FURTHER-FC

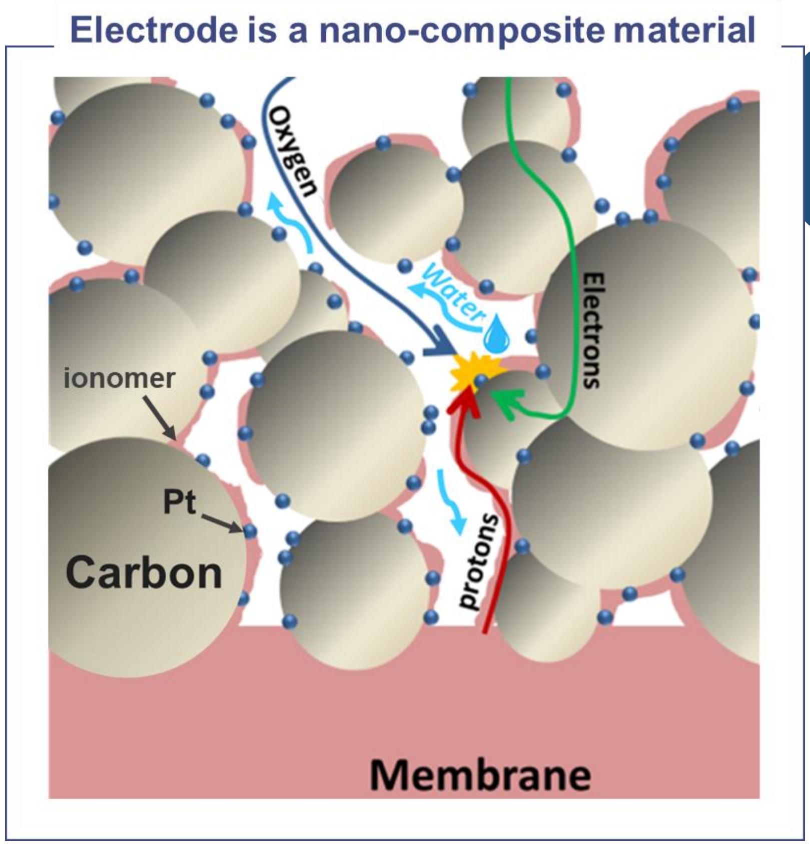
Further **U**nderstanding **R**elated to **T**ransport limitations at **H**igh current density towards future **E**lect**R**odes for **F**uel **C**ells

Characterization of the CCL structure by electron and AFM microscopy

Final Workshop

Introduction

Objectives : To have a better understanding of the cathode catalyst layer (CCL) microstructure parameters that could contribute to the performance limitation



CCL MICROSTRUCTURE PARAMETERS

- Porosity
- Distribution of the Pt/C catalyst
- Distribution of the ionomer

Cathode Catalyst Layer

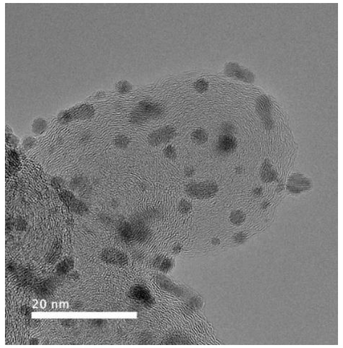
TOYOTA

Clean Hydrogen Partnership

Co-funded by the European Union

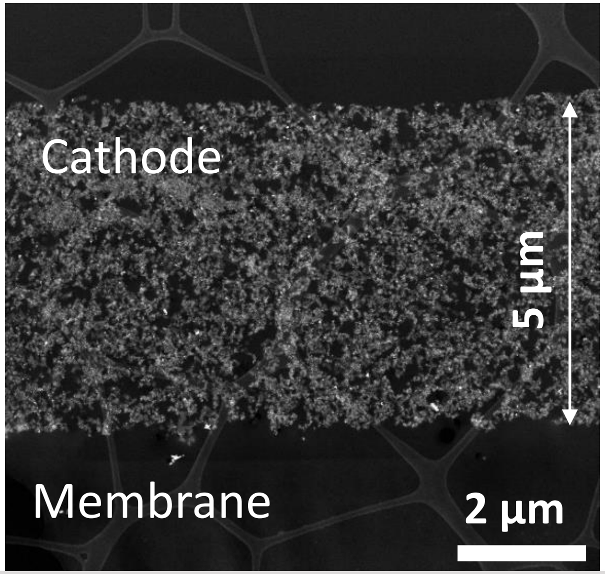
Reference MEA

- **Catalyst: TEC10E50E from TKK *(50 wt. % Pt / HSAC- high surface area carbon)***
- **Ionomer: Nafion D2020.**
- **Ionomer/carbon ratio = 0.8**
- **Pt loading : 0.2 $mg_{Pt}cm^{-2}$**

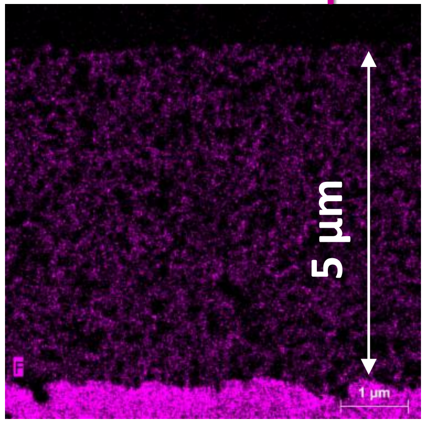


HAADF / STEM images and X-ray EDS analysis

Thin MEA cross section



F elemental map



⇨ **CCL shows homogeneous structure and ionomer distribution**

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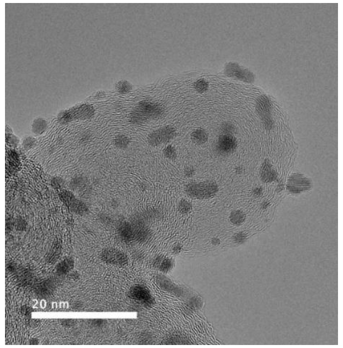

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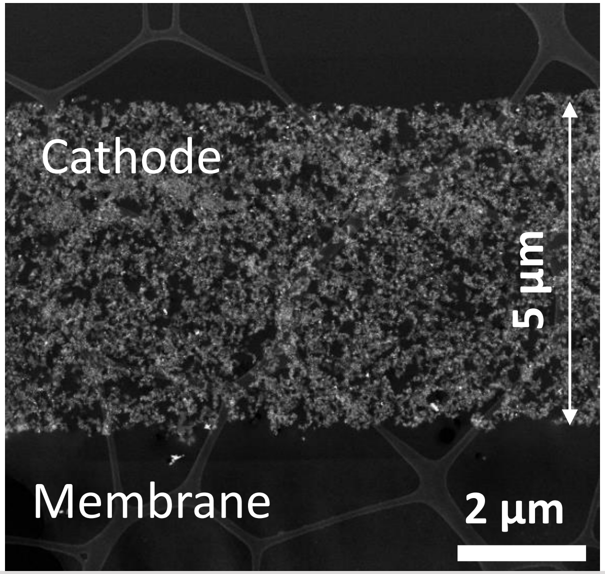
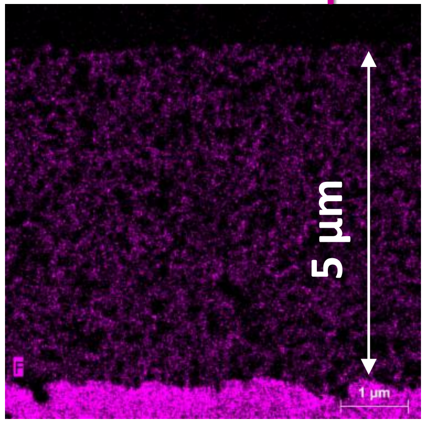


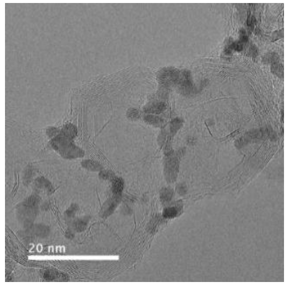
F elemental map



⇨ **CCL shows homogeneous structure and ionomer distribution**

Customized MEAs

- **Ionomer/carbon ratio = 0.5 and 1.1**
- **Ionomer: HOPI (high oxygen permeable ionomer)**
- **Catalyst:** TEC10EA30E **from TKK** (*30 wt. % Pt / graphitized carbon*)



Cathode Catalyst Layer

TOYOTA

Clean Hydrogen Partnership

Co-funded by the European Union

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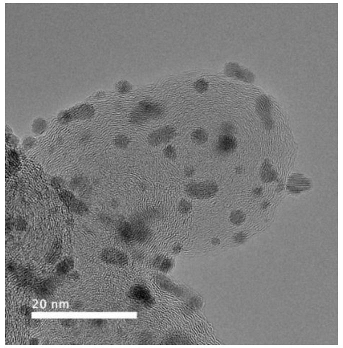

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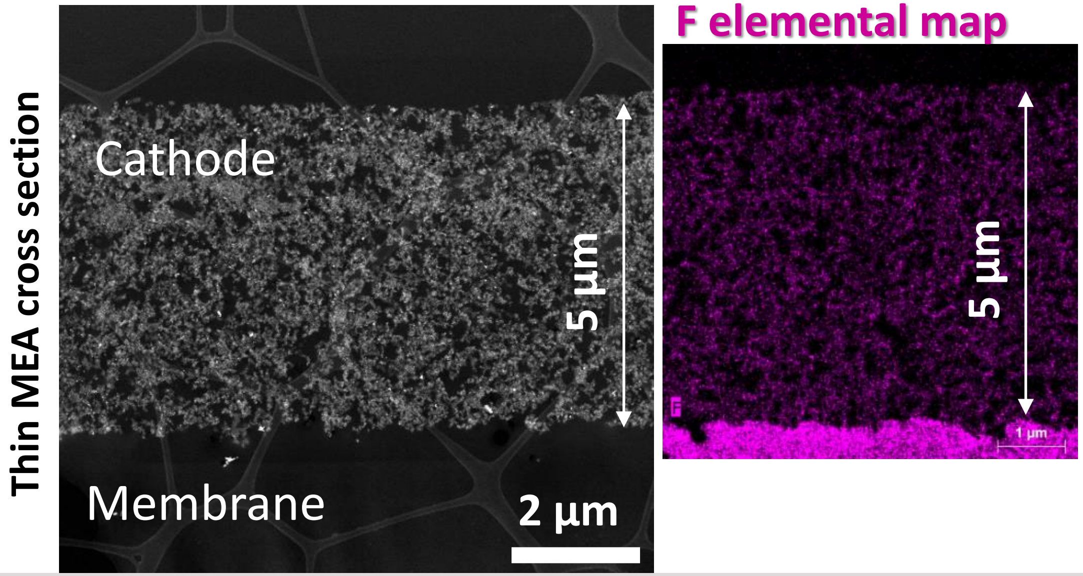

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AFM

Cathode Catalyst Layer

TOYOTA

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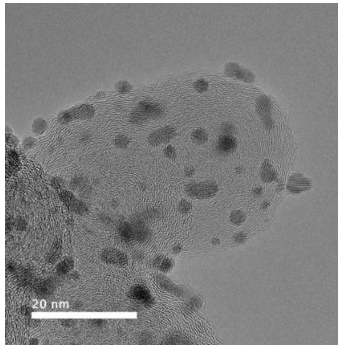

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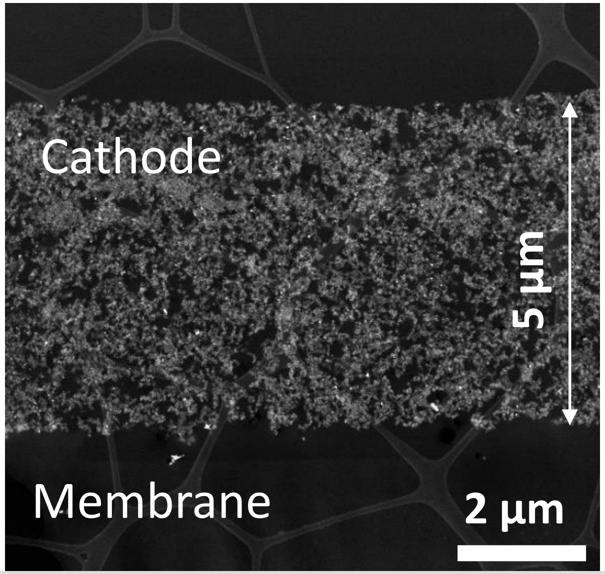

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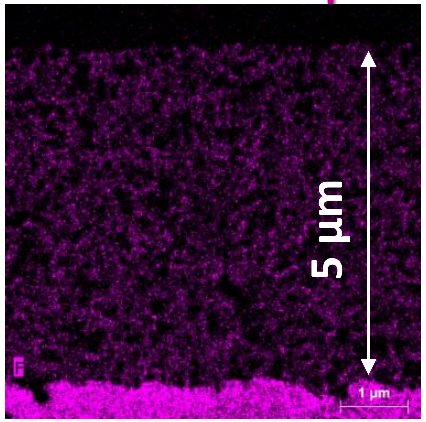
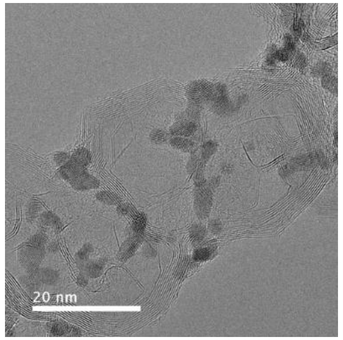


⇨ **CCL shows homogeneous structure and ionomer distribution**

Customized MEAs

TEM

- **Catalyst:** TEC10EA30E **from TKK**
  (*30 wt. % Pt / graphitized carbon*)



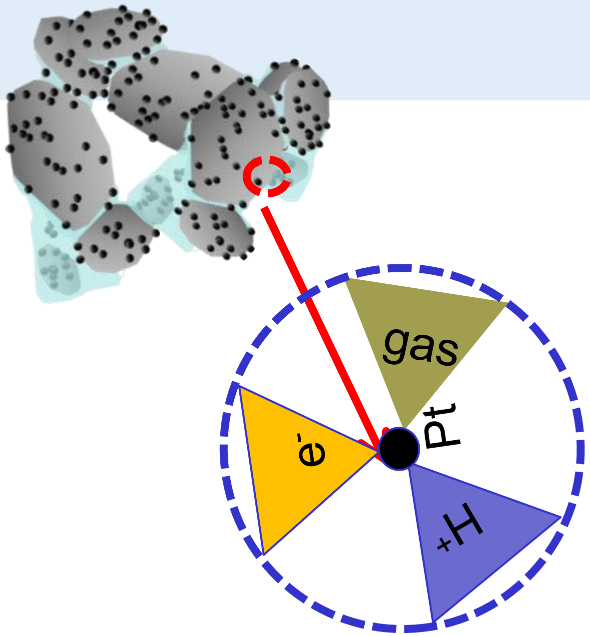
1. Atomic Force Microscopy (AFM)

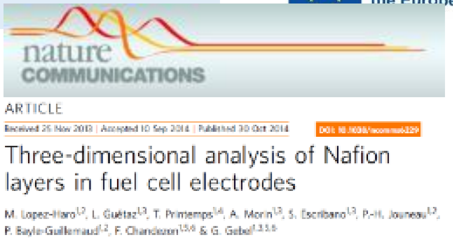
Basics and General Observations

Introduction

Electrodes / CL: Composite of ionomer, Pt catalyst covered mesoporous carbon, and pores

→ Reaction at 3-phase boundary
Performance & Durability

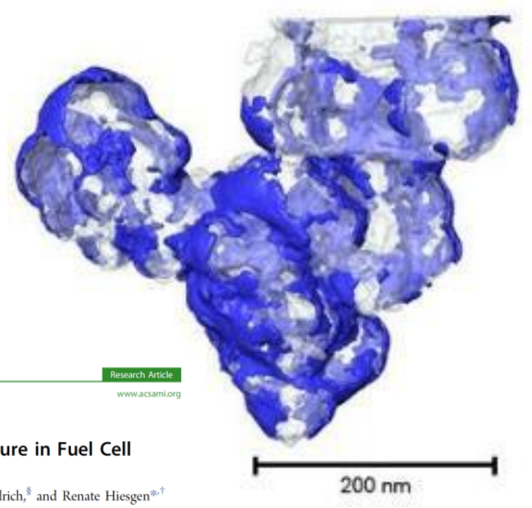



nature COMMUNICATIONS

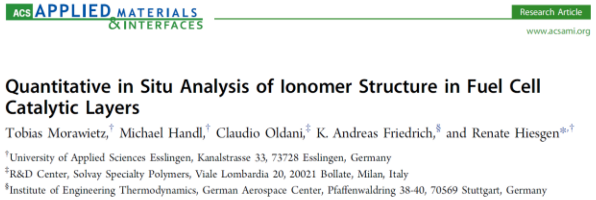
ARTICLE

Three-dimensional analysis of Nafion layers in fuel cell electrodes

M. Lopez-Haro, L. Guétaz, T. Printemps, A. Morin, S. Escribano, P.-H. Jouneau, P. Bayle-Guillemaud, F. Chandezon & G. Gebel



