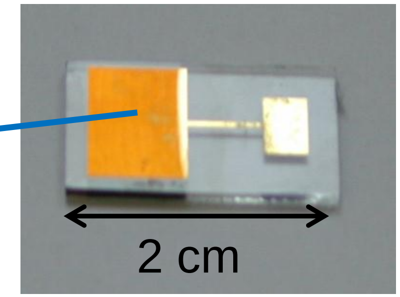
II - Platinum Organically Grafted Electrocatalyst feature

Early reported O_2 reduction on Pt grafted nanoparticles in Langmuir-Blodgett thin film structures









- Direct and significant response towards O_2 (Organic capping still grafted)
- One Monolayer or sub-monolayers structures exhibit optimized responses in term of platinum loading

Motivation for making “real” fuel cells electrodes…

Cavaliere S. Raynal, F. Etcheberry A., Herlem M., Perez H. Electrochem. Solid State Let. 7 (10): A358-A360 ***2004***

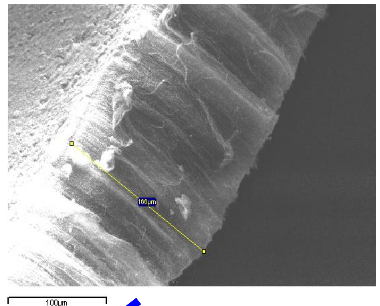
Cavaliere S, Raynal F, Etcheberry A, Herlem M, Perez H Solid State Phenomena 106 ***2005*** *31*

S. Cavaliere-Jaricot, J. Haccoun, A. Etcheberry, M. Herlem, H. Perez Electrochimica Acta 53 ***2008*** *5992*

III- Porous electrode formation and feature

Capped Pt nanoparticles

Carbone Nanotubes (CNT)

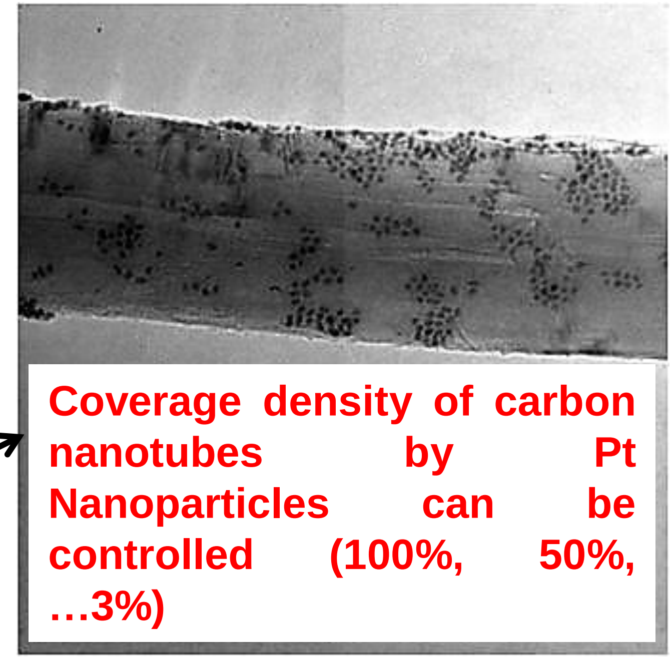


DMSO
[C] defined

+

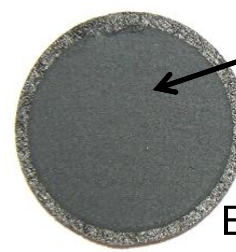
Isopropanol
[C] defined

mixing



Coverage density of carbon nanotubes by Pt Nanoparticles can be controlled (100%, 50%, …3%)

Filtration of a controlled volume on carbon felt



Active layer
Capped NP / NT

Electrode with a controlled Platinum Loading over a wide range

*M. Pinault, M. Mayne-L'Hermite, C. Reynaud, O. Beyssac, J. N. Rouzaud and C. Clinard Diamond and Related Materials 13 (**2004**) 1266*

*B. Baret, P-H Aubert, M. Mayne-L'Hermite, M. Pinault, C. Reynaud, A. Etcheberry, H.Perez, Electrochim. Acta 54 (**2009**) 5421.*

III- Porous electrode formation and feature

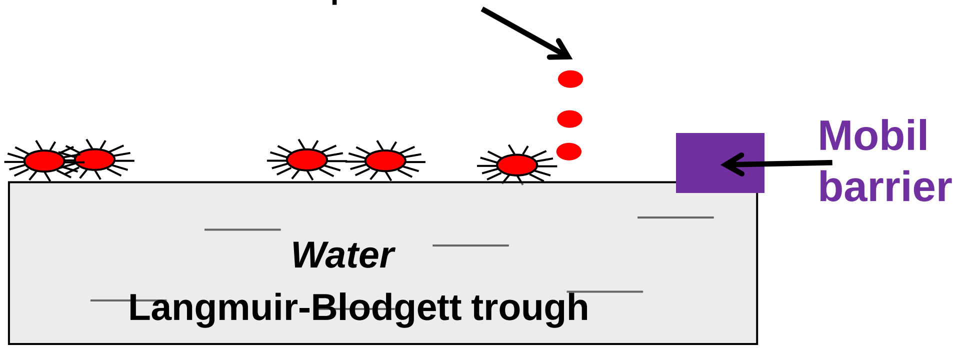
→ Tuning the coverage density of grafted nanoparticles at carbon nanotube surface

Specific surface areas are used :

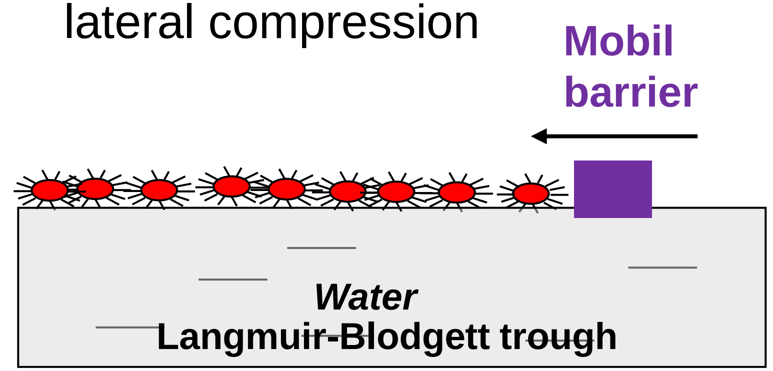
Nanotubes : classical measurement by Nitrogen adsorption (BET)

Pt grafted nanoparticles: monolayer compression isotherm recorded at the air-water interface (Langmuir-Blodgett trough)

