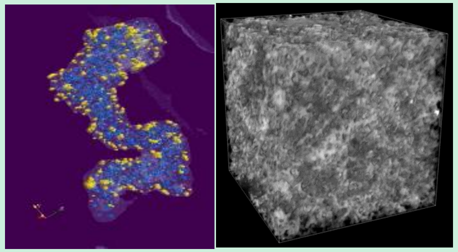
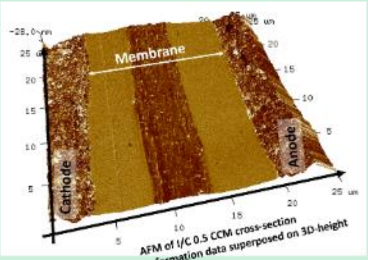
# WELCOME TO THE 1st FURTHER-FC WORKSHOP!

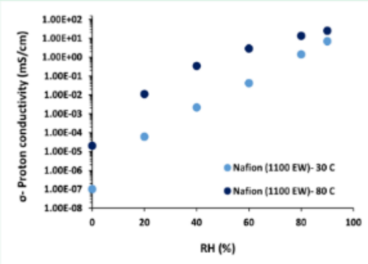
## Multiscale characterization



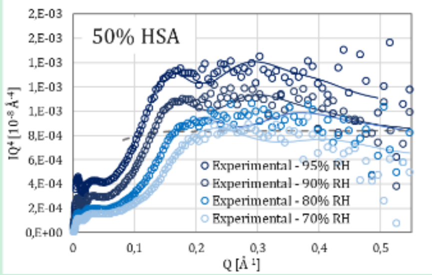
*3D TEM and FIB/SEM*



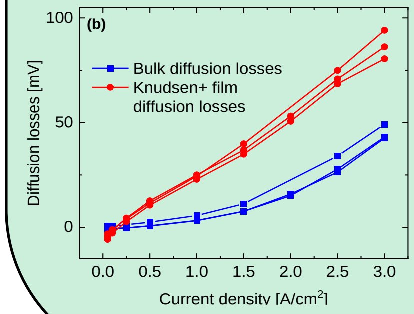

*AFM*



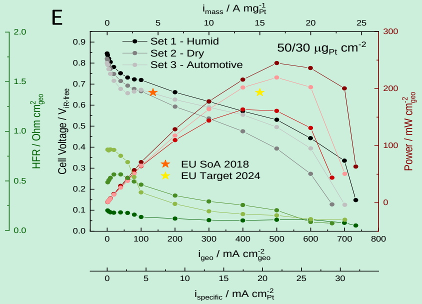

*Ionomer transport properties*



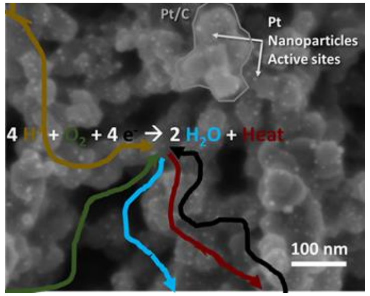

*Small Angle Scattering*

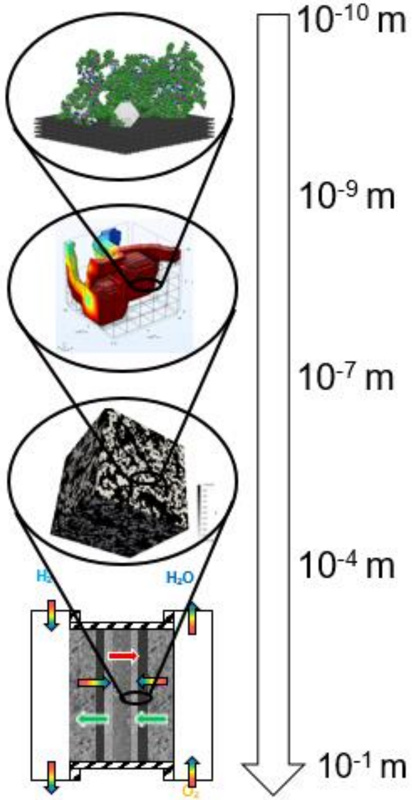



*Mass transport losses*



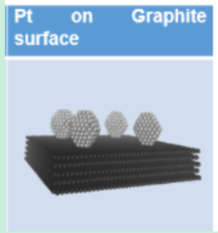

*Ultra-thin electrode*

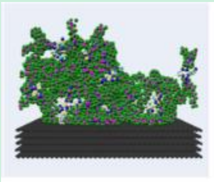


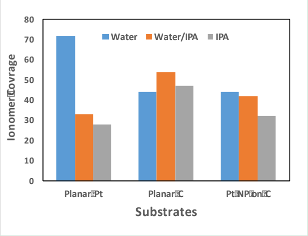




## Multiscale modeling

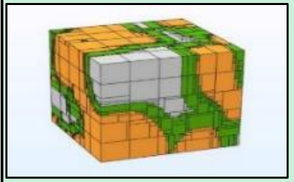
*Ionomer film scale*



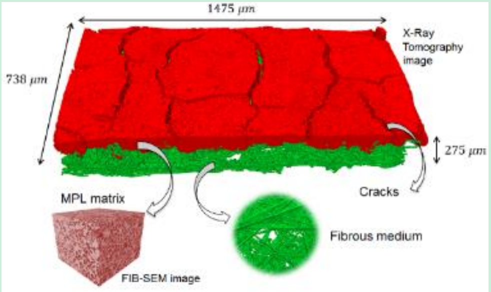





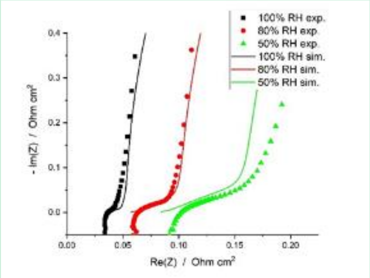

*Sub µm scale*

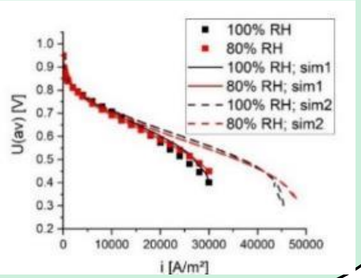


*CCL scale*




*Cell scale*




Public workshop, 06/07/2022, DLR/Stuttgart + visio

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

# FURTHER-FC

**F**urther **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

## Spatial distribution of the materials

((A. Morin (CEA), T. Morawietz (Esslingen Univ.), H. Kaess (Esslingen Univ.),

L. Guétaz (CEA), A. Ghorbel (CEA), T. David (CEA), Z. Saghi (CEA)

# Outline

1. Introduction
2. Atomic Force Microscopy
3. Electron Microscopy
4. Conclusions

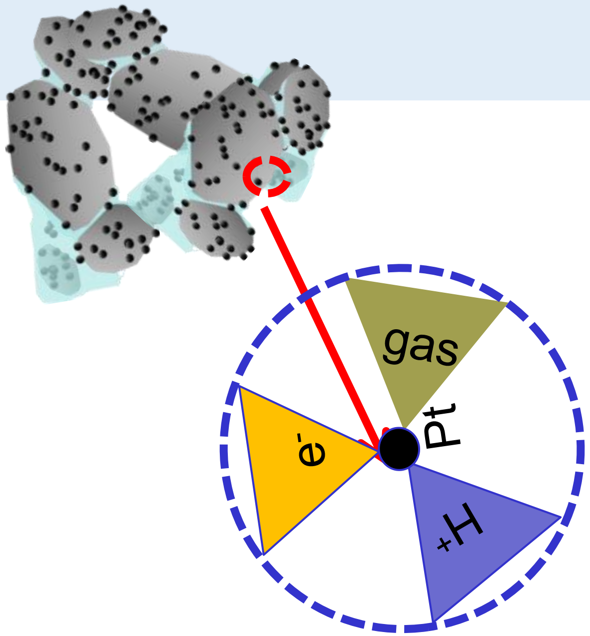
# Introduction

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

→ Reaction at 3-phase boundary

Performance & Durability

- electronic conductivity
- ionic conductivity
- gas supply ükü




nature COMMUNICATIONS

ARTICLE

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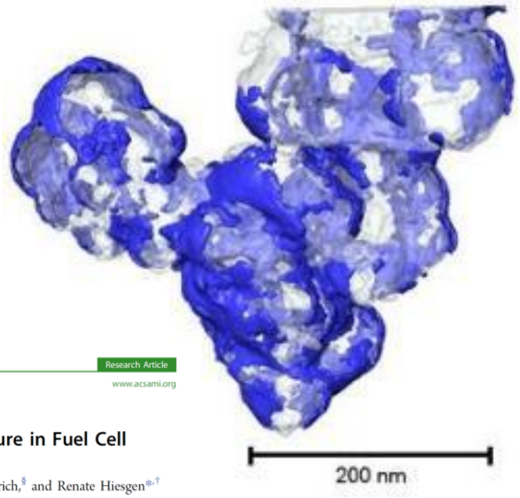
Three-dimensional analysis of Nafion layers in fuel cell electrodes

M. Lopez-Haro[1,2], L. Guétaz[1,3], T. Printemps[1,4], A. Morin[1,3], S. Escribano[1,3], P.-H. Jouneau[1,2], P. Bayle-Guillemaud[1,2], F. Chandezon[1,5,6] & G. Gebel[1,3,5,6]




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.

