Bottom-up approach for the elaboration of nanocomposite model structures based on organically capped platinum nanoparticles electrocatalyst

H. Perez*, S. Cavaliere†, B. Baret*, L. Akrou*, J. Haccoun †, C. Cremona*, C. Reynaud*, A. Etcheberry†

* CEA - Saclay
DSM/DRECAM/SPAM-LFP Groupe Edifices-Nanométriques

† IREM-CNRS, UMR 8637, University of Versailles Saint Quentin
Polymer Exchange Membrane Fuel Cell is an electrochemical device…

**Active layer contains an electrocatalyst**

**Cathode:**

\[ \frac{1}{2} O_2 + 2H^+ + 2e^- \xrightarrow{\text{electrocatalyst}} H_2O \]

**Anode:**

\[ H_2 \xrightarrow{\text{electrocatalyst}} 2H^+ + 2e^- \]
**INTRODUCTION**

**PEMFC and electrocatalyst**

Platinum as electrocatalyst

---

**Polarisation curve of PEMFC**

- $E_0$ = 1.23 V ($O_2/H_2O$)
- $V_{Max}$ « Activation over-potential »
  (essentially at cathode)

Platinum exhibits the lowest over-potential

Using platinum cannot be bypassed for PEMFC development, but it is rare and expensive…

---

Current (A/cm²)

Potential Volt
OPTRODUCTION

Platinum as electrocatalyst

Optimization of platinum loading is a challenge...and requires model electrodes

- Control the platinum loading over a wide range
- Control the polydispersity of nanoparticles (shape and size)
- Control the manipulation of catalyst

Bottom up approach offers such possibilities:

- Solution chemistry from molecular precursors affords capped or stabilized platinum nanoparticles with low polydispersity which can be handled in solution
The capping or stabilizing agent conflicts with electrochemical characterization.

Hydrogen under potential deposition (upd):

\[ \text{H}_2\text{SO}_4 \ 1 \text{ M, 100 mV/s} \]

“Clean” Bulk polycrystalline platinum

Surfactant contaminated Bulk polycrystalline platinum

Unsymmetrical adsorption and desorption

Cycling at high potential strongly disturbs nanoparticle feature

Electrochemical oxidation treatments:

- Capped or stabilized Platinum as electrocatalyst

Strongly disturb nanoparticle features!

Removing capping/stabilizing agent while keeping the nanoparticle core surface realistic?

INTRODUCTION

Capped or stabilized Platinum as electrocatalyst

- Control of platinum nanoparticle features versus electrochemical activity characterization

Hydrogen underpotential deposition may be observed while a stabilizing agent is used… (polyacrylate-capped nanoparticles)

For electrocatalysts few information concerning:

- the relation between the feature of capping/stabilizing agent and the electrochemical behaviour

- the influence of the nature of the interaction between capping/stabilizing agent and the nanoparticule surface on the electrochemical behaviour…

Bottom-up approach for the elaboration of nanocomposite model structures based organically capped platinum nanoparticles electrocatalyst

1 – Organically capped platinum nanoparticles

2 - Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

3- nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

4 -Conclusion
PART 1: SYNTHESIS AND CHARACTERIZATION OF NANO-OBJECTS

Organically capped platinum nanoparticles

→ 4-mercaptoaniline functionalized platinum nanoparticles

Isolated solid powder: 15 % organic content

Proposed a chemical formula: \( \text{Pt}_{265} (-\text{S} -\text{NH}_2)_{80} \)

Averaged molar weight: \( \sim 60000 \text{ g/mole} \)

X-ray diffraction (wide angles)
FCC Structure
Core diameter (scherrer) \( \sim 2 \text{ nm} \)

X-Rays diffraction (small angles)
Low size polydispersity
(defined averaged interparticle distance)

Capping molecules allow spontaneous solubilisation as individual nanoparticles.
PART 1: SYNTHESIS AND CHARACTERIZATION OF NANO-OBJECTS

Making different bricks from by modification through « over-grafting » reactions

Mother brick

Derivatized/overgrafted nanoparticles

- Control of nanoscale environment of platinum core
- Long term stability of stock solutions
PART 1: SYNTHESIS AND CHARACTERIZATION OF NANO-OBJECTS

Characterizing partial over grafting

Over-grafting ratio ( % of reacted amine functions) :

7%  19%  39%  42%  43%

Governed by steric effects
PART 1: SYNTHESIS AND CHARACTERIZATION OF NANO-OBJECTS