Spreading controlled amount of Pt nanoparticle from solution

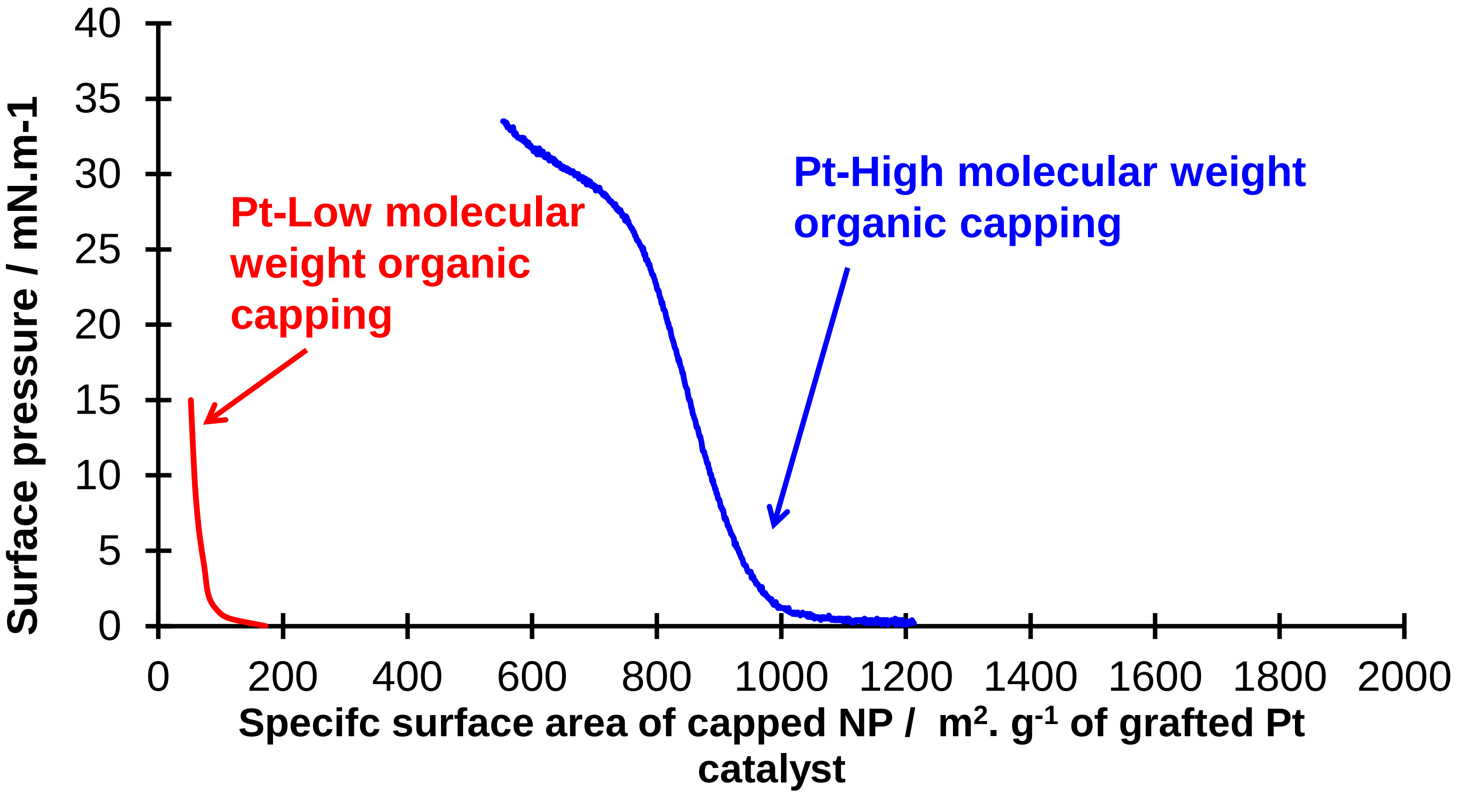


Monolayer formed by lateral compression



III- Porous electrode formation and feature

Specific surface area of grafted Pt-nanoparticles from compression isotherm :



Pt-Low molecular weight organic capping : 50m^2/g

Pt-High molecular weight organic capping : 1000 m^2/g

III- Porous electrode formation and feature

→ Setting the coverage density of capped nanoparticles at the carbon nanotube surface:

