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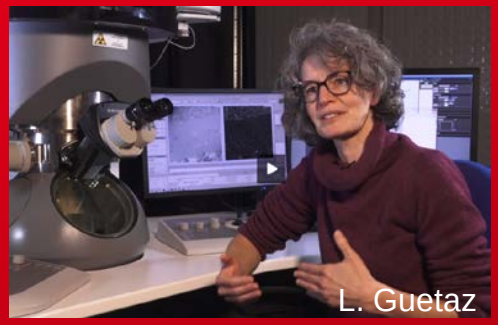
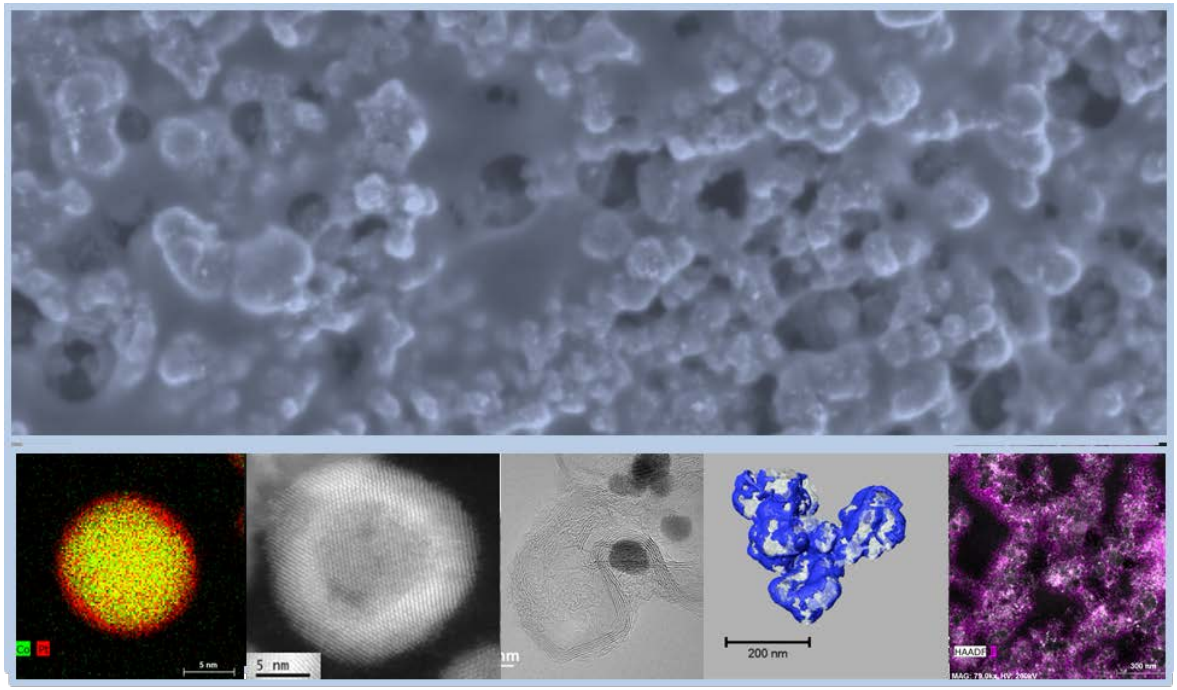
FROM RESEARCH TO INDUSTRY

cea tech



ADVANCED MICROSCOPY TECHNIQUES FOR STUDYING THE DURABILITY OF FUEL CELLS



Laure Guétaz, Sylvie Escribano, Fabrice Micoud

CEA-LITEN, Grenoble, France

Introduction

The durability of PEMFCs remains, with their cost, one of the main barriers to the widespread commercialization of fuel-cell electric vehicles.

The first generation fuel cell vehicles (Toyota Mirai) have demonstrated their good performance:

- **by using MEA with quite high Pt loading (0.37 mg_{Pt}/cm^2)**
- **probably through the development of good system mitigation strategies**

*Borup et al., Current Opinion in Electrochemistry 2020, **21**, 192*

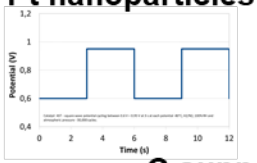
To reduce the MEA Pt loading and to simplify the system management
⇨ it is crucial to still improve the durability of MEA components

MEA degradation studies

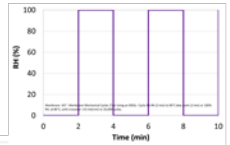
Two main strategies

Ageing tests in single cell under accelerating stress test (AST) protocols

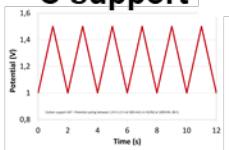
Pt nanoparticles



Membrane



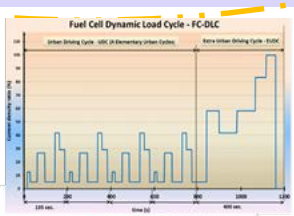
C support



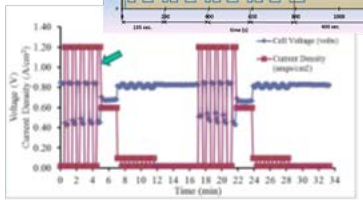
https://energy.gov/sites/prod/files/2016/10/f33/fcto_myrdd_fuel_cells.pdf

- Screening and selection of the MEA materials and components
- Accurate understanding of the degradation mechanisms of each component.

Ageing tests in stack under near real automotive application conditions



G. Tsotridis et al., EU Harmonised test protocols for PEMFC MEA testing in single cell configuration for automotive applications JRC Science for Policy report, 2015; EUR 27632 EN.



Stariha et al., JES, F492-501, 2018 & U. S. DoE "Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan" (2016). https://energy.gov/sites/prod/files/2016/10/f33/fcto_myrdd_fuel_cells.pdf

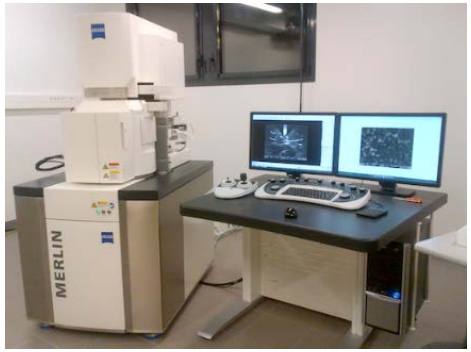
- Which MEA components are degraded and by which mechanisms?
- Do the observed degraded components explain the performance losses?

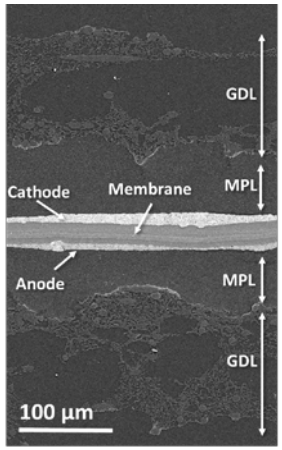
Electron microscopy techniques

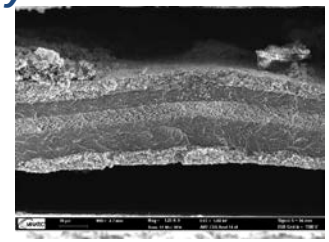
Powerful tools to progress in degradation mechanisms understanding

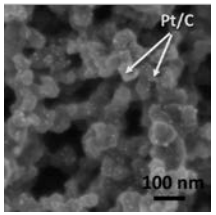
SEM

Scanning Electron Microscopy



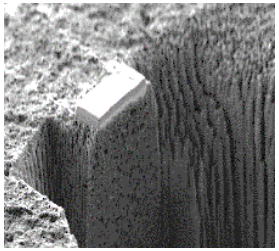


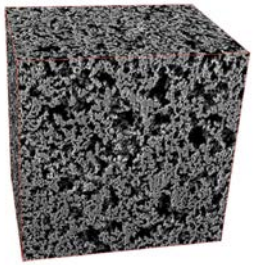




FIB/SEM

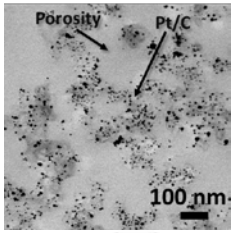
Focused Ion Beam / Scanning Electron Microscopy-

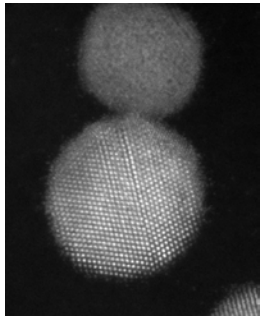


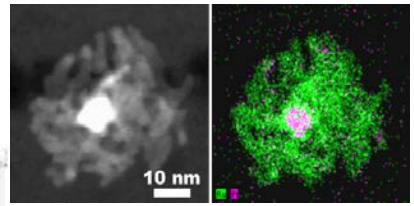


TEM

Transmission Electron Microscopy







OUTLINE

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Introduction

Pt and Pt alloy nanoparticle degradation

- Pt nanoparticles
  - Electrochemical Ostwald ripening: Pt nanoparticle growth
  - Pt membrane precipitation band
- Pt-Co nanoparticles
  - Electrochemical Ostwald ripening: Pt shell thickness increase
  - Ionomer contamination by Co cations
- Role of the carbon support
  - Pt nanoparticles can be localized on or inside the carbon

Carbon corrosion

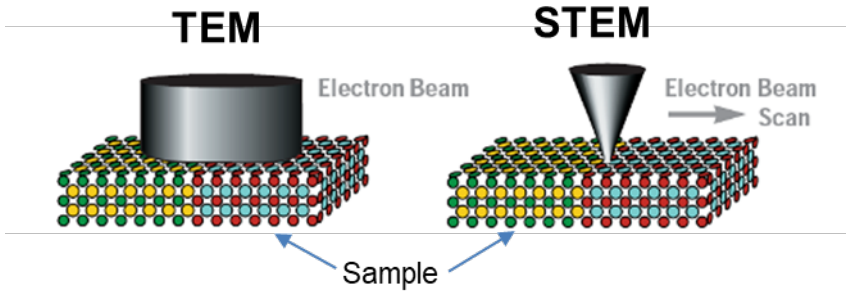
- Compaction of the cathode and effect on the Pt band localization
- Possibility to measure the porosity evolution by FIB-SEM

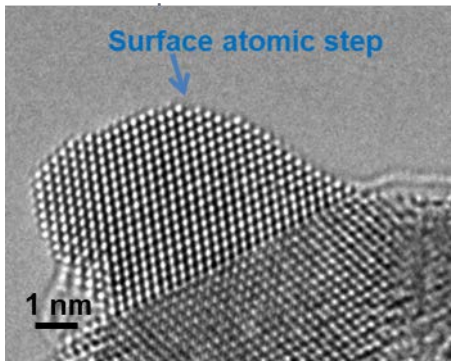
Membrane and cathode ionomer degradation

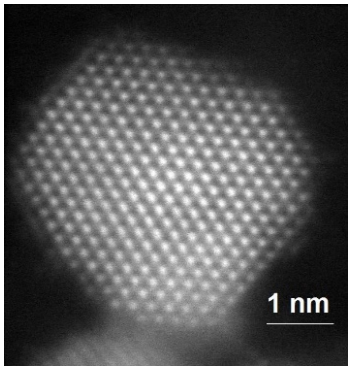
- Different locations of the membrane degradation