Characterizing over grafting

- Infrared spectroscopy:
PART 1: SYNTHESIS AND CHARACTERIZATION OF NANO-OBJECTS

Characterizing over grafting

→ X-ray photo-electron spectroscopy (XPS)
Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

ELaboration and features of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

→ Langmuir-Blodgett procedure

1- Spreading

Spreading with a controlled ratio of

Fatty acid

nanoparticles

\(\text{CH}_3-(\text{CH}_2)_{20}-\text{COOH}\)

2- Compression at controlled surface pressure: mixed film formation

Note: contrôle of platinum density 2 µg/cm² to 0.2 µg/cm²
Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

ELaboration and features of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

- Control of platinum density in one monolayer
- Control of the number layers

Two ways to control platinum density on the solid substrate

H. Perez, R. M. Lisboa de Sousa, J-P. Pradeau and P-A. Albouy

H. Perez, V. Noël, S. Cavaliere, A. Etcheberry, P-A. Albouy

Note: fatty acid can be eliminated after film deposition
PART 2: ELABORATION AND CHARACTERIZATION OF SOLID STATE NANOSTRUCTURES FROM PREFORMED NANO-OBJECTS

Characterization of Langmuir-Blodgett films

Infrared spectroscopy

\[ \text{CH}_2 \text{COOH} \]

H. Perez, V. Noël, S. Cavaliere, A. Etcheberry and P-A. Albouy

*Thin Solid films in press*
Evidence of fatty acid removal by washing procedure (skeletonization)

H. Perez, V. Noël, S. Cavaliere, A. Etcheberry and P-A. Albouy
Thin Solid films in press
Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Behaviour towards a classical probe

$[\text{FeCN}_6]^{3/-4-}$ redox probe

$5 \text{mM } [\text{FeCN}_6]^{3/-4-} \text{ in } 0.1 \text{ M Na}_2\text{SO}_4 @ 20 \text{ mV s}^{-1}$

Bare gold electrode

$[\text{FeCN}_6]^{3/-4-}$ behaves as quasi reversible system with Pt 1

5 layers Pt 1 / fatty acid (50/50)
Thiol capped platinum nanoparticles exhibits H upd feature of « contaminated » surface

- $Q' \neq Q''$
- Low electroactive surfaces...
Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Nanoparticles exhibit a direct significant response to oxygen reduction

**Graph:**
- E (mV) / ENH
- i (µA cm⁻²)

**Equation:**
\[ HClO_4 \ 1 \text{ mol L}^{-1}, \ 20 \text{ mV s}^{-1} \]

**Table:**

<table>
<thead>
<tr>
<th></th>
<th>before cycling</th>
<th>after cycling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt 4f/S 2p 161-166eV</td>
<td>3.77</td>
<td>4.04</td>
</tr>
<tr>
<td>Pt 4f/Au 4f</td>
<td>0.15</td>
<td>0.16</td>
</tr>
</tbody>
</table>

**Cavaliere S. Raynal, F. Etcheberry A., Herlem M., Perez H.**

Prolonged cycling keep the organic crown essentially unchanged
[FeCN₆]³⁻/⁴⁻ redox probe

5 mM [FeCN₆]³⁻/⁴⁻ in 0.1 M Na₂SO₄ @ 20 mV s⁻¹

Electrochemical response is blocked with Pt 2
(Residual response could be due to pinholes)

Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Electrochemical behaviour: effect of organic crown in mixed films

Oxygen reduction

Pt 1

Pt 2

Exhibit no electrochemical activity towards oxygen reduction

Pt 2

Effect of the fatty acid matrix?
Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Electrochemical behaviour: Effect of organic crown versus fatty acid elimination

$O_2$ saturated 1 M HClO$_4$ @ 20 mV s$^{-1}$

Before washing

After washing

effect nanoparticle environment:
- Surrounding (fatty acid)
- Local (organic crown)
Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Electrochemical behaviour: Effect of platinum loading

- O₂ reduction (mixed films)

Two ways to modify platinum density

A

Fixed density in the layer
Increasing number of layers

B

Fixed number of layer density in one monolayer ~ 0.1 µg/cm² to ~ 0.8 µg/cm²

Both kinds of dilution lead to the same strong effect on current and potential

\[ \text{O}_2 \text{ saturated } 1 \text{ M HClO}_4 \@ 20 \text{ mV s}^{-1} \]
Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Electrochemical behaviour: Effect of platinum loading

Platinum density effect after fatty acid elimination (50/50 Pt-1/fatty acid ratio)

\[(\text{O}_2 \text{ saturated } 1 \text{ M } \text{HClO}_4 @ 20 \text{ mV s}^{-1})\]