Amount of nanotube giving 100 m^2 area

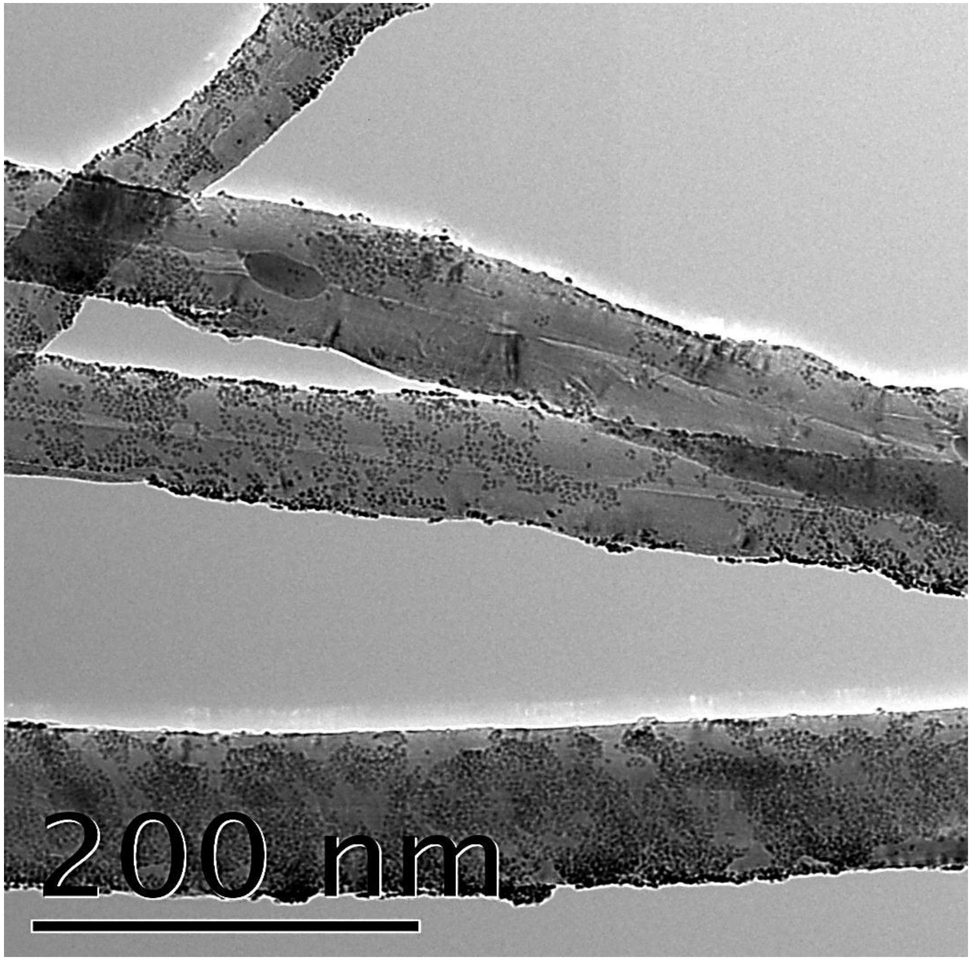
\+

Amount of nanoparticle for 100 m^2 area → 100 % coverage density

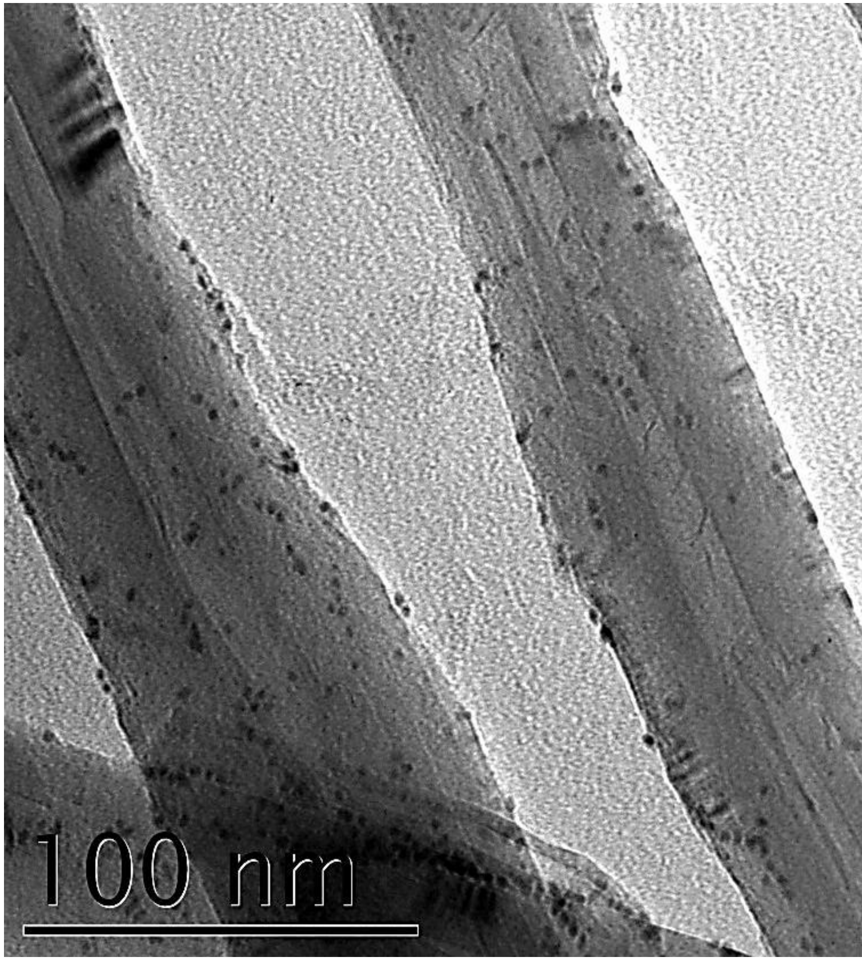
Amount of nanoparticle for 3 m^2 area → 3 % coverage density

III- Porous electrode formation and feature

→ different coverage densities setting for the same capped nanoparticles at CNT surface:



Coverage density 20 %



Coverage density 3 %

(Low molecular weight organic capping)

III- Porous electrode formation and feature

Setting the coverage density of capped nanoparticles at the carbon nanotube surface:

Amount of nanotube giving 100 m^2 area

+

Amount of nanoparticle for 100 m^2 area → 100 % coverage density

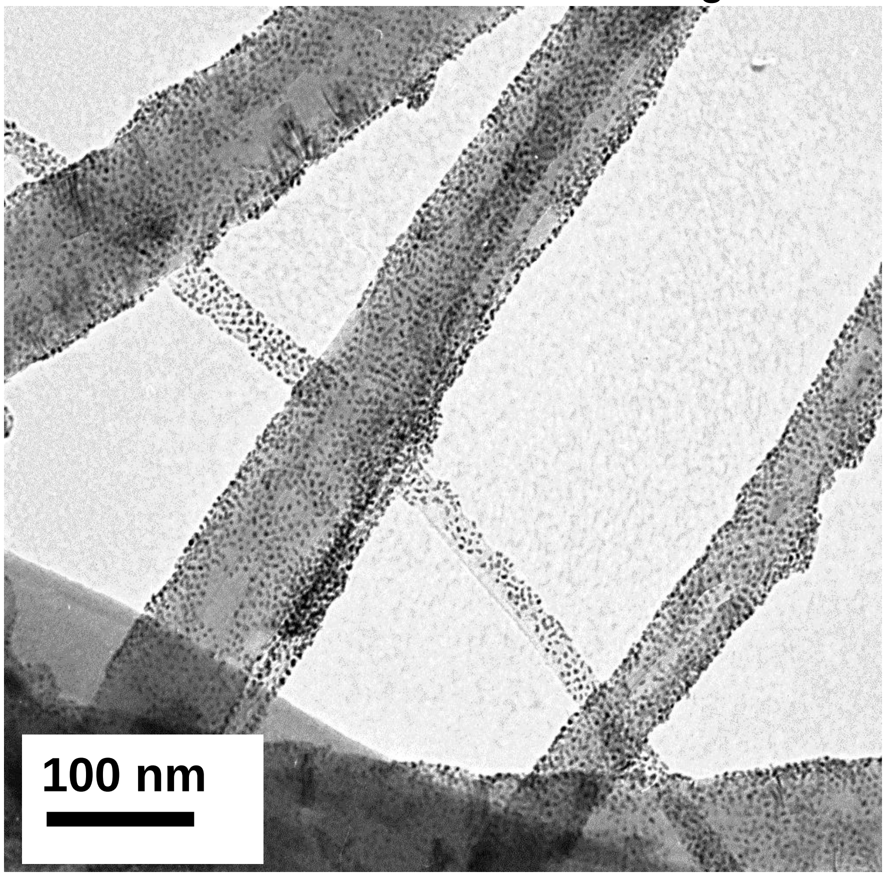
Amount of nanoparticle for 3 m^2 area → 3 % coverage density

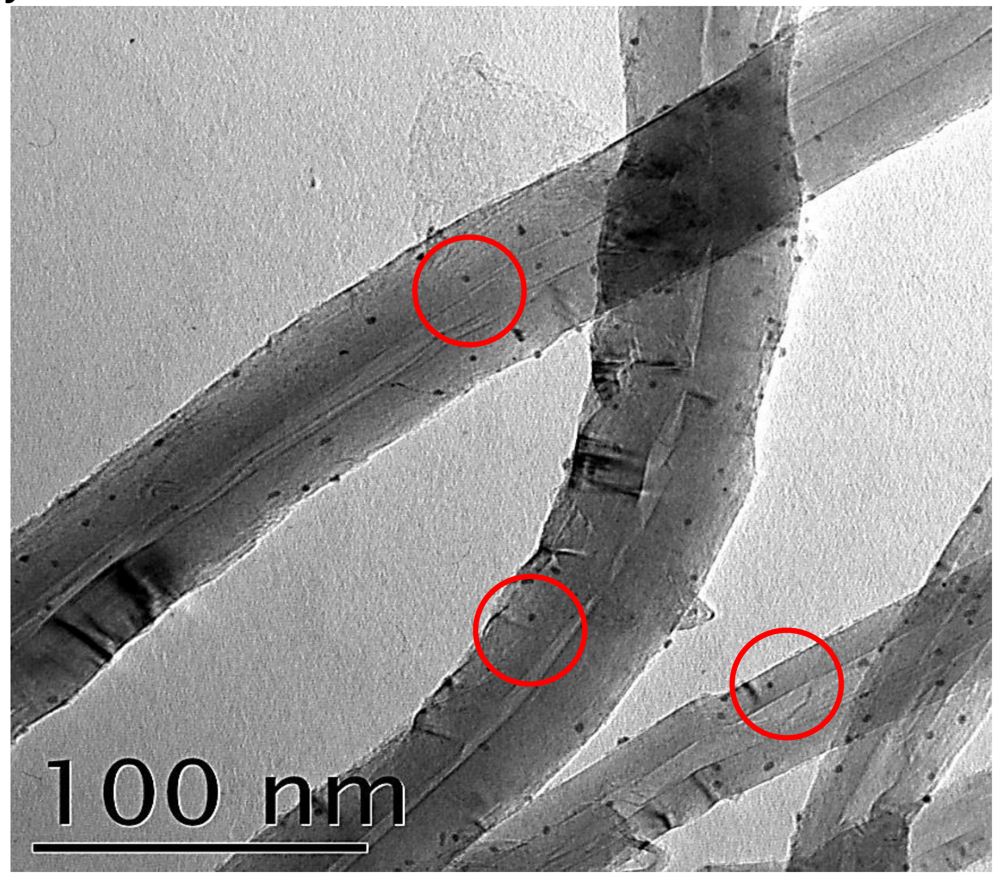
Note: Specific surface area for nanoparticles obtained from compression isotherms include the organic capping