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

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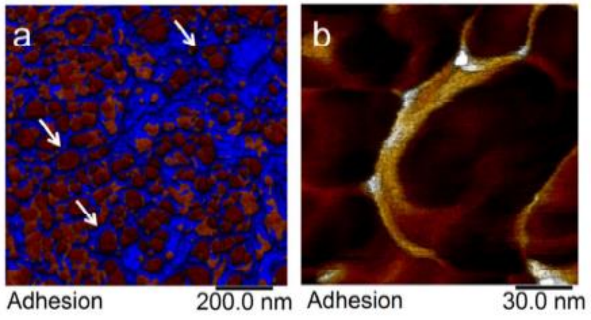
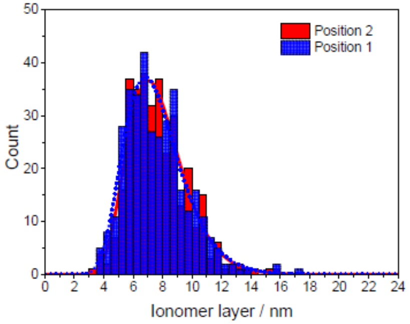
[§]Institute of Engineering Thermodynamics, German Aerospace Center, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany

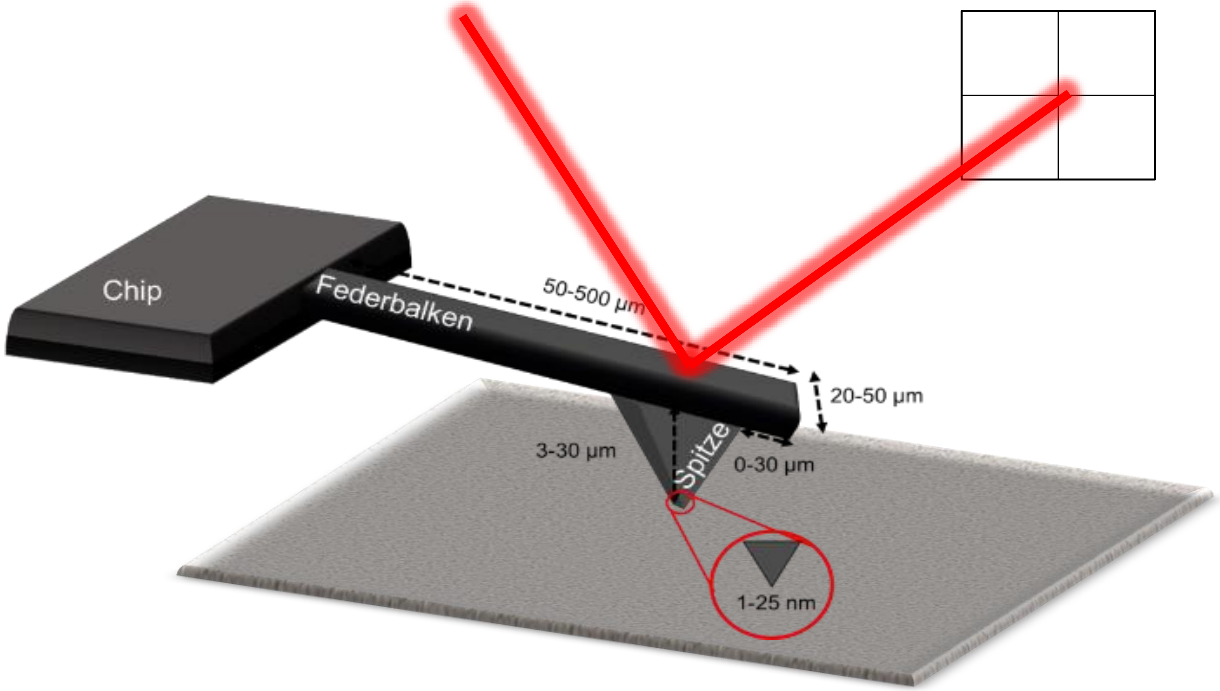


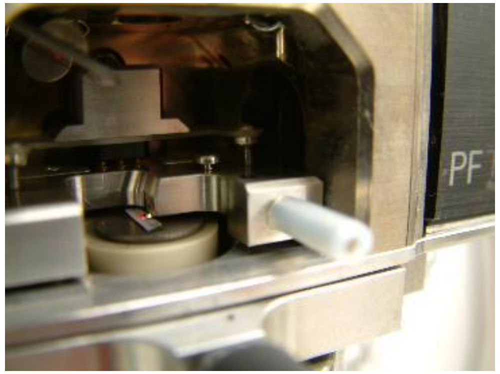
# Atomic Force Microscopy

# Atomic Force Microscopy (AFM)

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

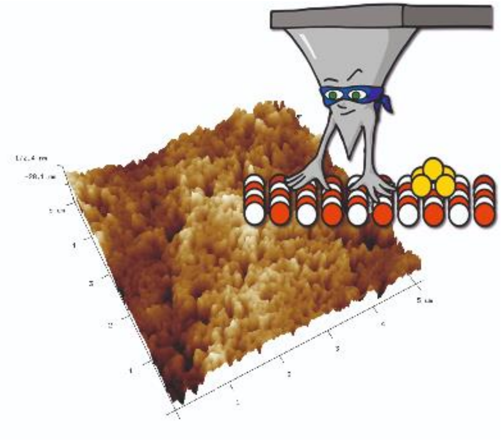


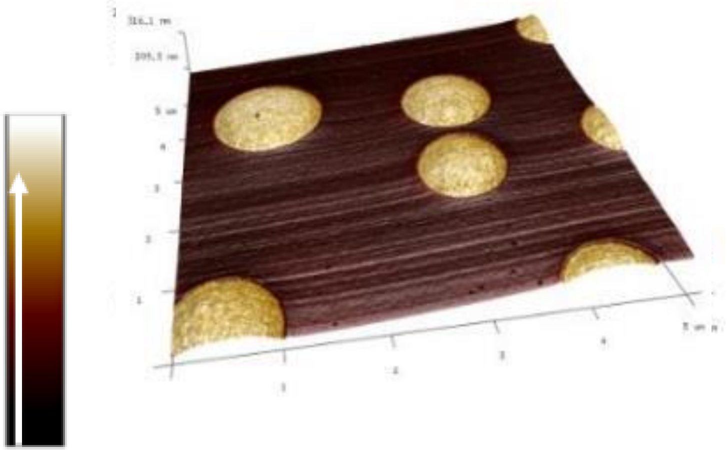




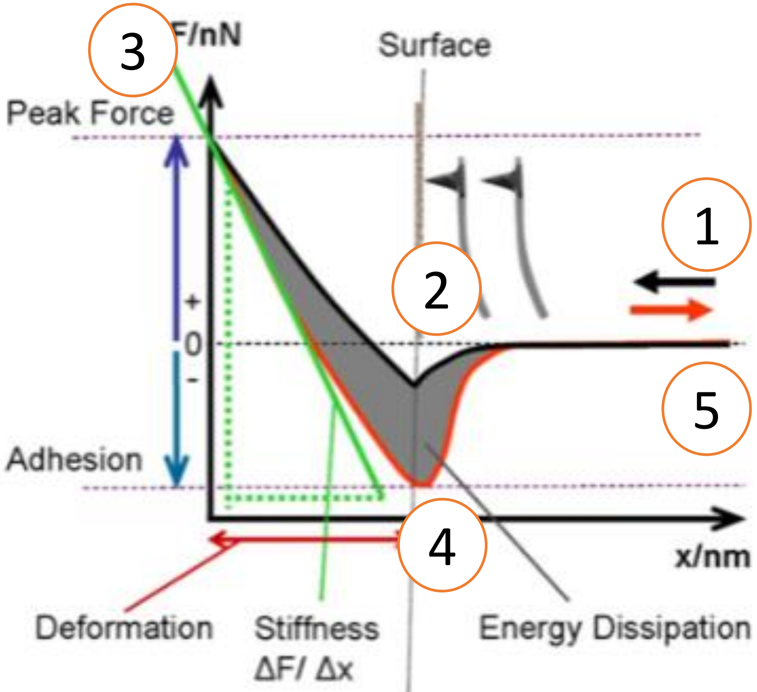
# Atomic Force Microscopy (AFM)

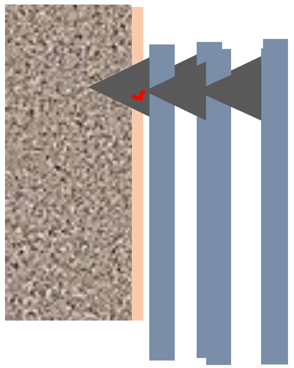
- Tapping PeakForce QNM/TUNA-Mode (Bruker Corp.):
- Evaluation and mapping of adhesion force, phase shift, stiffness (DMT modulus), maximal force, dissipation energy, deformation and current.





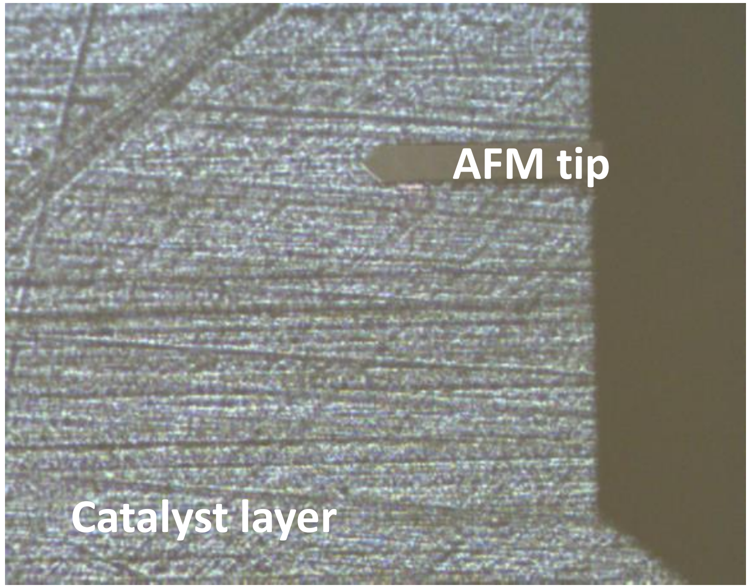
PS-LDPE Adhesion (5 µm)