![Diagram showing electrochemical behaviour](image)

- Slow improvement of electrochemical response
Platinum density effect after fatty acid elimination (50/50 Pt-1/fatty acid ratio)

(O₂ saturated 1 M HClO₄ @ 20 mV s⁻¹)

After fatty acid elimination one layer loading gives the same electrochemical response as several layers

Main goal: To make model porous electrodes with controlled platinum loading and controlled nanoparticle feature which can be characterized ex-situ (three-electrode cell) and in fuel cells.
Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

Association of platinum nanoparticles and carbon nanotube through **Bottom-up approach**:

NP Solution in solvent 1  +  NT Suspension NT in solvent 2  →  Mixture under stirring

Control of relative amount allows nanocomposites liquid dispersion formation with controlled coverage of nanotubes.
Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

Characterization of nanocomposite dispersions by Transmission Electron Microscopy

NP/NT = 1/2

NP/NT = 1/5

NP/NT = 1/10
Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

Characterization of nanocomposite dispersions by Transmission Electron Microscopy

NP/NT = 1/100
Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

Electrode formation by filtration of the liquid nanocomposite dispersion

As a function of volume and NP/NT ratio, platinum loading can be controlled over a wide range.
Platinum loading can be controlled over a wide range
Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

Electrochemical behaviour

Same feature for H upd….
Electrochemical behaviour towards oxygen reduction

Oxygen reduction can be evidenced over a wide range of platinum loadings and up to ultra low loading.

Platinum loadings:
- a) 75 µg/cm²
- b) 29 µg/cm²
- c) 10 µg/cm²
- d) 0.8 µg/cm²
- e) No platinum

B. Baret Ph-D Thesis 2008
Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

Fuel cell test preliminary results

Fuel cell test electrode

ex-situ characterization (three-electrode cell)

S = 44 cm²

S = 2.3 cm²
Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

• Fuel cell test (A. Morin CEA Technological Research Division Grenoble):

  Reference Membrane Electrode Assembly: Commercial Anode et cathode 500 µg/cm²
  Test Membrane Electrode Assembly : Anode 500 µg/cm² cathode nanocomposite (115 µg/cm²) No activation treatment

  Demonstrate the possibility to decrease significantly the cathode platinum loading (close to factor 5) while keeping high performances
Capped platinum nanoparticles can provide efficient oxygen reduction catalyst

- the sites concerned by oxygen reduction?

- reliability of H upd measurement versus oxygen reduction potentialities?

Determine electrochemical parameters directly related to oxygen reduction in nanocomposite porous electrodes …
Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Specifical behaviour towards Hydrogen underpotential deposition

- \( Q' \neq Q'' \)
- Low electroactive surfaces
  - Reliable measurement?
Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Modify the platinum core....
Part 2: Mixed LB films based on organically capped platinum nanoparticles

Synthesis and characterization of nano-objects

Controlled manipulation in solution

Elaboration and characterization of solid state nanostructures from preformed nano-objects

Part 3: Electrochemistry...

Understanding of phenomena related to nanoscale features

Study of properties

DEVELOPMENT AND ELECTROCHEMICAL BEHAVIOUR OF PLATINUM BASED NANOCOMPOSITE MODEL STRUCTURES BUILT USING THE BOTTOM UP APPROACH
PART 3: ELECTROCHEMICAL PROPERTIES

Oxygen reduction: a direct electrochemical activity

\[ \text{HClO}_4 \, 1 \text{ mol L}^{-1}, \, 20 \text{ mV s}^{-1} \]

\[ \begin{array}{c}
\text{Pt 4f/S 2p} \\
S 2p \, 161-166eV \end{array} \]

\[ \begin{array}{c}
\text{Pt 4f/Au 4f} \\
0.15 \end{array} \]

\[ \begin{array}{c}
\text{Pt 4f/S 2p} \\
3.77 \end{array} \]

\[ \begin{array}{c}
\text{Pt 4f/Au 4f} \\
0.16 \end{array} \]

Prolonged cycling keep the organic crown essentially unchanged

PART 3: ELECTROCHEMICAL PROPERTIES

Stability of stock solution towards $\text{O}_2$ reduction

$\text{O}_2$ reduction $\text{HClO}_4$ 1 mol L$^{-1}$, 20 mV s$^{-1}$

<table>
<thead>
<tr>
<th>E mV/ ENH</th>
<th>FRESH SOLUTION</th>
<th>ONE YEAR SOLUTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