Consequence : Low molecular and high molecular weight organic Pt grafted nanoparticles at the same coverage density results in different Pt core density at the carbon nanotube surface

III- Porous electrode formation and feature

Pt core density variation for Pt Low and High molecular weight organic capping set at the same CNT coverage density





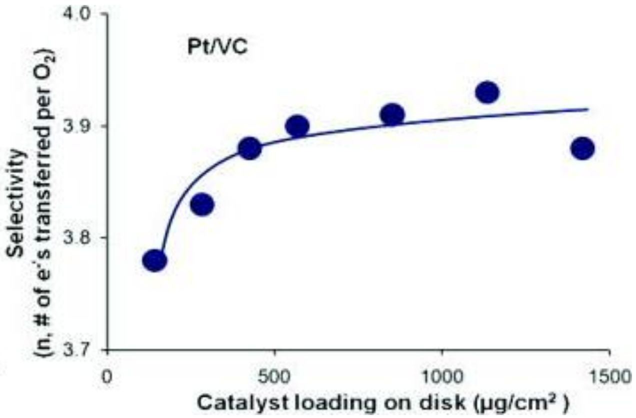
Pt-Low molecular weight organic capping
coverage density 100 %

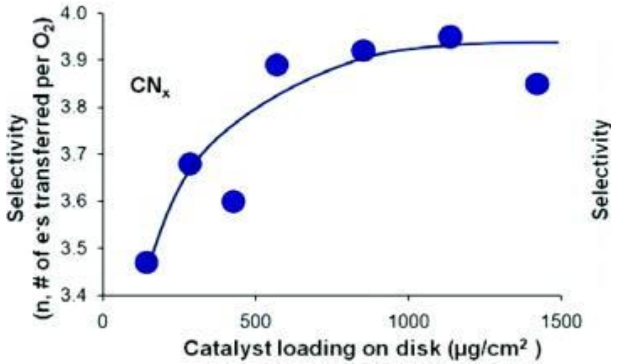
Pt-High molecular weight organic capping
coverage density 100 %

IV- New approaches for the characterization of the ORR in porous electrodes

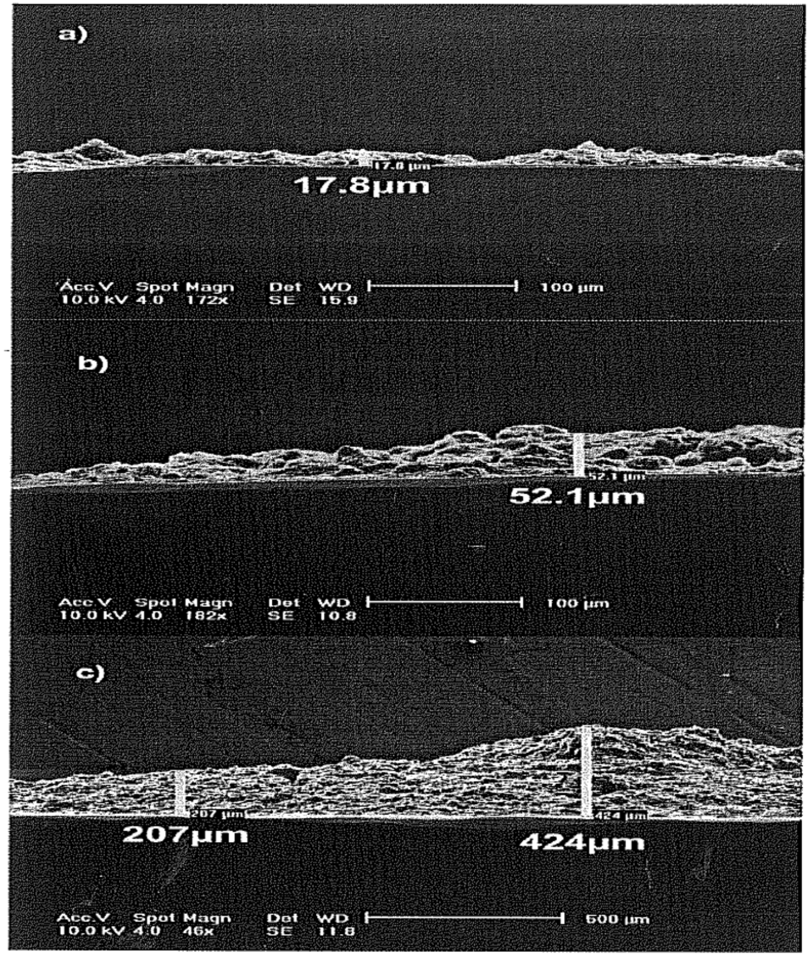
The selectivity of the ORR depend on the catalyst density…

(Rotating electrode)





After E. J. Biddinger et al J. Electrochem. Soc., ***2011****, Vol. 158, No. 4, p. B402*



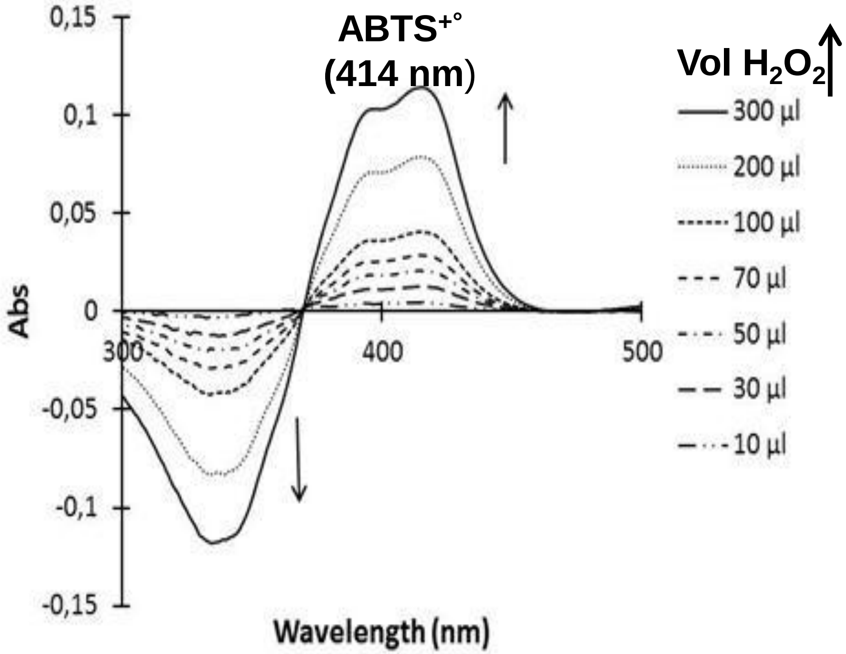
Control of active layer thickness and homogeneity is difficult on rotating electrodes…

Numerous attempts with our composite Nanoparticle/Nanotubes dispersions gave very poor reproducibility for selectivity measurements…

