PEMFC degradation mechanism studied by Transmission Electron Microscopy

Laure Guétaz, Sylvie Escribano, Benoît Vion-Dury
LITEN, CEA-Grenoble ,France

Outline

I. Experimental conditions of aging tests

1) Open Circuit Voltage (OCV)
2) Steady state at fixed current (i=0.6 A/cm²)
3) On/Off cycles (0 – 0.6 A/cm²)

II. TEM analysis of the electrocatalyst distribution in the aged MEA

- Anode
- Cathode

III. Catalyst degradation mechanisms

- Electrochemical Ostwald ripening
- Mobility of particles on the carbon support surface
- Carbon corrosion

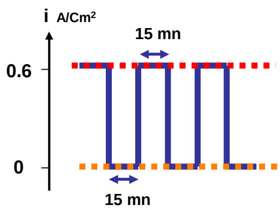
Conclusions and future works

Experimental conditions of the aging tests

- MEA : 25 cm²
  - CCB hot-pressed
  - Membranes: Nafion NRE212
  - Electrodes: ELAT Single side LT140EW-SI (0.5 mgPt/cm² with 30% Pt/C XC72)
- Single cell nominal operating conditions
  - P = 1.5 bars
  - T = 80℃
  - St 1,2/2 @i on load
  - St 1,2/2 @120mA/cm² at OCV
  - Gases humidification:
    - Dry H_2 / fully humidified air

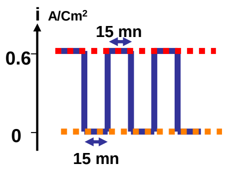
3 aging tests

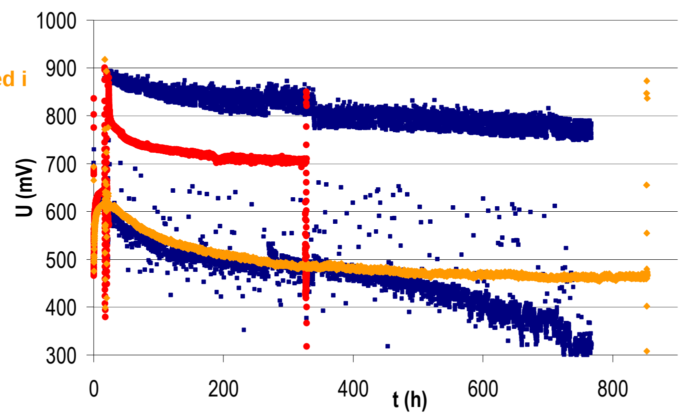
- ❑ OCV
- ❑ Steady state at fixed I (0.6 A/cm²)
- ❑ On/Off cycles (O – 0.6 A/cm², 15-15 mn)



Performance during the aging tests

- ❑ OCV
- ❑ Steady state at fixed i
- ❑ On/Off cycles

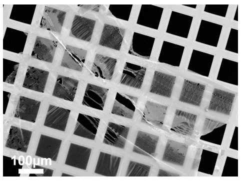




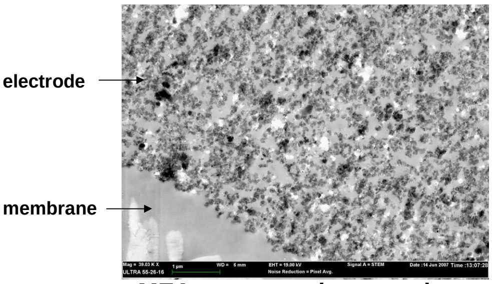
What are the electrocatalyst distribution evolutions during these tests ?

MEA TEM observations

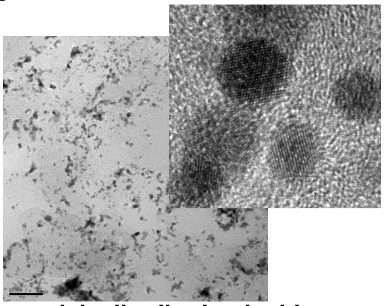
Sample preparation by ultramicrotomy



- ♦ A piece is taken from MEA near the gas exit side
- ♦ Embedding in a epoxy resin.
- ♦ Thin slices (70 nm) are cut with a diamond knife and deposit on a copper grid