LB films from fresh solution

LB films from 1 year aged solution

$\text{S 2p}$
PART 3: ELECTROCHEMICAL PROPERTIES

Influence of different parameters on the electrochemical behaviour

- Effect of organic crown modification
- Effect of fatty acid elimination (versus organic crown effect)
- Effect of platinum density
- Effect of fatty removal (versus platinum density effect)
PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)

$[\text{FeCN}_6^{3-/4-}]$ redox probe

5 mM $[\text{FeCN}_6^{3-/4-}]$ in 0.1 M Na$_2$SO$_4$ @ 20 mV s$^{-1}$

Bare gold electrode

$[\text{FeCN}_6^{3-/4-}]$ behaves as quasi reversible system with Pt 1

5 layers Pt 1 / fatty acid (50/50)
PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)

[FeCN₆]³⁻⁴⁻ redox probe

5 mM [FeCN₆]³⁻⁴⁻ in 0.1 M Na₂SO₄ @ 20 mV s⁻¹

[FeCN₆]³⁻⁴⁻ electrochemical response is blocked with Pt 2
(Residual response could be due to pinholes)
PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)

Oxygen reduction

![Chemical structures](image)

\[ E \text{ (mV)} / \text{ ENH} \]

\[ i \text{ (µA cm}^{-2} \text{)} \]

\[ \text{HClO}_4 1 \text{ mol L}^{-1}, 20 \text{ mV s}^{-1} \]

Strong effect of local environment on
The electrochemical activity
PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)

→ Reasons for Pt 2 inactivity?

Different features of Pt 1 and Pt 2

- D.C. conductivity
  
<table>
<thead>
<tr>
<th>Particule</th>
<th>$\sigma_{//} (S , cm^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-1</td>
<td>$8.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>Pt-2</td>
<td>$3.0 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

- Steric hindrance in Pt 2?

- Pt 2 is soluble in non-polar solvents: Hydrophobicity and wettability?
PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)

Reasons for Pt 2 inactivity D.C. conductivity?

Behaviour of sandwich like structures

Pt-2

n = 6

n = 2-60

Pt-1

n = 5

[Fe(CN)₆]³⁻/⁴⁻ 5 mmol L⁻¹ dans Na₂SO₄ 0.1 mol L⁻¹, 20 mV s⁻¹

E (mV) / ENH

i (µA cm⁻²)
PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)

Reasons for Pt 2 inactivity D.C. conductivity?

Behaviour of sandwich like structures

Pt-2

Pt-1

n = 6

n = 2-60

n = 5

[Fe(CN)₆]³⁻/⁴⁻ 5 mmol L⁻¹ dans Na₂SO₄ 0,1 mol L⁻¹, 20 mV s⁻¹
PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)

Reasons for Pt 2 inactivity D.C. conductivity?

Behaviour of sandwich like structures

Pt-2

n = 6

Pt-1

n = 2-60

n = 5

[Fe(CN)$_6$]$^{3-/4-}$ 5 mmol L$^{-1}$ dans Na$_2$SO$_4$ 0,1 mol L$^{-1}$, 20 mV s$^{-1}$
PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)

Reasons for Pt 2 inactivity D.C.conductivity?

Behaviour of sandwich like structures

Pt-2

n = 6

n = 2-60

n = 5

Pt-1

[Fe(CN)₆]³⁻/⁴⁻ 5 mmol L⁻¹ dans Na₂SO₄ 0,1 mol L⁻¹, 20 mV s⁻¹

S. Cavaliere-Jaricot Ph.D Thesis 2006 University of Versailles Saint Quentin

S. Cavaliere-Jaricot, A. Etcheberry, V. Noël, M. Herlem, H. Perez
PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)

Same behaviour when a simple variable resistance is intercalated for electrochemical measurements

n = 6
n = 2-60
n = 5

Conductivity estimated to $10^{-8}$ S.cm
PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)

→ Reasons for Pt 2 inactivity  D.C.conductivity?

Pt-1

Pt-2

HClO₄ 1 mol L⁻¹, 20 mV s⁻¹

D.C.conductivity does not look responsible for Pt-2 inactivity

Steric hindrance for redox species?