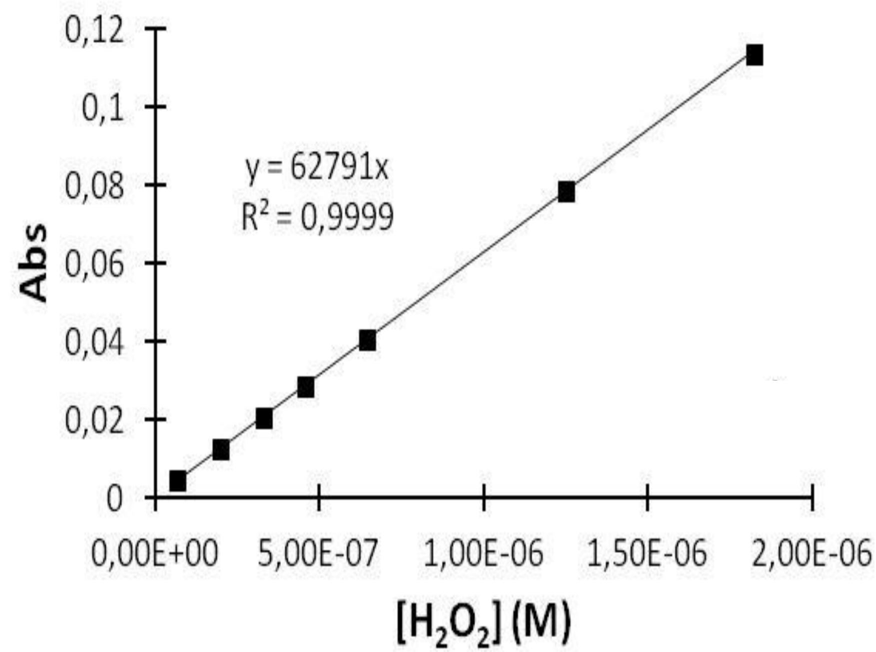
IV- New approaches for the characterization of the ORR in porous electrodes

→ An alternative method to Rotating electrodes for the determination of the selectivity :

Based on spectrophotometric assay of H_2O_2 using an enzyme and a dye



UV-Visible Spectroscopy with HRP/ABTS /H_2O_2



Exemple of calibration curve

ABTS (340 nm) —HRP / H_2O_2→ $ABTS^{+°}$ (414 nm)

Enzyme : Horseradish peroxydase (**HRP**)
Dye : 2,2'-azino-bis 3-ethylbenzothiazoline-6-sulfonate (**ABTS**)

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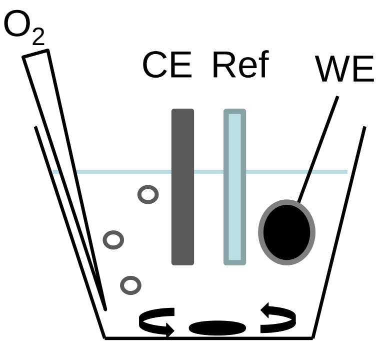
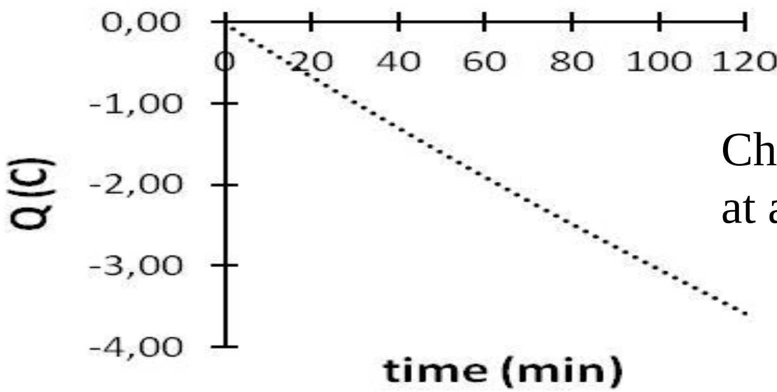
IV- New approaches for the characterization of the ORR in porous electrodes

→ An alternative method to Rotating electrodes for the determination of the selectivity :

chronoamperometry



30mL $HClO_4$ 0.1 M



Charge involved in the ORR at a given time t

H_2O_2 assay in the electrolyte at given time t → Total amount of H_2O_2 at t M_{H2O2}

$$M_{2e-} = 2 \times M_{H2O2}$$

$$n = 2 \times H_2O_2\% + 4 \times (1 - H_2O_2\%)$$

$$H_2O_2\% = M_{2e-} / Mt_{e-} \times 100\%$$

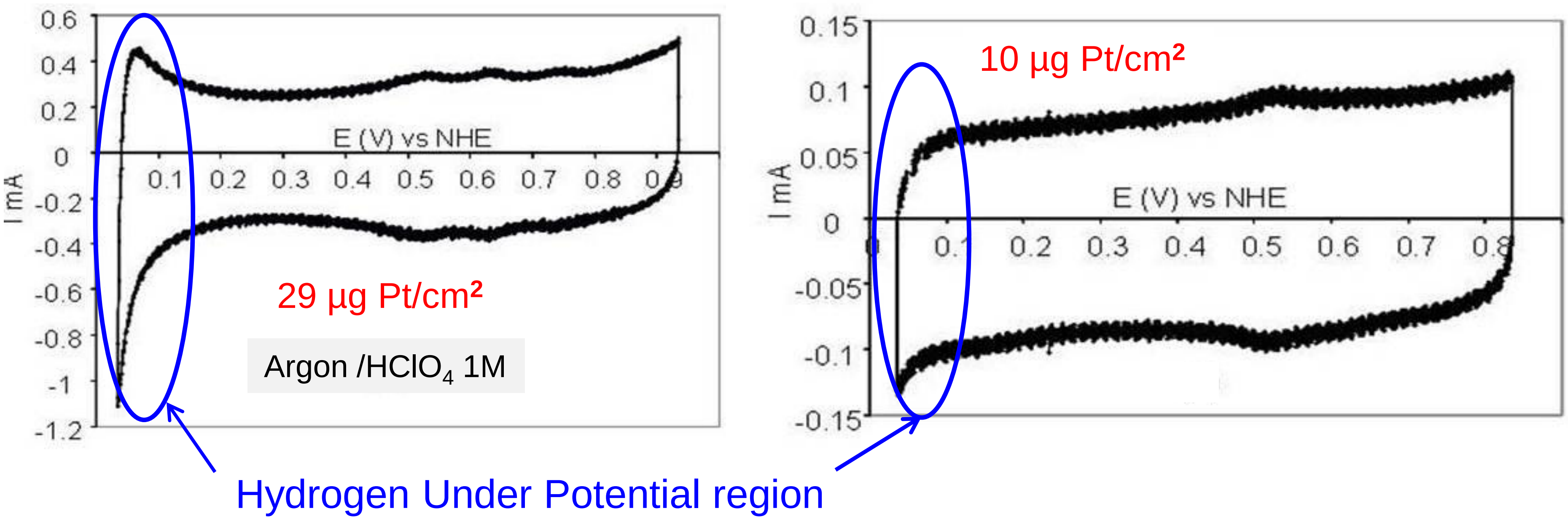
Method can be implemented on porous or bulk electrodes with various shapes (n=4 for bulk platinum, n=2 for porous carbon electrode….)

*X. Cheng, L. Challier, A. Etcheberry, V. Noël, H. Perez, Int. J. Electrochem. Sci., 7 (**2012**) 6247*

IV- New approaches for the characterization of the ORR in porous electrodes

→ Why attempting at measuring an electrode area related to O_2 reduction ?

A consequence of the organic grafting at the Platinum nanoparticle surface….