Conclusions

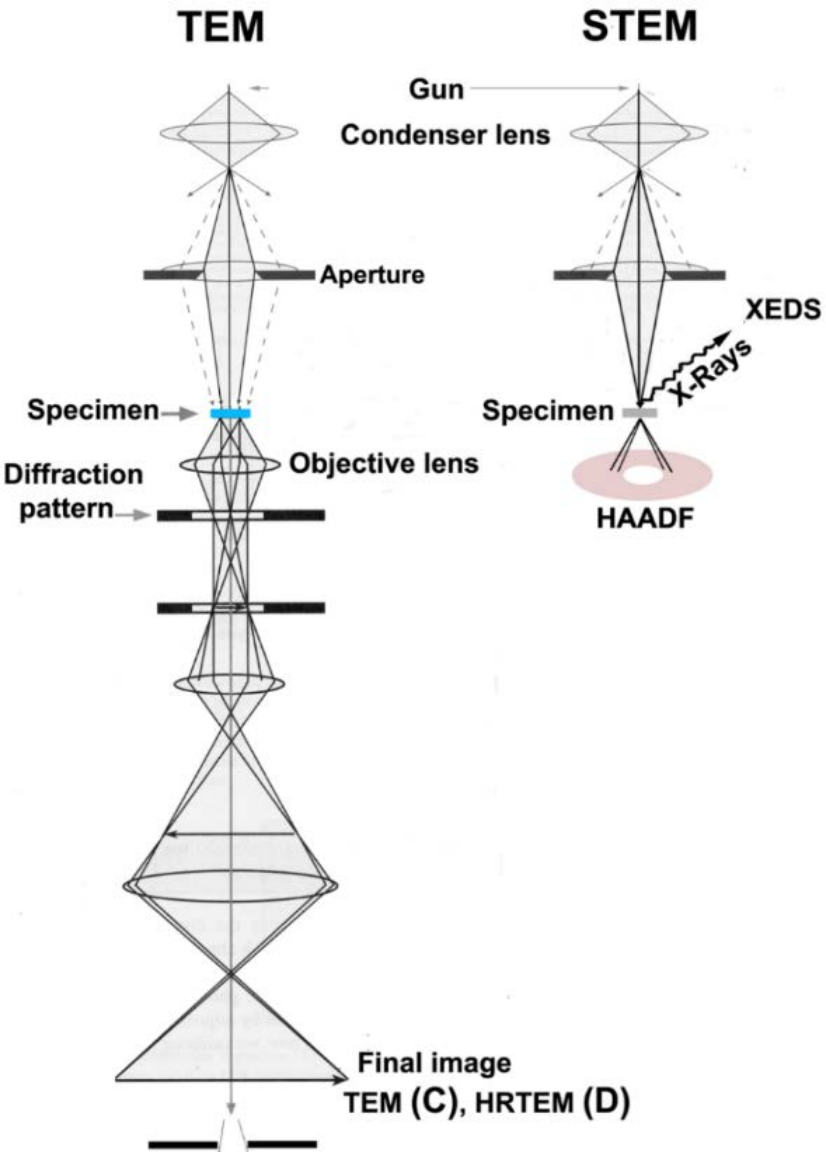
TEM or STEM for nanoparticle structure analyses





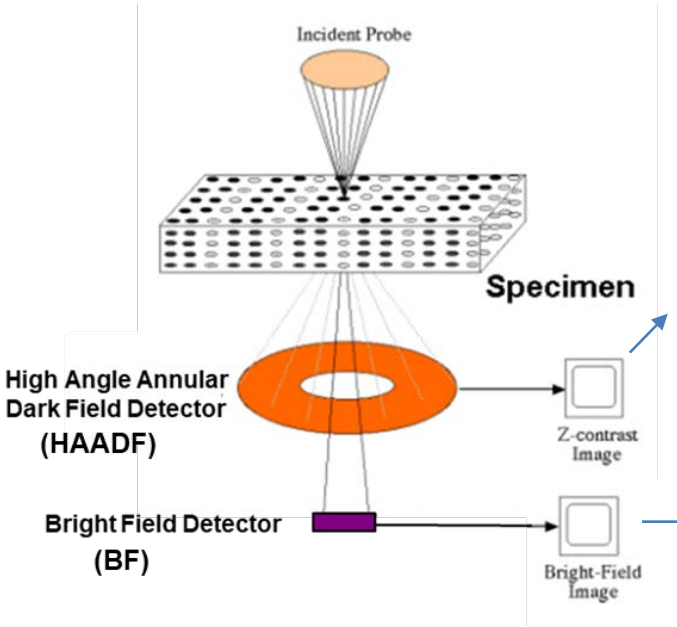


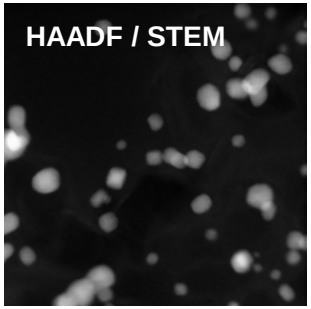
Atomic structure of Pt nanoparticles

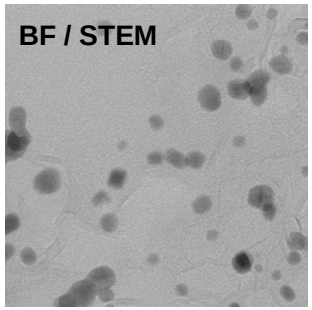


HAADF/STEM for nanoparticle structure analyses

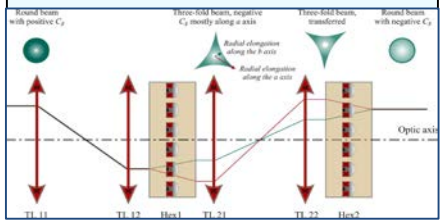
HAADF / STEM

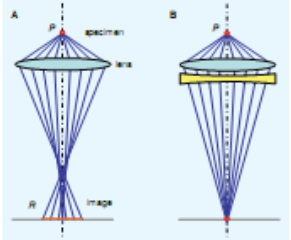




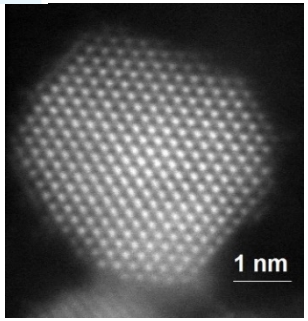


Cs aberration corrector





Atomic resolution



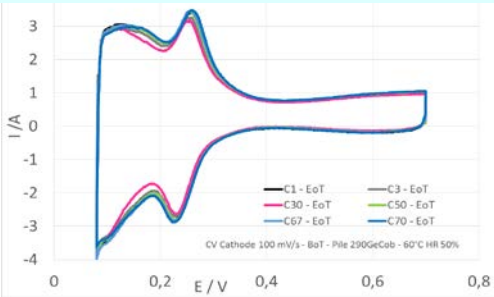
Advantages of HAADF/STEM

- **Chemical contrast (Z-contrast)**: heavier atoms scatter electrons more intensely than lighter atoms
- Possibility to analyze the **chemical composition of the atomic columns** during the scan by **EELS or X-EDS**

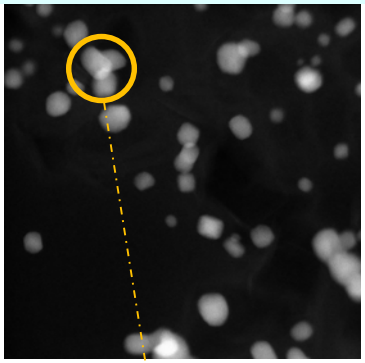
Pt Nanoparticles

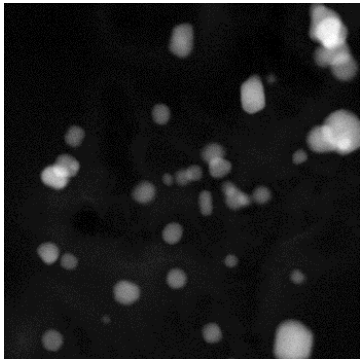
Nanoparticle size distribution is the main microstructural parameter

Electrochemical Surface Area (ECSA)



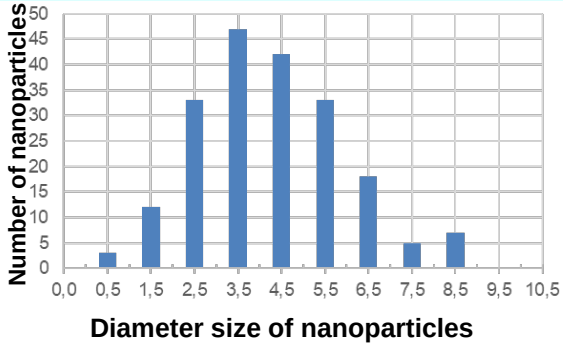
TEM or HAADF / STEM images





200 nanoparticles

Nanoparticle size histogram



Nanoparticle size can be measured using image analysis software

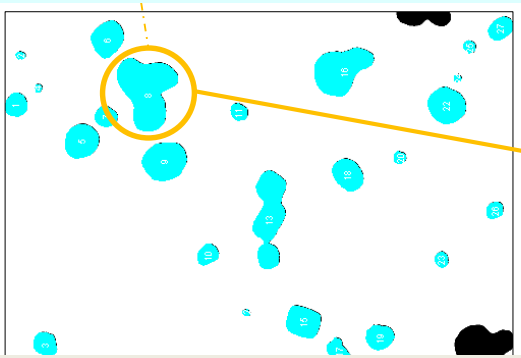
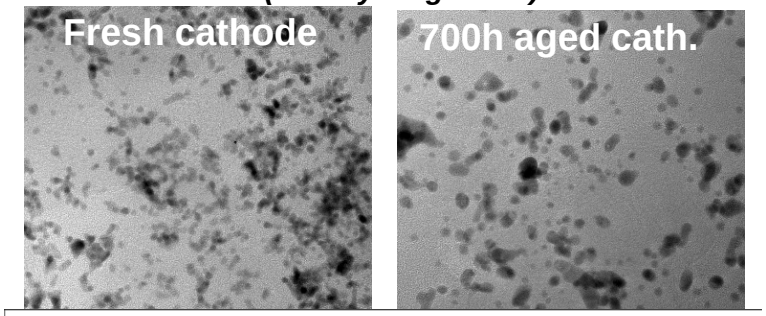


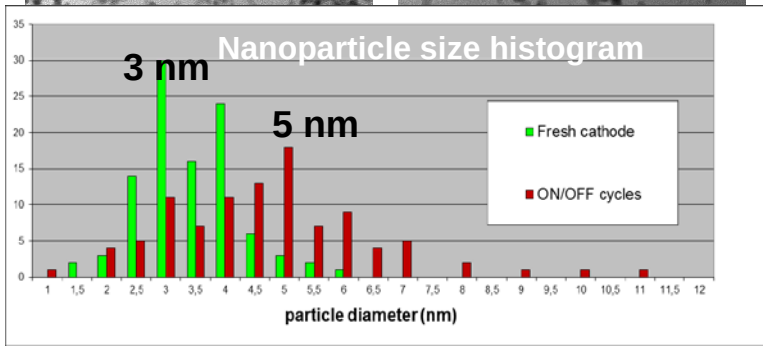
Image overlapping of nanoparticles that are not at the same level in the sample thickness is often measured as large nanoparticles ⇨ increase of the number of large nanoparticles

Pt Nanoparticle Degradation
Electrochemical Ostwald ripening mechanism

Nanoparticle size increases during fuel cell operation

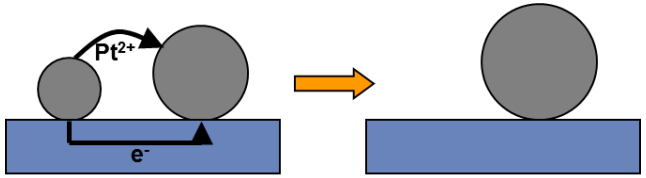
Ageing tests representative of automotive application
(load cycling mode)





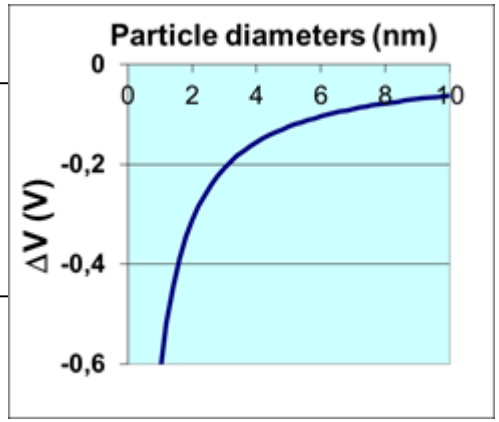
Pt surface area loss can be of 40-50% in few hundred hours of fuel cell operation time.