Hydrophobicity and wettability disturb Helmotz layer?
PART 3: ELECTROCHEMICAL PROPERTIES

Effect of fatty acid elimination

→ Fe(CN)$_6^{3-/4-}$ and O$_2$

Before whashing

After whashing

Fe(CN)$_6^{3-/4-}$ 5 mmol L$^{-1}$, Na$_2$SO$_4$ 0, 1 mol L$^{-1}$, 20 mV s$^{-1}$

HClO$_4$ 1 mol L$^{-1}$, O$_2$, 20 mV s$^{-1}$

Strong modification appears in oxygen reduction (improvement)
PART 3: ELECTROCHEMICAL PROPERTIES

Effect of organic crown versus fatty acid elimination

\[ \text{O}_2 \text{ saturated 1 M HClO}_4 \text{ @ 20 mV s}^{-1} \]

The effect of organic crown is still present

Before washing

After washing

Differences between actives particles tend to vanish
PART 3: ELECTROCHEMICAL PROPERTIES

Effect of platinum loading on \( \text{O}_2 \) reduction

Effect of platinum density towards \( \text{O}_2 \) reduction (mixed films)

Two ways to modify platinum density

A

Fixed density in the layer
Increasing number of layers

B

Fixed number of layer
Density in one monolayer \( \sim 0.1 \, \mu\text{g/cm}^2 \) to \( \sim 0.8 \, \mu\text{g/cm}^2 \)

Both kinds of dilution lead to the same strong effect on current and potential

\( \text{O}_2 \) saturated 1 M HClO\(_4\) @ 20 mV s\(^{-1}\)
PART 3: ELECTROCHEMICAL PROPERTIES

Effect platinum loading before fatty acid elimination

Platinum density effect after fatty acid elimination (50/50 Pt-1/fatty acid ratio)

Slow improvement of electrochemical response

(O₂ saturated 1 M HClO₄ @ 20 mV s⁻¹)
Effect platinum loading after fatty acid elimination

Platinum density effect after fatty acid elimination (50/50 Pt-1/fatty acid ratio)

After fatty acid elimination one layer loading gives the same electrochemical response as several layers.

(O$_2$ saturated 1 M HClO$_4$ @ 20 mV s$^{-1}$)

PART 3: ELECTROCHEMICAL PROPERTIES
Nanostructures based on carbon nanotubes and platinum nanoparticles through the bottom-up

M. Pinault, M. Mayne-L'Hermite, C. Reynaud, O. Beyssac, J. N. Rouzaud and C. Clinard
Nanostructures based on carbon nanotubes and platinum nanoparticles through the bottom-up
RECENT DEVELOPMENTS

Nanostructures based on carbon nanotubes and platinum nanoparticles through the bottom-up

MEB images:
P. Bonnaillie
CEA-DEN-SRMP-Saclay France
Nanostructures based on carbon nanotubes and platinum nanoparticles through the bottom-up

Platinum density 50 µg/cm²

Electrochemical study in progress (B. Baret Ph.D Thesis)…

Fuel cell related studies, confidential…

Evaluating LB approach
The bottom up approach presents real advantages to realize model systems in electrochemistry as shown in the case of platinum electrocatalysts.

- Very good control of electroactive material amount (µg scale)
- Evidence of the influence the local environment of electrocatalyst (organic crown effect)
- Evidence of the effect at mesoscopic scale (effect of the fatty acid matrix)

Coupling of modelling and experimental results recorded on such well controlled nanostructures is an interesting tool to understand electrochemical responses...
A. Etcheberry, IREM-CNRS Versailles University UMR 8637

P-A Albouy, Paris-Sud University IREM-CNRS UMR 8502

S. Cavaliere Ph.D Thesis University of Versailles Saint Quentin 2006

B. Baret (Ph.D Student), M. Mayne-L’hermitte, C. Reynaud, CEA-Saclay
Réponse de « type 1 »

Réponse de « type 2 »
CHARACTERIZATION ON LB FILM STRUCTURES

X-ray photo-electron spectroscopy (XPS)

\[ \text{Counts} \]

\[ \text{S 2p} \]

\[ \text{B. E. (eV)} \]

\[ 170 \quad 165 \quad 160 \]

LB films from fresh solution

LB films from 3 months aged solution

precipitate

F. Raynal, A. Etcheberry, S. Cavaliere, V. Noël, H. Perez

Making of nanocomposites structures

Bulk substrates

Finely divided substrates
Effet de l'élimination de l'acide gras
(réduction de O2 HClO4 1M 20 mV.s-1)

Comportement électrochimique
NANOPARTICULES DE PLATINE A ENROBAGE ORGANIQUE MODIFIABLE

Comportement électrochimique

Effet de l’élimination de l’acide gras selon la sonde redox

Avant lavage

Avant la sonde redox

Après lavage

HClO₄ 1 mol L⁻¹, O₂, 20 mV s⁻¹

Fe(CN)₆³⁻/⁴⁻ 5 mmol L⁻¹, Na₂SO₄ 0, 1 mol L⁻¹, 20 mV s⁻¹
NANOPARTICULES DE PLATINE A ENROBAGE ORGANIQUE MODIFIABLE

Comportement électrochimique

Effet de l’enrobage organique des nanoparticules (après élimination de l’acide gras)