- electronic conductivity
- ionic conductivity
- gas supply


ACS APPLIED MATERIALS & INTERFACES

Research Article

www.acsami.org

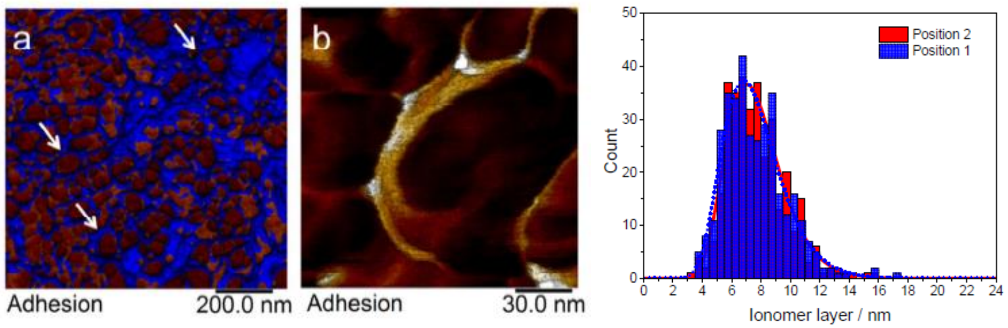
Quantitative in Situ Analysis of Ionomer Structure in Fuel Cell Catalytic Layers

Tobias Morawietz,[†] Michael Handl,[†] Claudio Oldani,[‡] K. Andreas Friedrich,[§] and Renate Hiesgen*[,†]

[†]University of Applied Sciences Esslingen, Kanalstrasse 33, 73728 Esslingen, Germany
[‡]R&D Center, Solvay Specialty Polymers, Viale Lombardia 20, 20021 Bollate, Milan, Italy
[§]Institute of Engineering Thermodynamics, German Aerospace Center, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany

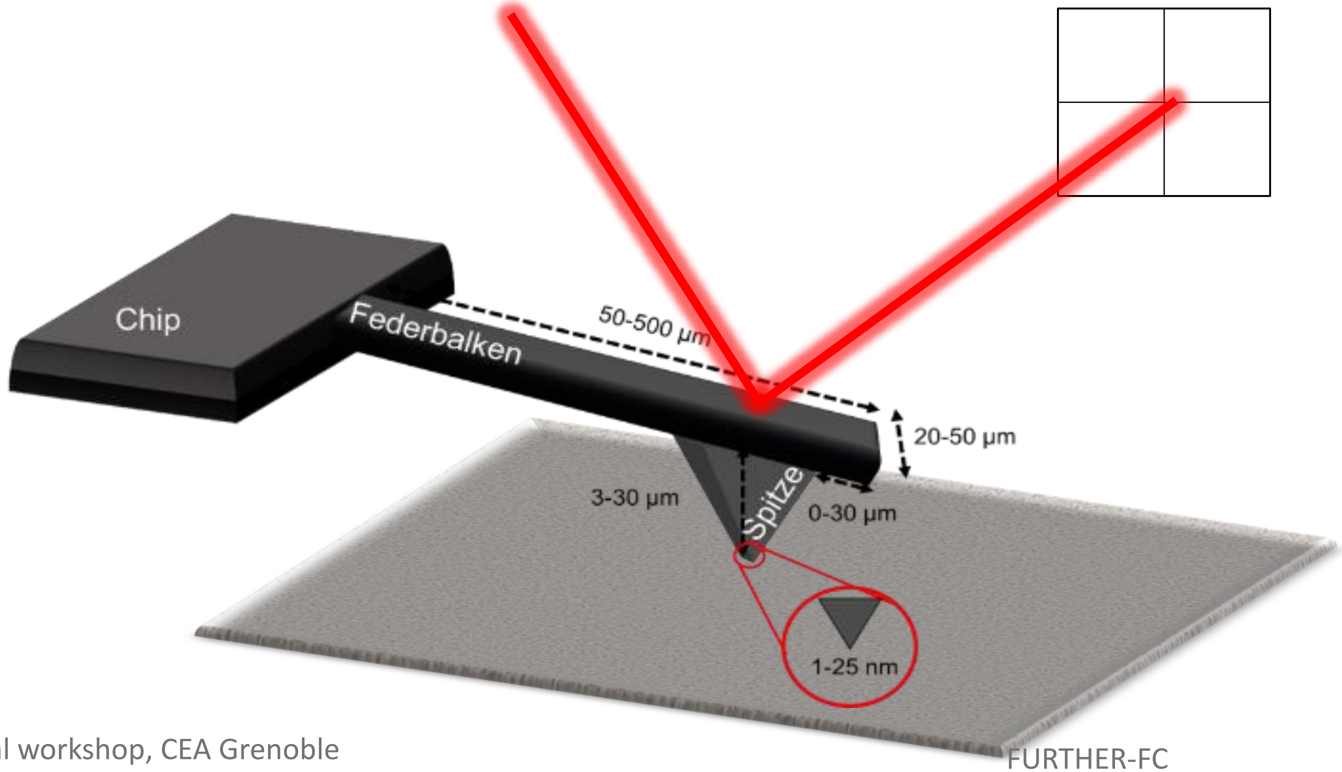
Uncertainty about ionomer distribution inside the electrode.
Quantitative analysis is difficult:

- Small size in the order of few nanometers, depends on humidity and temperature
- 3D-geometry
- Lopez-Haro, Guetaz et al. (CEA): Thickness of 7 nm with electron tomography (HAADF-STEM) at model electrodes
- Morawietz et al. (UES): Thickness measured with adhesion analysis of catalyst layers. Distribution from ~ 4-12 nm.



Atomic Force Microscopy (AFM)

- AFM uses a small tip (1-25 nm) to scan the surface of an sample to get topographic information and several other properties simultaneously.
- Measurements can be done at ambient conditions and temperature and RH controlled environment

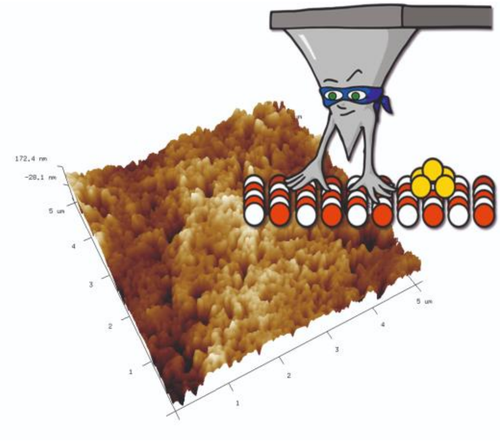


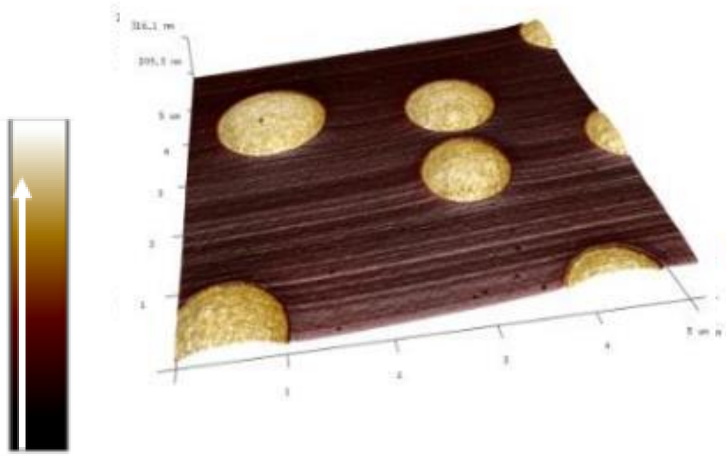
Bruker Multimode 8

Bruker Icon XR

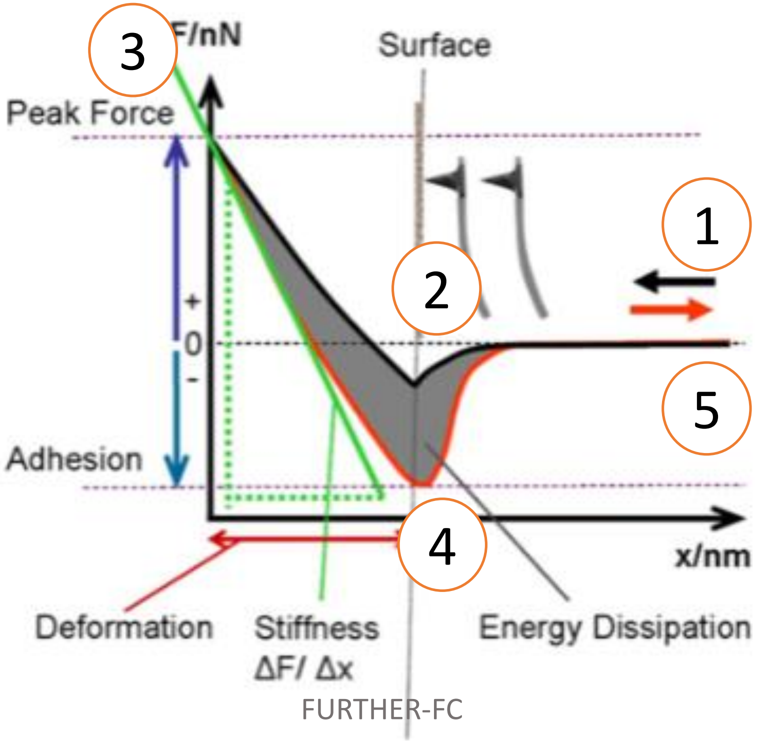
Atomic Force Microscopy (AFM)

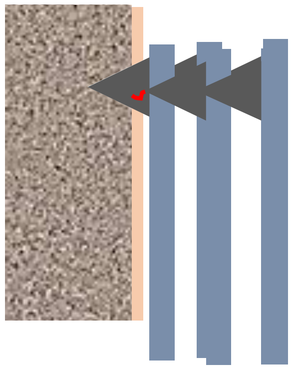
- Tapping PeakForce QNM/TUNA-Mode (Bruker Corp.):
- Evaluation and mapping of adhesion force, phase shift, stiffness (DMT modulus), maximal force, dissipation energy, deformation and current.





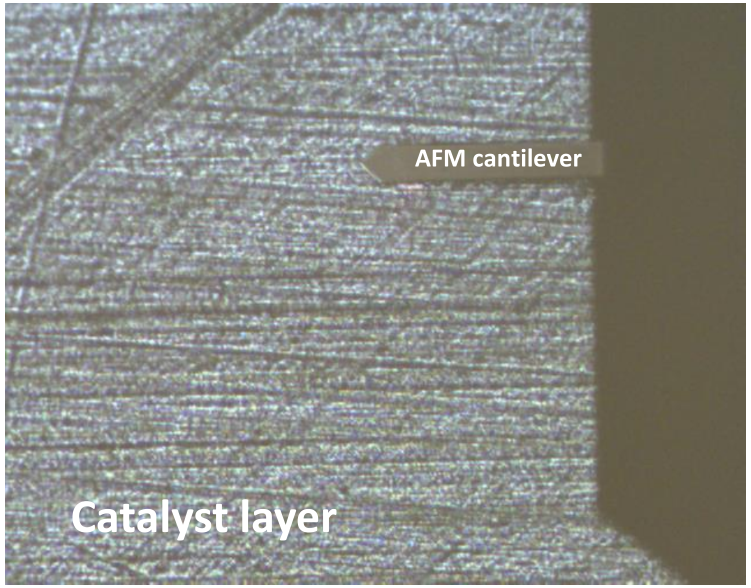
PS-LDPE Adhesion (5 µm)



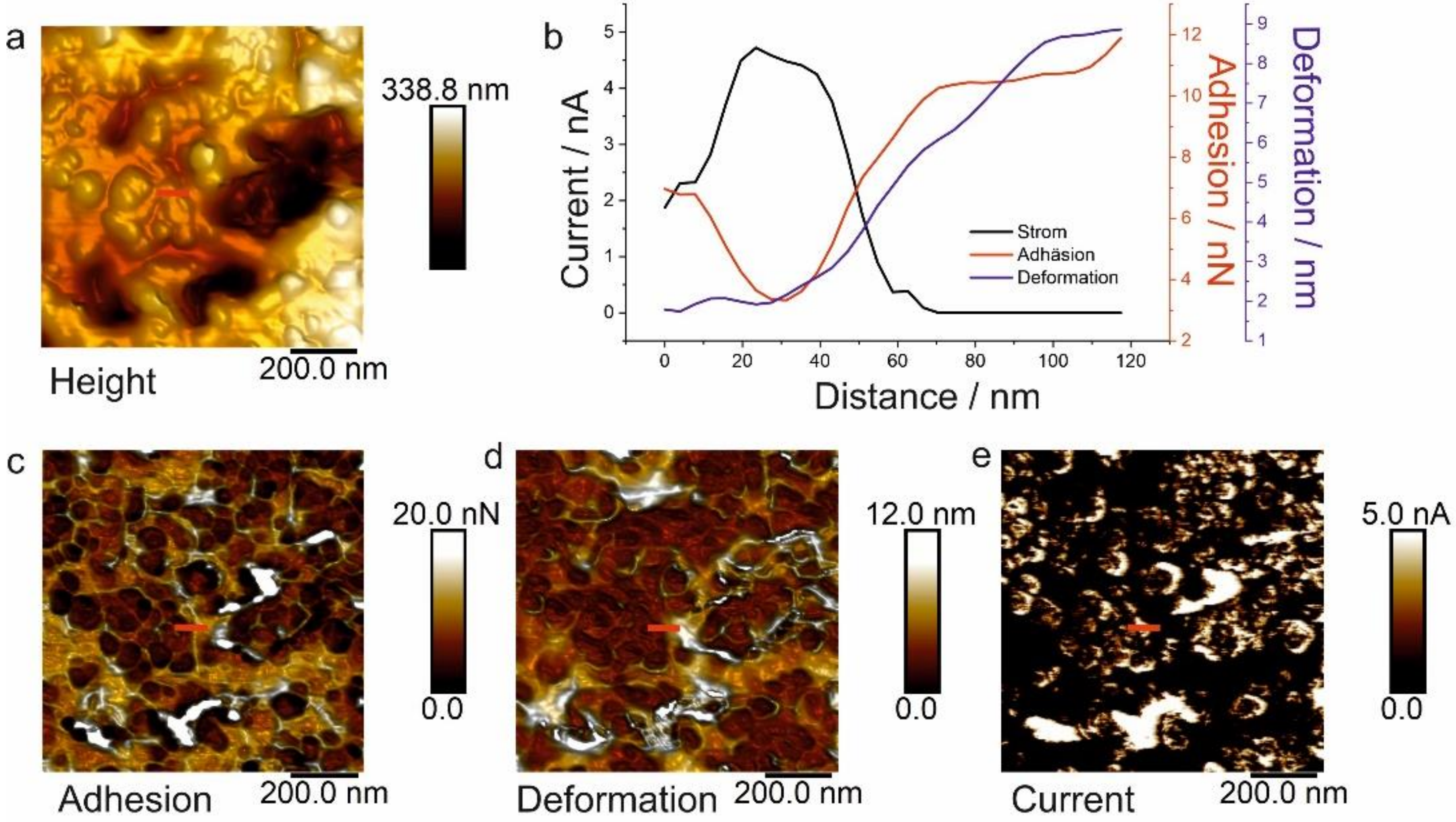


Atomic Force Microscopy (AFM)

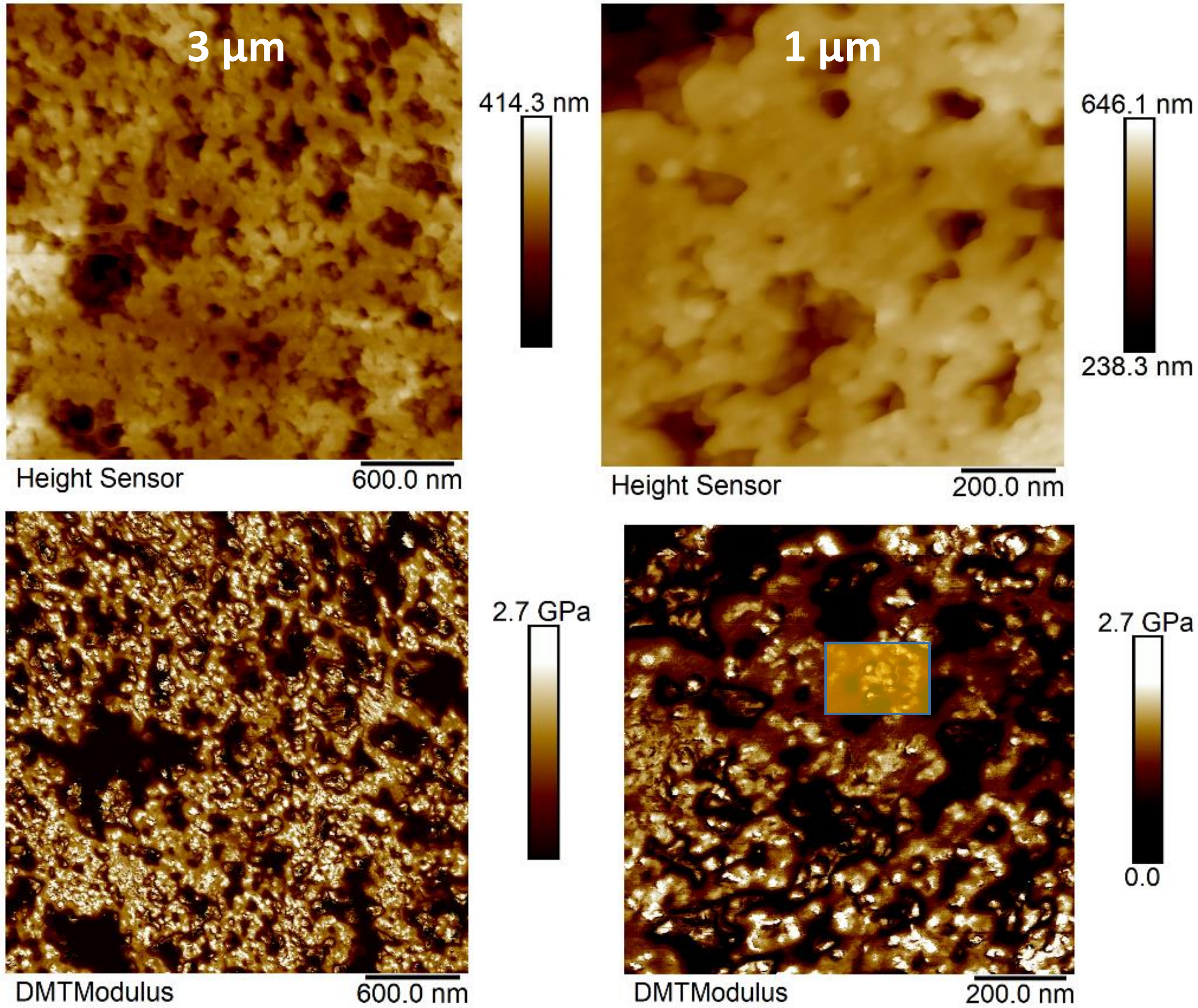
Using AFM one can discern the different components in the PEMFC and PEMWE electrodes. They consist of catalyst, support materials and (ionomer) binder, the distribution of these components affects MEA performance and degradation rates.