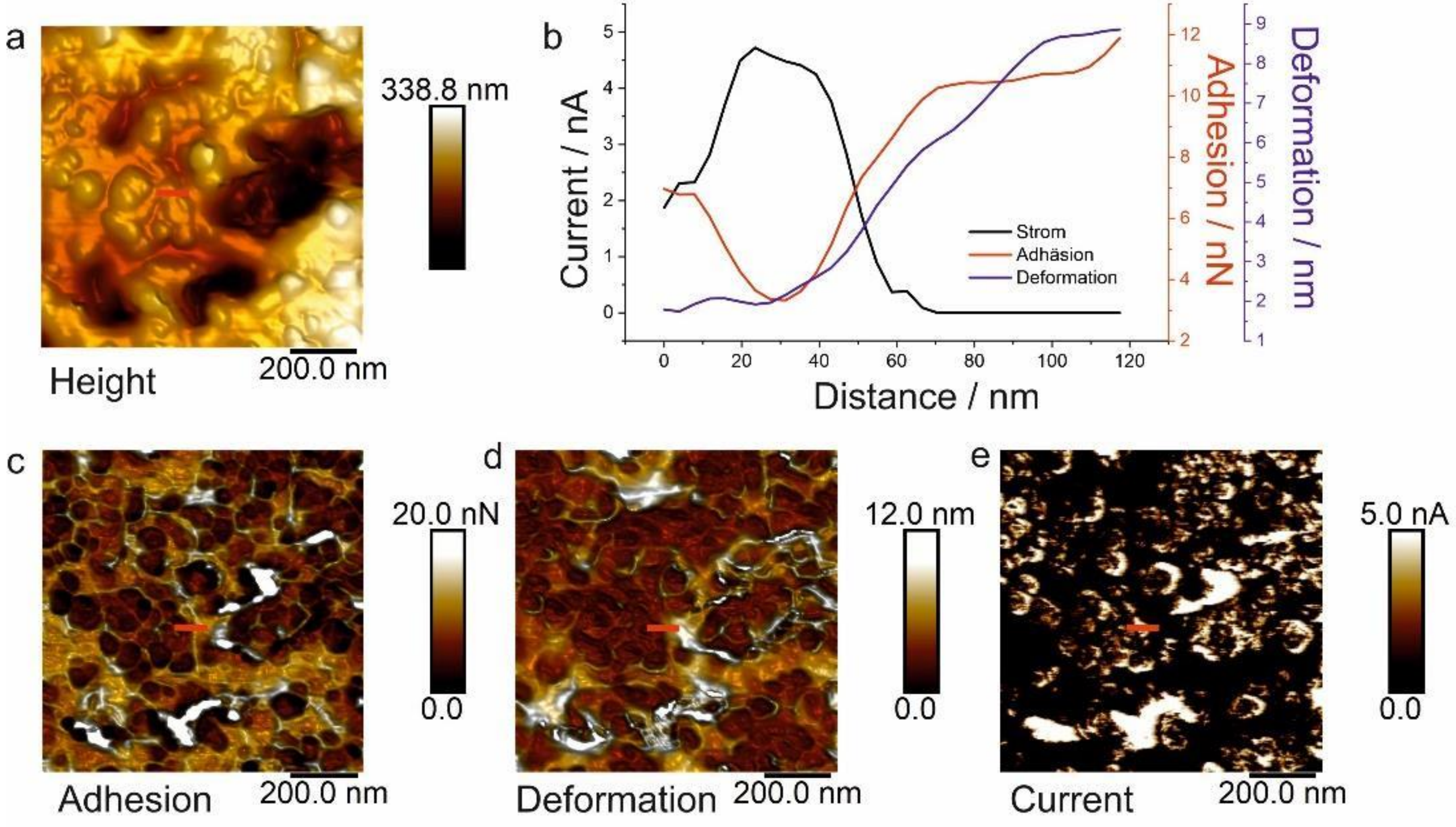



# Atomic Force Microscopy (AFM)

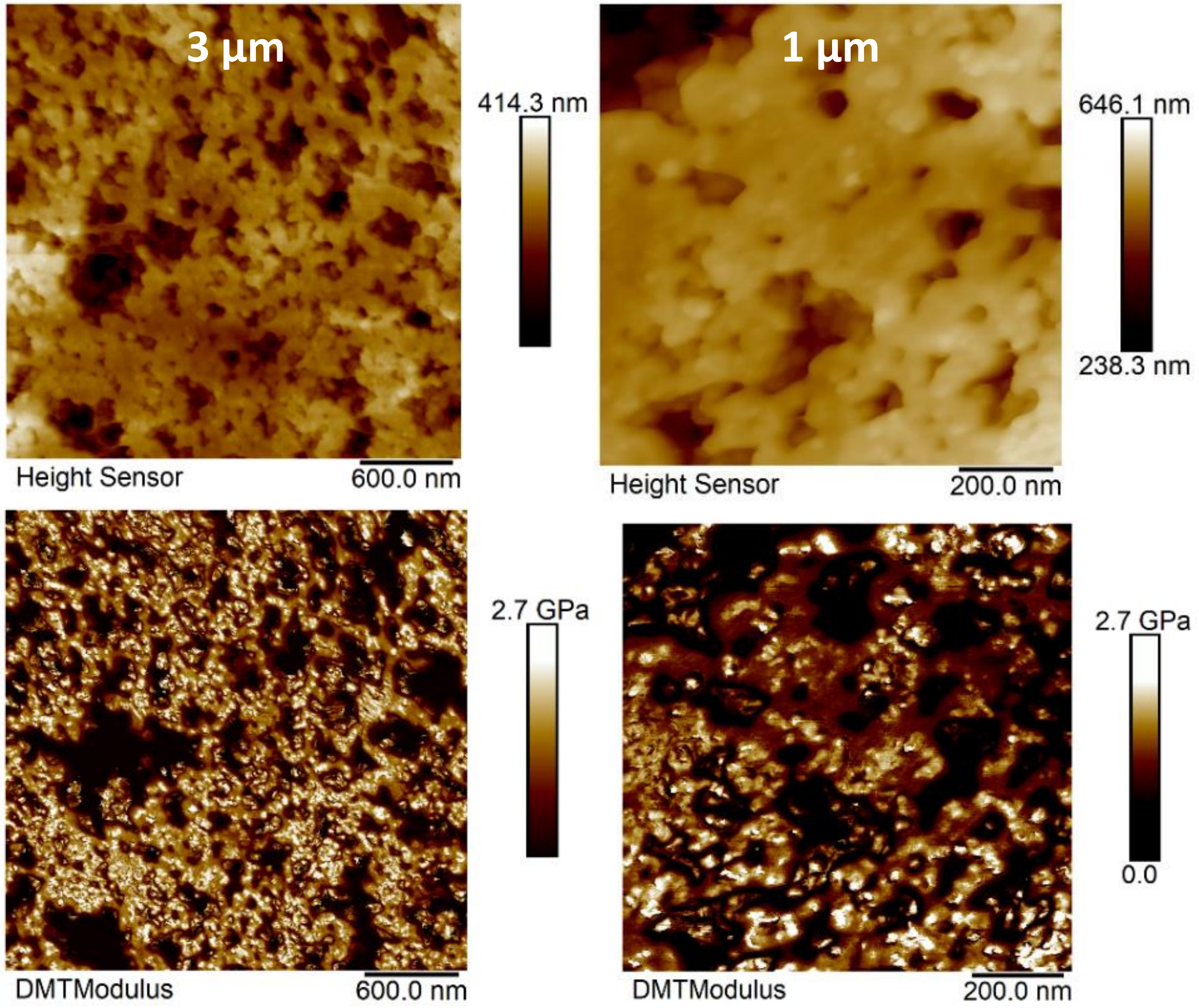
- Using AFM one can discern the different components in the PEMFC and PEMWE electrodes. They consist of catalyst, support materials and (ionomer) binder, the distribution of these components affects MEA performance and degradation rates.



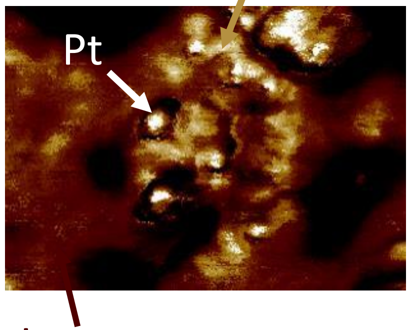

Optical microscope



# Analysis of the CCL surface



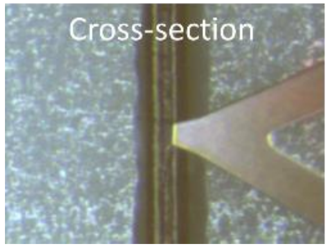

Ionomer bridges

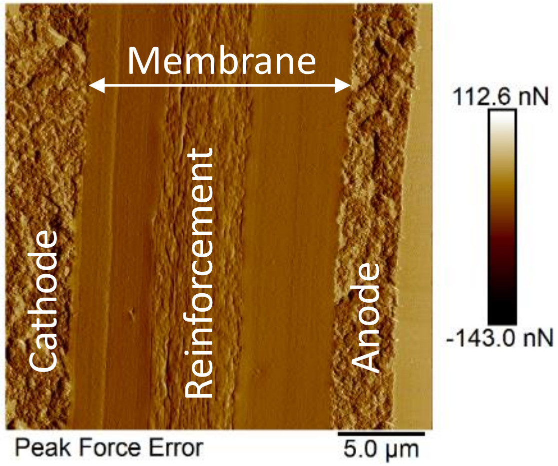


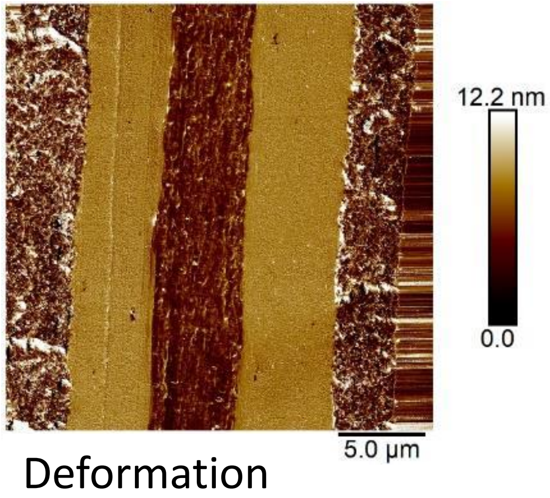


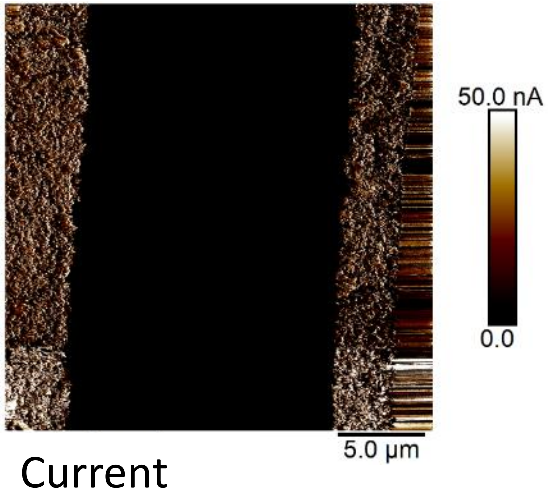
- Nanomechanics AFM measurement with high resolution tips → < 2 nm tip radius
- 3 different phases visible in stiffness, adhesion and deformation channels
- Pt particles may be seen under a layer of ionomer
- Analysis of single Pt Particles difficult