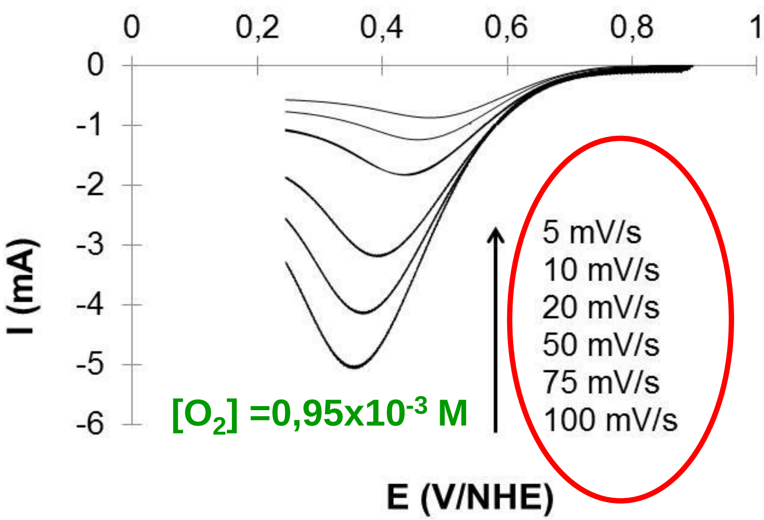
The platinum electroactive surface area cannot be measured when the platinum loading is too low …

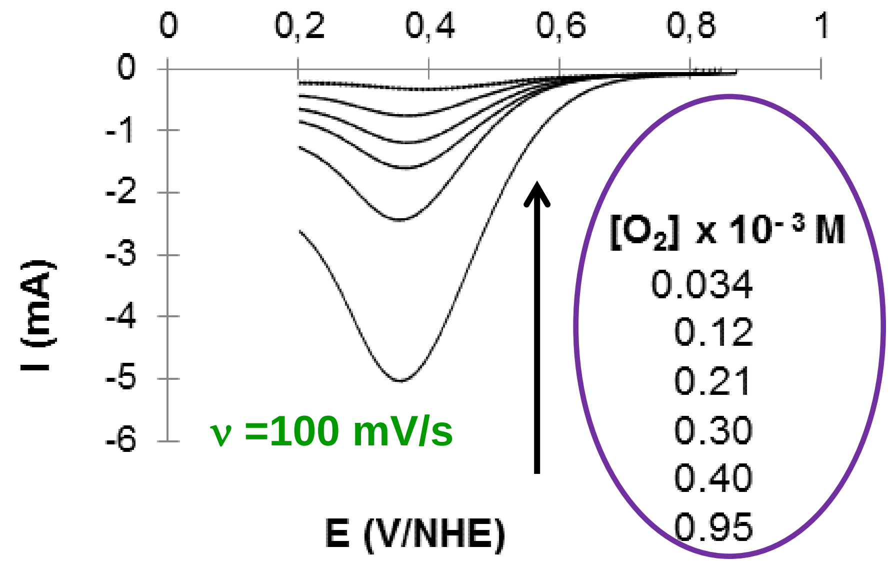
→ Determination of the specific area of porous electrode A related to the ORR

Cyclic voltammetry for an irreversible redox couple

(1) $$E_{peak} = E^{0'} - \frac{RT}{\alpha F}\left[0{,}78 + \ln\left(\frac{D_o^{1/2}}{k^0}\right) + \ln\left(\frac{\alpha F}{RT}\right)^{1/2}\right] - \frac{RT}{2\alpha F}\ln \nu$$

(2) $$I_{peak} = 2.99\times 10^5 \times n \times \alpha^{1/2} \times A \times C_0^* \times D_o^{1/2} \times \nu^{1/2}$$





Electrode behavior consistent with equations describing E peak and I peak

A the area of the electrode can be determined *(see reference below for details)*

G. March, F. Volatron, F. Lachaud, X. Cheng, B. Baret, M. Pinault, A. Etcheberry, H. Perez
*Electrochimica Acta 56 (**2011**) 5151*

IV- New approaches for the characterization of the ORR in porous electrodes

Determination of the specific area of porous electrode A O_2 related to the ORR

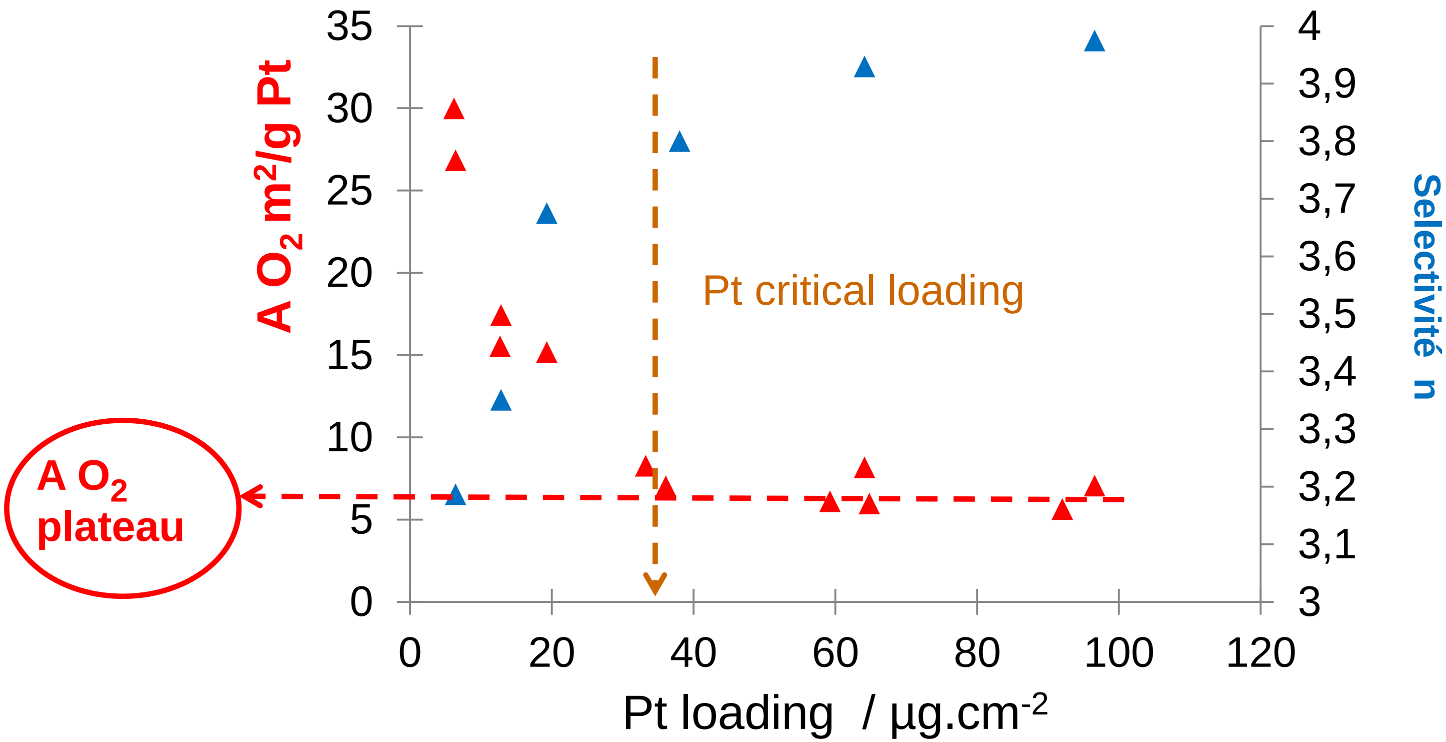
Because we have a very good control of the catalyst loading in the

electrodes we can calculate a

specific value for A_{O_2} which is expressed in m^2/ g of catalyst

→ Determination of **specific A O_2 in m^2/g Pt** **and** **selectivity** as a function of Pt loading