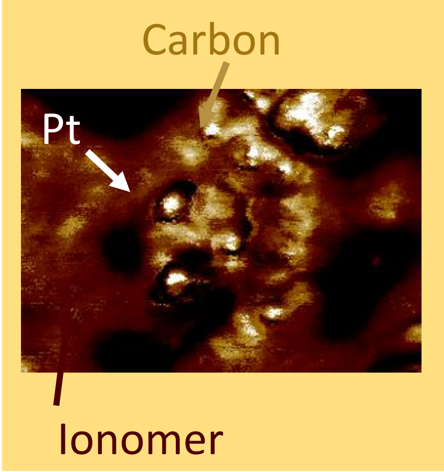
Optical microscope

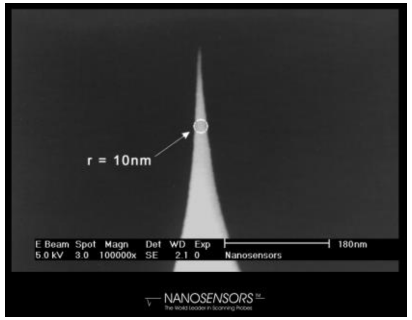


Analysis of the CCL surface



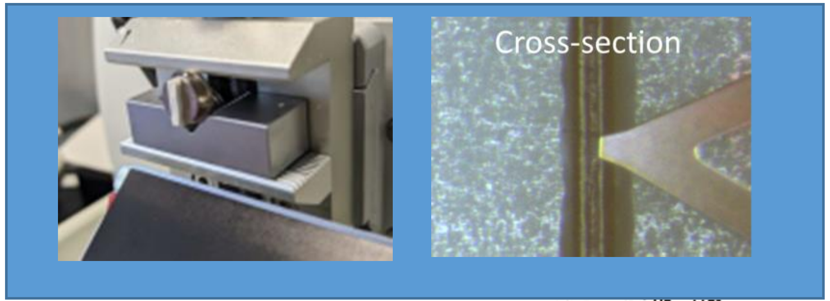
Ionomer bridges

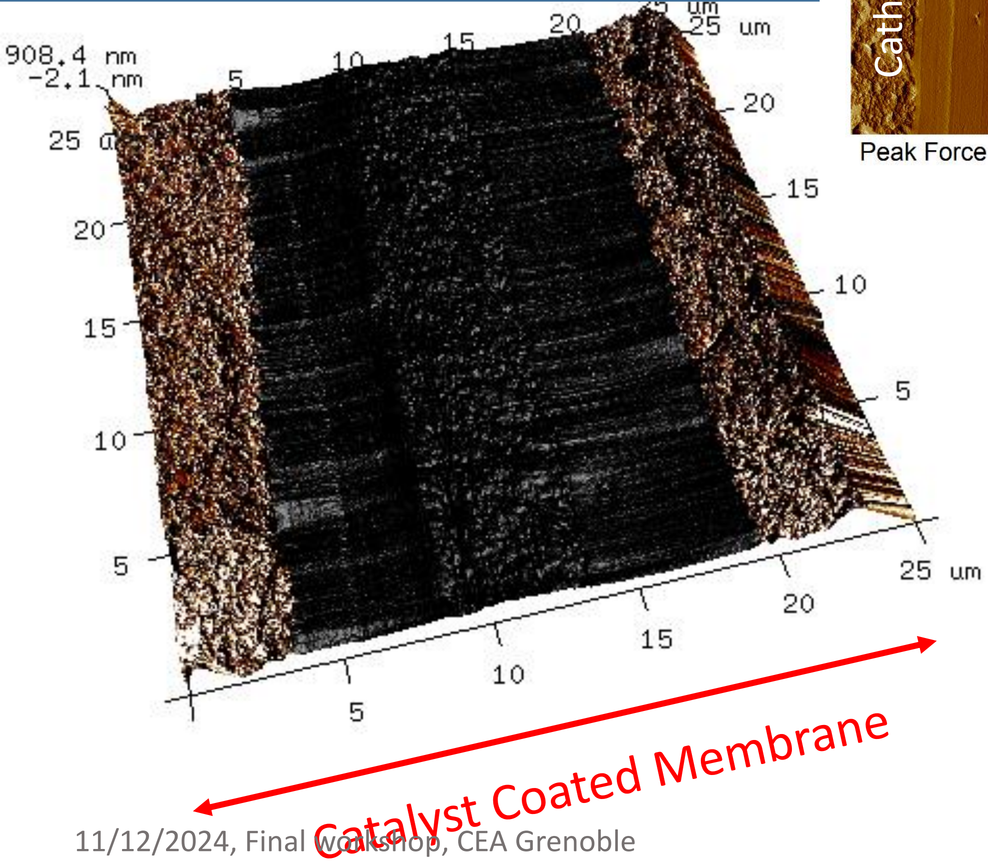


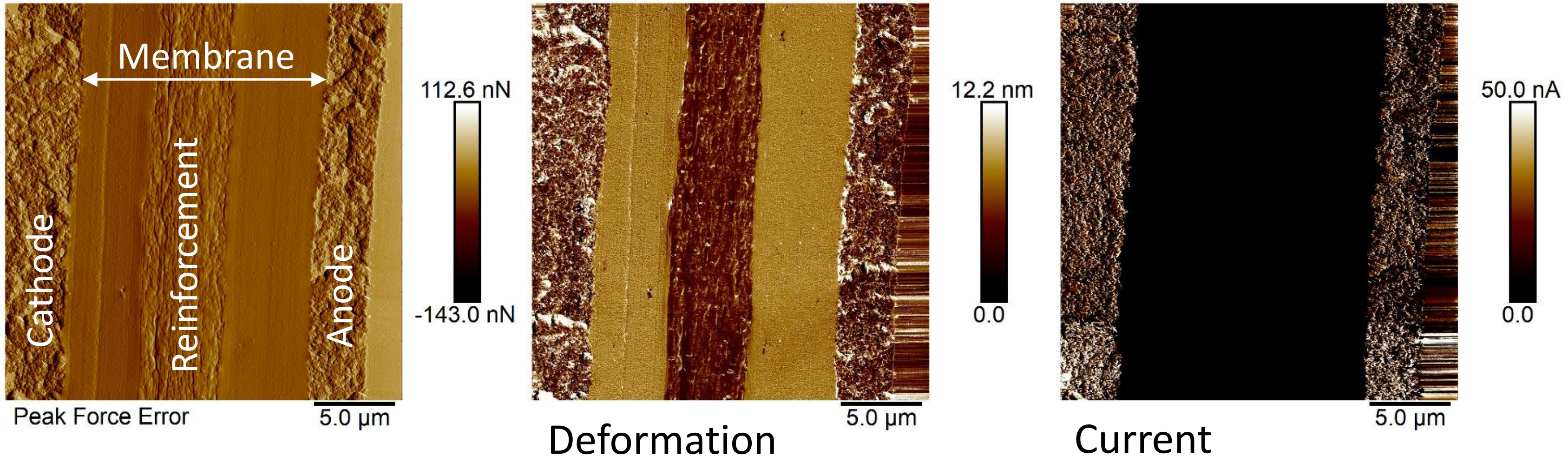


- Nanomechanics AFM measurement with high resolution tips → < 2 nm tip radius
- 3 different phases visible in stiffness channel
- Pt particles may be seen under a layer of ionomer
- Analysis of single Pt Particles difficult

AFM on CCM cross-sections





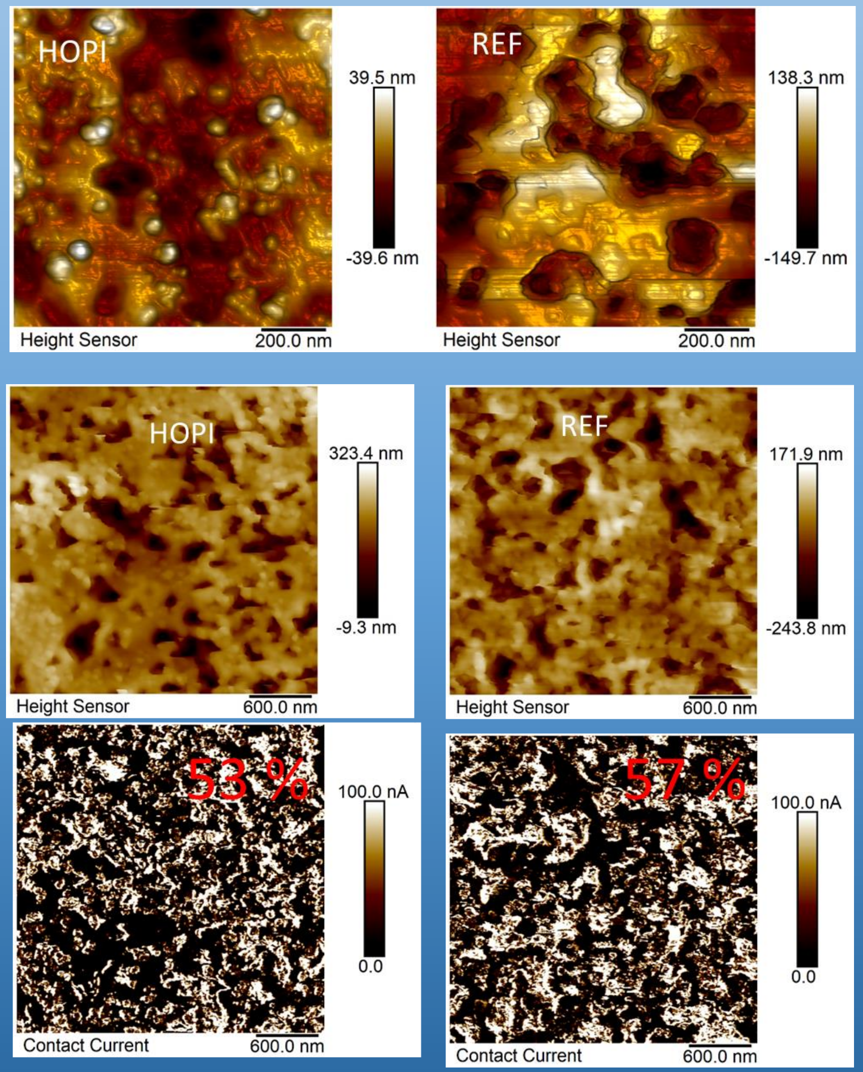


- Cutting with microtome without embedding
  - Clamped between Polystyrene plates for cutting
  - Measurement of "Blockface"
- Different layers can be analyzed due to different electrical and mechanical properties
- Thickness and material distribution
- Measurement of conductivity possible due to metal coated AFM tips (r_{tip} = 25 nm)

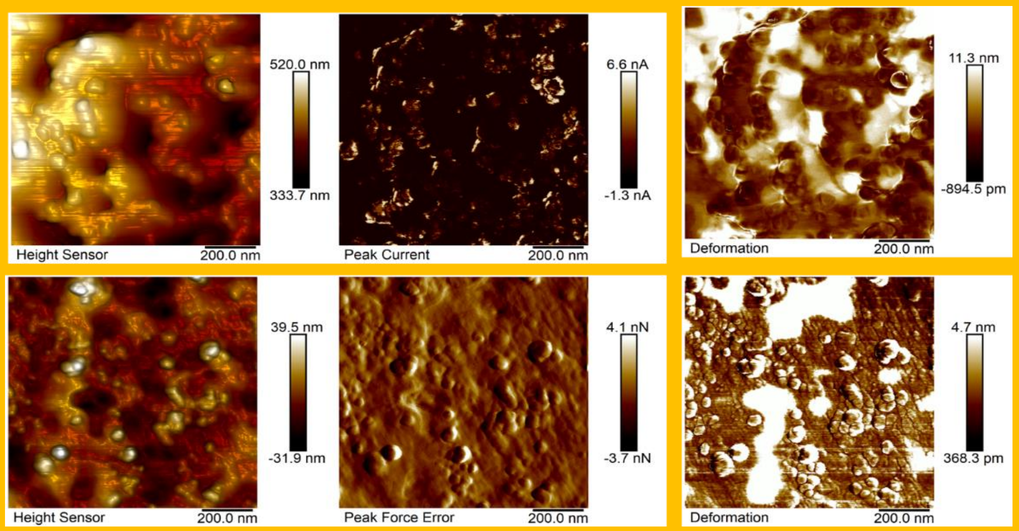
1. Atomic Force Microscopy (AFM) Influence of Ionomer Type

Catalyst layer structure HOPI/D2020

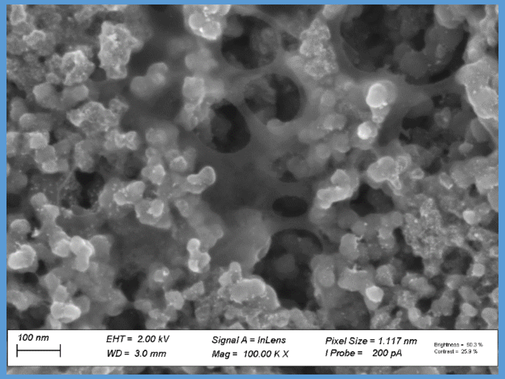
- The porosity of HOPI catalyst layers is lower as compared to D2020. As the performance in mass transport is still high, permeability of the ionomer is sufficient anyway. (1st row is measured with high-res AFM tip; 2nd and 3rd with conductive AFM tip.)
- The electronic conductive area is lower for HOPI, thus the overall coverage of the surface with ionomer is higher.

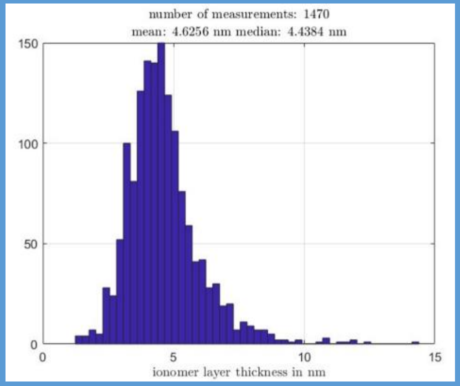


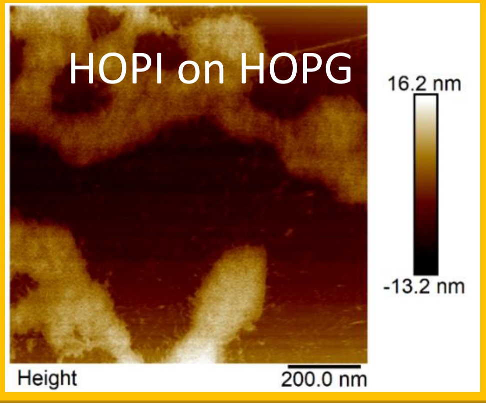
Ionomer agglomerates at HOPI MEA

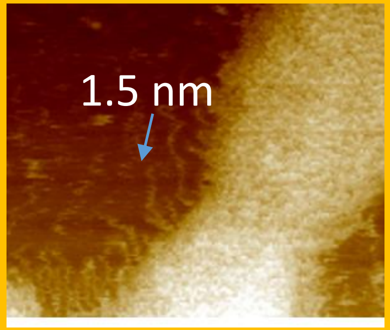


- Ionomer agglomerates with HOPI measured on CCL surface with AFM and SEM
- Ionomer layer thickness was evaluated with automated MATLAB script
- Lower thickness (4.4 nm) compared to D2020 ionomer layer thickness
- Thin film experiments revealed even layers below 2 nm



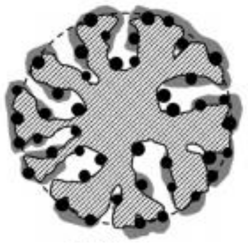
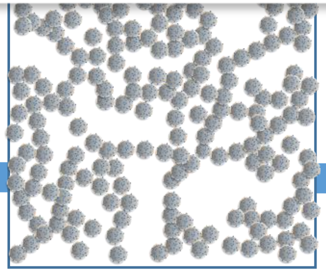