Electrochemical Ostwald ripening mechanism



- ✓ **Driven by the nanoparticle size dependence of the standard potential.**

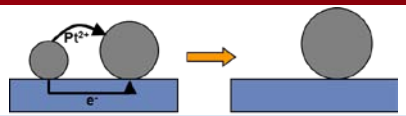
Negative shift in the standard electrode potentials of small nanoparticles (Plieth 1982)



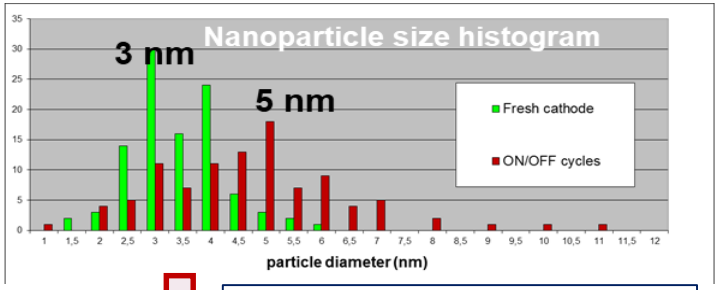
- ✓ **Migration of Pt ions (and electron transfer) between neighboring nanoparticles.**
- ✓ **Enhanced by liquid water content due to higher ionomer ionic conduction.**
- ✓ **Slows down when nanoparticles become larger.**

Pt Nanoparticle Degradation
Electrochemical Ostwald ripening mechanism

Particles with diameters ≥ 4.0 nm are stable

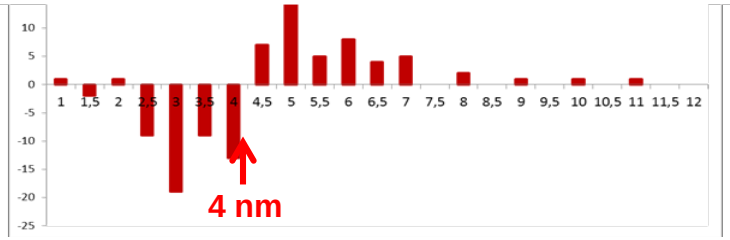


Electrochemical Ostwald ripening mechanism

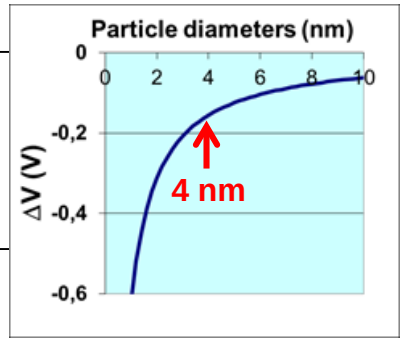


Evolution of Pt NP number for the different NP diameters

Aged Cathode Histogram –Fresh Cathode Histogram



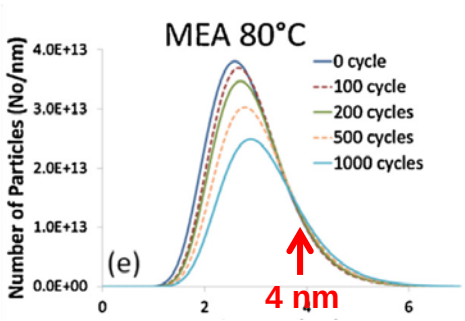
Negative shift in the standard electrode potentials of small nanoparticles (Plieth 1982)



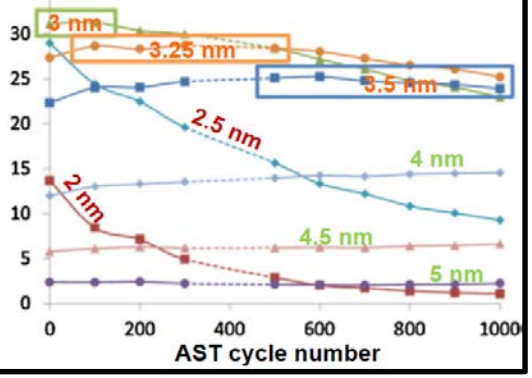
Similar results have been highlighted in studies performed by Operando A-SAXS during AST

(Gilbert et al., Electrochimica Acta 173, 2015, 223)

Nanoparticle size histogram evolution



Evolution of Pt NP number during AST for different NP diameters



Optimization of the electrode microstructure by using larger nanoparticles (4-5 nm)

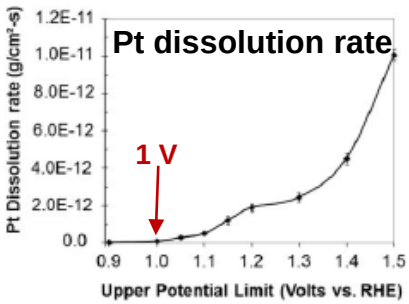
Pt Nanoparticle Degradation

Membrane Pt precipitate band

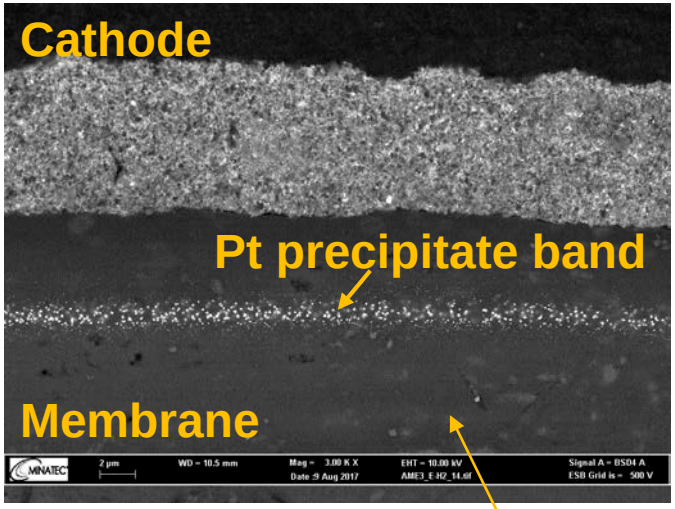
For potential larger than 1 V, a large amount of Pt is dissolved

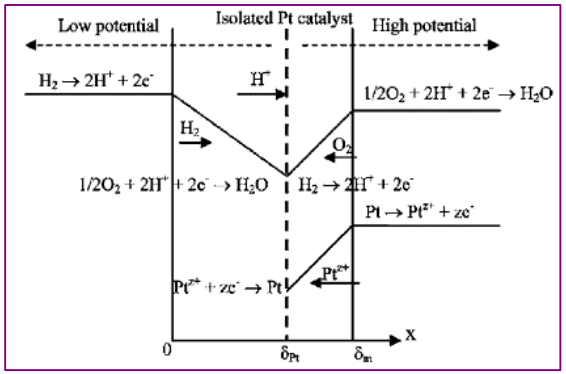
1. **Pt ions migrate toward the membrane**
2. **Pt ions are reduced by H_2 crossover**

Formation of a Pt precipitate band



Myers et al. , J. of Electrochem Soc.,165 (6), 2018,F3178





J. Zhang, J. of Electrochem Soc.,(2007),154 (10) B1006.

- **The position of this band depends on H_2/O_2 crossover.**
- **It is located where the crossover molar flux of O_2 equals one half of the crossover molar flux of H_2**

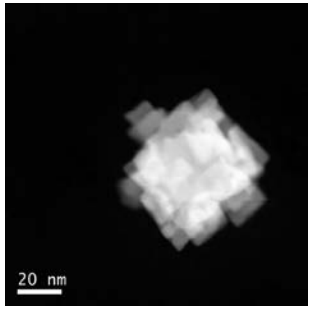
Small precipitates also appear in the whole area between the band and the anode.

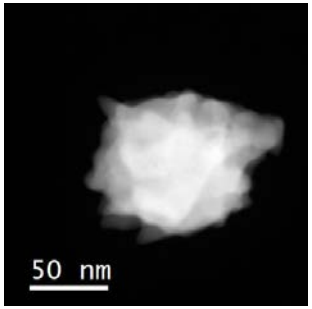
Pt Nanoparticle Degradation

Membrane Pt precipitate band

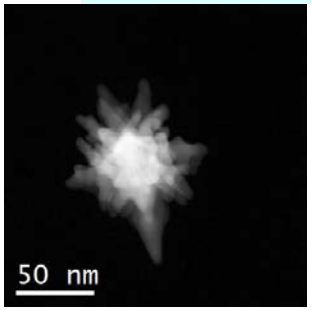
The membrane Pt precipitates have different morphologies

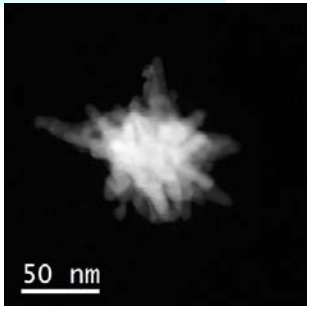
Shape close to the cube





Star/dendritic shape



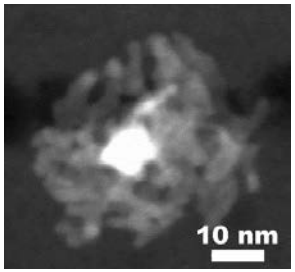


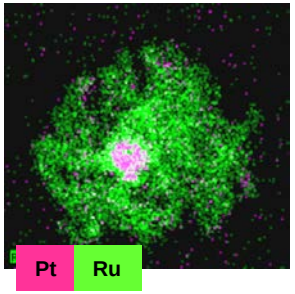
The precipitate shape probably results from the intensity fluxes of the Pt ions and/or H_2

(Ferreira et al. *Electrochemical and Solid-State Letters,* **10** 3 2007, B60)

Lower Pt ion flux ⇨ shape close to the cube

Higher Pt ion flux ⇨ star/dendritic shape





Star shaped precipitates are also observed when Pt-Ru anode is used: they are Pt-Ru precipitates

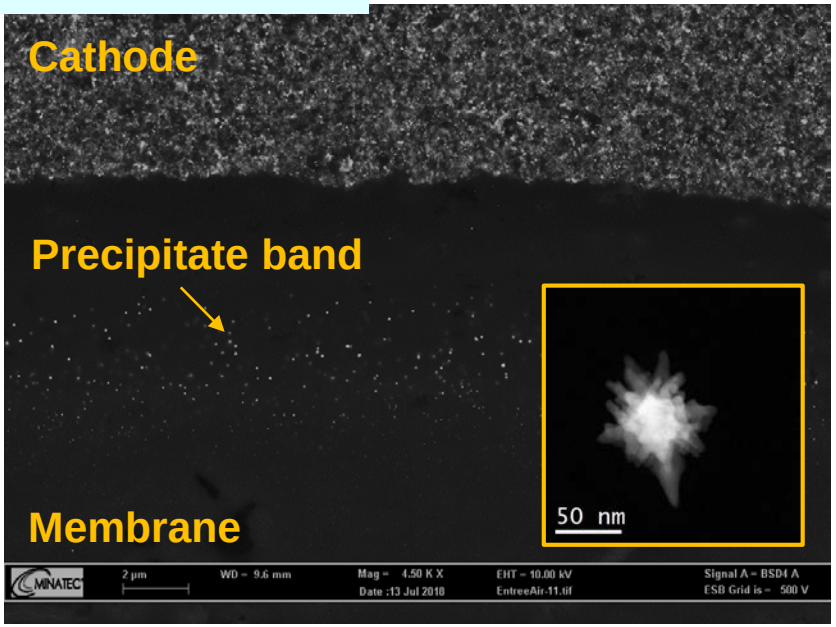
P.A. Henry et al., J. Power Sources 275 (2015) 312

Pt Nanoparticle Degradation

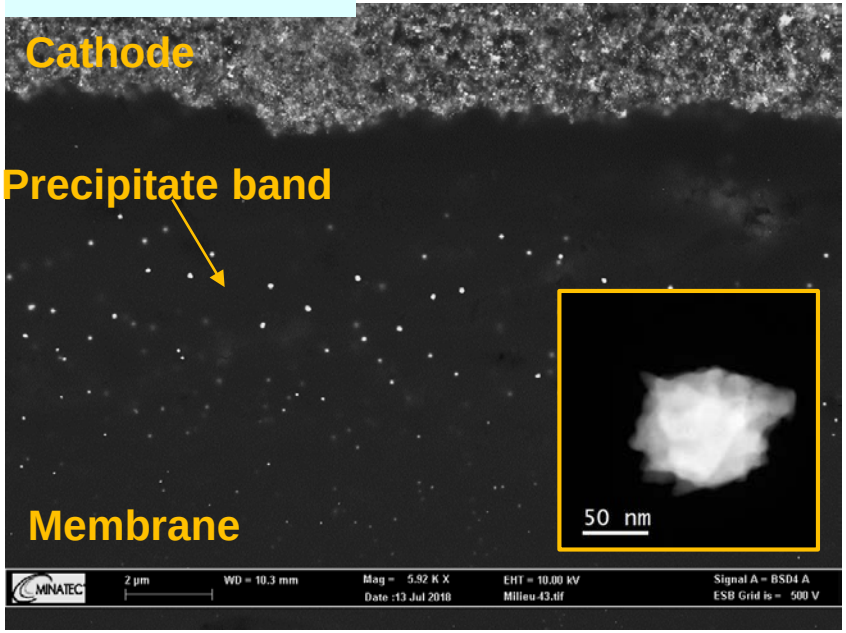
Membrane Pt precipitate band

The morphology of the membrane precipitates can provide some information on the MEA local conditions that could appear during the ageing test.