General trends for all the structures :

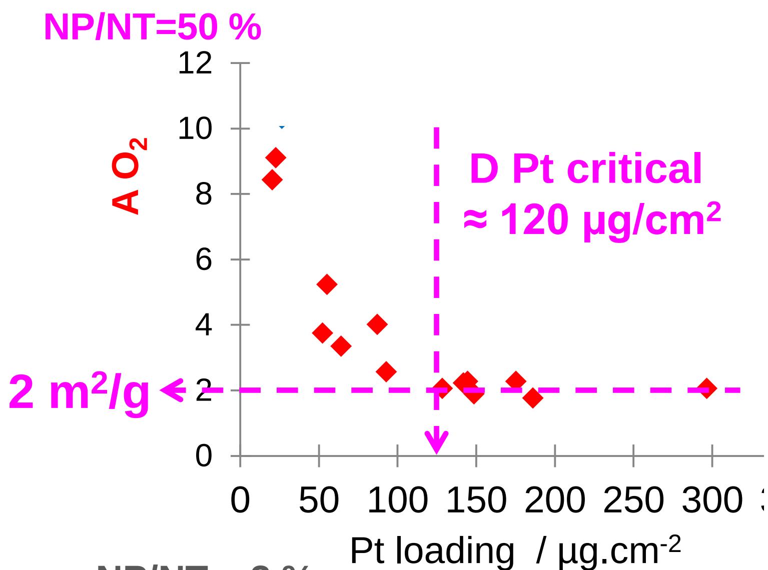


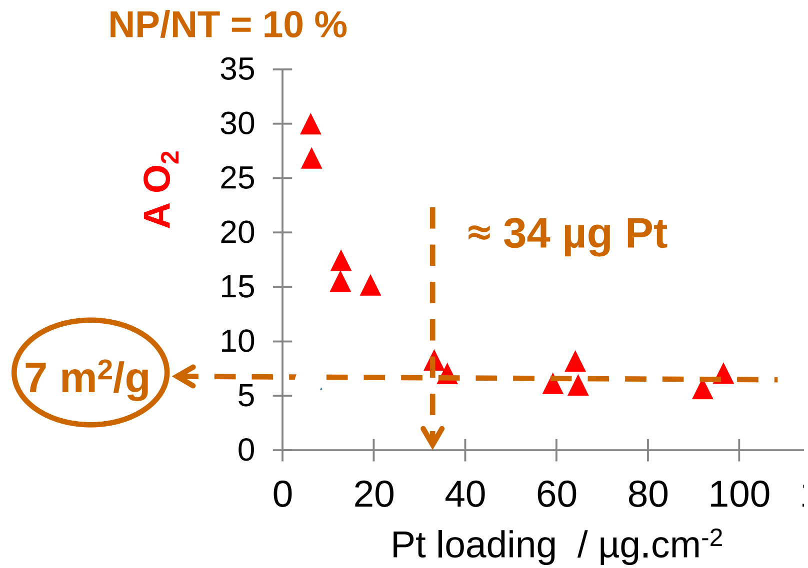
Two feature parameters : A O_2 plateau and critical catalyst loading

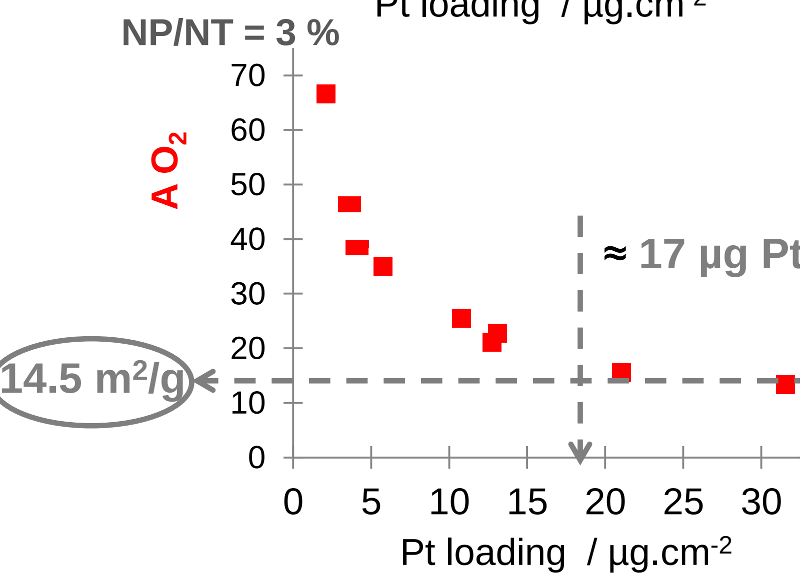
Correlation between specific A O_2 trends and the selectivity (n)

Above critical catalyst loading the selectivity is close to 4

Determination of **specific A O_2 in m^2/g Pt** as a function of Pt loading
(Low molecular weight organic capping (here three different Pt coverage densities)







A strong correlation is revealed between feature parameters specific A O_2 and D Pt critical for the different systems based on the same Pt-grafted catalyst !

(2 / 7) x 120 ≈ 34 µg Pt (D Pt critical)

(2 / 14,5) x 120 ≈ 17 µg Pt (D Pt critical)

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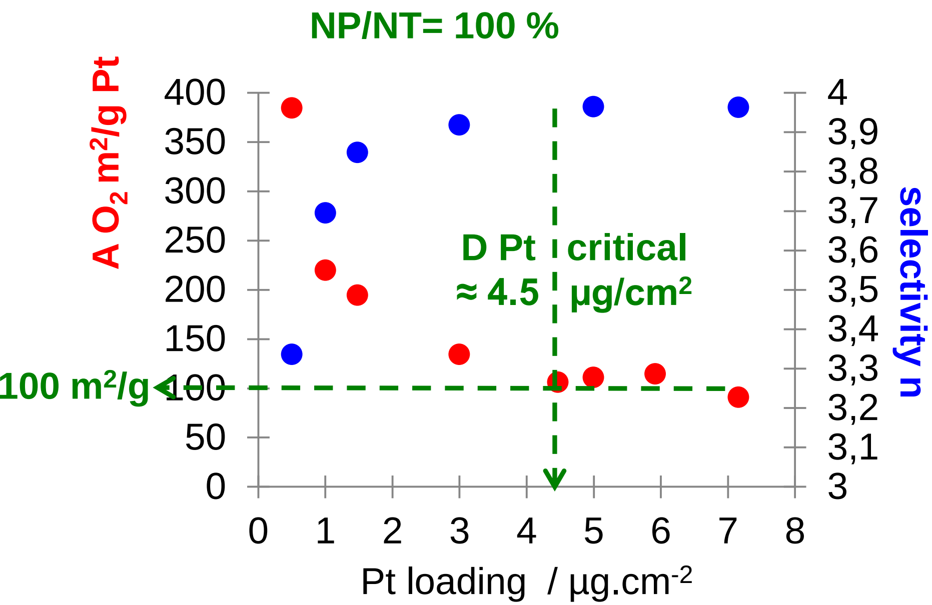
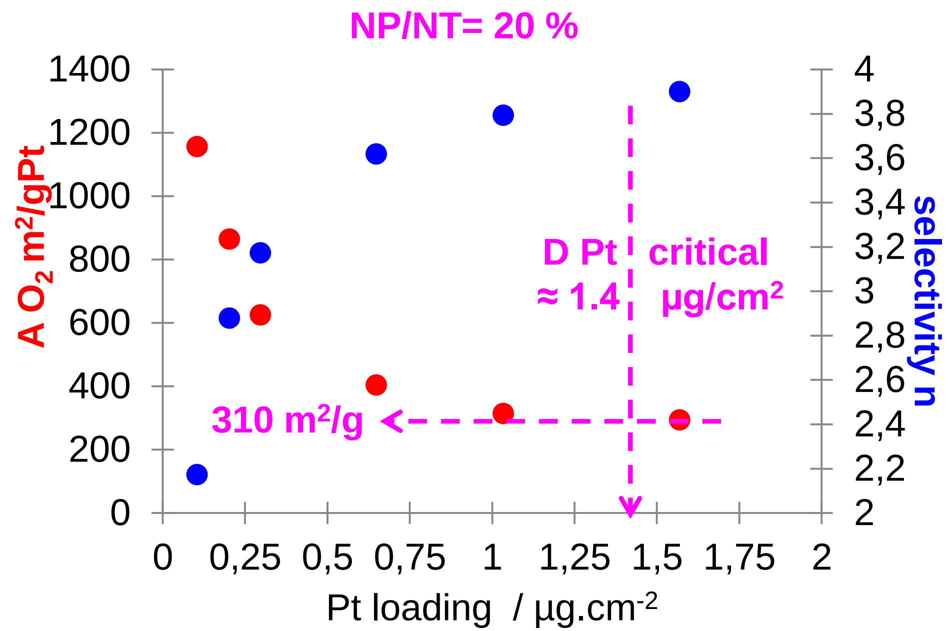
IV- New approaches for the characterization of the ORR in porous electrodes