2. Electron Microscopy

Different scales of characterization

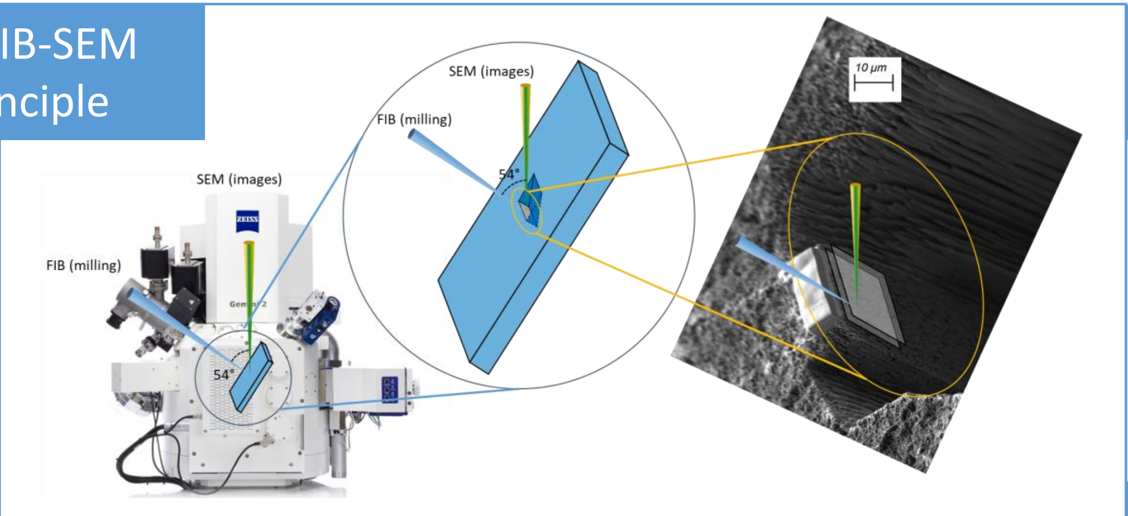
	Nano-scale	Micro-scale
		
	Carbon primary particle	*CCL*
◇ Porosity		1
◇ Distribution of the Pt/C catalyst	2	3
◇ Distribution of the ionomer	4	5

Electrode porosity by 3D FIB-SEM

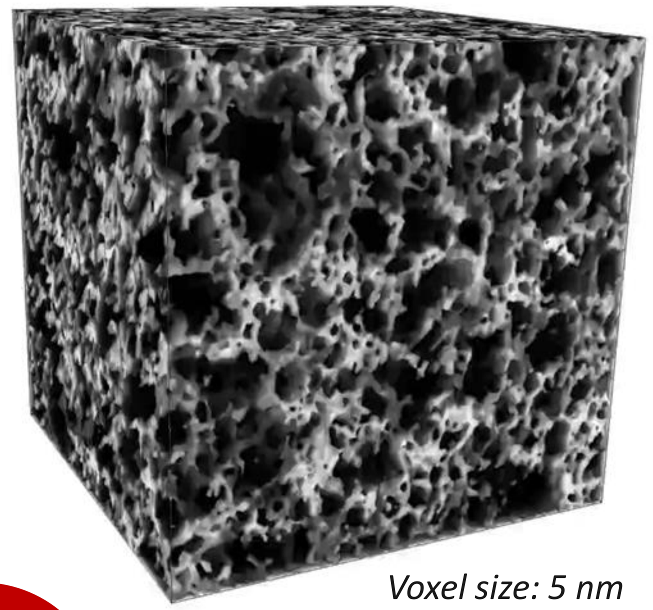
1

Focused Ion Beam – Scanning Electron Microscopy

3D FIB-SEM principle



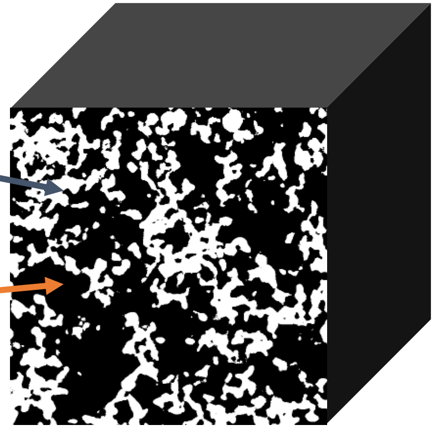
Stack of image acquisition

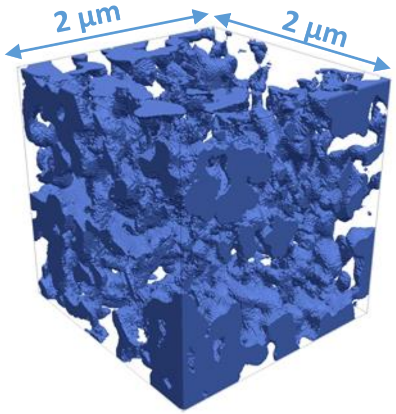


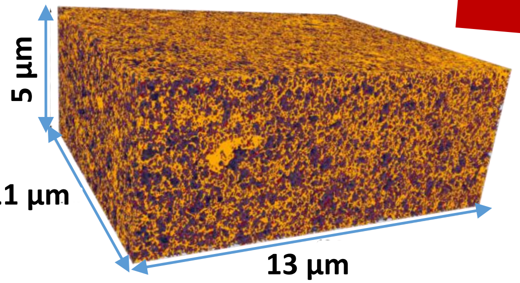
Voxel size: 5 nm

Porosity 55%

Representative electrode volume after image segmentation







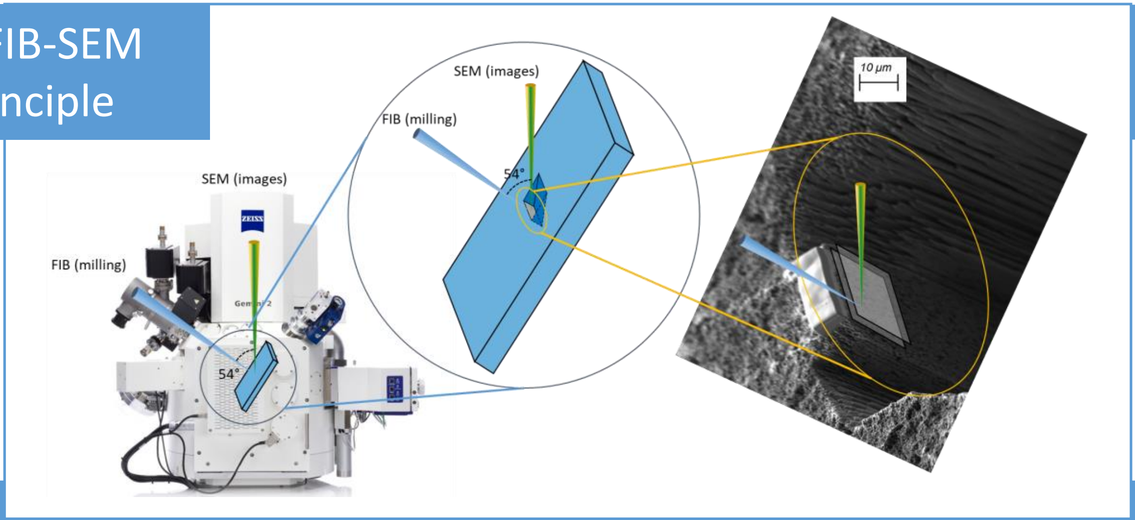
3D image of electrode porosity is used to model gas transport through the electrode

Electrode porosity by 3D FIB-SEM

1

Focused Ion Beam – Scanning Electron Microscopy

3D FIB-SEM principle



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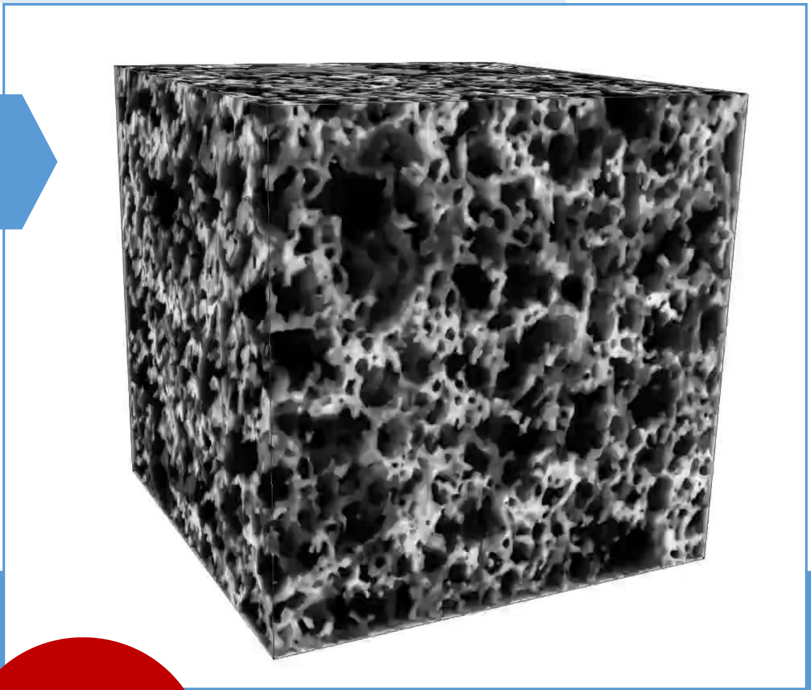

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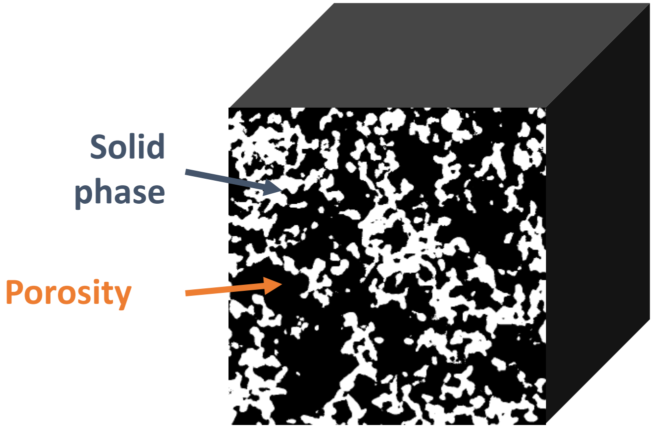
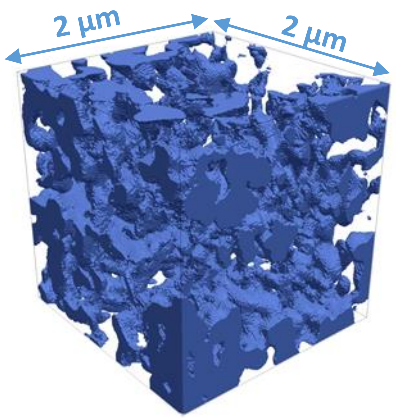
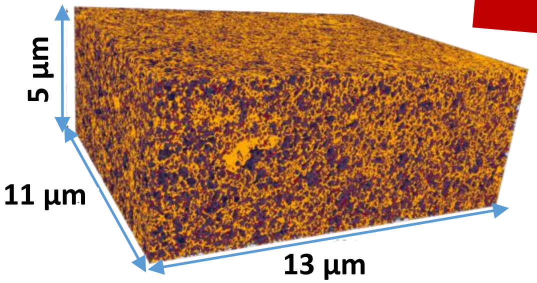






3D image of electrode porosity is used to model gas transport through the electrode

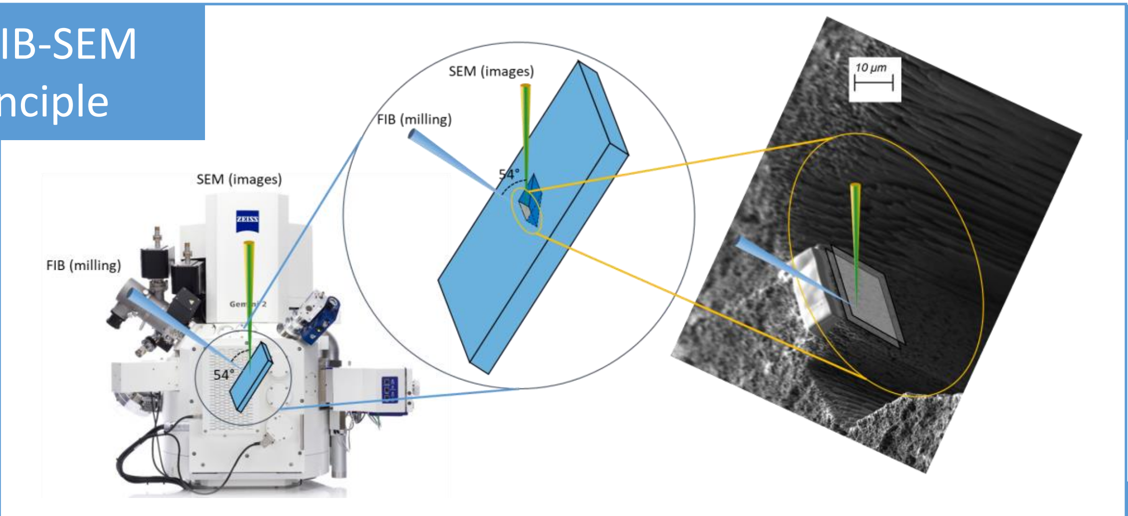
Electrode porosity by 3D FIB-SEM

1

Focused Ion Beam – Scanning Electron Microscopy

Clean Hydrogen Partnership
Co-funded by the European Union

3D FIB-SEM principle



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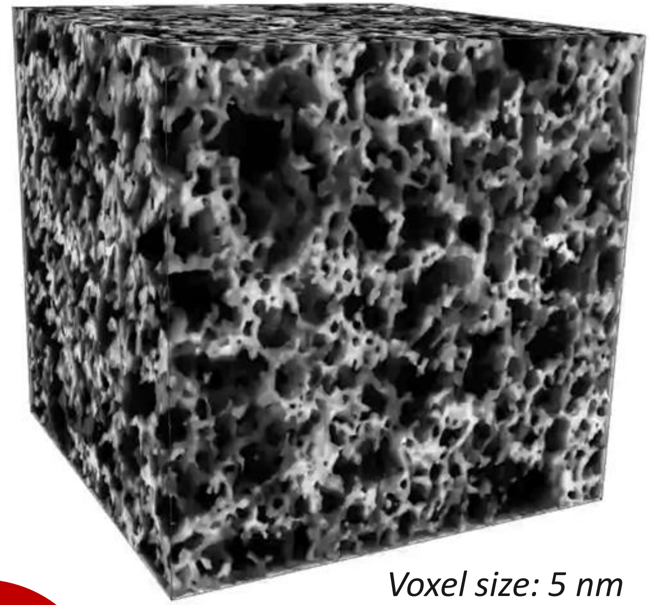

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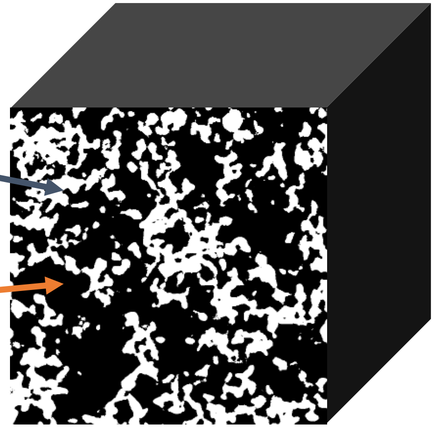
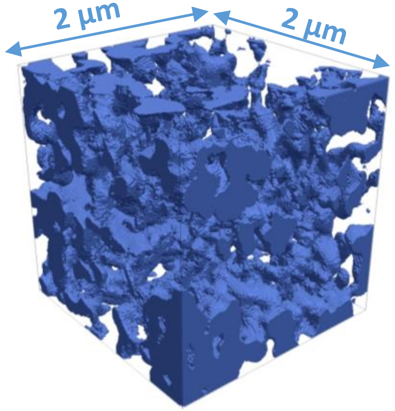
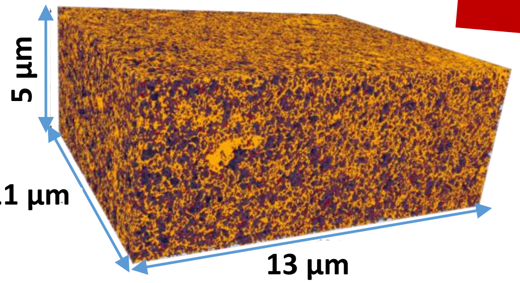




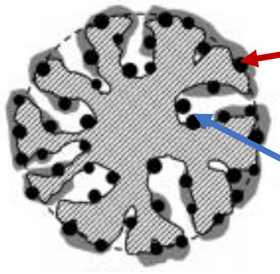


Porosity 55%

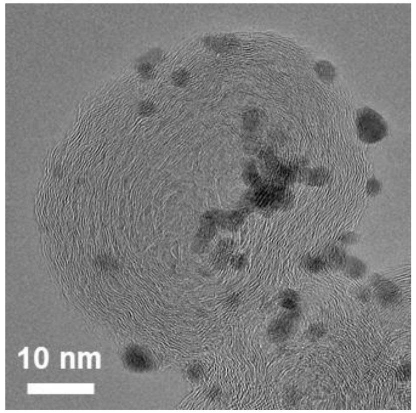
3D image of electrode porosity is used to model gas transport through the electrode

Pt nanoparticle distribution on the carbon support by electron tomography

2

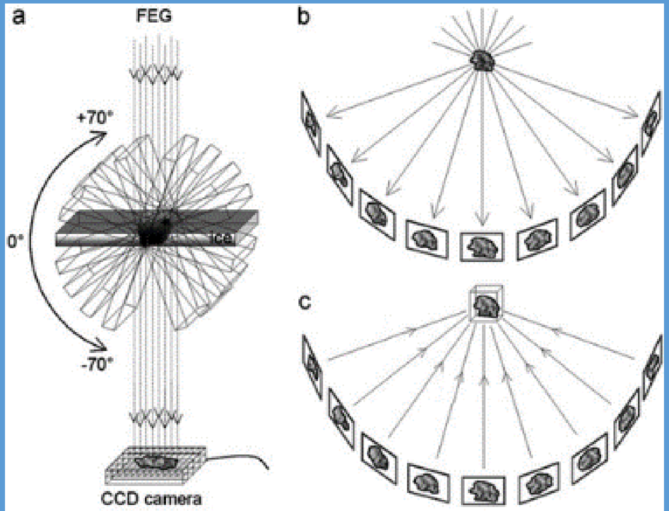


High surface area carbon



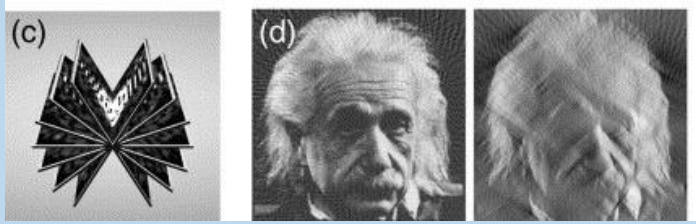
Electron tomography analyses is needed to determine the inner and outer Pt nanoparticles