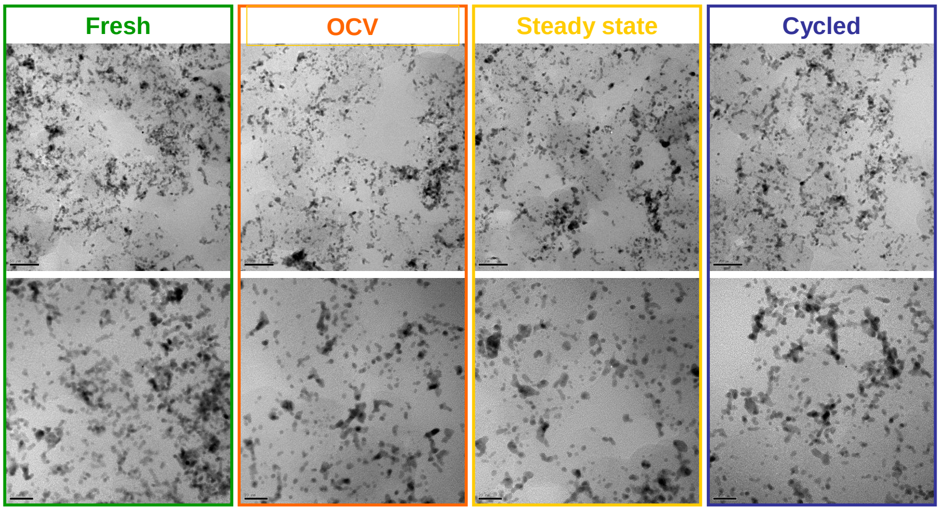


MEA cross-section sample



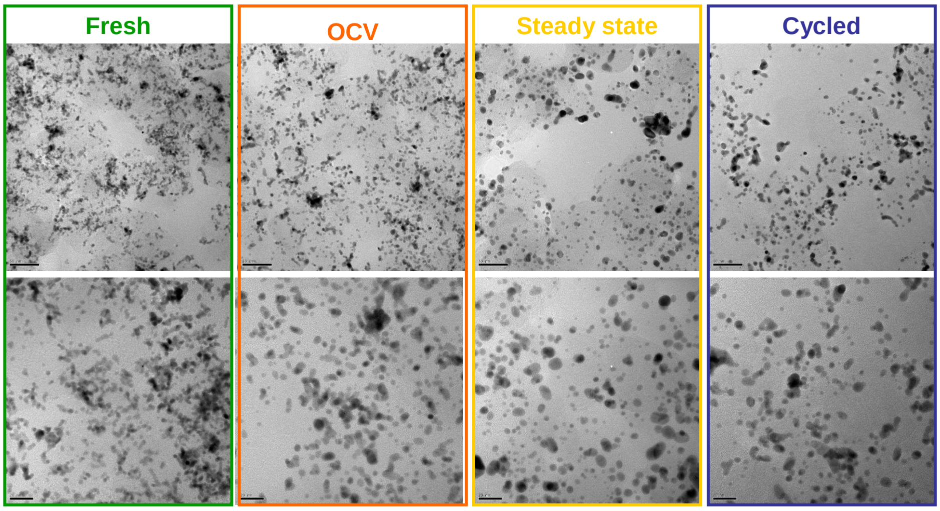
Pt particle distribution inside the electrodes

Anode side



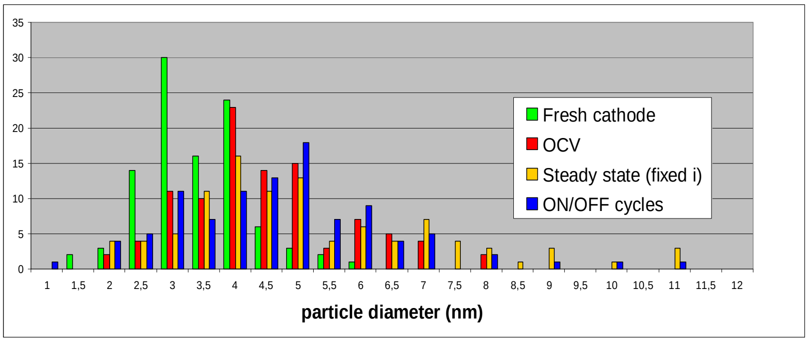
⇨ No significant change is observed at the anode