→ Determination of **specific A DiffO$_2$ in m^2/g Pt and selectivity** as a function of Pt loading
(High molecular weight organic capping (two different Pt coverage densities)





Same correlation between specific A O$_2$ and n…

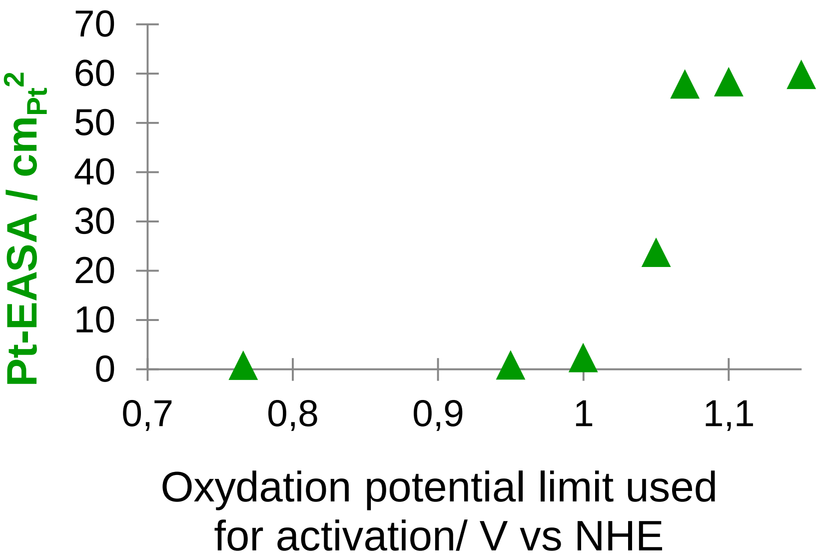
Same correlation between feature parameters (specific AdiffO$_2$ and DPt critical) from one coverage density to another one :

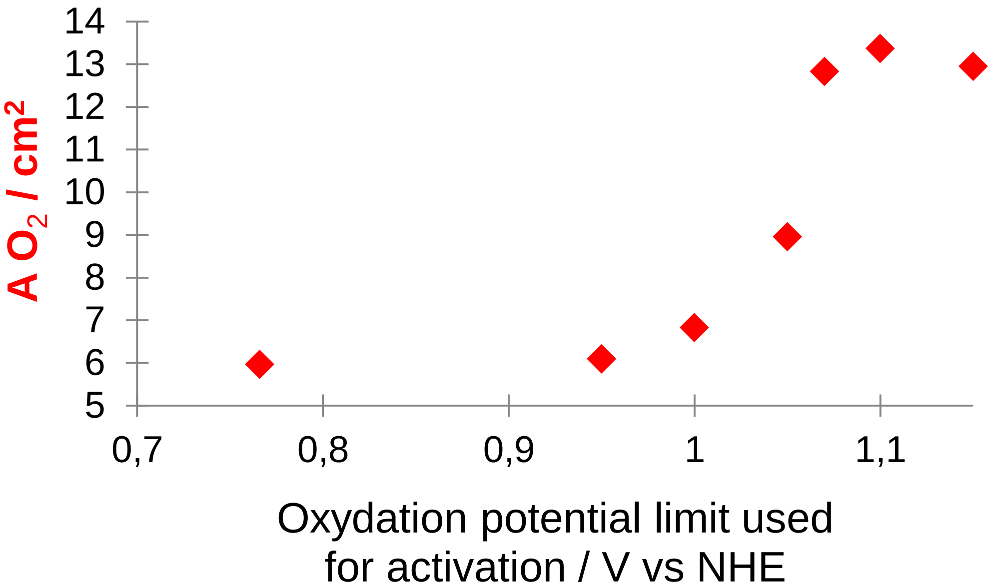
(100 /310) x 4,5 ≈ 1.4 µg

X. Cheng, F. Volatron, A. Borta, G. Carrot, E. Pardieu, C. Reynaud, M. Mayne, M. Pinault, A. Etcheberry, H. Perez Electrochim. Acta 89 (2013) 1

IV- New approaches for the characterization of the ORR in porous electrodes

Comparison of **Pt EASA** and AO_2 trends on electrochemically activated Pt-capped electrocatalyst:





Strong correlation between Pt-EASA and A O_2 !

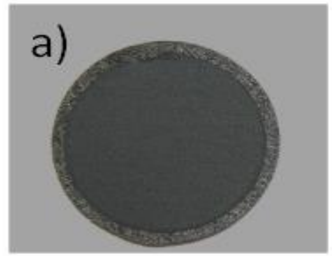
Manuscript in preparation

IV- Conclusion and prospects

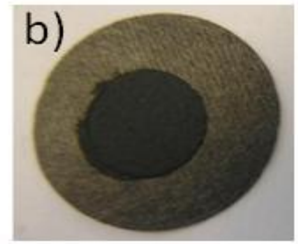
Our research on porous electrodes based on carbon nanotubes and organically grafted Pt-electrocatalyst allowed to establish :

- New method for the determination of ORR selectivity in porous electrodes

Same total amount of Pt 50 µg



D Pt= 19,3 µg/cm²
n= 3,68



D Pt= 94,1 µg/cm²
n=3,93

- Specific value (m²/g electrocatalyst) of the porous electrode area related to ORR as an interresting feature parameter :

  Here it varies from ≈ 2 m²/g Pt to ≈ 310 m²/g Pt !

- Current studies in progress to get more insights in AO_2 parameter…

- Such new approaches are currently exploited for the characterization of non-noble metal ORR electrocatalysts

Acknowledgement

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Thank you for your attention