Air Inlet zone



Middle zone



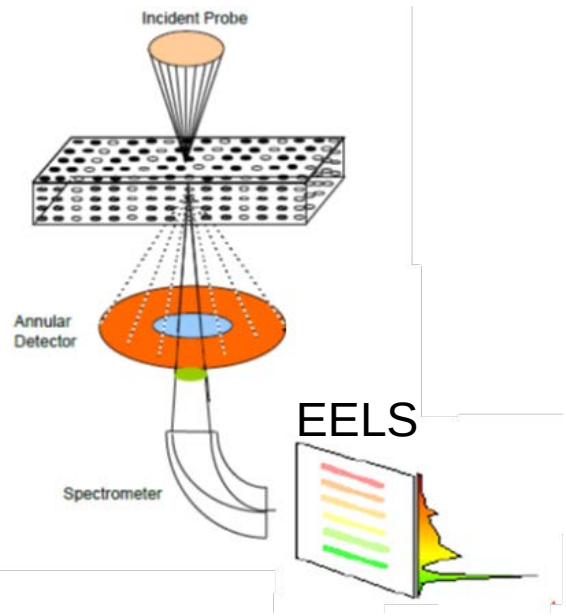
The precipitate star/dendritic morphology indicates that probably a high-potential phase occurred during start/stop steps

Pt Alloy Nanoparticles

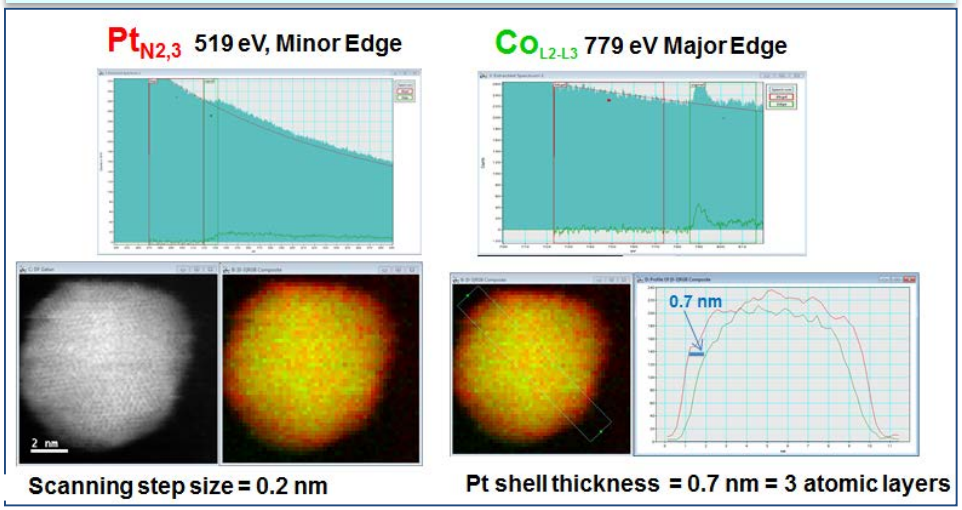
Pt alloys (Pt-Ni, Pt-Co): Higher Oxygen Reduction Reaction activity than pure Pt

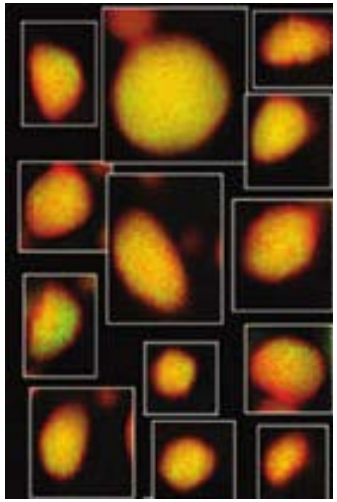
Protection of the metal dissolution *(ionomer contamination)* by a Pt shell (acid leaching, heat treatment)

Chemical analysis at the atomic scale is needed



Electron energy loos spectroscopy EELS

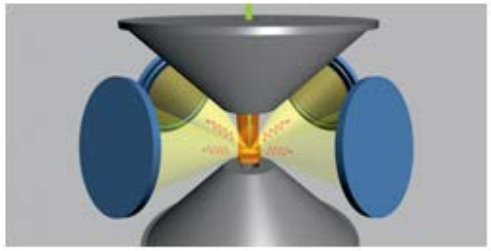


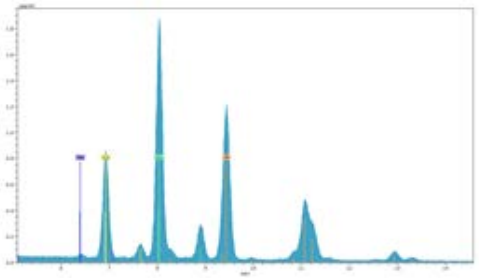


Xin et al., Nano Lett. 2012, 12, 1, 490

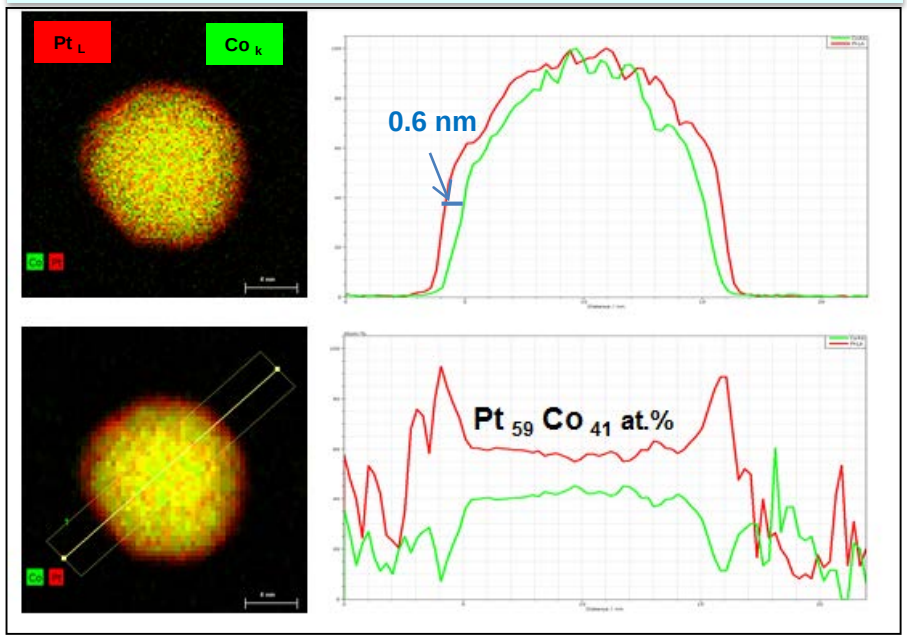
Pt Alloy Nanoparticles

Chemical analysis at the atomic scale is needed





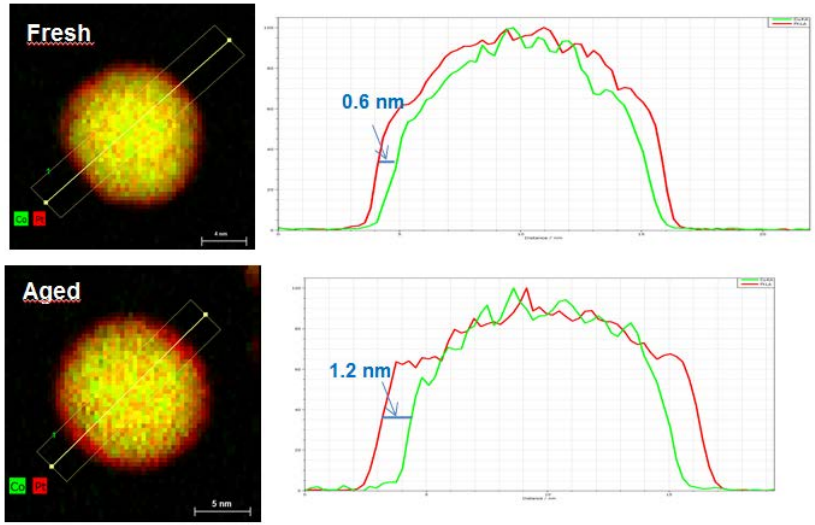
Xray energy dispersion spectroscopy X-EDS

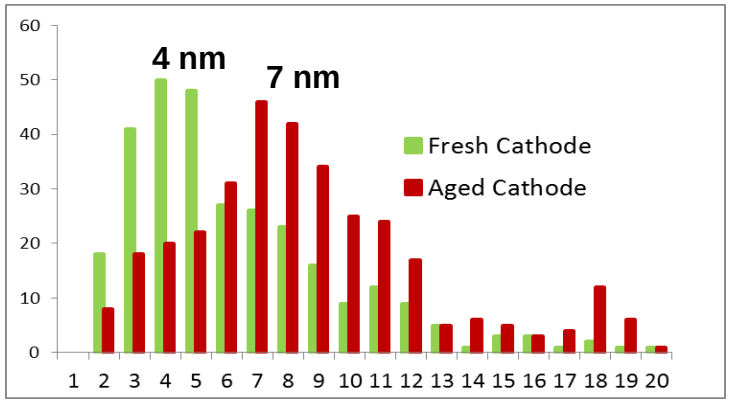


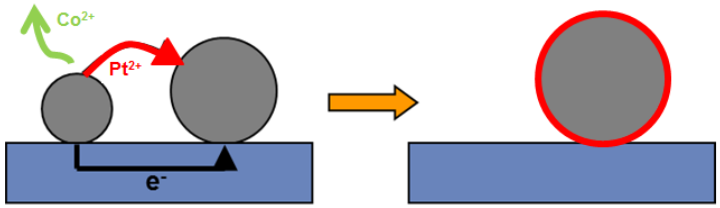
One nanoparticle X-EDS or EELS elemental map acquisition time: 5-10 min
► Difficulty to have statistically representative data when the catalysts are not homogeneous

Pt-Co nanoparticle degradation

Ageing tests representative of automotive application







Electrochemical Ostwald ripening mechanism

1. Co and Pt dissolution of the small nanoparticles

2. Co ions migration through the ionomer (ionomer contamination),

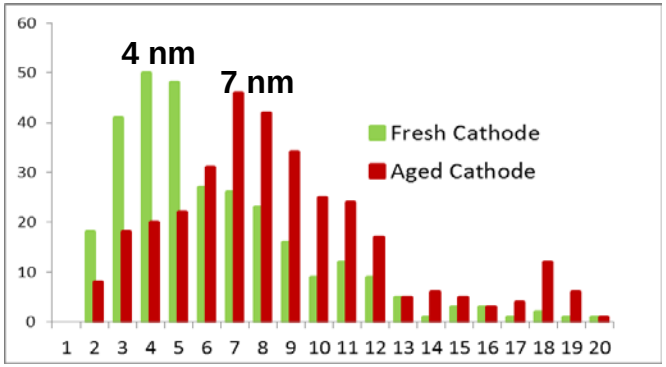
Standard electrode potential $Co^{2+}/Co = - 0,28 < 0$