Electron-tomography principle



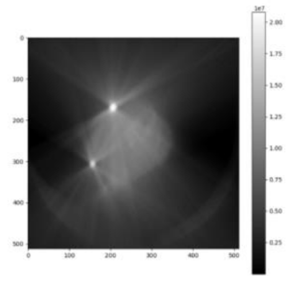
Challenges of 3D image reconstruction

- Effect of the missing wedge



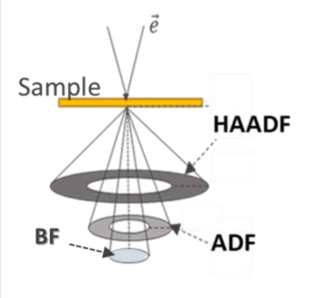
-90° to +90° -60° to +60°

- Effect of C density << Pt density



➡Use of different detectors

- Pt NPs ⇨ ***HAADF-high angle annular detector*** *to avoid* ***diffraction contrast.***
- C support ⇨ ***ADF-annular or BF detector*** *to enhance* ***C contrast.***



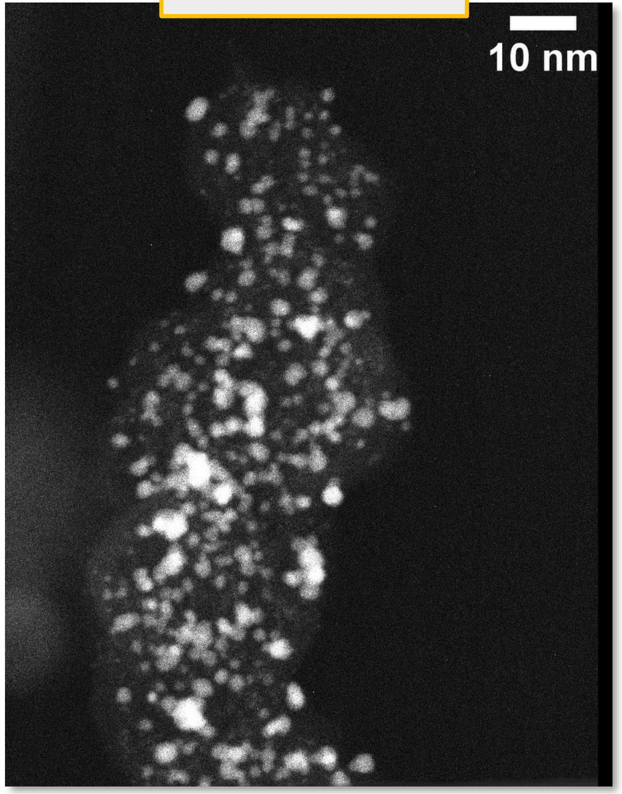
➡Use of advanced algorithm for 3D image reconstruction that reduces the missing wedge artefacts

Pt nanoparticle distribution on the carbon support by electron tomography

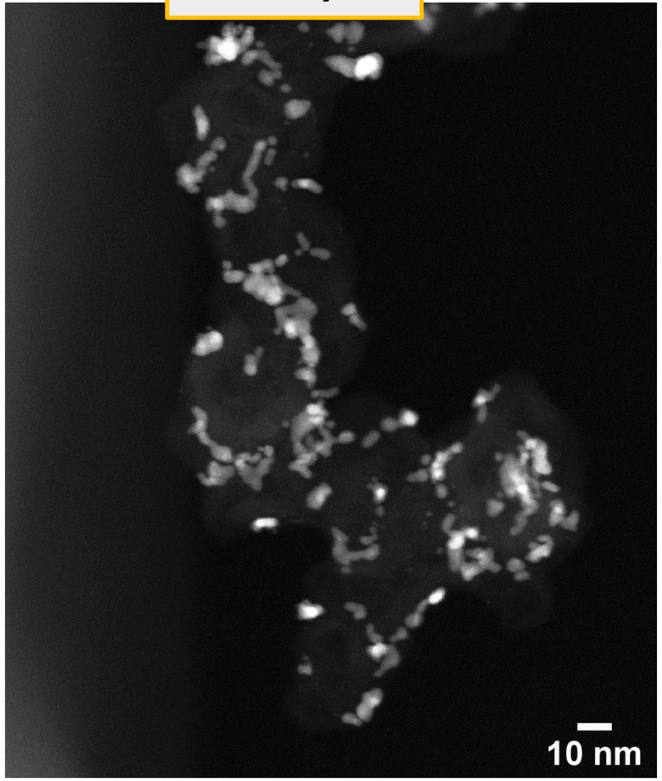
2

Acquisition: stack of images for the two catalysts

50% Pt/HSAC



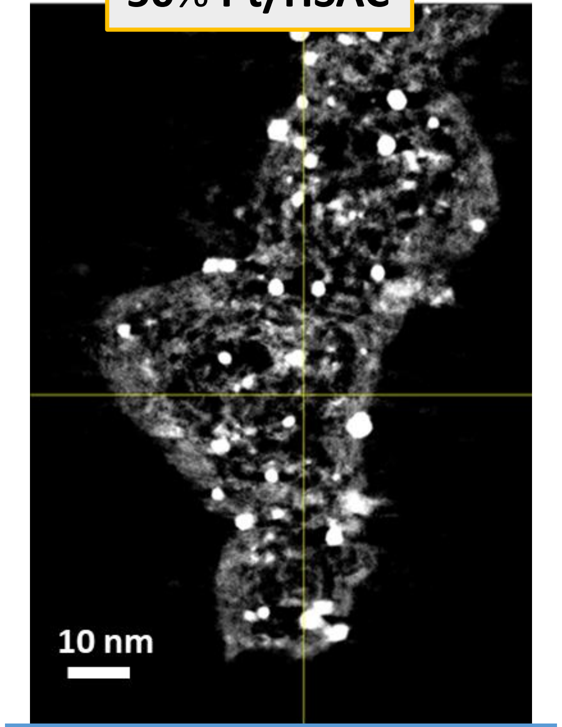
30% Pt/GC



After 3D reconstruction

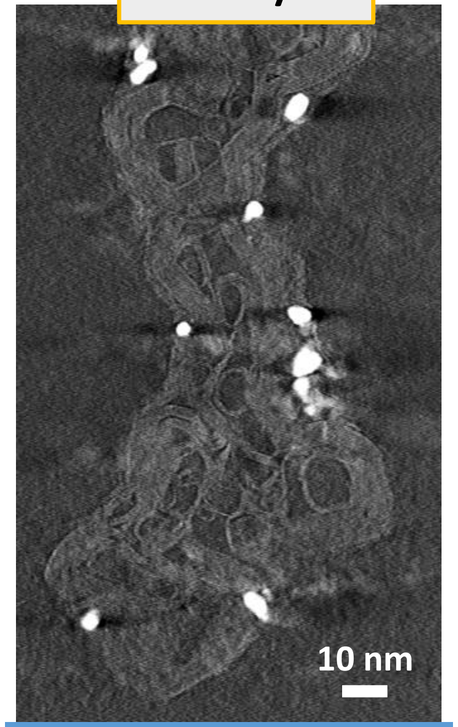
One slice of the volume

50% Pt/HSAC



A large number of Pt NPs are inside the C

30% Pt/GC

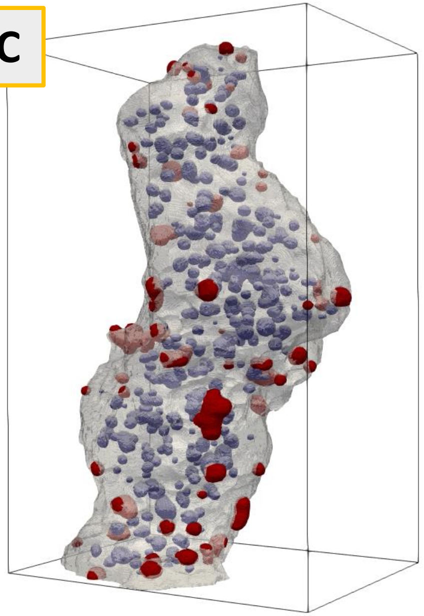


All the Pt NPs are on the C surface

Pt nanoparticle distribution on the carbon support by electron tomography

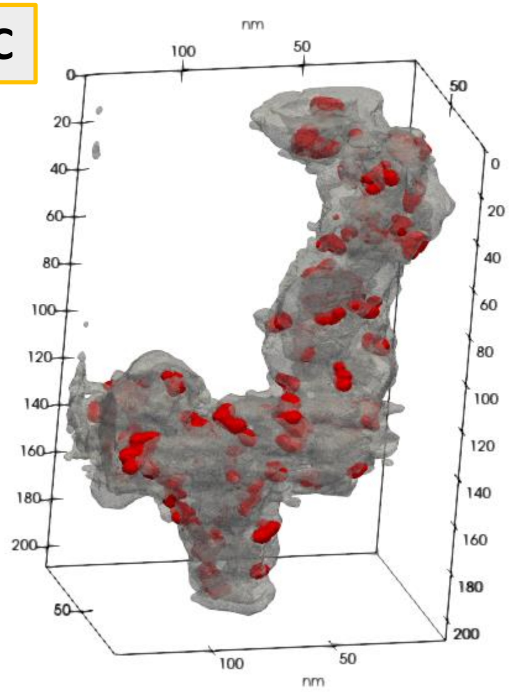
2

50% Pt/HSAC

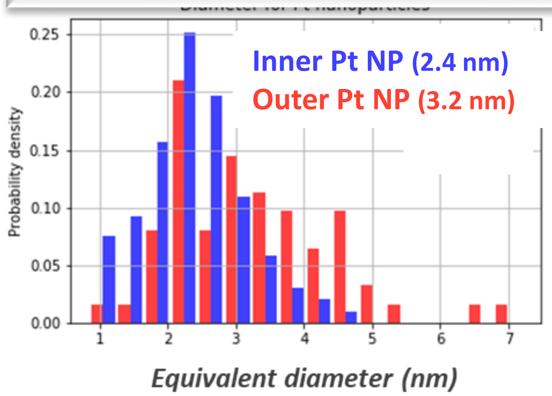


Outer Pt
Inner Pt
Carbon

30% Pt/GC



Quantitative analyse



Number of NPs

- 82% are internal
- 18% external

Surface area of Pt NPs

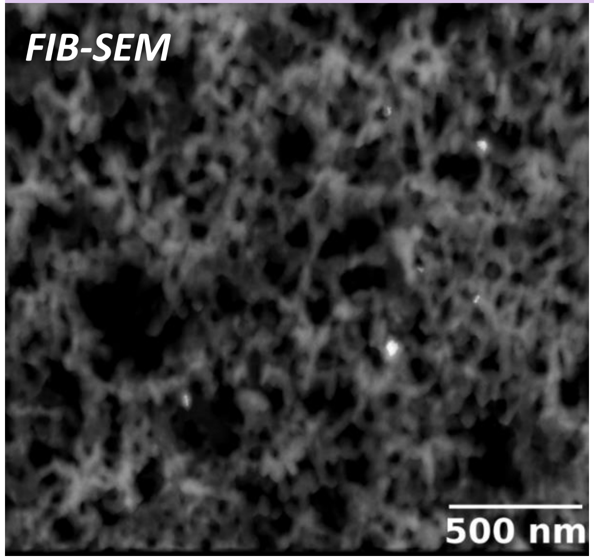
- 70% are internal
- 30% external

3D image of the Pt NP distribution is used to model the difference of local transport resistance between the inner/outer Pt nanoparticles

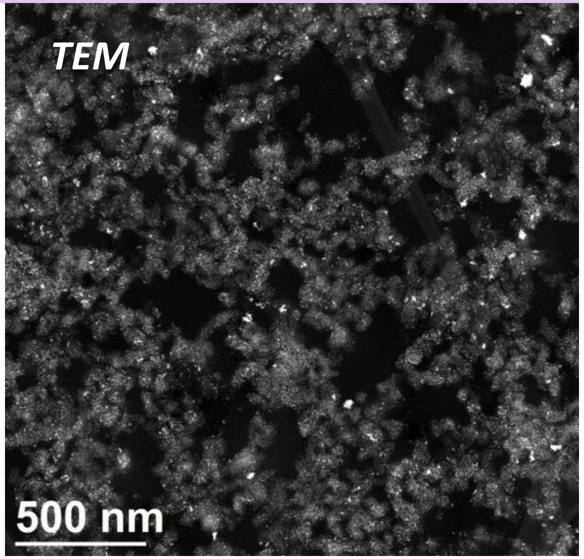
3 Pt/C distribution in the CCL by electron tomography

50% Pt/HSAC

Comparison of 3D FIB-SEM images with TEM images



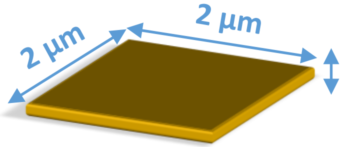
Pixel size : 5 nm



Pixel size : 0.5 nm

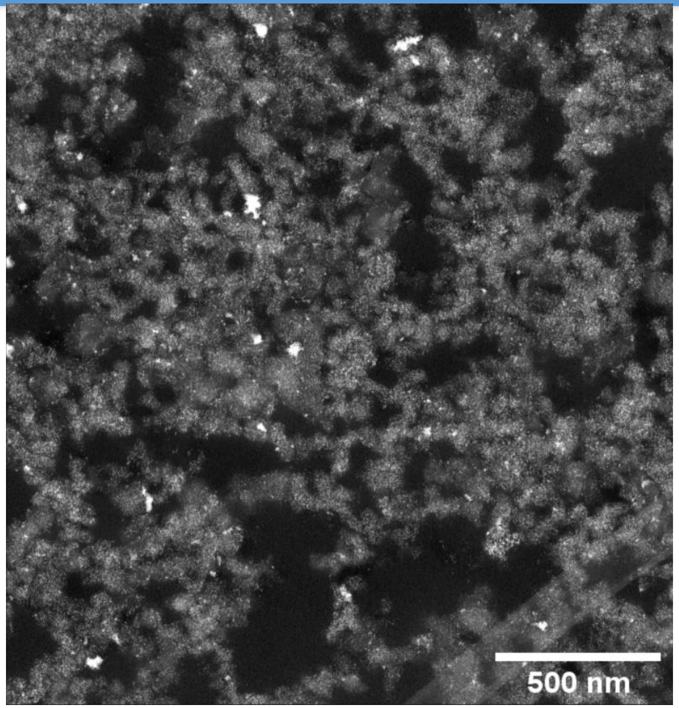
Electron tomography on thin sample (100 nm)

Size of the analyzed cathode volume



Thin sample of MEA embedded in epoxy resin cut by ultramicrotomy

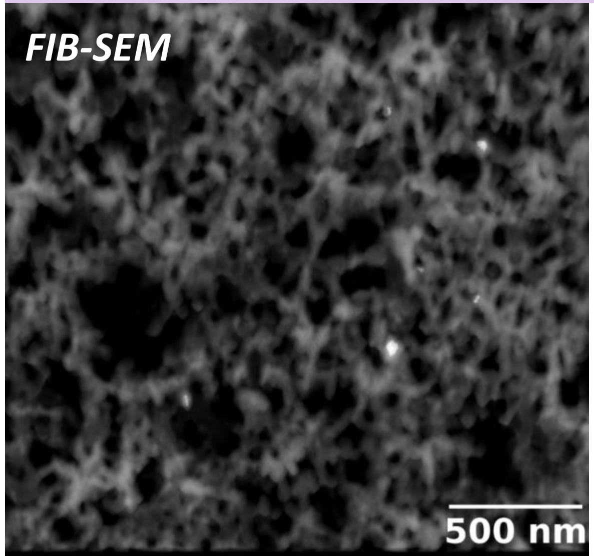
Tilt series image acquisition



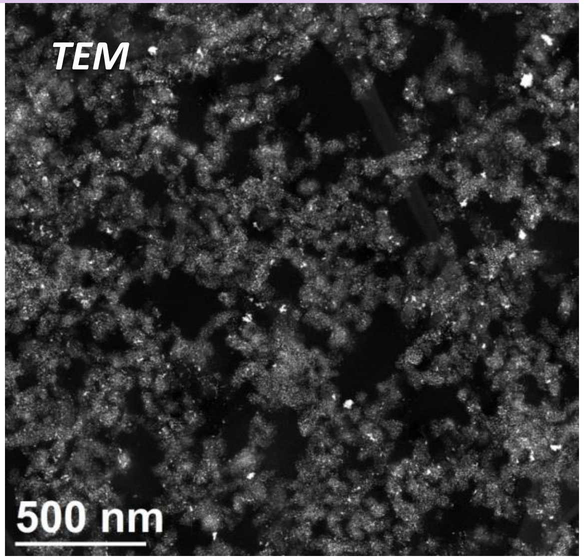
3 Pt/C distribution in the CCL by electron tomography

50% Pt/HSAC

Comparison of 3D FIB-SEM images with TEM images



Pixel size : 5 nm



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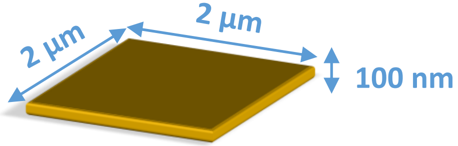