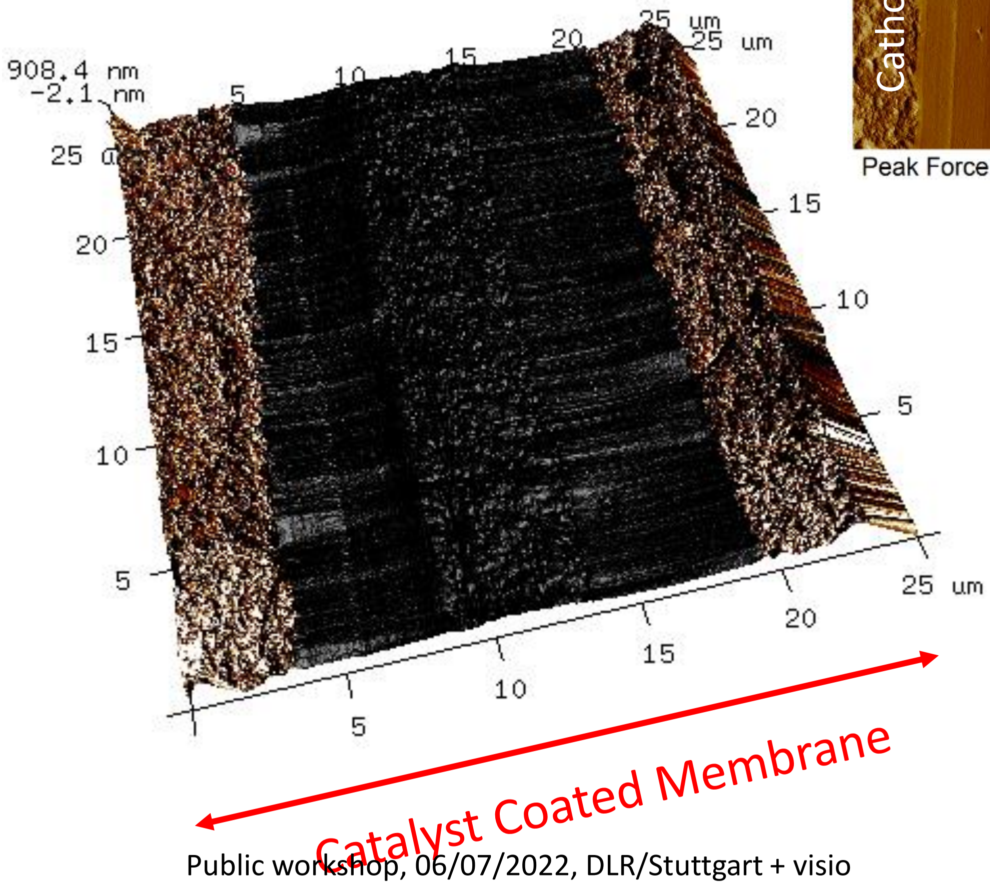
# AFM on CCM cross-sections



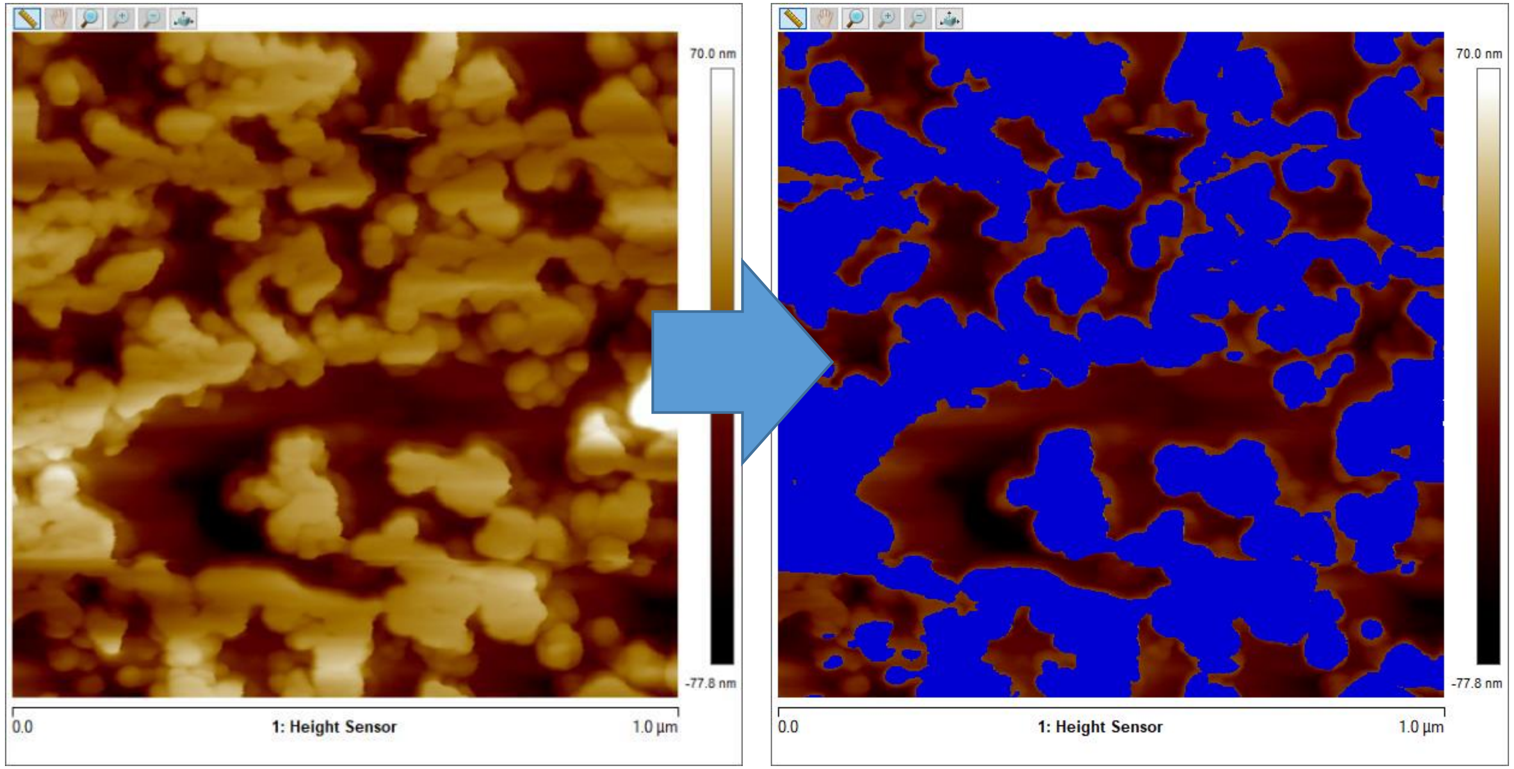



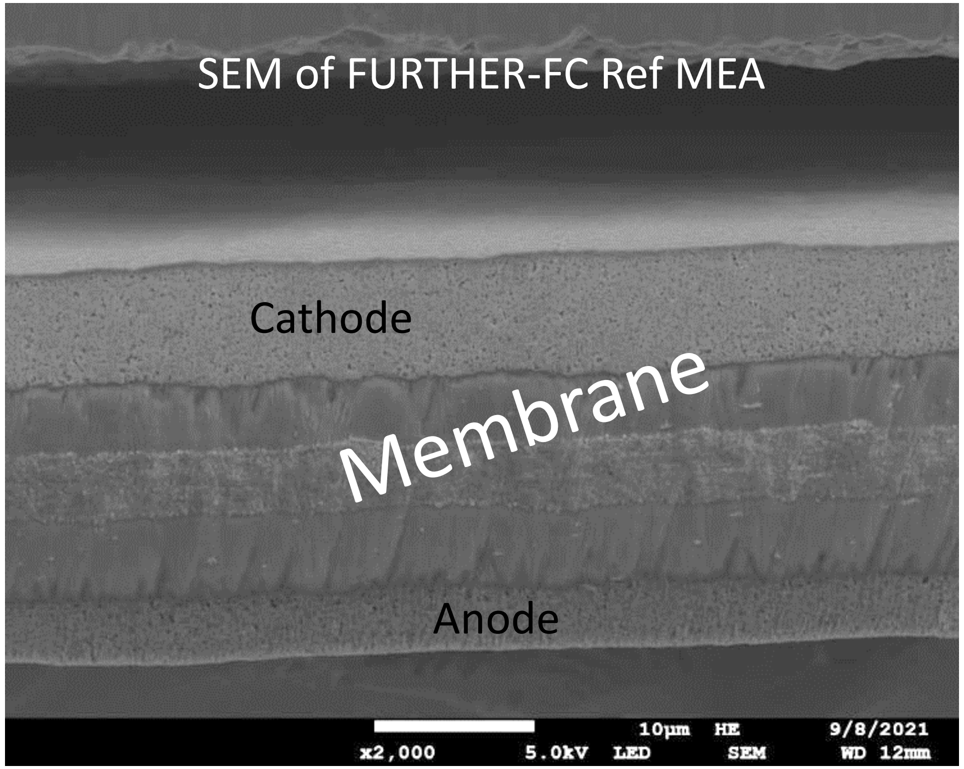




- Cutting with microtome without embedding
  - Clamped between Polystyrene plates for cutting
  - Measurement of “Blockface”
- Different layers can be analyzed due to different electrical and mechanical properties
- Thickness and material distribution
- Measurement of conductivity possible due to metal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