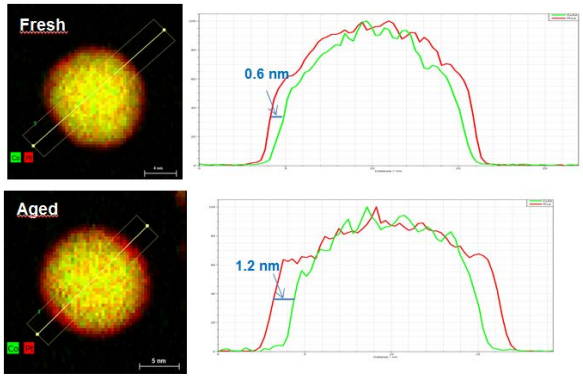
3. Pt re-deposition on largest nanoparticles
   ⇨ Thicker Pt shells (> 1 nm)

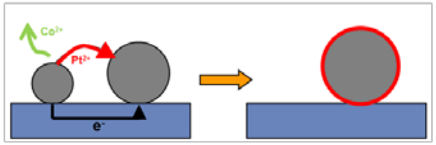
The electrochemical Ostwald ripening mechanism leads to thicker Pt shell surrounding the Pt-Co nanoparticles

Pt-Co nanoparticle degradation

Ageing tests representative of automotive application







Electrochemical Ostwald ripening mechanism

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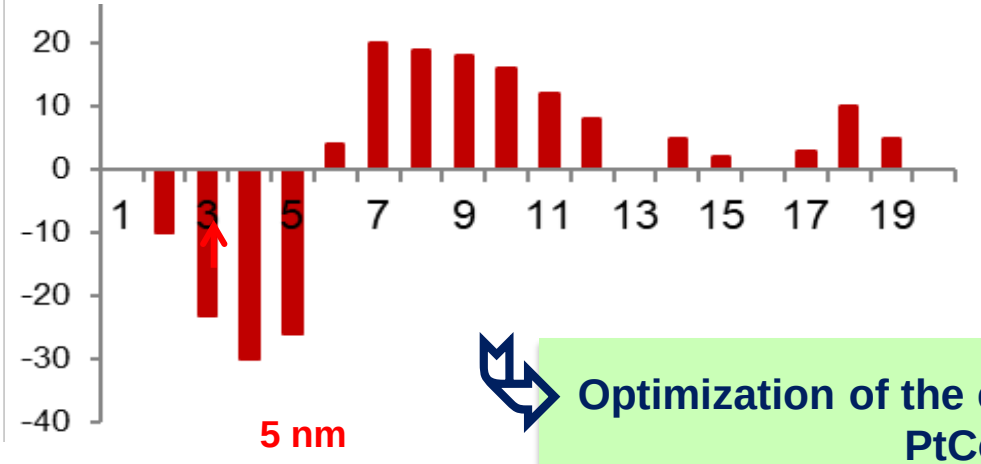
   ⇨ Thicker Pt shells (> 1 nm)

Evolution of Pt NP number for the different NP diameters

Aged Cathode Histogram –Fresh Cathode Histogram



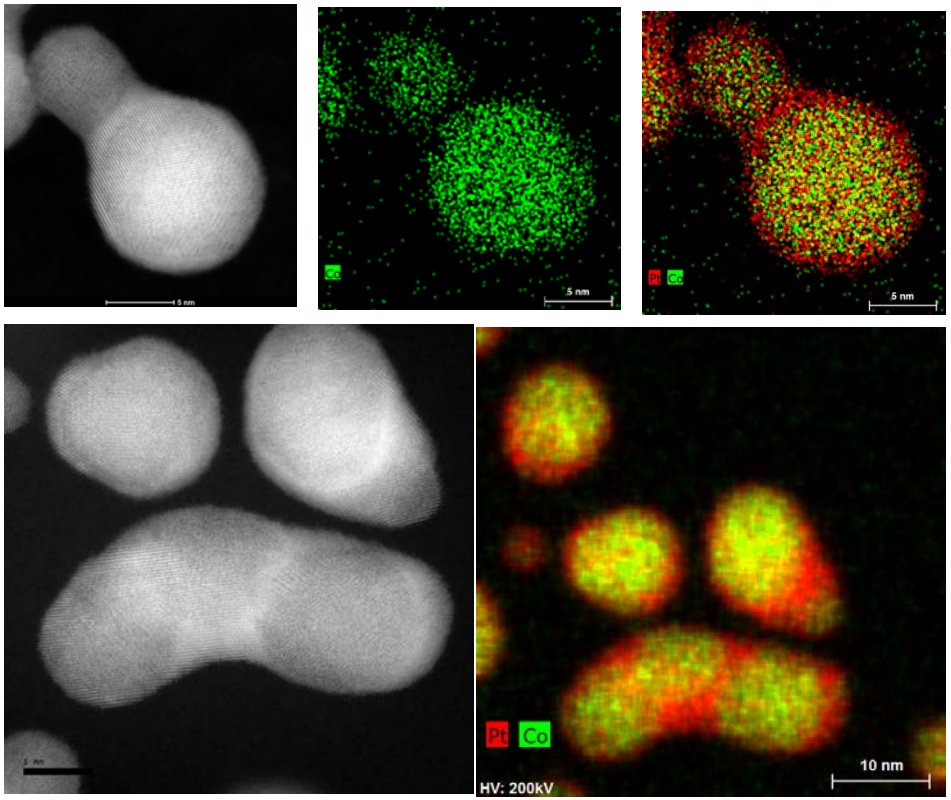
Nanoparticles smaller than 4-5 nm are dissolved (Pt shell is also dissolved)

Pt shell protects Co dissolution only for the larger nanoparticles

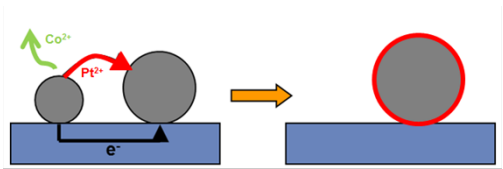
Optimization of the electrode microstructure by using larger PtCo nanoparticles (4-5 nm)

Pt-Co nanoparticle degradation

Pt re-deposition on neighboring Pt-Co nanoparticles leads to their coalescence



Nanoparticle sintering by Pt re-deposition



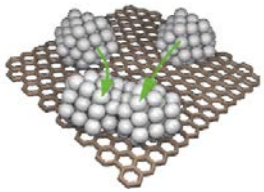
Electrochemical Ostwald ripening mechanism

1. Co and Pt dissolution of the small nanoparticles
2. Co ions migration through the ionomer (ionomer contamination),

Standard electrode potential $Co^{2+}/Co = -0{,}28 < 0$

3. Pt re-deposition on largest nanoparticles
   ⇨ Thicker Pt shells (> 1 nm)

Coalescence of neighboring NP appears to result from Pt re-deposition rather than from nanoparticle migration



Nanoparticle migration

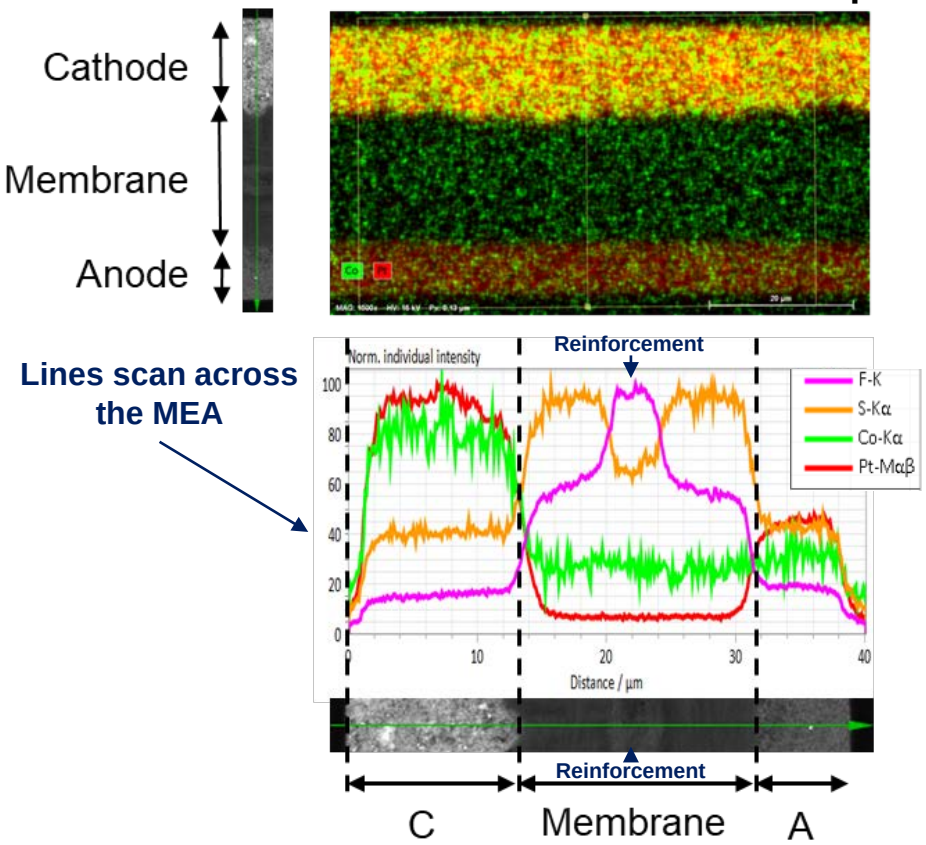
Membrane contamination by Co cations

As the standard electrode potential of $Co^{2+}/Co < 0$ V, the released Co cations remain in the ionomer

Contrary to the Pt ions, Co ions are not reduced within the MEA.

Fresh MEA

Pt and Co X-EDS elemental maps



The membrane contamination can be detected on MEA cross-section by X-EDS analysis in a SEM

In order to avoid the contamination of the membrane during the sample preparation, the embedded cross-section was cut by microtomy in dry conditions

No Co cation are detected in the membrane of the fresh MEA

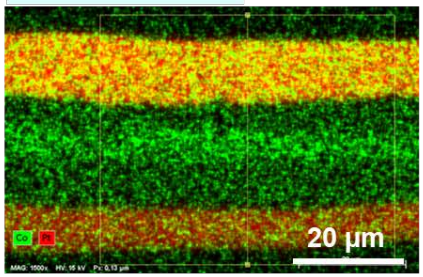
Membrane contamination by Co cations

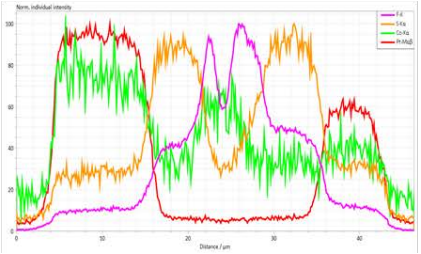
A high level of Co cation contamination is detected in the membrane