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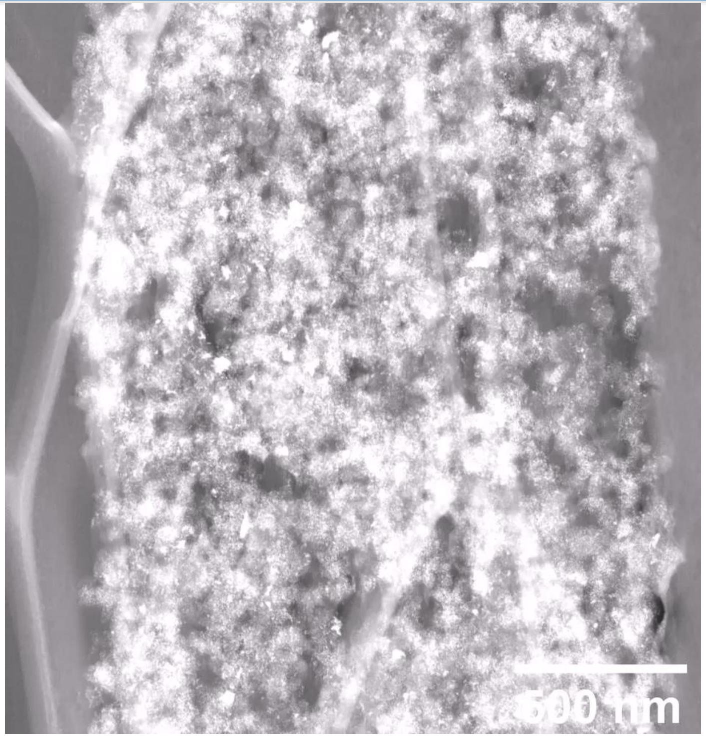
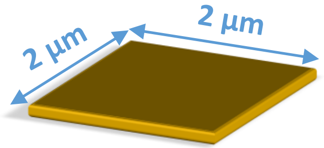
Tilt series image acquisition

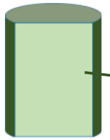


3 Pt/C distribution in the CCL by electron tomography

Size of the analyzed cathode volume

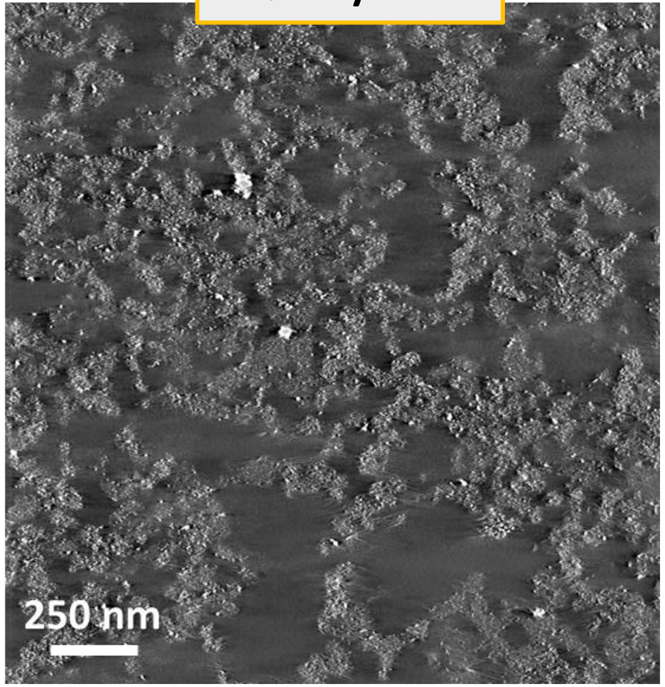


After 3D reconstruction

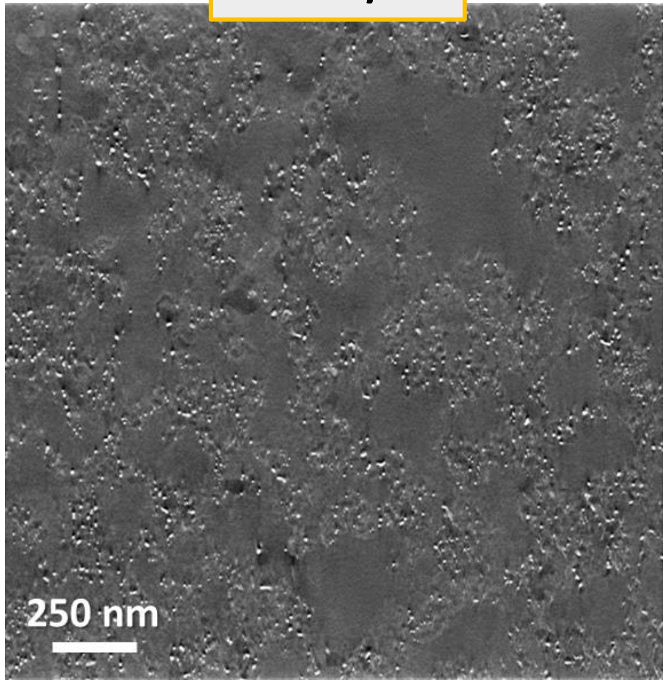


One slice of the volume (Volume : 2 µm x 2µm x 100 nm)

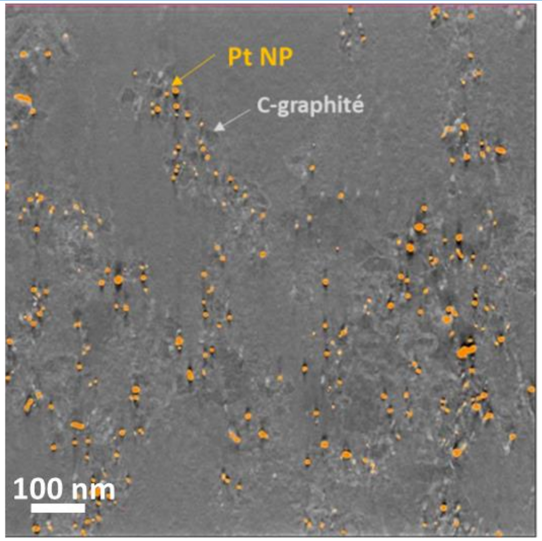
50% Pt/HSAC



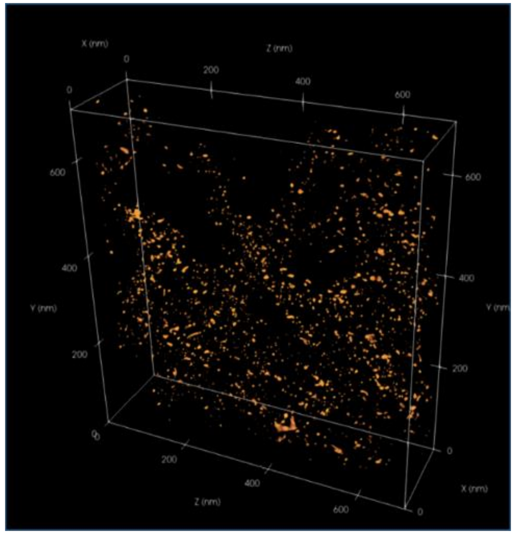
30% Pt/GC



Pt NP distribution in the slice



Pt NP distribution in the volume



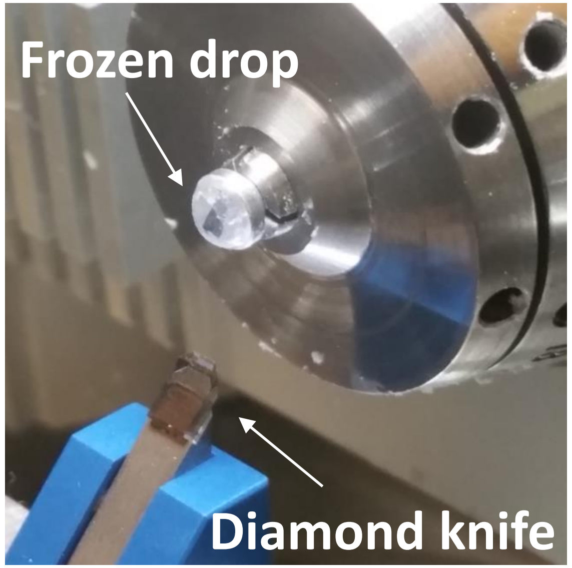
Segmentation of the carbon support in the image is more difficult (in progress)

Ionomer distribution on the carbon support

Clean Hydrogen Partnership

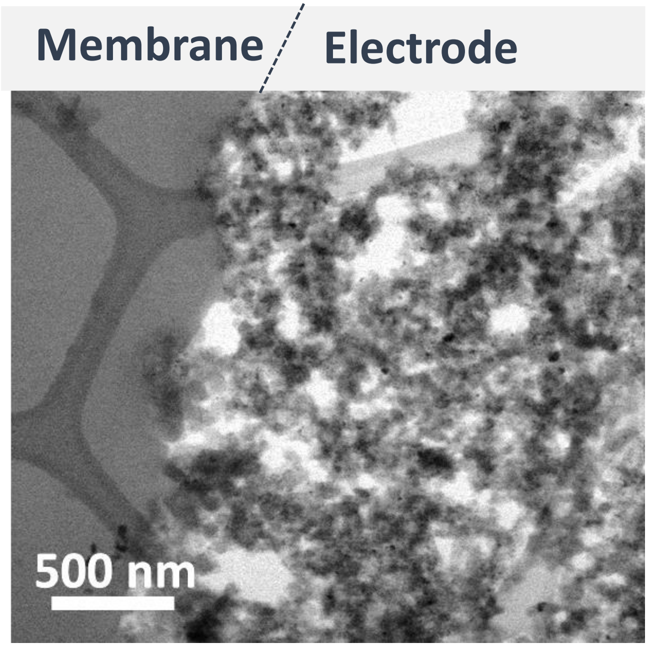
Co-funded by the European Union

Development of the cryo-ultramicrotomy preparation technique by embedding the MEA in a drop of frozen water

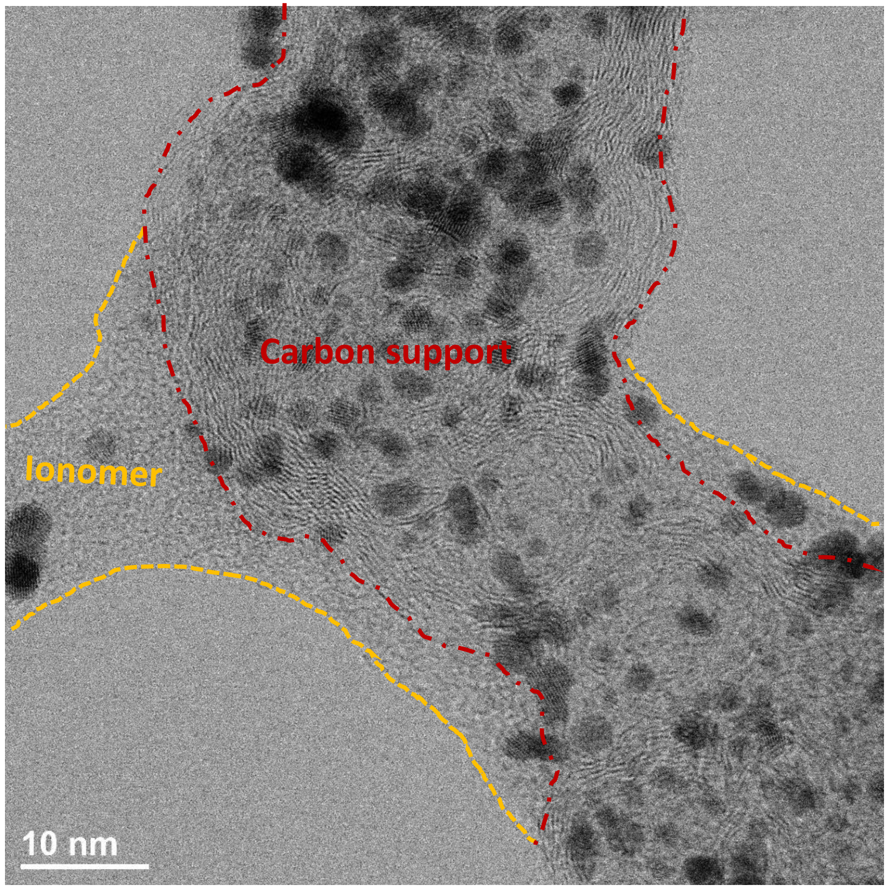


Salvado et al.,
J. Power Sources, (2021)

Thin slice of cut MEA was successfully deposited on TEM grid



The ionomer thin layer can be observed

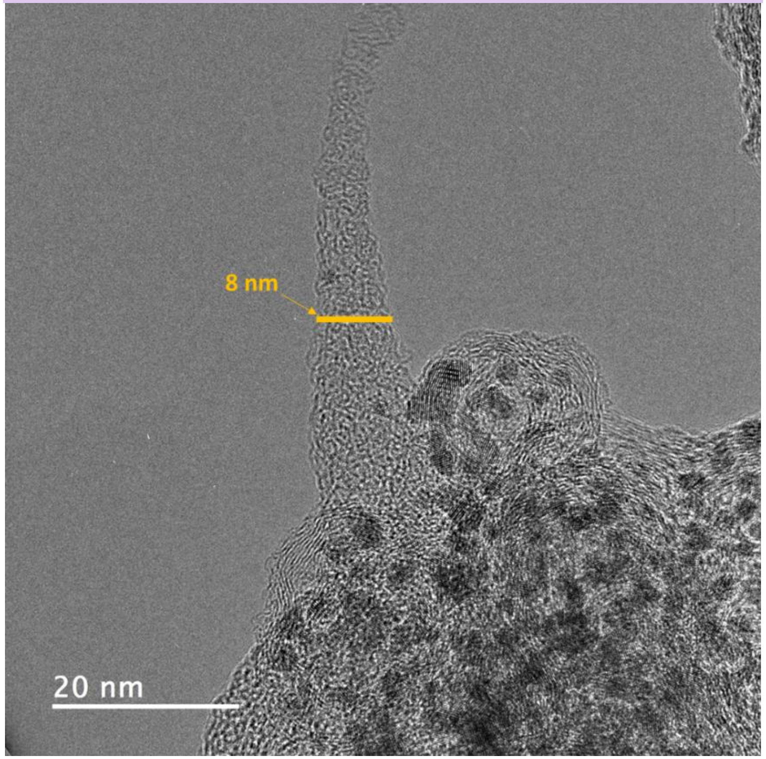


Ionomer distribution on the carbon support

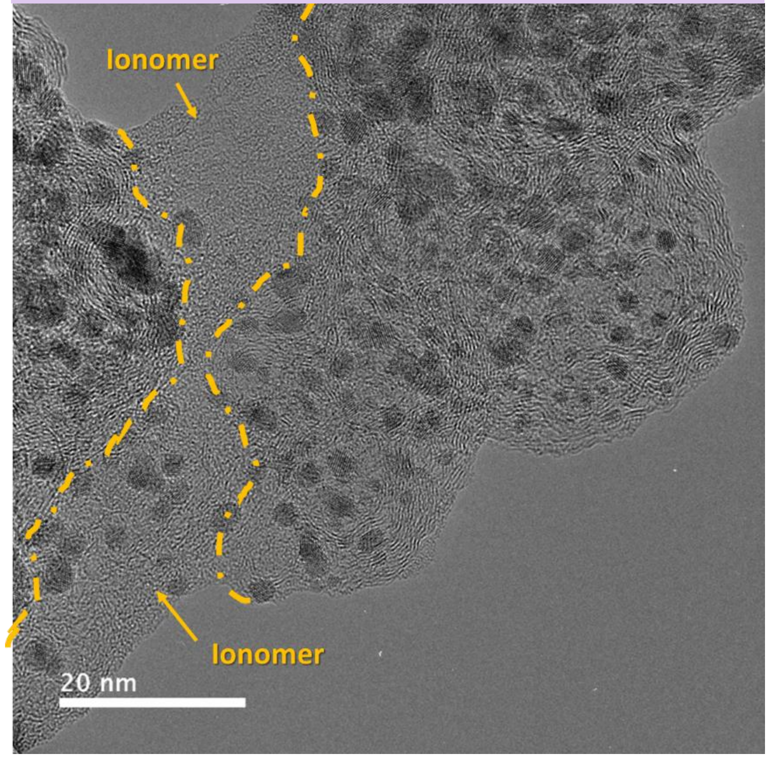
4

50% Pt/HSAC

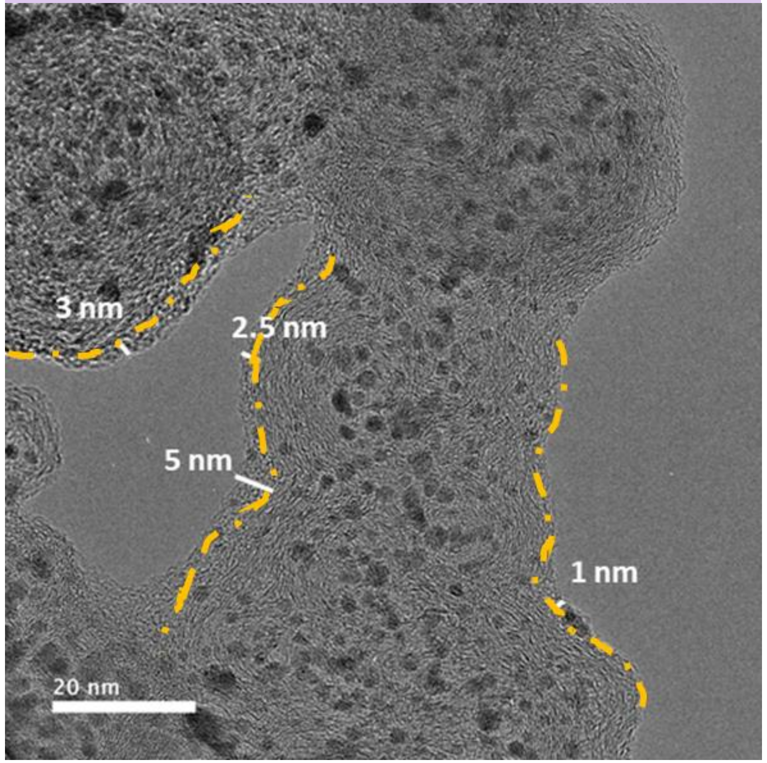
Ionomer filament bridging two Pt/C agglomerates