Cathode side near the membrane



⇨ **Particle coarsening is observed for the three aging conditions**

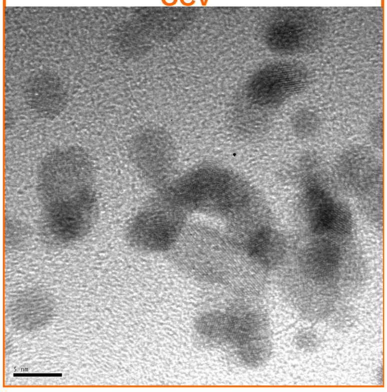
Particle size distribution at the cathode



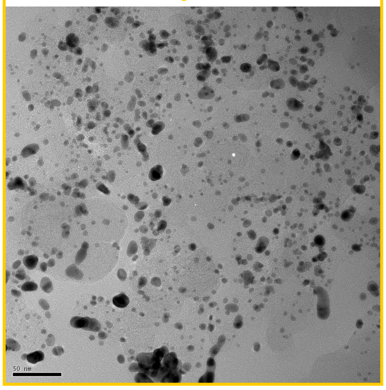
- **For the 3 aged cathodes :**
  - **Particle coarsening**
  - **Presence of particles larger than 6 nm that did not exist in the fresh cathode.**
  - **No significant difference of the particles size distribution between the 3 aged cathodes.**

Large particle morphology after aging

OCV



Steady state

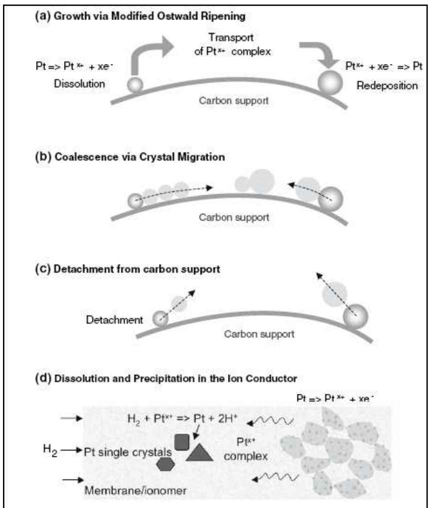


OCV : agglomerates composed of several particles (polycrystalline agglomerates)
Steady state : large spherical single crystal particles

How can we explain this morphology difference ?

Catalyst degradation mechanisms

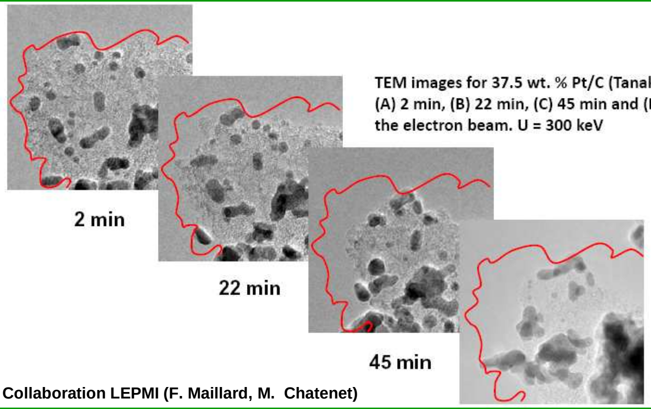
- Electrochemical Ostwald ripening
- Mobility of particles on the carbon support surface
- Carbon corrosion



Y. Shao-Horn, W.C. Sheng, S. Chen, P.J. Ferreira, E.F. Holby, D. Morgan,(2007) Top. Catal., 46, 285.

Carbon degradation during TEM experiments

- Carbon is damaged by the TEM electron beam (300kV)



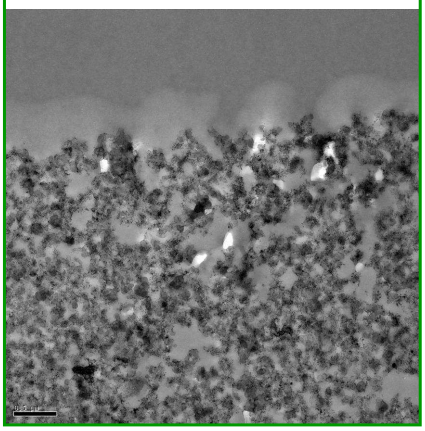
TEM images for 37.5 wt. % Pt/C (Tanaka) taken after (A) 2 min, (B) 22 min, (C) 45 min and (D) 65 min under the electron beam. U = 300 keV