Co cations form high concentration band in the membrane

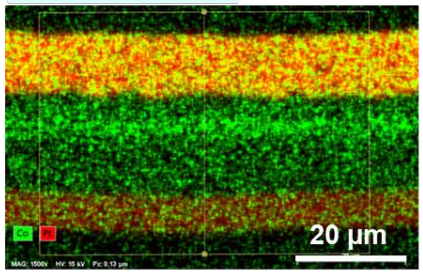
Aged MEA

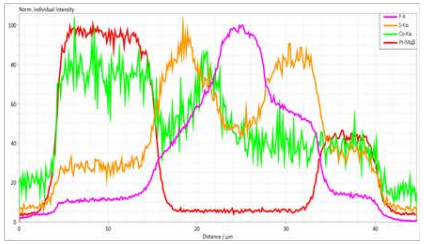
Air inlet zone



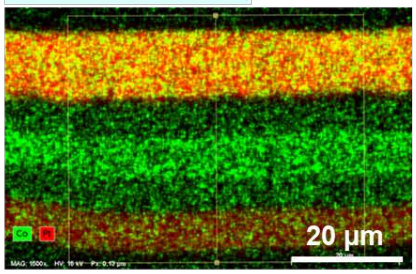


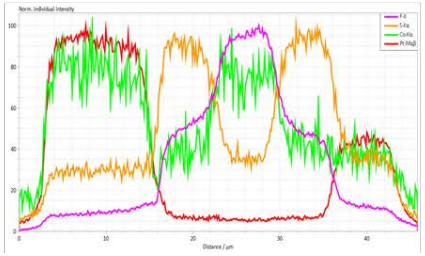
Middle zone





Air outlet zone





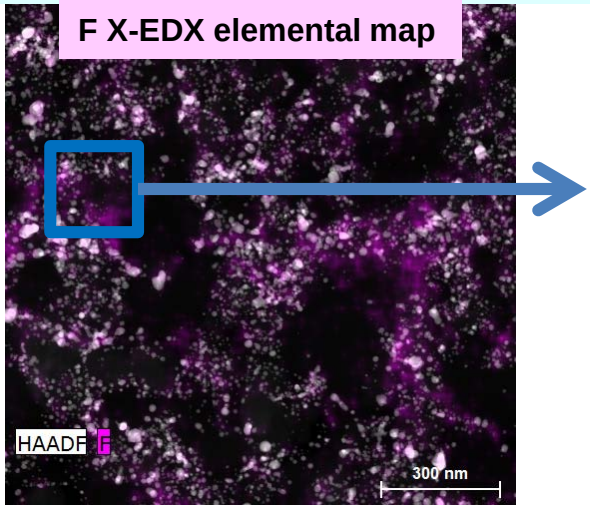
- **The position of the band in the membrane varies in the different zones of the MEA**
- **The band is often located in the reinforcement** (leading probably to a high Co^{2+}/SO^{3-} ratio)

Results in large performance losses particularly at high current density

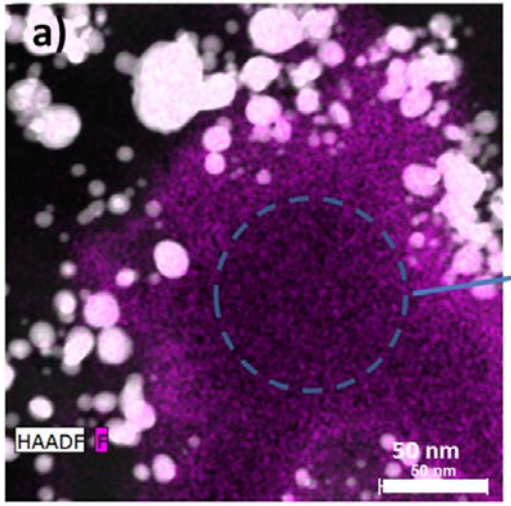
Co contamination of the cathode ionomer by Pt_3Co catalyst degradation

The ionomer in the cathode could be even more contaminated by Co cations than the membrane

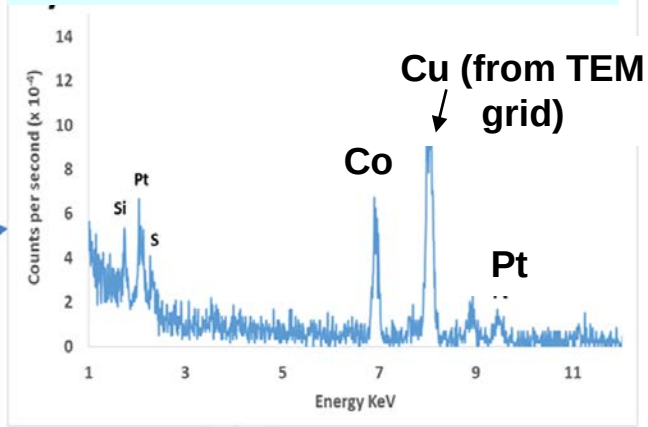
HAADF/STEM image of the cathode



Pore filled with Nafion



EDS spectrum in the pore filled with Nafion



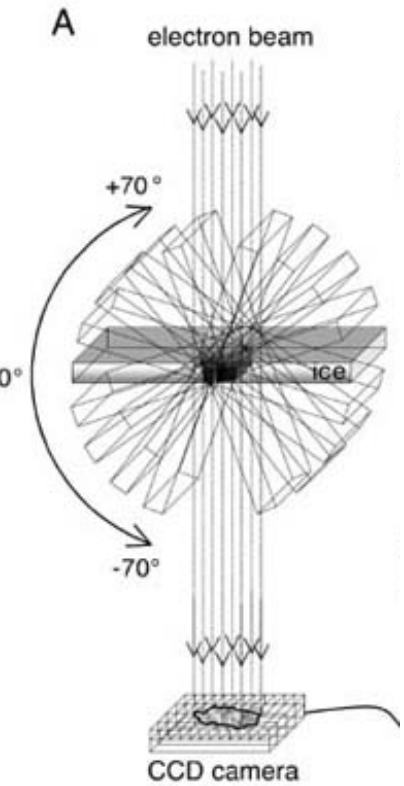
Large amount of Co is detected in the pore filled with Nafion

To reduce the ionomer contamination, it is important to lower the Co content in the catalysts (~10 at.% Co instead of 25 at.%)

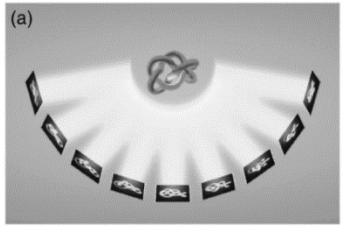
*Borup et al., Current Opinion in Electrochemistry 2020, **21**, 192*

Carbon support and nanoparticle dispersion

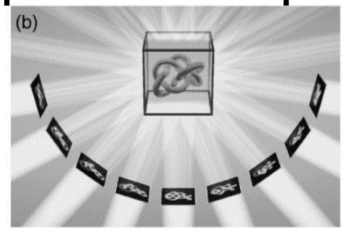
Electron tomography analyses have shown that for the high surface area carbon (HSAC) support, many nanoparticles are located inside the carbon

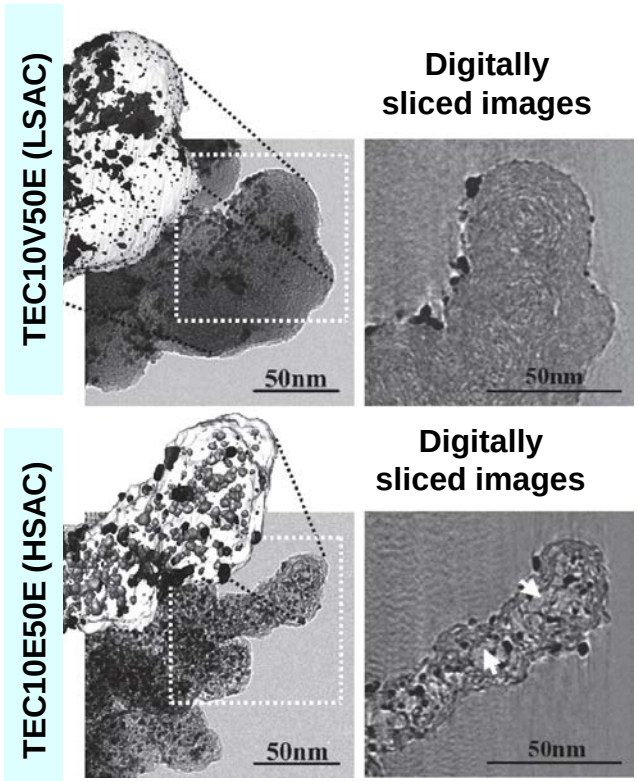


Tilt series of images is recorded

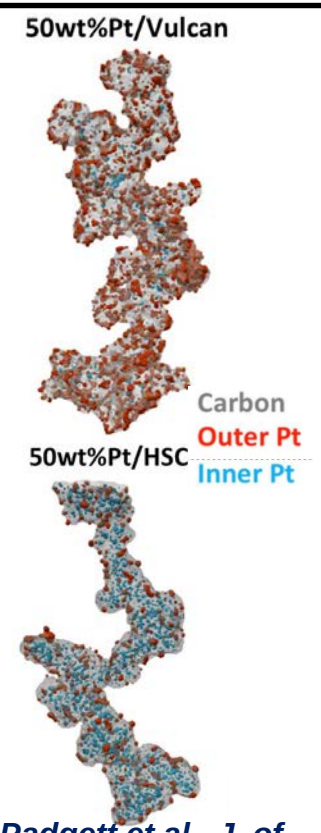


3D structure of the specimen is computed





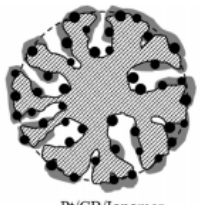
Ito et al., Electrochemistry, 79, 2011, 374



Padgett et al., J. of The Electrochem. Society, 165 (3), 2018, F173

Carbon support and nanoparticle dispersion

The interior nanoparticles appear to be active, however they could be more sensitive to the local conditions (RH, current…)

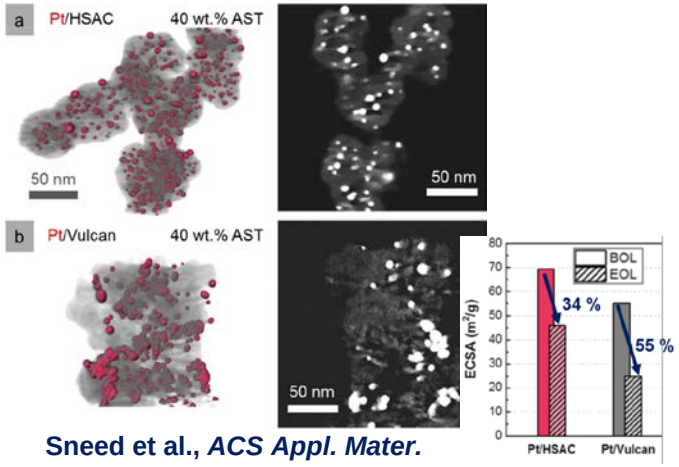


Nanoparticles in the interior of the CB are:

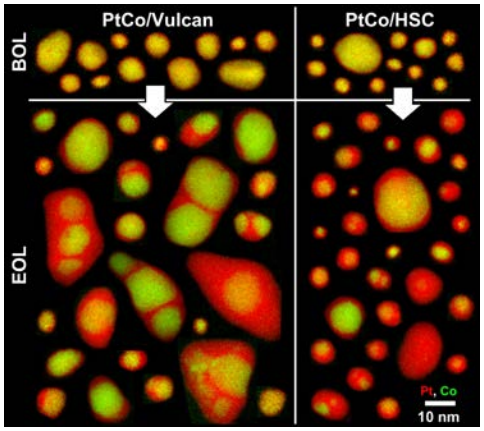
- ✓ **active in low current density region**
- ✓ **no active in the high current density region due to their too low proton and O_2 accessibility**

Park et al., J. Power Sources 315 (2016), 179

Are the interior nanoparticles less sensitive to coarsening ?



Sneed et al., *ACS Appl. Mater. Interfaces*, 9, 29839 (2017).



Padgett et al., J. of The Electrochem. Society, 166, 2019, (4) F198

- ➢ **First studies suggest that the confinement of nanoparticles in C pores reduces the coalescence of neighboring nanoparticles**
- ➢ **It is yet not known whether their coarsening by the electrochemical Ostwald ripening is also limited**

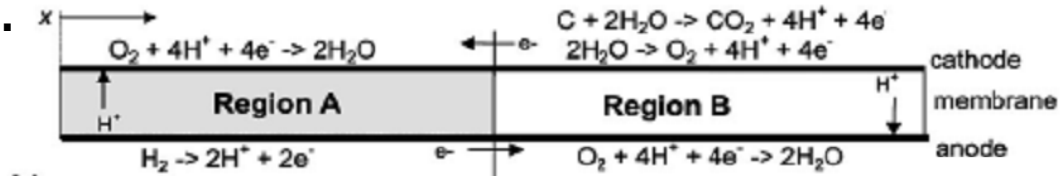
The optimization of carbon supports seems to be a promising path for the development of more efficient and resistant catalysts.