Réd. $O_2$ dans $\text{HClO}_4$ 1 M, 20 mV s$^{-1}$
NANOPARTICULES DE PLATINE
A ENROBAGE ORGANIQUE MODIFIABLE

Comportement électrochimique

Etude des faces cristallines actives (réduction H+, désorption H+)

\[
\text{Pt} + \text{H}_3\text{O}^+ + \text{e}^- \rightleftharpoons \text{Pt-H}_{\text{ads}} + \text{H}_2\text{O}
\]

cycles \(E_a > 0,8 \text{ V/ESH}\)

Défauts cristallins (110)

[Graphs showing electrochemical behavior with current (i) vs. potential (E) for 90 cycles]
Etude des faces cristallines actives en $O_2$ activité selon le milieu

Comportement électrochimique

NANOPARTICLES DE PLATINE
A ENROBAGE ORGANIQUE MODIFIABLE

$\text{Pt (111)}$ essentiellement responsable de l’activité ?

Sur monocristaux de Pt (littérature) :

- $H_2SO_4$ : $\text{Pt}(110) > \text{Pt}(100) > \text{Pt}(111)$
- $\text{HClO}_4$ : $\text{Pt}(110) > \text{Pt}(111) > \text{Pt}(100)$
- $\text{NaOH}$ : $\text{Pt}(111) > \text{Pt}(110) > \text{Pt}(100)$
Etude de la dégradation du platine

Comportement électrochimique

Diminution de l’aire électro-active  →  Dissolution Pt ?
Etude des espèces chimiques qui « empoisonne » le catalyseur (effet $S^{2-}$)

Comportement électrochimique
Q_H = 115 µC cm^{-2}

Surface Active = \frac{Q_H}{[Pt]} \times 0.21


Surface Active = 55 m^2 g^{-1}

(140 m^2 g^{-1} pour NP de 2 nm “nue”)

≅ 40% Surface Active

EFFET DE L’ENROBAGE ORGANIQUE

Probable désorption enrobage

11 couches Pt-thiophène/BHA 50/50, HClO_4 1 mol L^{-1}, 100 mV s^{-1}
DEVELOPPEMENT D' ELECTROCATALYSEURS
MODELES DE PAC PAR L’APPROCHE BOTTOM-UP

CONCLUSION

L’approche adoptée permet d’accéder à des systèmes dont les caractéristiques sont assez bien déterminées

-Quantité de catalyseur mise en jeu

-Structure et environnement de la couche catalytique…

Les systèmes à base de platine couplés à des études de modélisations peuvent probablement apporter des éléments de compréhension des phénomènes fondamentaux mis en jeu dans les catalyseurs de PEMFC…
PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)

Pt 1

Pt 2

Pt 3

5 mM $\text{Fe(CN}_6^{3-/4-}$ in 0.1 M $\text{Na}_2\text{SO}_4$ @ 20 mV s$^{-1}$

$E$ (mV) / ENH

$i$ (µA cm$^{-2}$)

More pronounced in oxygen reduction

$\text{O}_2$ saturated 1 M $\text{HClO}_4$ @ 20 mV s$^{-1}$
STABILITÉ DANS HClO₄
STABILITÉ DANS $\text{HClO}_4$

<table>
<thead>
<tr>
<th></th>
<th>Avant électrochimie</th>
<th>Après électrochimie</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pt 4f/S 2p</strong></td>
<td>3,77</td>
<td>4,04</td>
</tr>
<tr>
<td><strong>S 2p 161-166eV</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Pt 4f/S 2p</strong></td>
<td>3,77</td>
<td>3,49</td>
</tr>
<tr>
<td><strong>S 2p 161-171eV</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Pt 4f/Au 4f</strong></td>
<td>0,15</td>
<td>0,16</td>
</tr>
</tbody>
</table>

Sox représente 13% du soufre restant après électrochimie
STABILITÉ DANS NaOH

<table>
<thead>
<tr>
<th></th>
<th>Avant électrochimie</th>
<th>Après électrochimie</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt 4f/S 2p</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S 2p 161-166eV</td>
<td>3,85</td>
<td>7,04</td>
</tr>
<tr>
<td>Pt 4f/S 2p</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S 2p 161-171eV</td>
<td>3,85</td>
<td>4,68</td>
</tr>
<tr>
<td>Pt 4f/Au 4f</td>
<td>0,14</td>
<td>0,19</td>
</tr>
</tbody>
</table>