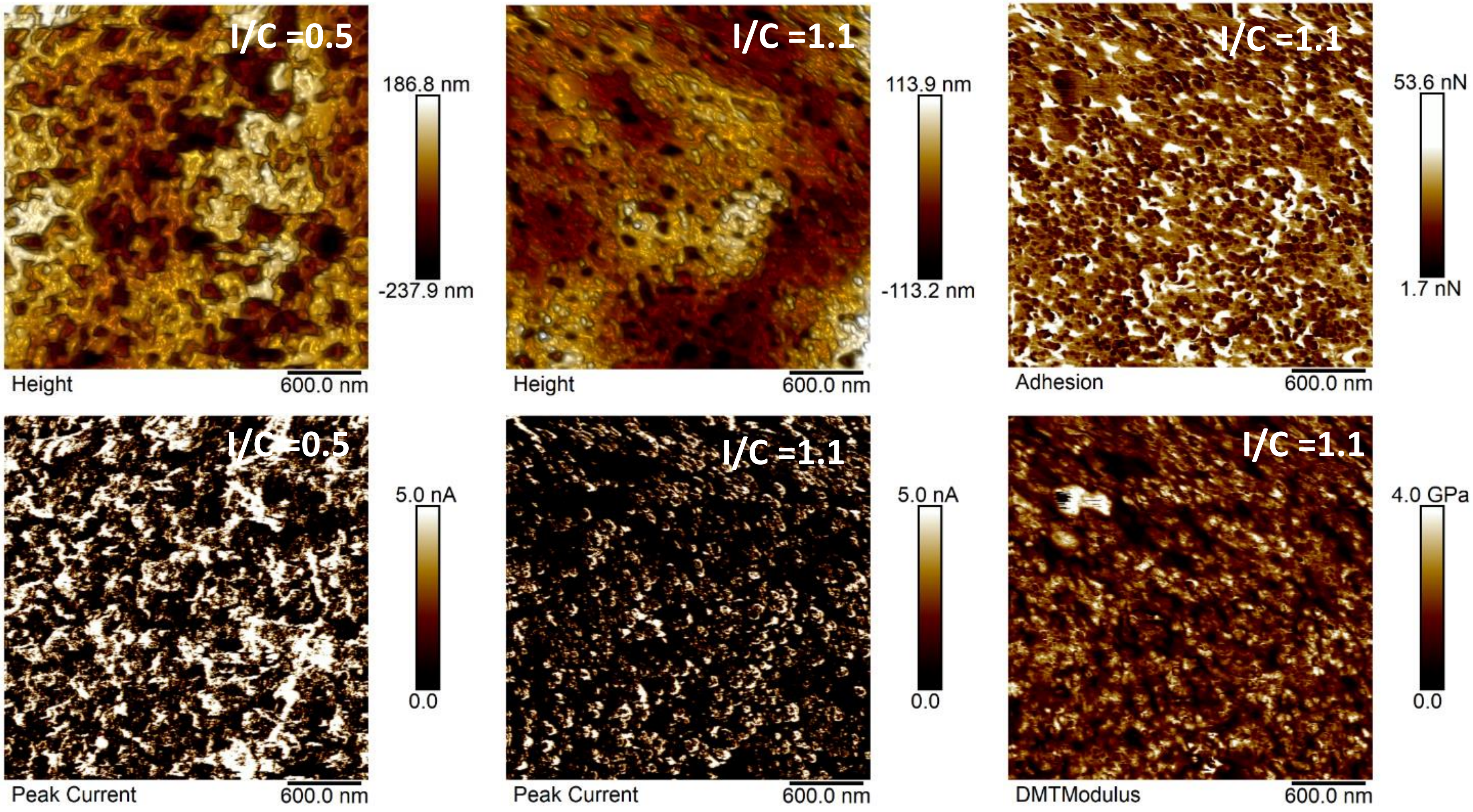
# AFM on CCM ion-cut cross-sections

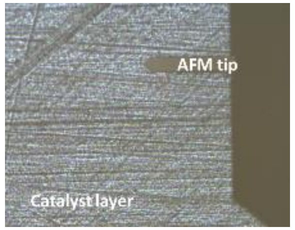
- Ion cutting at -100°C, smooth surface at CL
- Porosity using bearing area → 46 % for area of 1 µm²
- Measurement at ambient conditions gives different thickness of ionomer layers then measured with no humidity.



# Analysis of the CCL surface Electronic Conductivity



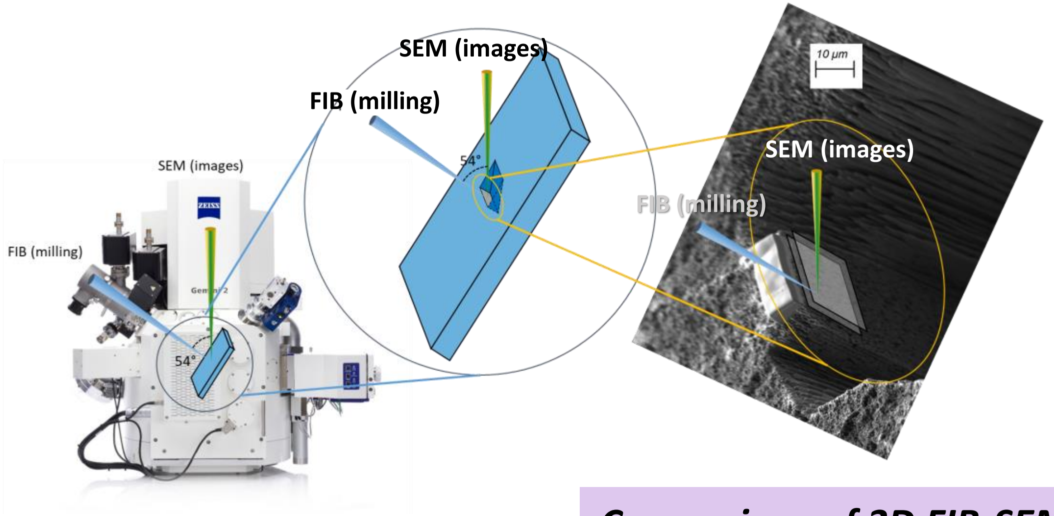




- Comparison of the electronic conductive area between I/C 0.5 and 1.1
- Ionomer distribution visible due to no electronic conductivity on ionomer layers, also adhesion and stiffness show same results
- Much lower conductive area for I/C 1.1 at the surface (27 % /55 %)

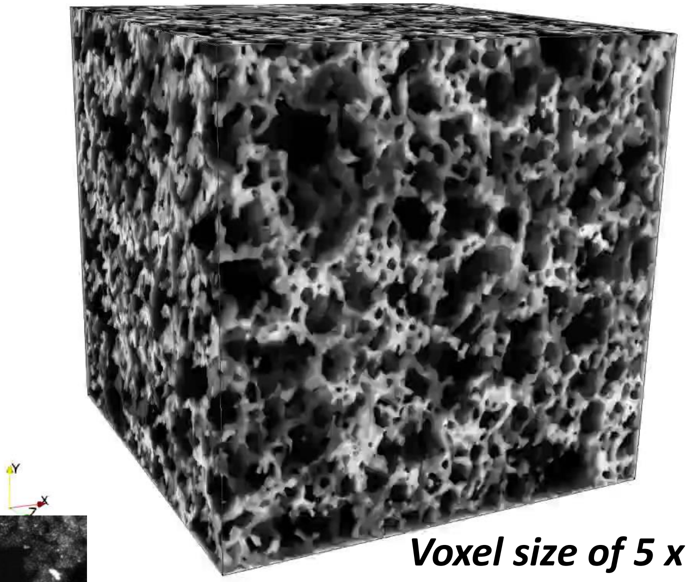
# Electron Microscopy

# 3D FIB SEM: CCL porosity

## 3D FIB-SEM principle

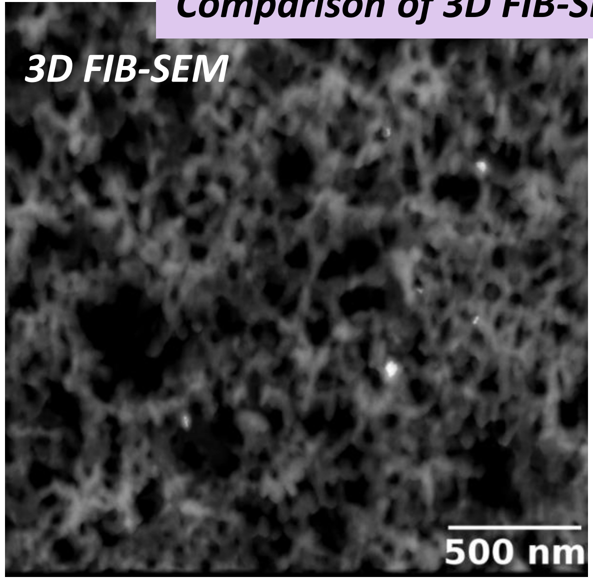


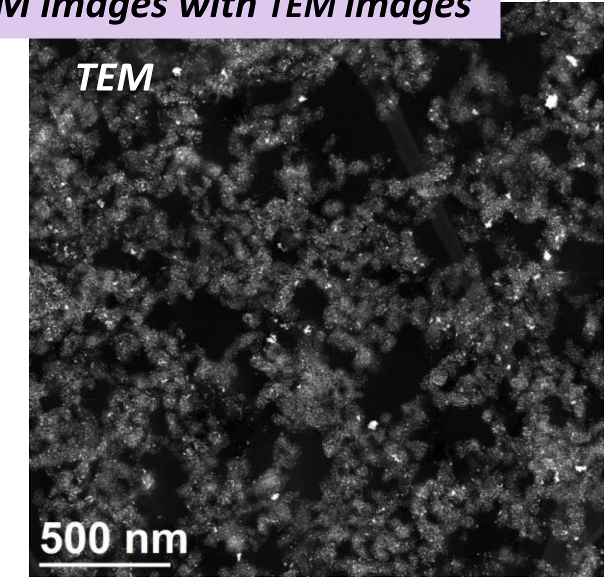

## Stack of image acquisition



*Voxel size of 5 x 5 x 5 nm³*

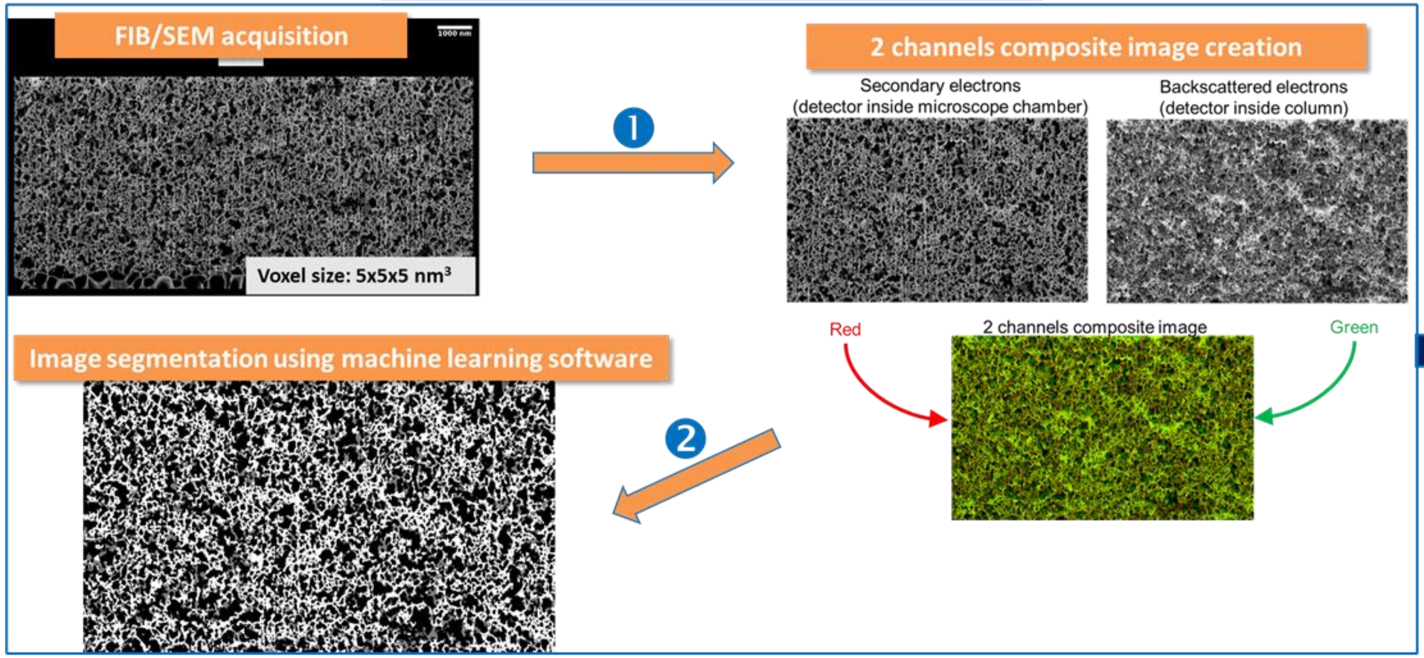
## *Comparison of 3D FIB-SEM images with TEM images*