CATHODE CARBON SUPPORT CORROSION

Carbon corrosion is often occurred during the start/stop procedure

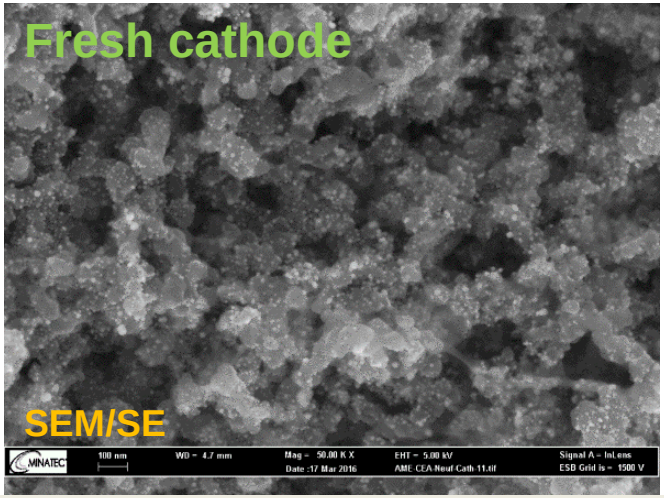
During start/stop procedure, the anode can be partially exposed locally to O2 creating a H_2 / O2 front.

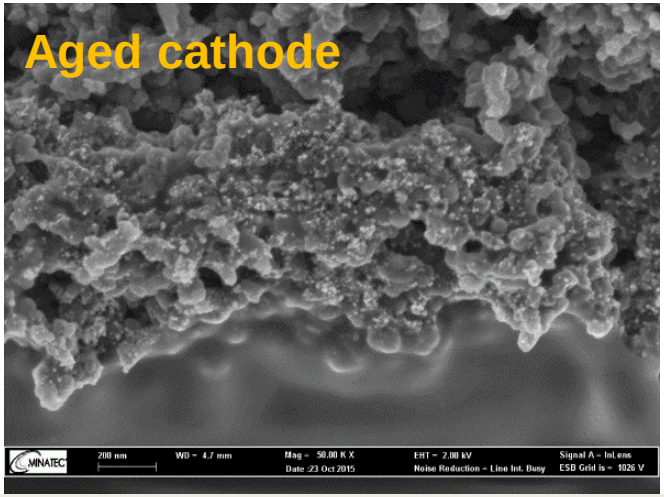
⇨ reverse current mechanism proposed by *Reiser (2005)*, *Electrochemical and Solid-State Letters*, 8 (6) A273.



The high cathode potential leads to the carbon corrosion

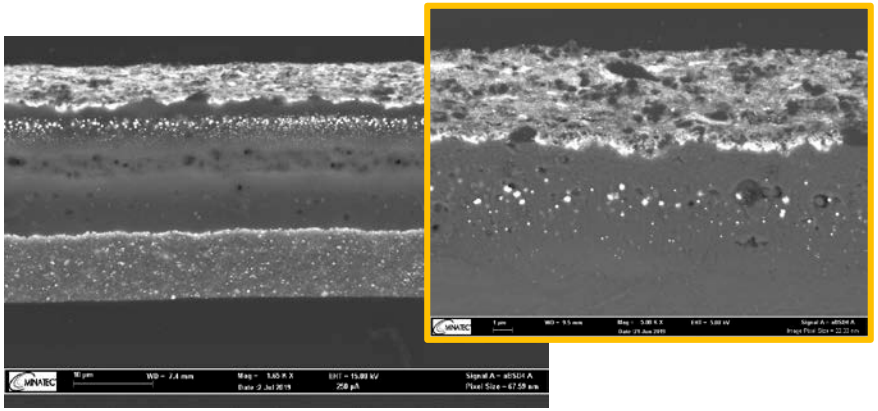
⇨ **Compaction of the cathode**





CATHODE CARBON SUPPORT CORROSION

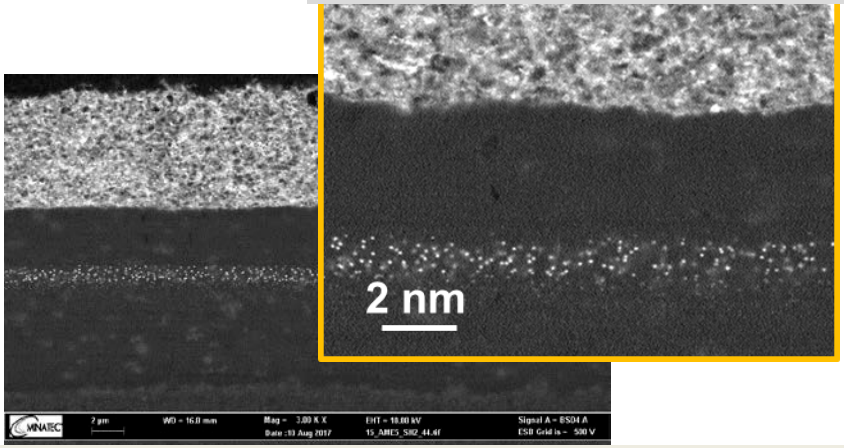
Carbon corrosion can modify the aspect of the cathode catalyst layer



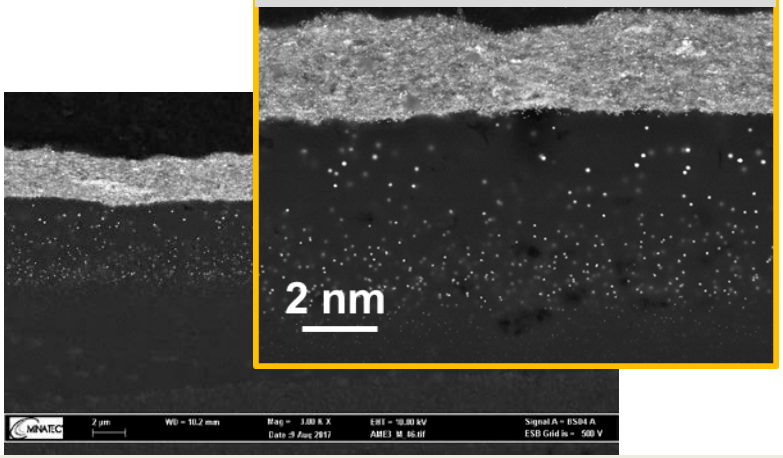
Carbon corrosion can change the position of the membrane Pt band

- Pt precipitates closer to the cathode revealing the presence of H_2 nearby the cathode / membrane interface
- That indicates that no more O_2 could diffuse into the membrane due to cathode compaction.

Cathode without compaction



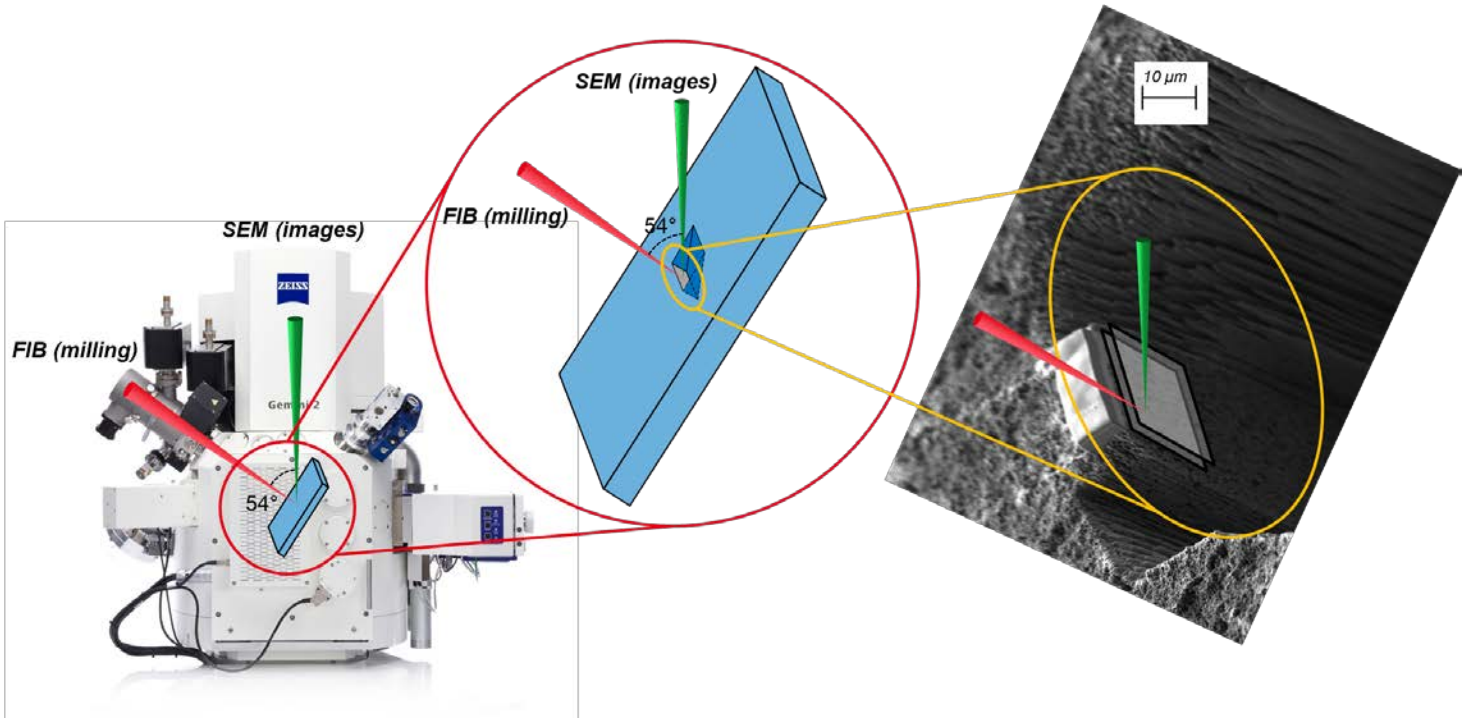
Compaction of the cathode



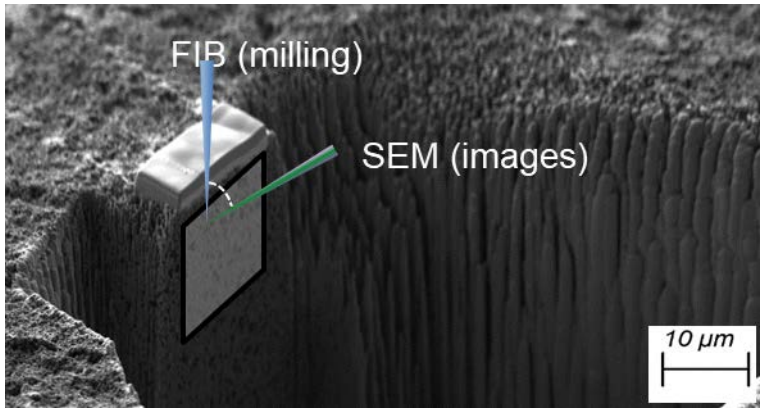
FIB/SEM

Focused Ion Beam / Scanning Electron Microscopy

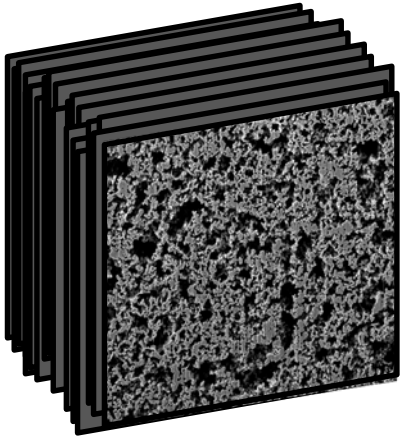
Cathode compaction can be analyzed quantitatively by measuring the evolution of cathode porosity