Ionomer linking two Pt/C agglomerates



Thin layer of ionomer on Pt/C agglomerates with different thickness

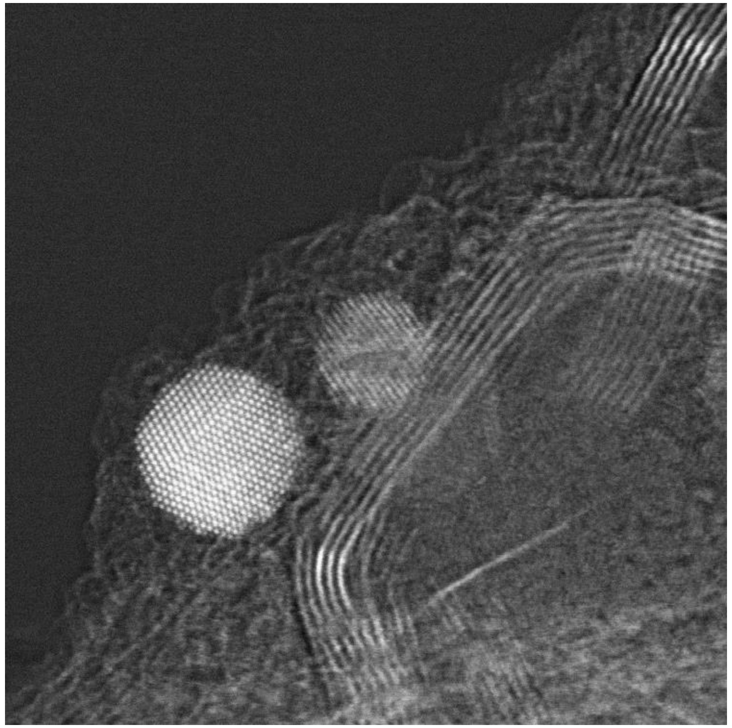


Ionomer distribution on the carbon support

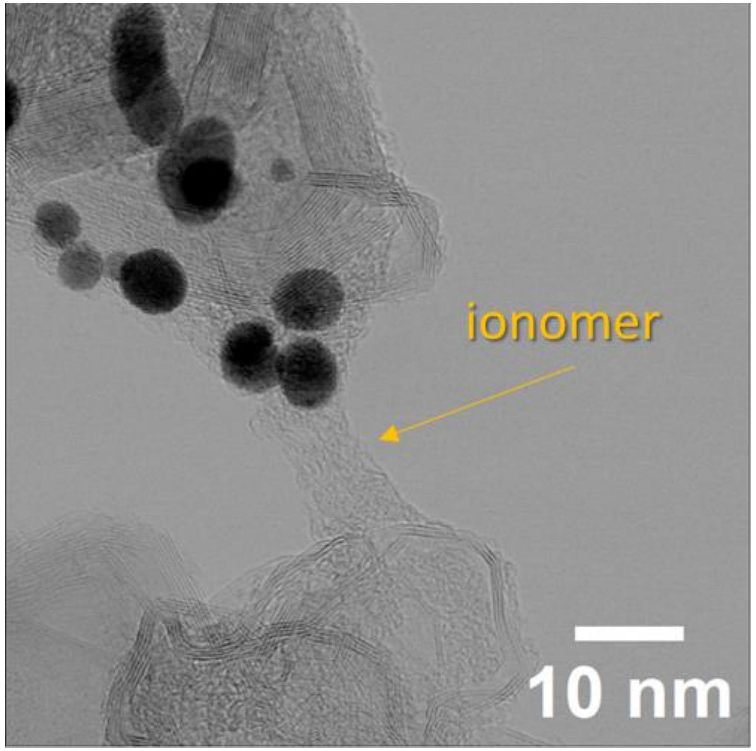
4

30% Pt/GC

Thin layer of ionomer on Pt/C agglomerates with different thickness



Ionomer filament bridging two Pt/C agglomerates

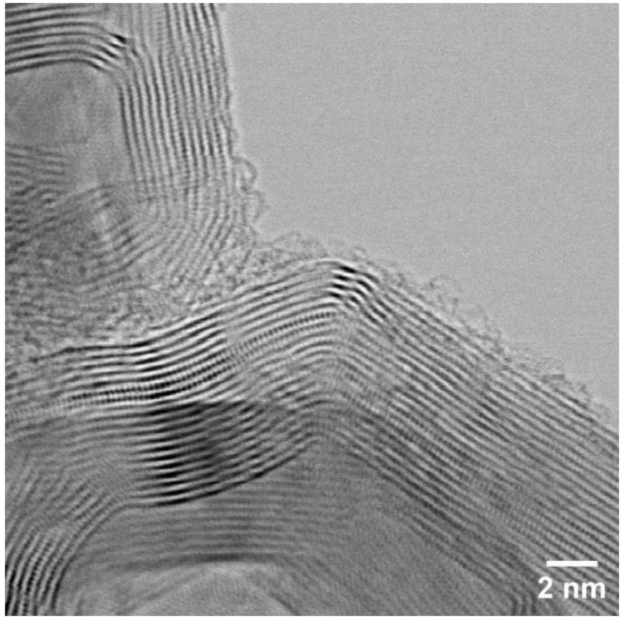


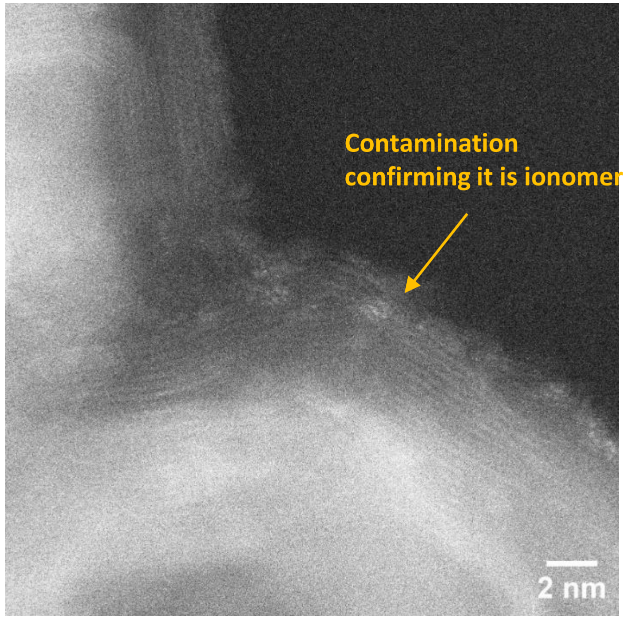
Ionomer distribution on the carbon support

4

30% Pt/GC

A thin layer < 2 nm of ionomer can also be observed on the Pt/C



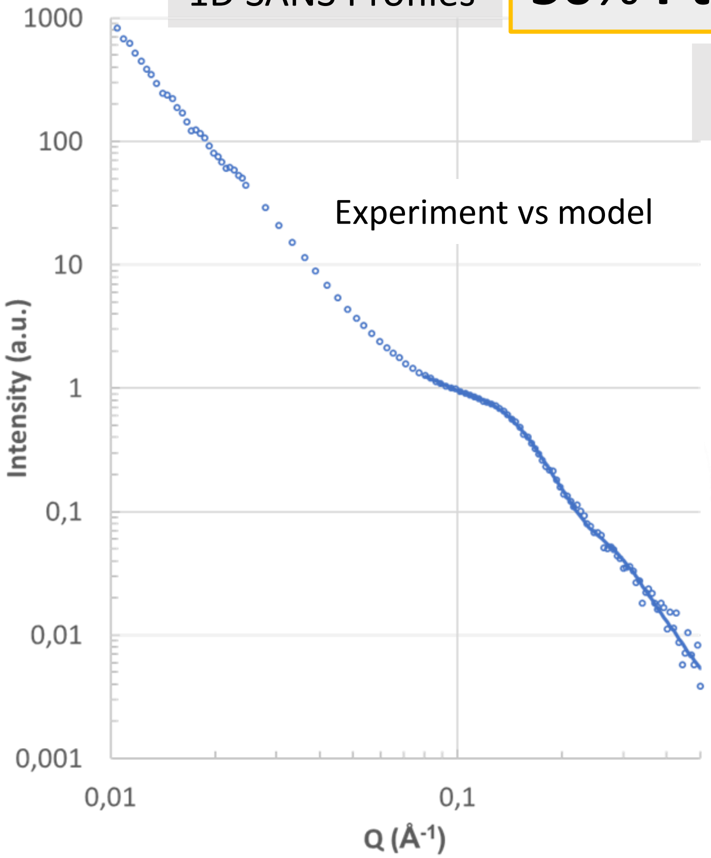


Similar ionomer layer < 2 nm is difficult to be detected on HSAC

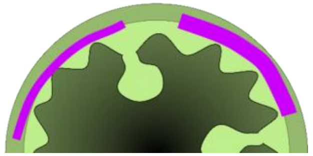
in agreement with SANS measurements (Arnaud Morin)

1D SANS Profiles

50% Pt/HSAC



Scheme of proposed structure
for hydrated ionomer coated carbon

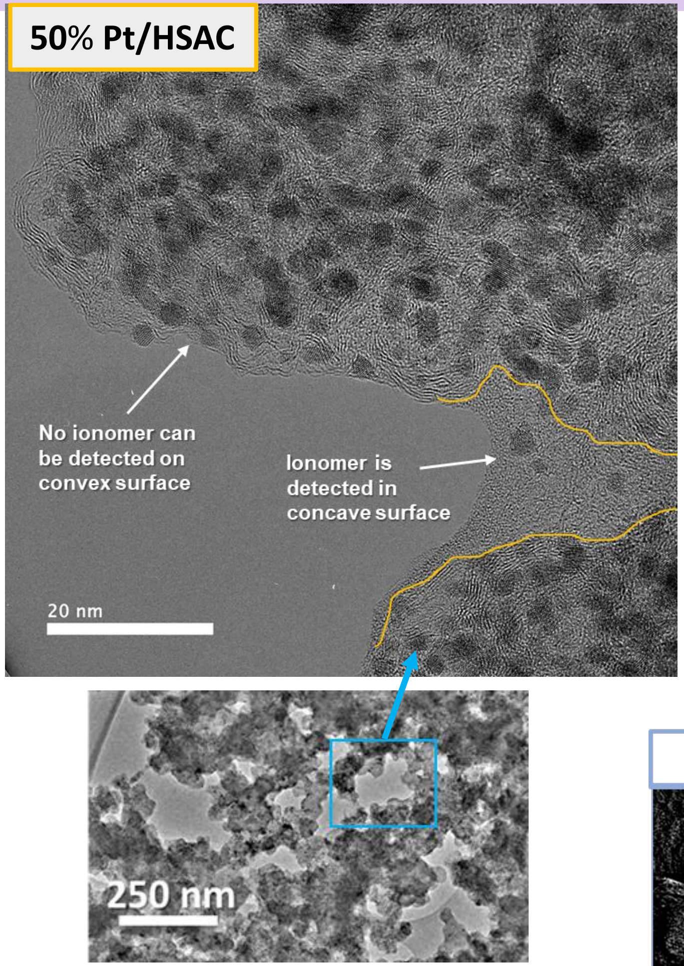


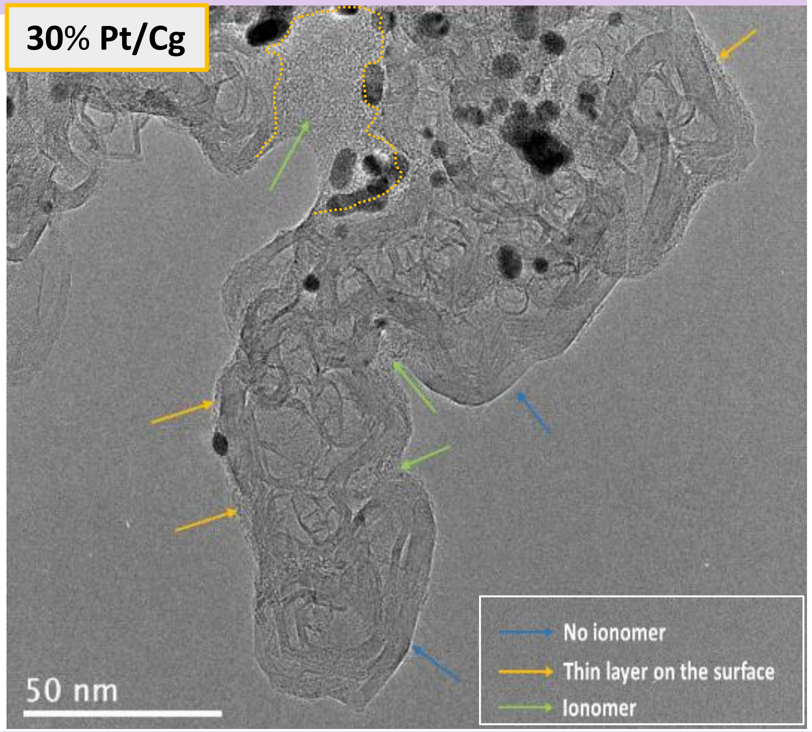
@95%RH
Ionomer film: ~2.5 nm (1 – 6 nm)
Water film: ~0.9 nm (0.3 – 1.5 nm)
Surface pores depth: ~3 nm (1 – 4 nm)

Chabot *et al.*, ACS Applied Energy Materials, 2023

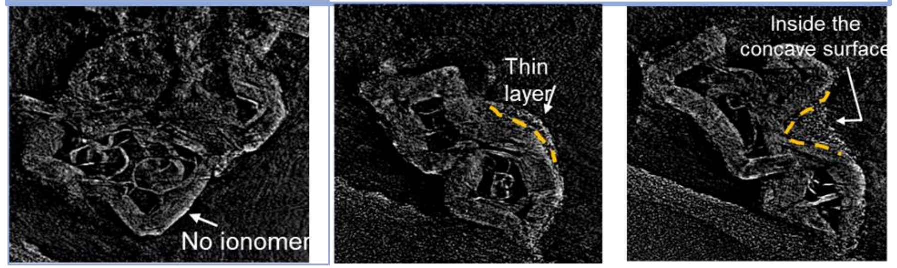
Ionomer distribution inside the CCL

Most of the ionomer observed by TEM is located in concave carbon surface





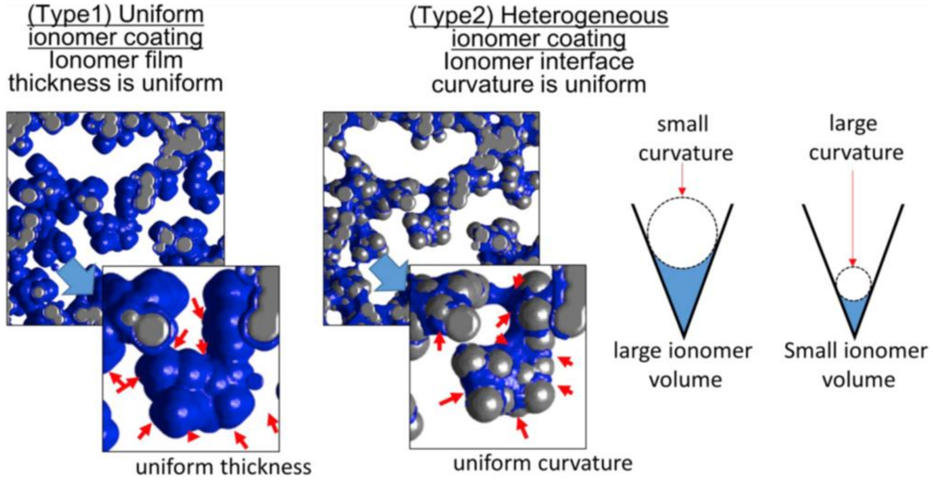
Slices of the 3D images (e-tomography)



G. Inoue et al., *Intern. J. Hydr. Energy* (2016)

"It is assumed that the gase/liquid interface moves with a uniform curvature in the entire interface during evaporation.

When the ionomer concentration becomes higher than the adhesion threshold concentration, ionomers adhere at this curvature."