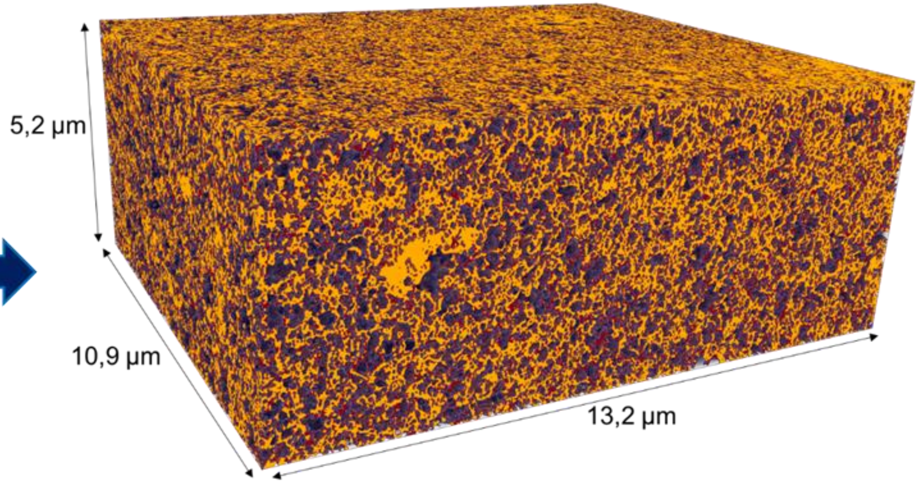


# 3D FIB SEM: CCL porosity

Segmentation of the 3D image




**Porosity: 55%**

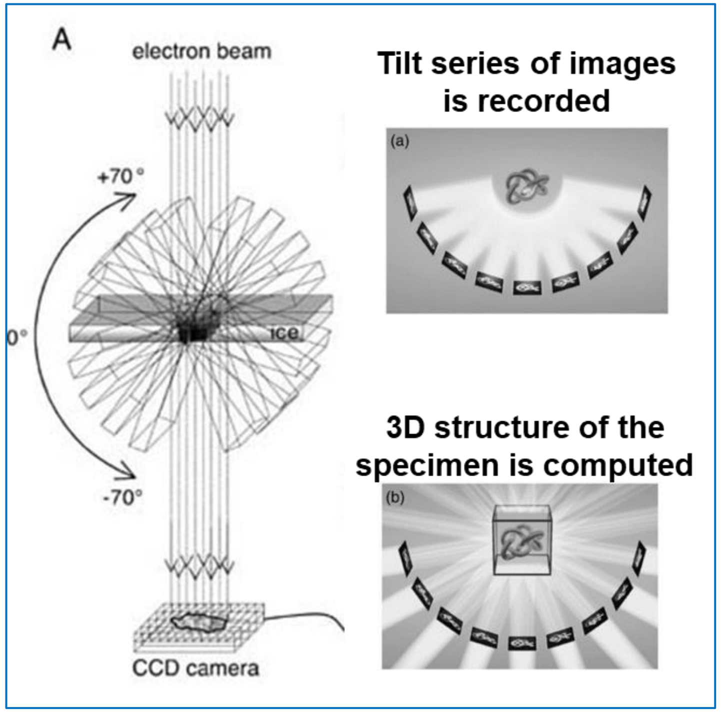
***The pore size distribution analysis will be presented by Ahmed Maloum ( INP-Toulouse) in the modelling presentation***

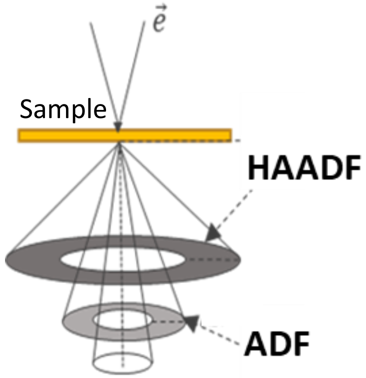
# E-tomography: Pt nanoparticle distribution on the carbon support

**Challenges of STEM tomography reconstruction due to C density << Pt density:**

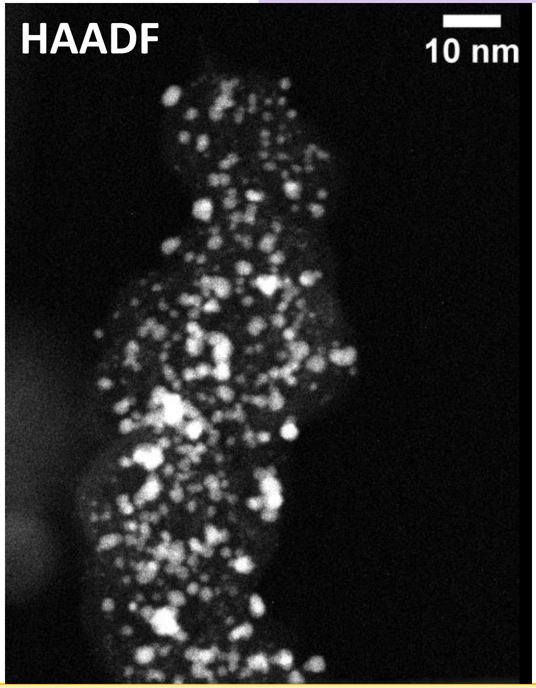
1. **Pt NPs ⇨ *HAADF-high angle annular detector*** *to avoid* ***diffraction contrast.***
2. **C support ⇨ *ADF-annular detector*** *to enhance* ***C contrast.***
3. **Use of advanced algorithm for 3D image reconstruction that reduces the NP artefacts**

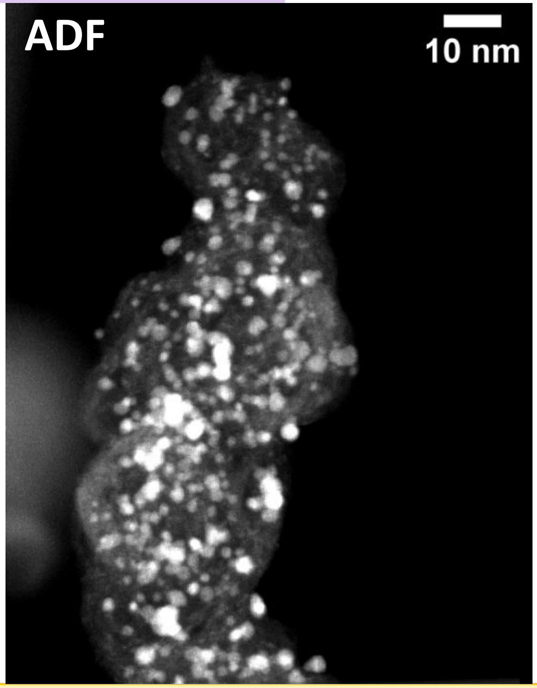
**Electron-tomography principle**




**Tilt series images acquisition**

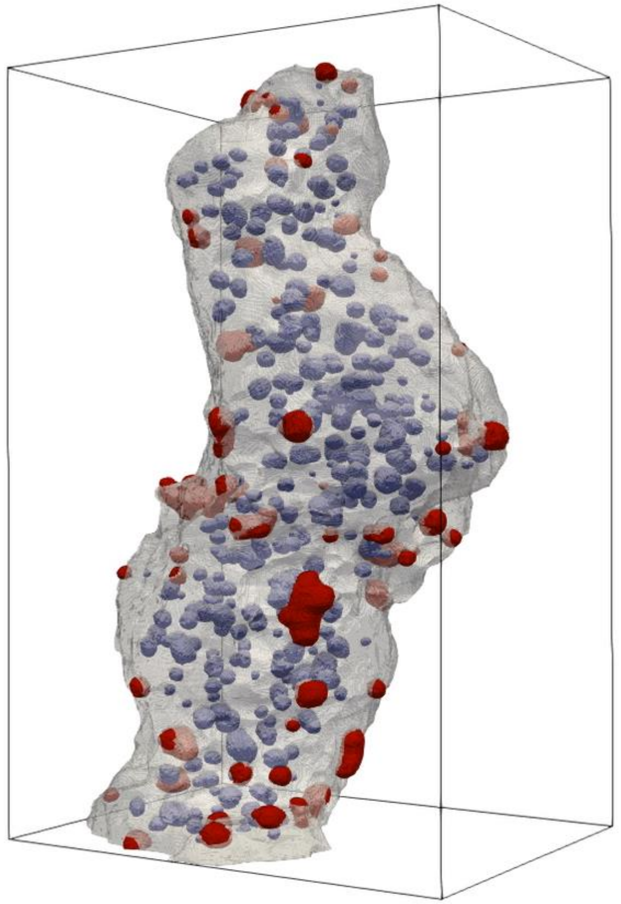



Catalyst powder from Tanaka (46.5 wt% Pt on high surface area carbon)

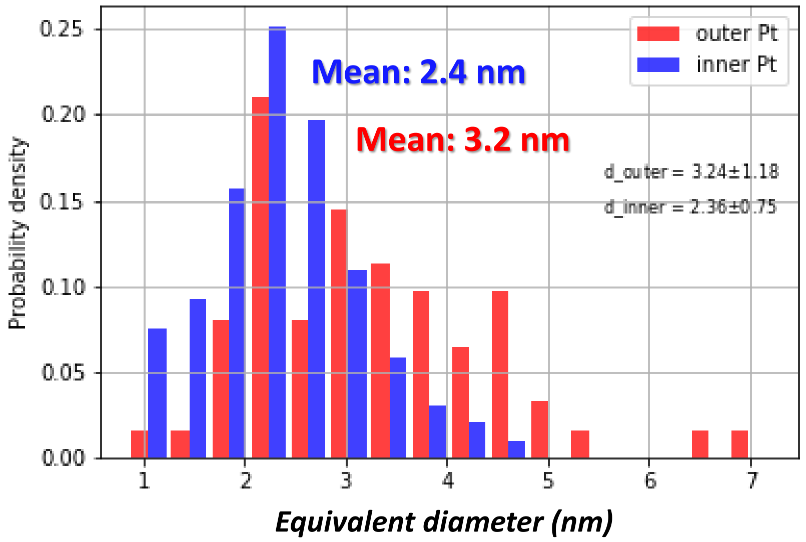
# E-tomography: Pt nanoparticle distribution on the carbon support