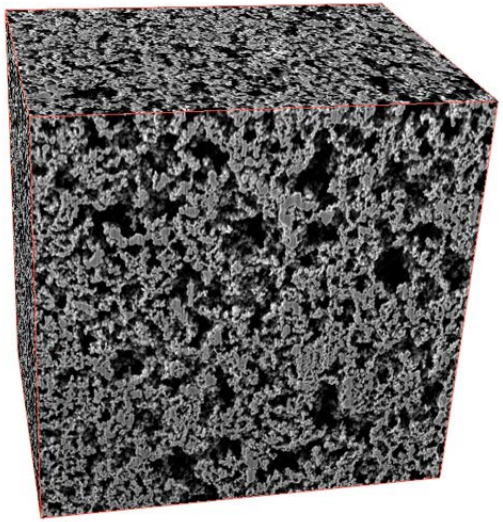
CATHODE CARBON SUPPORT CORROSION



Stack of SEM images



3D reconstruction of the MPL structure

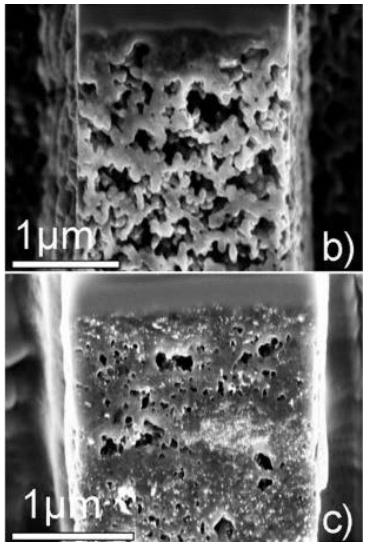


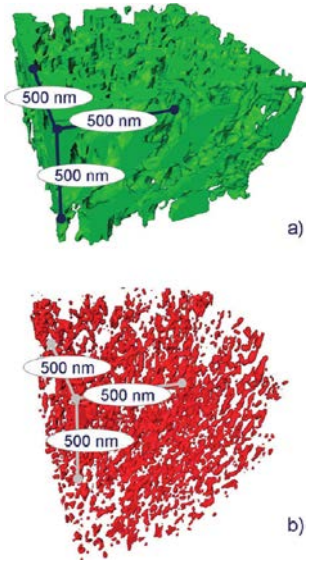
Courtesy of Thomas David, CEA-Liten

SEM images | **Porosity analysis**

Fresh Cathode

After 1000 cycles start-up/shut-down

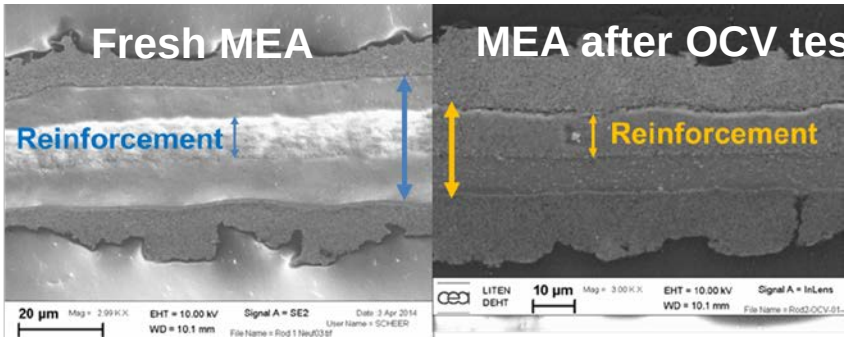




Schulenburg et al., J. Phys. Chem. C 2011, 115, 14236

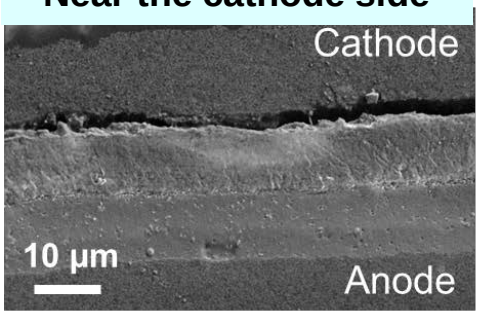
Membrane degradation

Degradation of the membrane, when it is severe, is visible on SEM MEA cross-sections

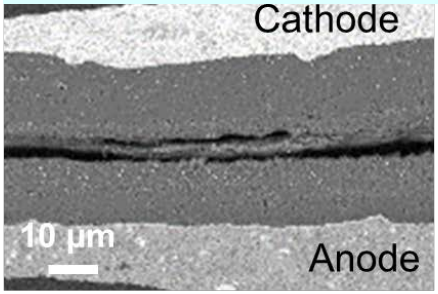


Membrane degradation can occur at different locations

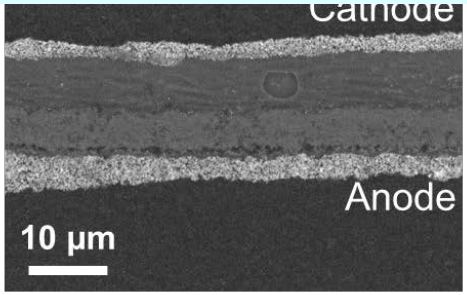
Near the cathode side



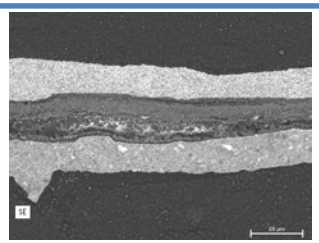
In the reinforcement

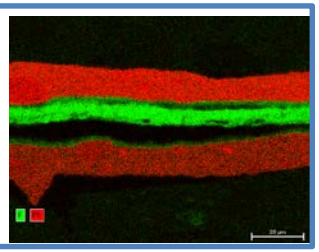


Near the anode side



The epoxy resin can fill the voids left by the membrane degradation : light contrast between membrane and epoxy resin



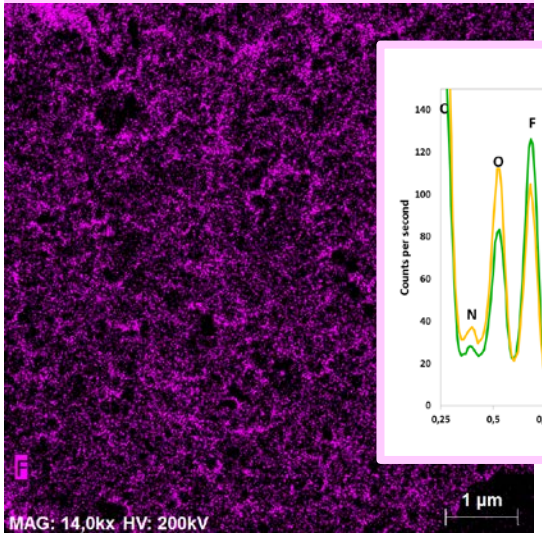


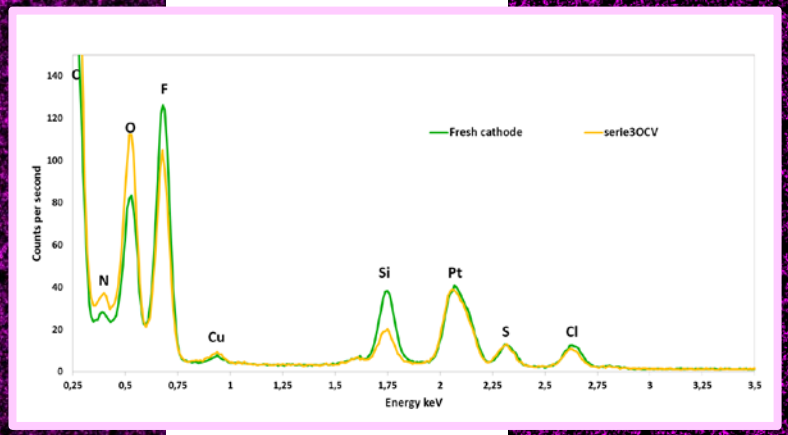
Cathode ionomer degradation

Comparison of F content in the fresh and aged cathodes

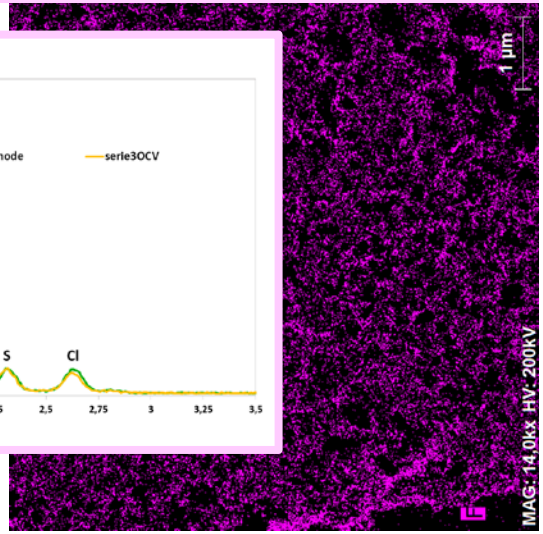
Fluorine EDS elemental maps are acquired using low electron dose at cryogenic temperature

F map in fresh cathode





F map in OCV aged cathode



Quantitative analysis (at.%):
F/Pt =88/12

=

Quantitative analysis (at.%):
F/Pt =87/13

⇨ **No degradation of the Nafion is detected in the cathode aged under OCV conditions, even if severe membrane degradation was observed**

Collaboration with Rod Borup (LANL)

Conclusions

To answer the question:

➢ **Which MEA components are degraded and by which mechanisms?**

The different electron microscopy techniques are powerful as they provide accurate analyses of the different MEA components and of their evolution after the ageing tests

- ✓ **Pt and Pt alloys nanoparticles degradation by the electrochemical Ostwald ripening mechanism**
- ✓ **Pt dissolution and precipitate band in the membrane**
- ✓ **Contamination of the ionomer by the Co cations**
- ✓ **Distribution of the nanoparticles on or in the carbon support**
- ✓ **Deterioration of the cathode porosity by the carbon corrosion**
- ✓ **Severe membrane degradations**

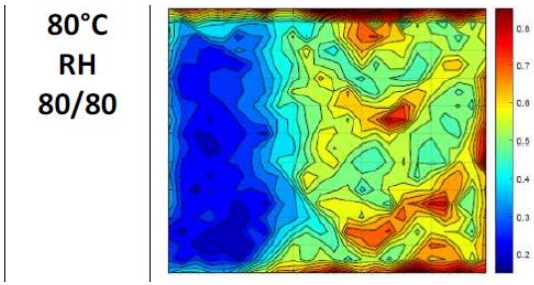
Conclusions

However, to answer the question:

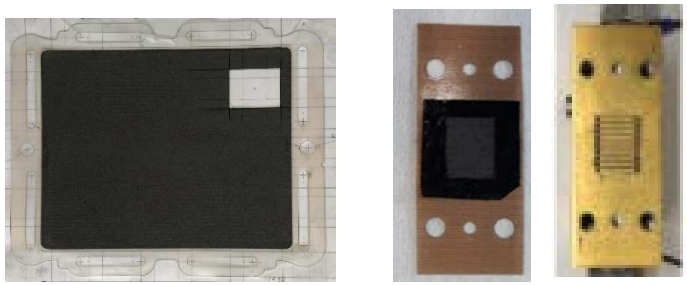
- **Do the observed degraded components explain the performance losses?**

Electron microscopy analyses must be combined with other local analyses techniques

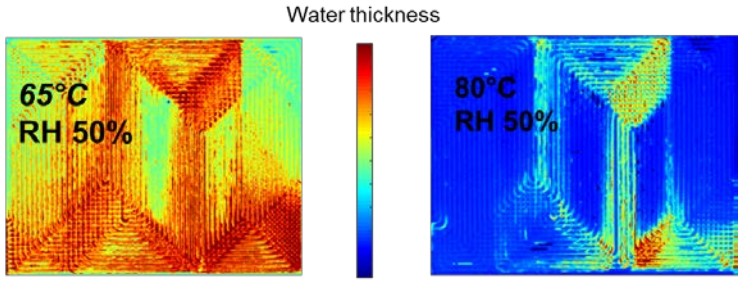
Measurement of the local current



Characterization of the local electrochemistry performances

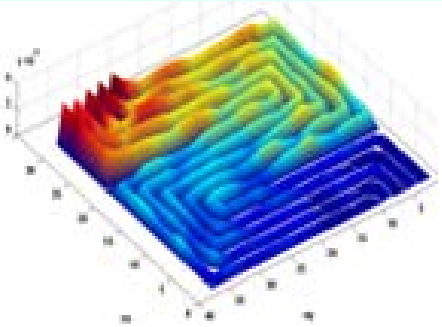


Measurement of the local water content



Neutron imaging on a reference stack
(Cf. E. Tardy)

Simulation of the local conditions and performances



ACKNOWLEDGEMENTS

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Thank you!