Collaboration LEPMI (F. Maillard, M. Chatenet)

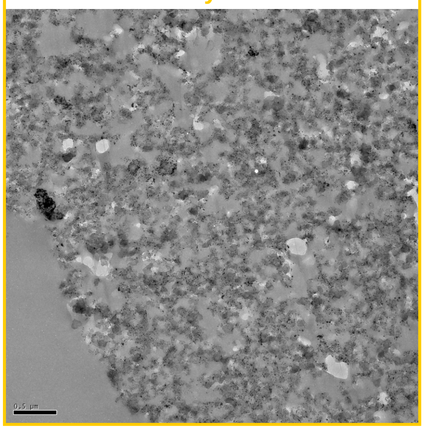
⇨ **the carbon degradation makes the particle getting closer and leads to their coarsening**

Porosity of carbon support

Fresh cathode

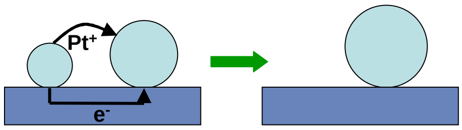


Steady state



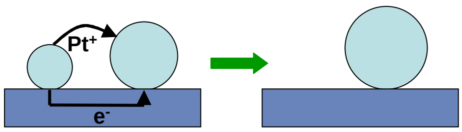
⇨ **no significant carbon corrosion that can lead to particle coarsening.**

Electrochemical Otwald ripening



⇨ **Driving force is the surface energy minimization**

Electrochemical Otwald ripening



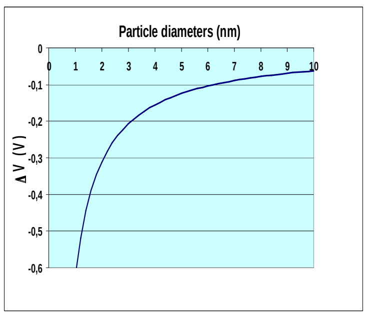
⇨ **Driving force is the surface energy minimization**

Negative shift in the standard electrode potentials of small particles (Plieth 1982)

$$E^{0}_{Particle} - E^{0}_{Bulk} = \frac{2\gamma\Omega_m}{zFr}$$

- γ: surface energy
- Ω_m : molar volume
- r: particle radius

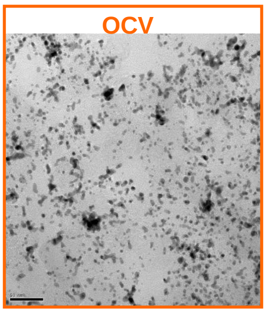
2 different size particles function as a galvanic cell !

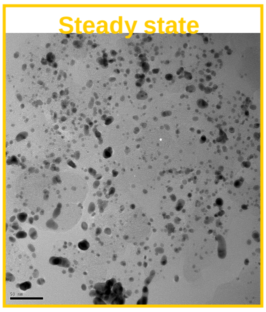


Main parameters that control the mechanism

- **Electrode potential**
- **Electric conductivity of the support**
- **Ionic conductivity of the electrolyte**

Difference in large particle morphology



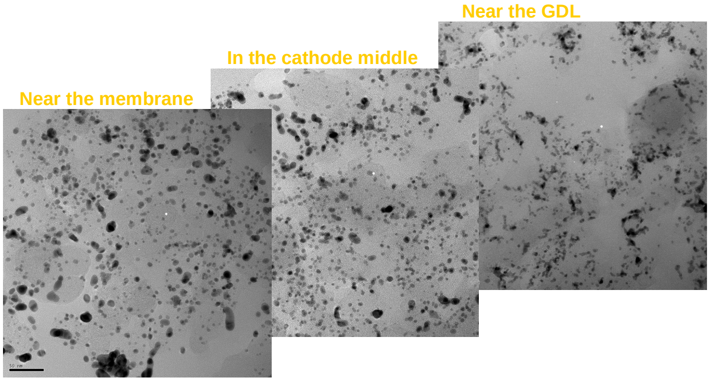


- **<u>Electrode potential</u>, higher in the OCV conditions can not explain this difference**
- **<u>Electric conductivity</u> of the support should be the same**
- **<u>Ionic conductivity</u> is probably higher in the cathode aged in steady state (fixed i) due to the water generated during the cell operation**

⇨ The difference in particle morphology can result from a difference in water content inside the electrode.