Sox représente 33% du soufre restant après électrochimie.
Avant électrochimie

Après électrochimie

Pt 4f

S 2p

Avant électrochimie

Après

Sox

Avant
ELECTRICAL AND ELECTROCHEMICAL PROPERTIES OF PLATINUM NANOPARTICLES ASSEMBLIES

Electrical behaviour

D.C. conductivity as function of the number of monolayers (mixed film 50/50 ratio area)

Possible influence of percolation, defects, nanoparticles domain size

Activation energy: \( \sigma = \sigma_0 \cdot e^{\frac{-E_a}{RT}} \)

Ea lies between 70 meV and 90 meV

Ea is mainly related to the core diameter
Electrical behaviour

- D.C. conductivity level and evolution

<table>
<thead>
<tr>
<th>Conductivity with fatty acid S.cm⁻¹</th>
<th>Functionalized Particle</th>
<th>Reaction Scheme 1</th>
<th>Reaction Scheme 2</th>
<th>Reaction Scheme 3</th>
<th>Reaction Scheme 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0. 10⁻²</td>
<td>Functionalized Particle</td>
<td>8.5. 10⁻⁴</td>
<td>2.5.10⁻⁴</td>
<td>7.5.10⁻⁴</td>
<td>3.0.10⁻⁷</td>
</tr>
</tbody>
</table>

- D.C. conductivity evolution is probably related to interparticle distance

<table>
<thead>
<tr>
<th>Interparticle distance nm</th>
<th>Functionalized Particle</th>
<th>Reaction Scheme 1</th>
<th>Reaction Scheme 2</th>
<th>Reaction Scheme 3</th>
<th>Reaction Scheme 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>dₚ/ₚ 3.7</td>
<td>dₚ/ₚ 3.7</td>
<td>4.1</td>
<td>4.3</td>
<td>4.0</td>
<td>4.8</td>
</tr>
<tr>
<td>dₚ/ₚ 3.6</td>
<td>dₚ/ₚ 3.6</td>
<td>3.6</td>
<td>3.5</td>
<td>3.3</td>
<td>5.2</td>
</tr>
</tbody>
</table>
Steps involved in the bottom-up approach

- Synthesis and characterization of nano-objects
  - Chemical composition
  - Size polydispersity
  - Structure cristalline
  - Forme géométrique, faces cristallines

- Making solution of individualized object with known concentration
  - Control of the amount of material
Electrical properties

- D.C. conductivity

<table>
<thead>
<tr>
<th>Conductivity with fatty acid S.cm⁻¹</th>
<th>Functionalized Particle</th>
<th>Reaction Scheme 1</th>
<th>Reaction Scheme 2</th>
<th>Reaction Scheme 3</th>
<th>Reaction Scheme 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0. 10⁻²</td>
<td>8.5. 10⁻⁴</td>
<td>2.5.10⁻⁴</td>
<td>7.5.10⁻⁴</td>
<td>3.0.10⁻⁷</td>
<td></td>
</tr>
</tbody>
</table>

Conductivity is probably related to interparticle distances

<table>
<thead>
<tr>
<th>Interparticle distance nm</th>
<th>Functionalized Particle</th>
<th>Reaction Scheme 1</th>
<th>Reaction Scheme 2</th>
<th>Reaction Scheme 3</th>
<th>Reaction Scheme 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.7</td>
<td>4.1. 10⁻⁴</td>
<td>2.5.10⁻⁴</td>
<td>7.5.10⁻⁴</td>
<td>3.0.10⁻⁷</td>
<td></td>
</tr>
</tbody>
</table>
Pt-2

![Chemical Structure](image)

**Graphs**

- **Graph 1:** Plot of $i$ (µA cm$^{-2}$) vs $E$ (mV) / ENH
  - X-axis: $E$ (mV) / ENH
  - Y-axis: $i$ (µA cm$^{-2}$)
- **Graph 2:** Plot of $i_a$ (µA cm$^{-2}$ at 515 mV) vs $n$
  - X-axis: $n$
  - Y-axis: $i_a$ (µA cm$^{-2}$ at 515 mV)
Platinum widely used in PEMFC and widely studied as electrocatalyst for oxygen reduction.

Some of the important points are:

- in PEMFC, having low loading/ high degree of utilization of Pt,
- In fundamental studies, having well defined system (structure, composition…)

To have a good control in the manipulation and the amount and environment of catalyst involved.

Way of synthesis of catalysts is a key point in order to reach such a control.