**3D image of Pt/C**




**Nanoparticle size histogram**

**356 Pt NPs = 294 Inner Pt NPs + 62 Outer Pt NPs**



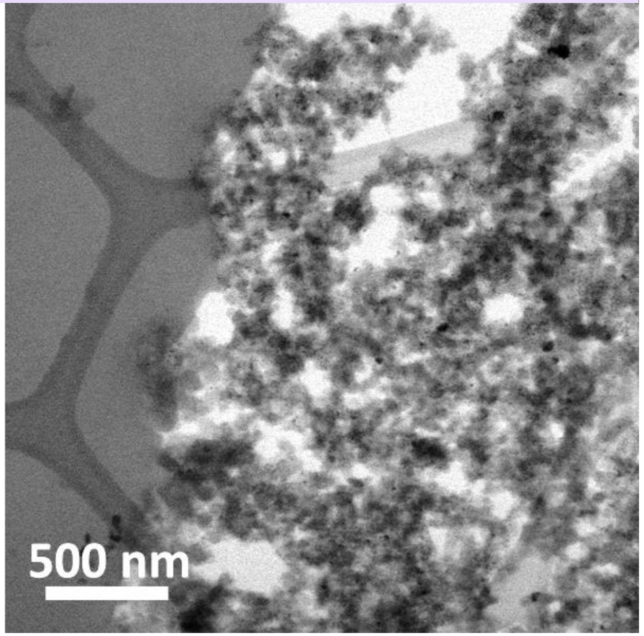
# Distribution of the ionomer within a real electrodes

Impossible to image by high resolution TEM the ionomer in the usual thin MEA cross-section that is embedded in epoxy resin

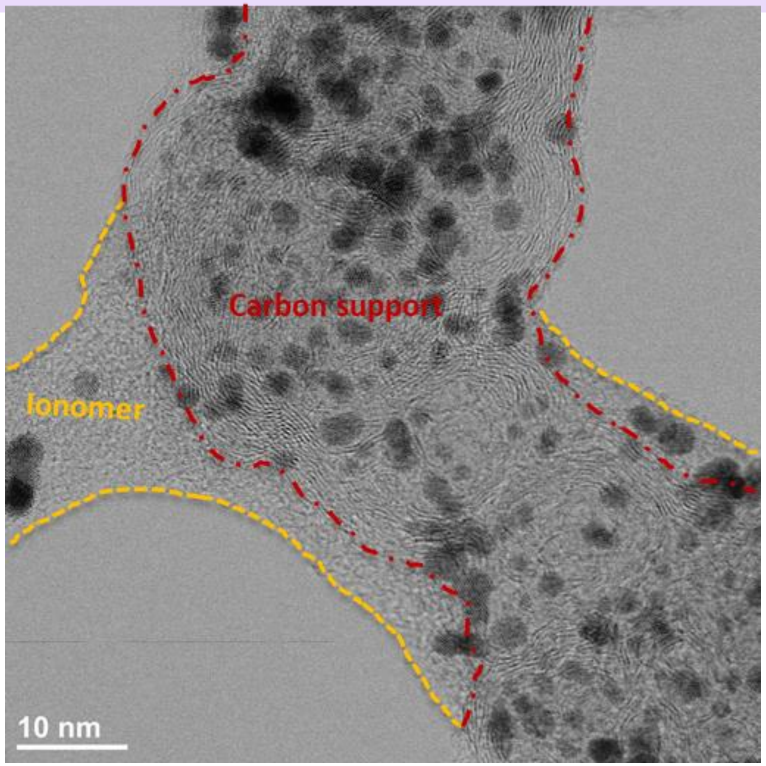
**Development of the cryo-ultramicrotomy preparation technique by embedding the MEA in a drop of frozen water**


*M. Salvado et al., J. Power Sources, 2021*

**Thin slice of cut MEA was successfully deposited on TEM grid**

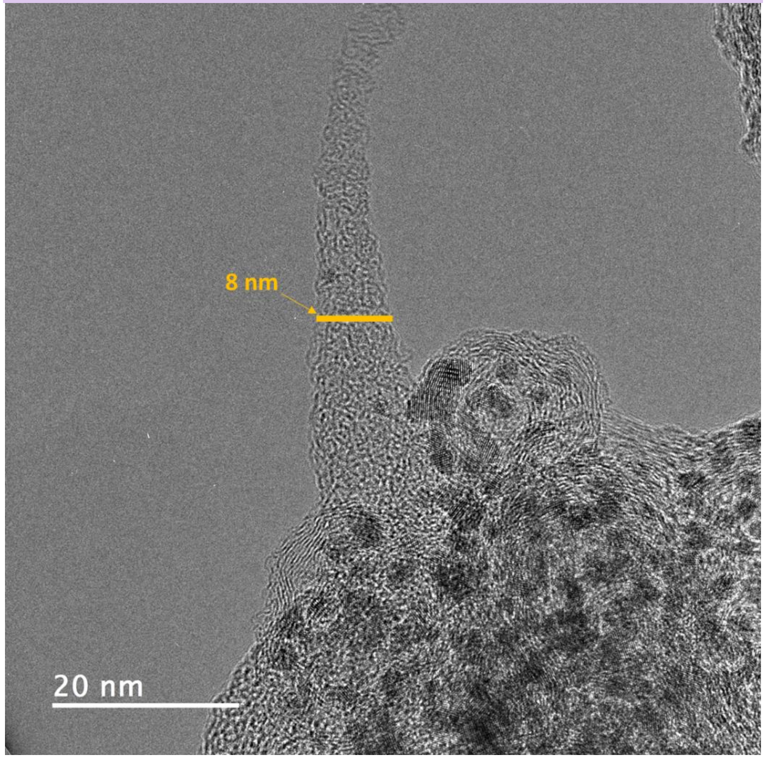



**The ionomer thin layer can be observed**

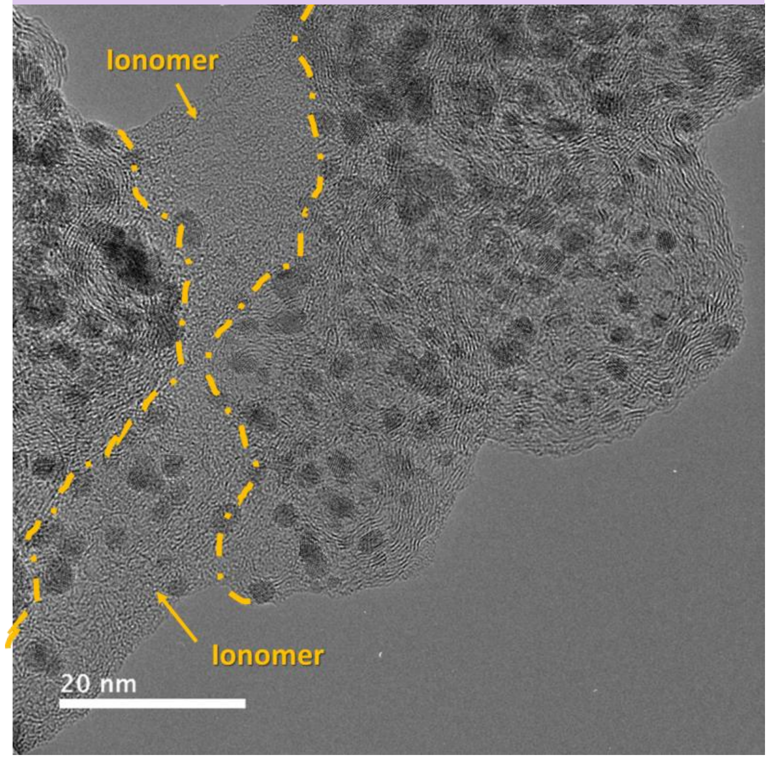


# Distribution of the ionomer within a real electrodes

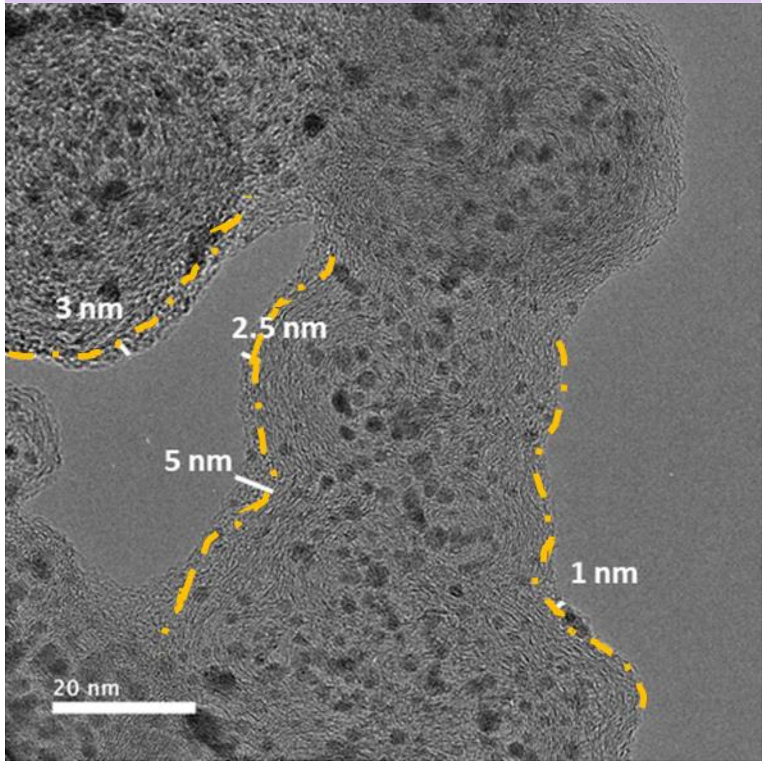
**Ionomer filament bridging two Pt/C agglomerates**