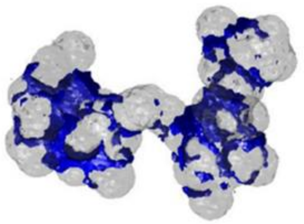


K. Park et al., J. Power Sources Advances (2022)

TEC10E50E, TKK,

50% Pt/HSAC

I/C = 0.8 (w/w)
Coverage = 0.819



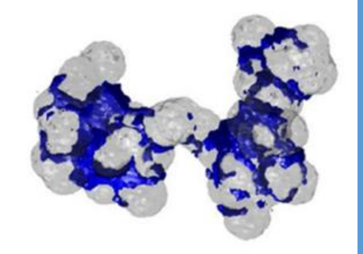
6

Ionomer distribution inside the CCL

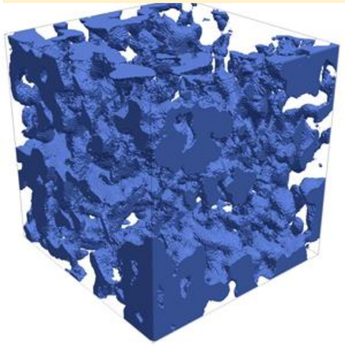
Digital reconstruction of ionomer coating on the 3D FIB-SEM image by considering the local curvature of the surface

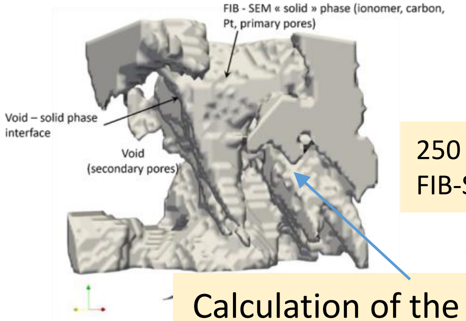
K. Park et al., J. Power Sources Advances (2022)

I/C = 0.8 (w/w)
Coverage = 0.819



3D FIB-SEM image



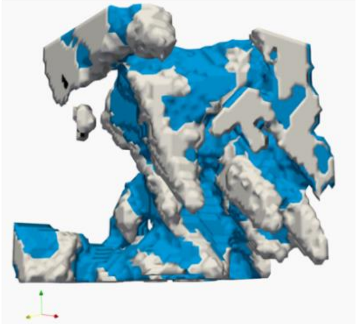


250 x 250 x 250 nm^3 of FIB-SEM image

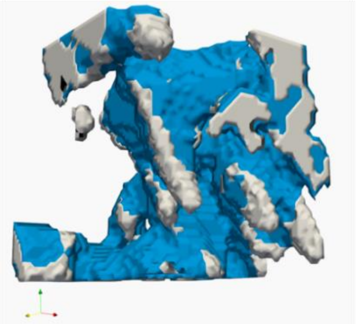
Calculation of the surface curvature

Ionomer coverage determined from thresholding the local solid surface curvature distribution

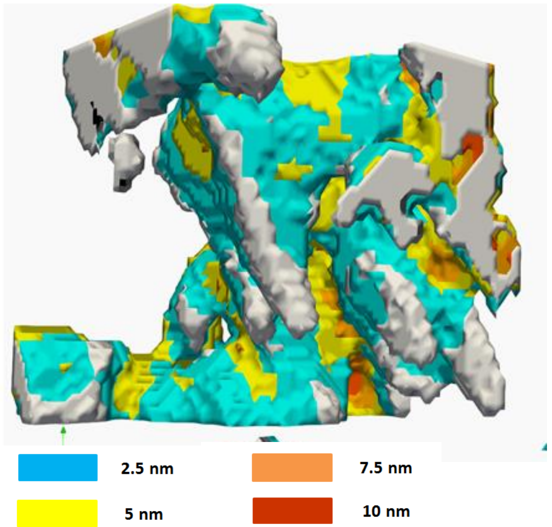
Coverage = 0.64
Curvature < 0.02 nm^{-1}



Coverage = 0.82
Curvature < 0.04 nm^{-1}

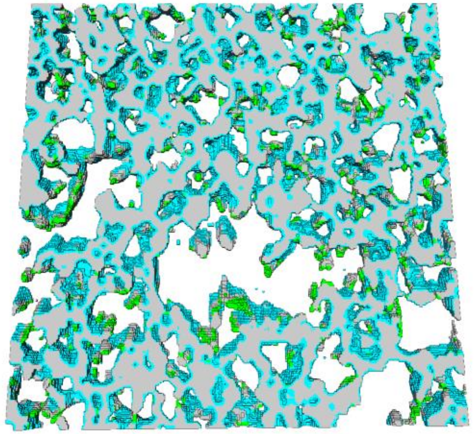


Thickness of the ionomer layer



Applied to a larger volume

Coating ionomer + Ionomer filaments + Pt/C



3D image of the CCL with distribution of ionomer used to model the CCL electrochemical properties

M Ahmed-Maloum et al., International Journal of Hydrogen Energy, 2024

Conclusions

AFM and electron microscopy are complementary techniques for CCL microstructural characterization

- **AFM :**

    - Measurement under different RH conditions

    - Measurement of mechanical and electrical properties gives high contrast between Pt/C and ionomer, atomic resolution difficult / not possible on catalyst layers. Best use-case is for microstructure.

    - Analysis of CCL surface revealed an ionomer layer particularly thick for the high I/C ratios *(electrical and mass transport properties are affected)*

- **Electron microscopy / electron tomography**

    - ***At the nano- scale (carbon primary particle)*:**
        - 3D image of the Pt NP distribution inside/outside the carbon support
        - Thin ionomer layer can be imaged on graphitized carbon but more difficult on HSAC carbon. 3D image of thin layer is still difficult.

    - ***At the micro-scale CCL scale***
        - FIB-SEM provided 3D image of the CCL porosity in representative volume (500 μm^3) but Pt NP and ionomer are not visible in the solid phase
        - E-tomography can provide a 3D image the Pt/C distribution in a smaller volume (1 x 1 x 0.1 μm^3)
        - The ionomer 3D distribution at µm scale is still difficult to be obtained: digital reconstruction on the FIB-SEM 3D image by taking in account the ionomer distribution features.

➪ **The 3D distribution of the ionomer is affected by ionomer ratio, ionomer type and catalyst**
Pt distribution is highly affected by the catalyst type

The TEAM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Dr. Pascal Schott

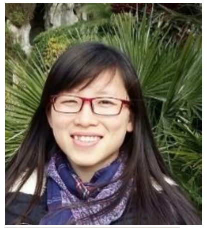

PhD Konrad Guelicher


Dr. Isotta Cerri


PhD Ahmed Maloum

Clean Hydrogen Partnership

Co-funded by the European Union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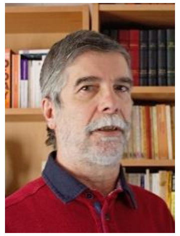
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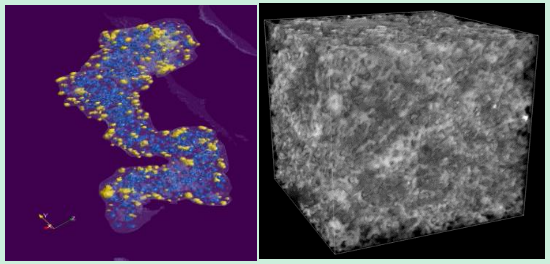
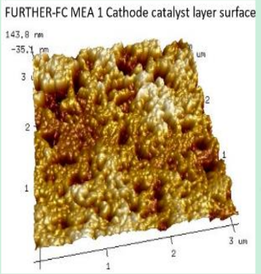
This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No **875025**. This Joint Undertaking receives support from the European Union’s Horizon 2020 Research and Innovation program, Hydrogen Europe and Hydrogen Europe Research.

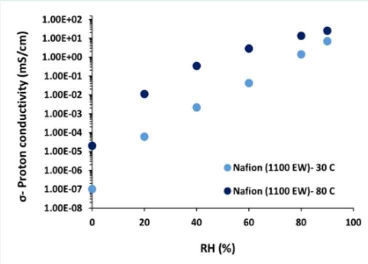
Thank you for your attention.
Your questions are welcome

Multiscale characterization

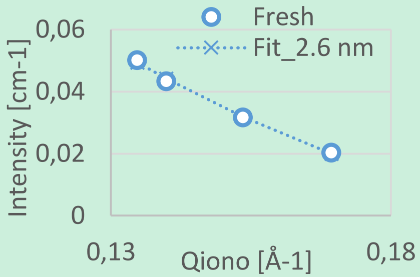




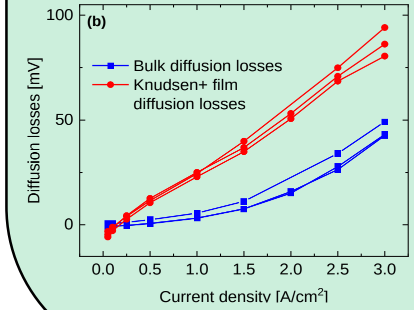
3D TEM and FIB/SEM *AFM*



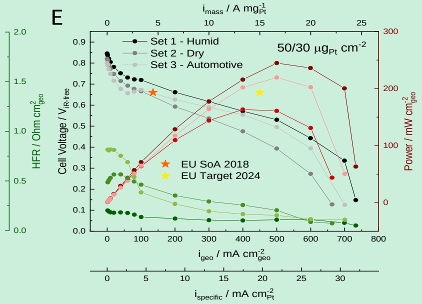
Ionomer transport properties



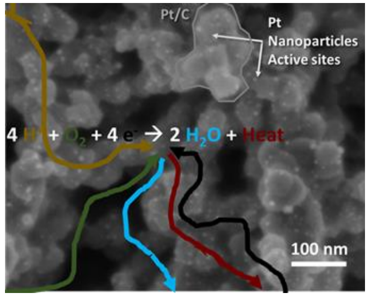
Ionomer swelling

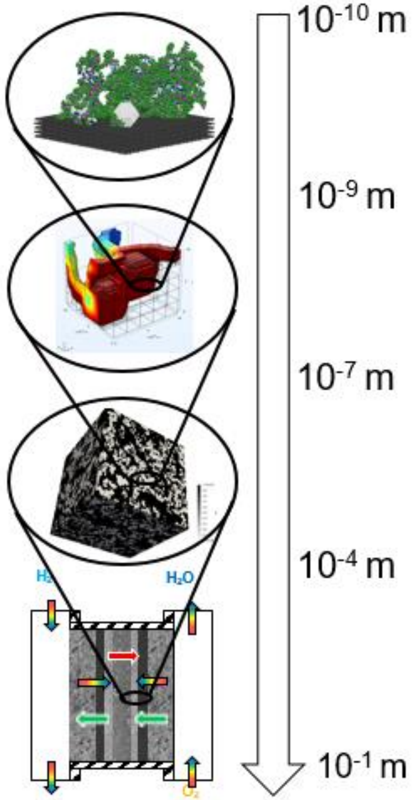


Mass transport losses



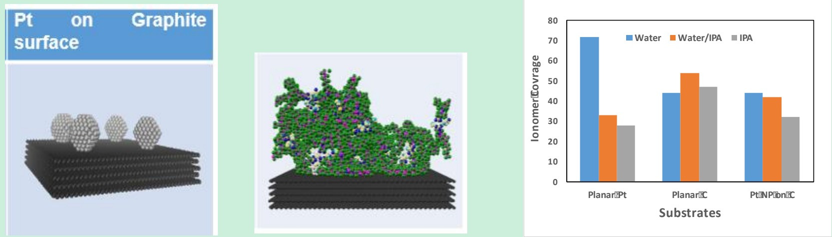
Ultra-thin electrode



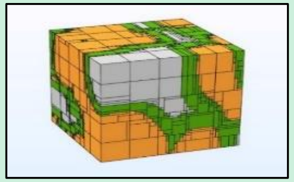


Multiscale modeling

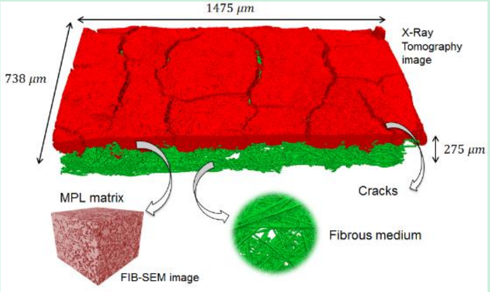
Ionomer film scale



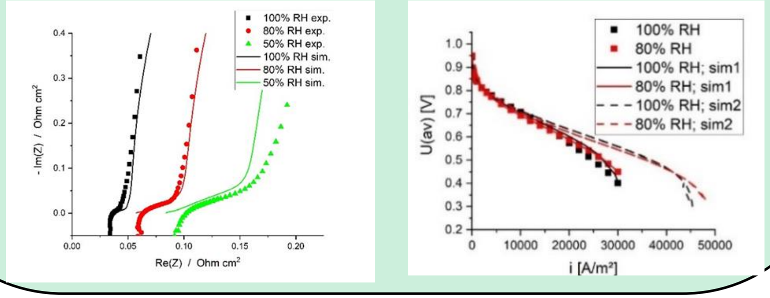
Sub µm scale



CCL scale



Cell scale

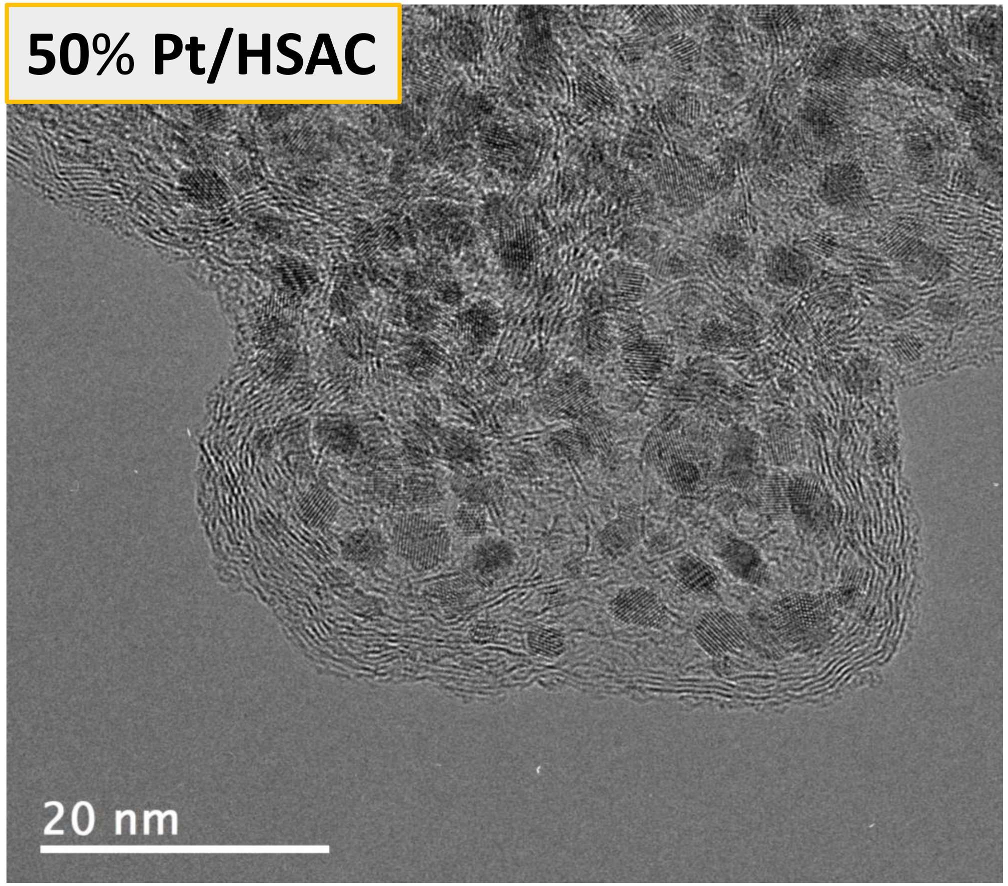


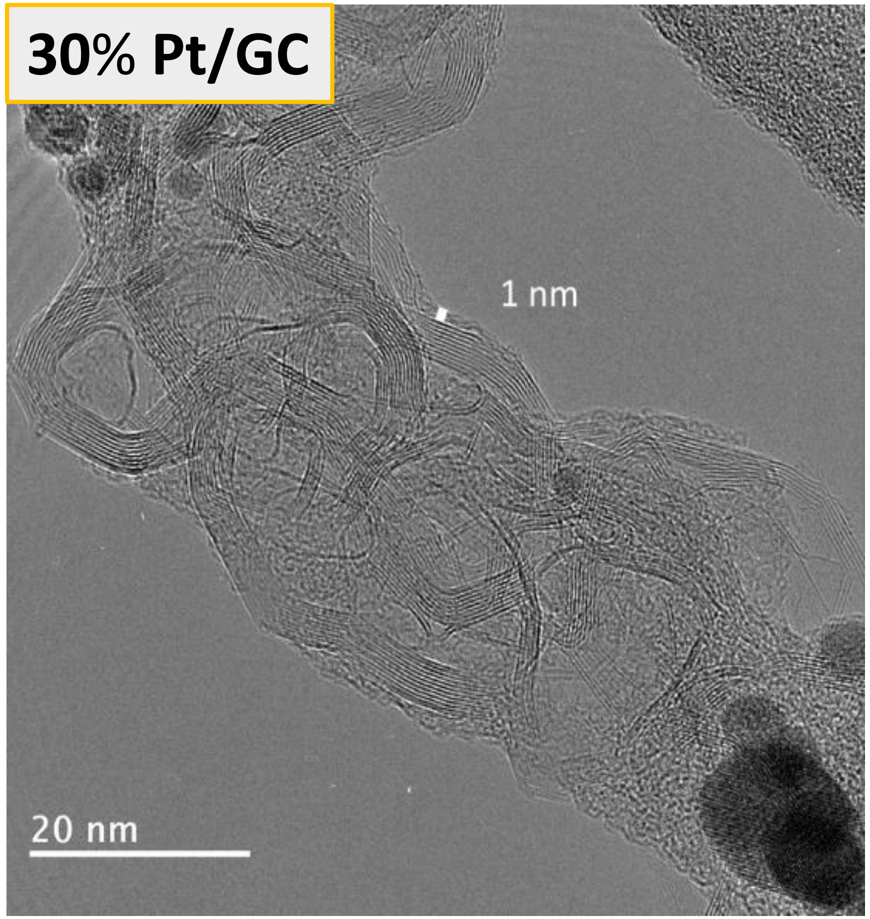
Coordinator: J. Pauchet (CEA); joel.pauchet@cea.fr

Ionomer distribution on the carbon support

4

Similar ionomer layer < 2 nm is difficult to be detected on HSAC





This very thin layer is probably difficult to be imaged in 3D