Different ways of synthesis of finely divided platinum:

- Impregnation/reduction (carbon support)
- Electrodeposition
- Sputtering, CVD
- Solution synthesis (wet chemistry) with capping agent

Isolable and redispersible particles are of special interest.
INTRODUCTION

Platinum, oxygen reduction and PEMFC

Sarah L. Horswell, Christopher J. Kiely, Ian A. O’Neil, and David J. Schiffrin

Eklund S.E. and D. E. Cliffel

S. Mandal, PR. Selvakannan, D. Roy, Raghunath V. Chaudhari and M. Sastry*
Chem. commun. 2002, 3002

Isolable, redispersible particles in solvents (like molecules or polymers)

New possibilities by combining with the bottom-up approach developed in nanosciences and nanotechnologies
PART 1: SYNTHESIS AND CHARACTERIZATION OF NANO-OBJECTS

Structural features of platinum nanoparticles

Nanoparticles are crystallized and faceted

X-ray diffraction (wide angles)
FCC Structure

High resolution T.E.M

Core diameter core RX: ~2 nm

Coll. P-A. ALBOUY LPS Paris-Sud Orsay

Cliché by J-N ROUZAUD ENS-Paris
PART 1: SYNTHESIS AND CHARACTERIZATION OF NANO-OBJECTS

Making different bricks from by modification through over-grafting reactions

Mother brick

Derivatized/overgrafted particles

Partial over grafting: Double crown structure
PART 1: SYNTHESIS AND CHARACTERIZATION OF NANO-OBJECTS

Organic content (Thermal Gravimetric Analysis)

Characterizing partial over grafting

→ Over grafting ratio: % of reacted $\text{NH}_2$ functions

13.7 à 14.9 %

18.6 à 19.07 %
PART 2: ELABORATION AND CHARACTERIZATION OF SOLID STATE NANOSTRUCTURES FROM PREFORMED NANO-OBJECTS

Characterization of Langmuir-Blodgett films

→ X-ray photo-electron spectroscopy (XPS)

![Diagram of molecular structures and XPS spectrum](image)

Coll. A. Etcheberry  IREM-UVSQ Versailles
PART 2: ELABORATION AND CHARACTERIZATION OF SOLID STATE NANOSTRUCTURES FROM PREFORMED NANO-OBJETCS

Characterization of Langmuir-Blodgett films

→ X-Rays diffraction at small angles

Continuous ring indicates a well defined first-neighbours distance $d$

Ring Ellipticity may be related to different distances $d_{||}$ and $d_{\perp}$

| Particule | $d_{||}$ (Å) | $d_{\perp}$ (Å) |
|-----------|--------------|----------------|
| Pt 1      | 41,0         | 36,0           |
| Pt-2      | 48,5         | 52,1           |

After fatty acid removal

| Particule | $d_{||}$ (Å) | $d_{\perp}$ (Å) |
|-----------|--------------|----------------|
| Pt 1      | 40,4         | 35,3           |
| Pt-2      | 49,6         | 40,8           |
Control of platinum nanoparticle features versus electrochemical activity characterization

Controlled surface decontamination by lowering the oxidation potential?

J. Solla-Gullon, V. Montiel, A. Aldaz, J Clavilier
J. Electroanal Chem. 491 (2000) 69
Capped or stabilized Platinum as electrocatalyst

- Control of platinum nanoparticle features versus electrochemical activity characterization

→ Activation steps by thermal treatments:

**FIG. 6.** Experimental and theoretical values of the

*PH. Buffat and J-P Borel Phys. Rev. A 13 (1976) 2287*

→ May change the features of low size nanoparticles!
Determination of electrocatalytical activity of capped/stabilized platinum nanoparticles raises many questions…

- Influence of capping or stabilizing agent on nanoscale nanoparticle features?
- Does H upd provide a reliable measurement of performances towards oxygen reduction in such a case?
- What is the effect of changing the nanoscale scale environment on the electrochemical features?

- Making capped platinum catalyst with different organic crowns well characterized (organic content)
- Control platinum loading in different kinds of nanostructures
- Characterize the electrocatalytical activity without changing the features of the catalyst (No “activation” step!)
Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

Association of platinum nanoparticles and carbon nanotube through **Bottom-up approach**:

Controle of relative amount allows to form Nanocomposites liquid dispersion with controlled coverage of nanotube.
Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

ELaboration and features of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Transcription Electron Microscopy
Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Hydrogen underpotentiel deposition (charge of proton adsorption-desorption)

Scanning at higher and higher potential results in usual features

But modify the platinum core....
Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

Electrochemical characterization do not alter the organic crown