**Ionomer linking two Pt/C agglomerates**

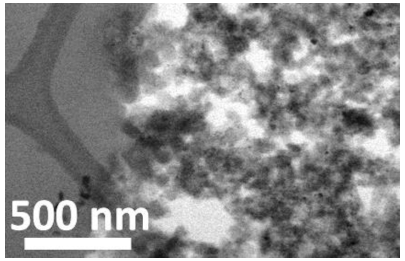



**Thin layer of ionomer on Pt/C agglomerates with different thickness**

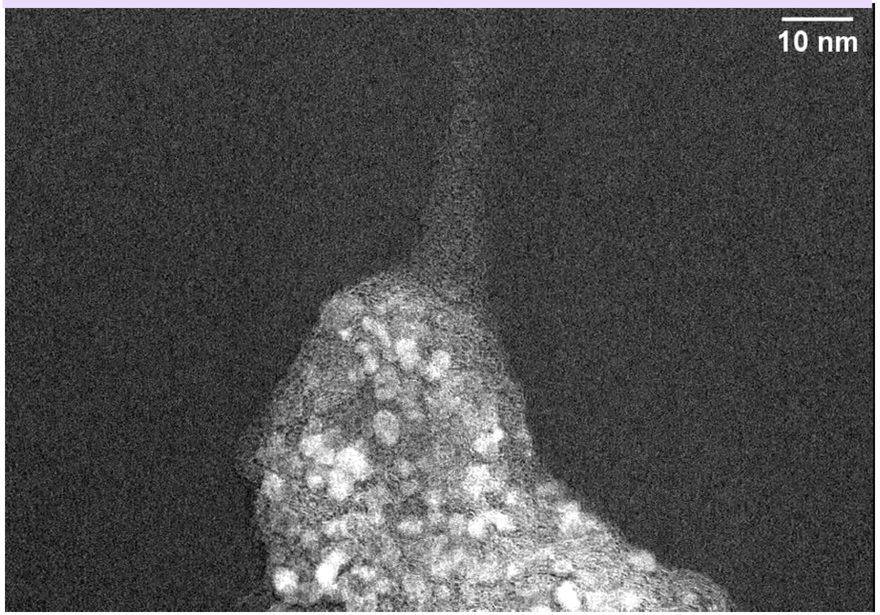


# Distribution of the ionomer within a real electrodes

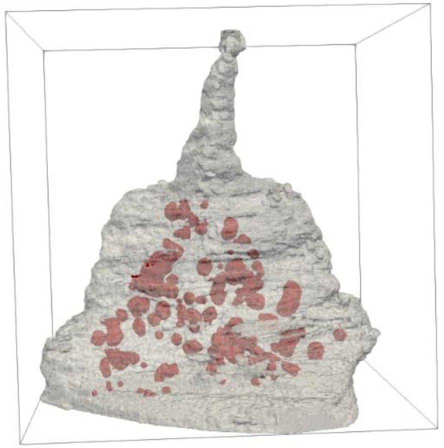
## E-tomography for 3D analysis

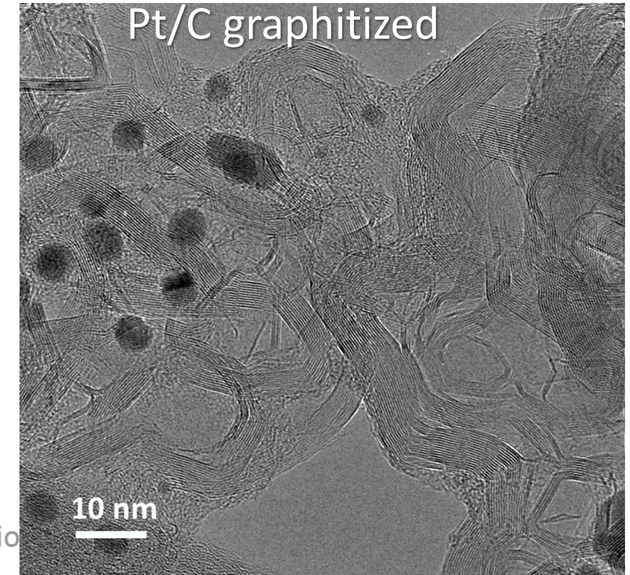



**ADF/STEM tilt series acquisition**




**3D volume reconstruction**




- **Difficulty in finding an area for high resolution tomography with no C support overlapping for the high tilt angle**
- **The 3D image reconstruction is still challenging due to the lack of contrast between the ionomer and C support ➡ *experiments will be performed on Pt deposited on graphitized carbon***

# Conclusions

**AFM and electron microscopy are complementary techniques for CCL microstructural characterization**

- **<u>AFM :</u>**

  - Measurement under different RH conditions

  - Measurement of mechanical and electrical properties gives high contrast between Pt/C and ionomer

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

- **<u>Electron microscopy</u>**

  ➢ *<u>3D FIB/SEM</u>* :

  - 3D image of the porosity in representative volume (500 μm$^3$) ⇨ to be compared with AFM to evaluate the porosity evolution with RH

  ➢ *<u>TEM</u>*

  - E-tomography : Pt NP distribution of Pt on carbon support

  - Resolution is high enough to see thin (>1 - 2 nm) layers of ionomer (higher resolution than AFM) however 3D is needed but difficult.

  - Images revealed some ionomer characteristic features (ionomer filaments, ionomer linking Pt/C agglomerates,

**⇘The 3D distribution of the ionomer is still under study: improvement of the different techniques and comparison of results are under progress**

# The TEAM

Co-funded by the European Union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Dr. Pascal Schott


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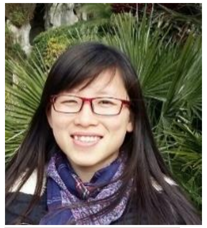
Dr. Isotta Cerri


PhD Ahmed Maloum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Dr. Thomas Jahnke


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Dr. Colleen Jackson


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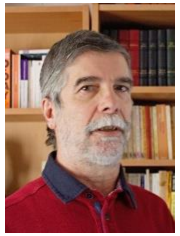
Dr. Michel Quintard


Dr. Marc Prat


PhD Florian Chabot

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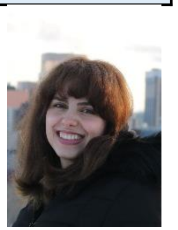
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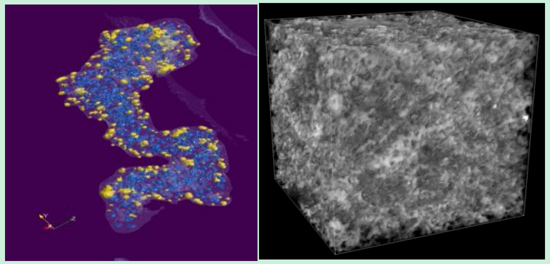
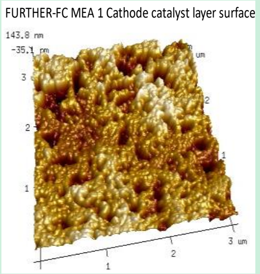
# Thank you for your attention.
# Your questions are welcome

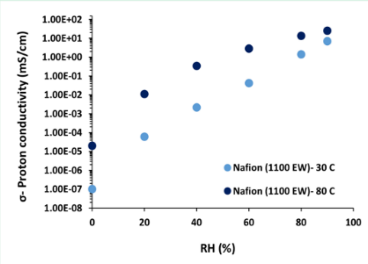
## Multiscale characterization



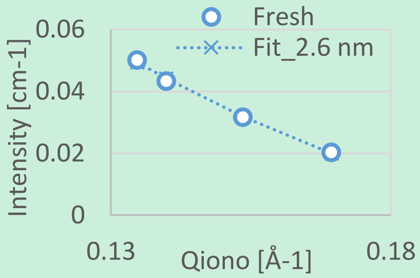
*3D TEM and FIB/SEM*



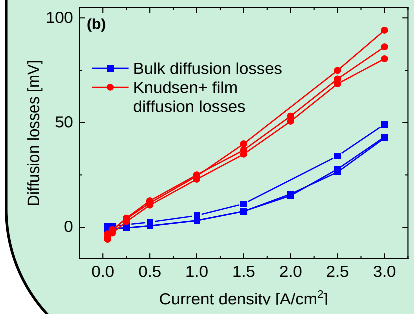

*AFM*



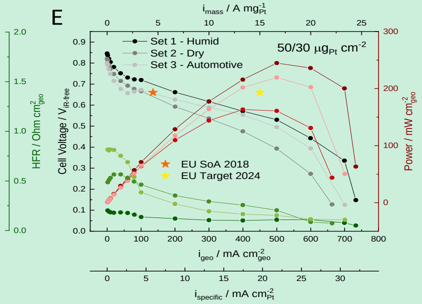

*Ionomer transport properties*



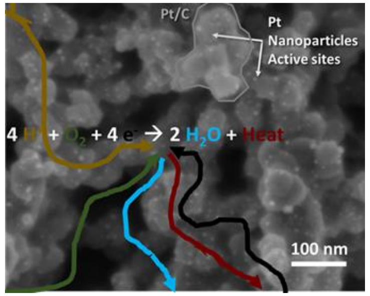

*Ionomer swelling*

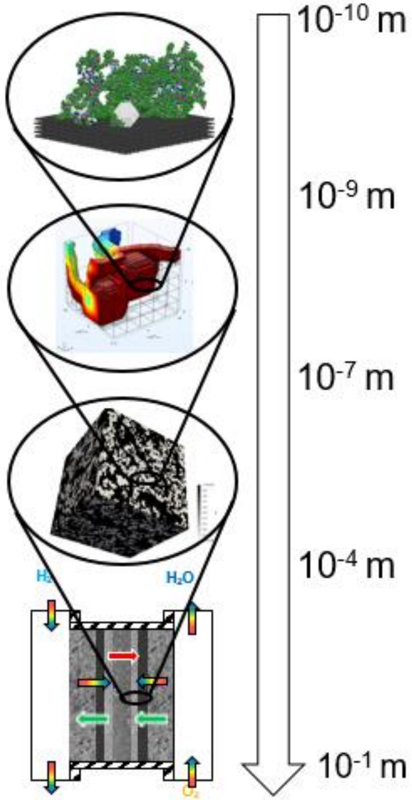



*Mass transport losses*



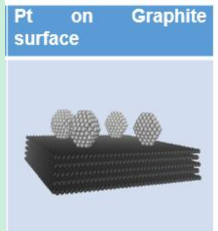

*Ultra-thin electrode*

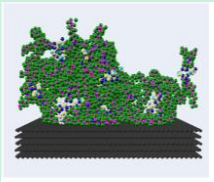


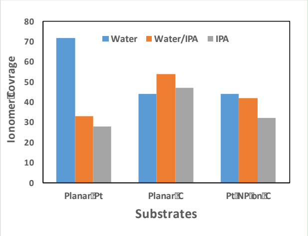




## Multiscale modeling

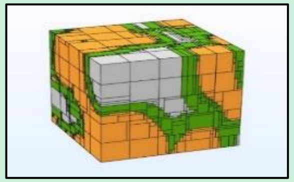
*Ionomer film scale*



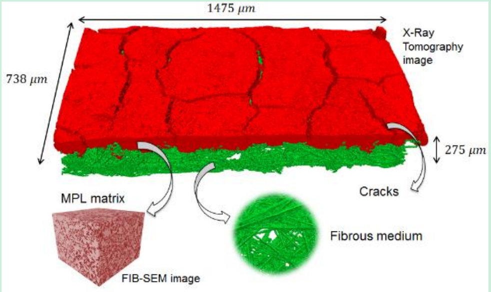





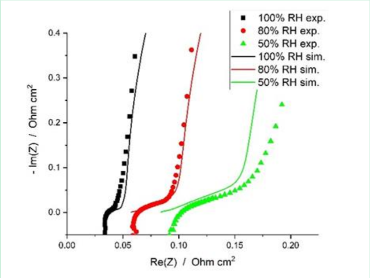

*Sub µm scale*

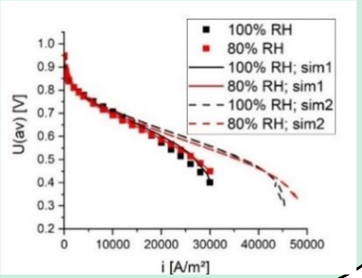


*CCL scale*




*Cell scale*






Public workshop, 06/07/2022, DLR/Stuttgart + visio



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