Across the cathode thickness

Cathode aged in steady state (fixed i) conditions



Particle coarsening is larger near the membrane than near the GDL.

⇨ Difference in water content trough the cathode can explain the difference in particle coarsening through the cathode

Conclusions

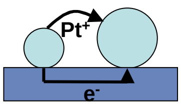
TEM is an important technique to study the catalyst degradation during fuel cell operation

- 3 aging test conditions (OCV, steady state-fixed i-, ON/OFF cycles) :
  - No significant catalyst evolution at the anode
  - Particle coarsening at the cathode

- Analysis of aged cathodes
  - Similar particle size distribution for the 3 aging conditions
  - Difference in the large particle/agglomerate morphology

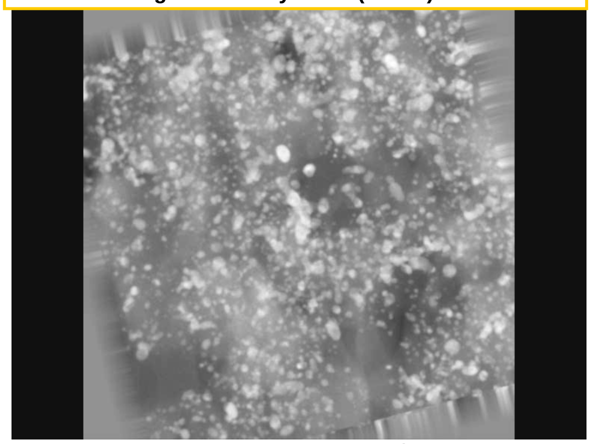
- Particle coarsening mechanism
  - Electrochemical Ostwald ripening seems to be the main mechanism
    - Not only the electrode potential but also the ionic conductivity are important factor for particle degradation
    - Water content inside the electrode has a strong impact on the particle coarsening

Electron Tomography



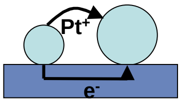
- <u>Distance between the particles</u> should also be an important parameter of electrochemical Oswald ripening mechanism

Cathode aged in steady state (fixed i) conditions



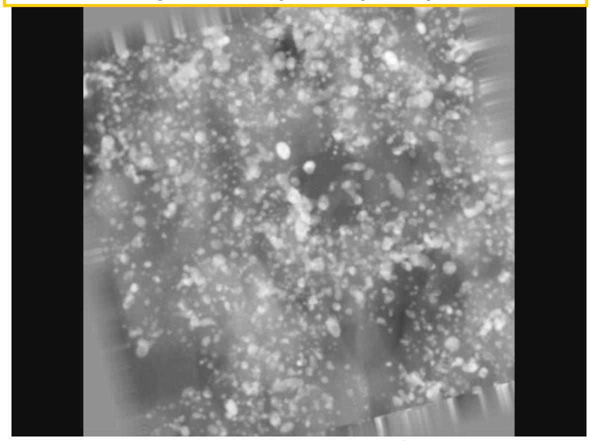
Electron tomography : P. Cherns, L. Guétaz

Electron Tomography



♦ <u>Distance between the particles</u> should also be an important parameter of electrochemical Oswald ripening mechanism

Cathode aged in steady state (fixed i) conditions



Electron tomography : P. Cherns, L. Guétaz

Future needs

♦ <u>**Need of a better understanding of the degradation mechanisms**</u>

- **Characterization of MEA aged in real conditions**
  - **What materials are damaged ?**
  - **Specific characterization technique developments.**
- **Characterization of MEA aged in more controlled electrochemical cell**
  - **Determination of the important parameters that control the degradation mechanisms**

ACKOWLEDGEMENTS

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DVDAME Project

Thank you for your attention