

## Toward 3D imaging of the PEMFC electrode microstructure

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### Background incl. aims

Proton Exchange Membrane Fuel Cells (PEMFCs) are being developed mainly for transport applications. Significant progress has been made over the last decade, leading to the commercialization of the first generation of fuel cell cars. More recently, R&D efforts have shifted to heavy-duty vehicles, where PEMFCs are more competitive with Li-ion batteries. However, their cost and durability are still the two barriers limiting the expansion of this market. To overcome these obstacles, we still need to optimise the components and structure of the electrodes and better understand their degradation mechanisms. PEMFC electrodes are a nano-porous material composed of carbon particles (30 nm) supporting platinum nanoparticles (3 nm) - the catalysts of electrochemical reactions - and linked together by ionomer (proton conducting polymer).

Scanning and transmission electron microscopies (SEM and TEM) are widely used for investigating the microstructure of PEMFC electrode. They have played a significant role in the improvement of electrode components and the understanding of their main degradation mechanisms. However, the currently available descriptions of the electrode microstructure do not allow yet to unambiguously identify the key microstructural parameters that limit gas and proton transport within the electrode. These factors are crucial as they govern PEMFC performance, especially at high current densities, and are therefore the subject of numerous studies, using either fine electrochemical measurements or modeling approaches. The aim of our work is to provide an improved description of the electrode microstructure in 3D to give quantitative information on its porosity, Pt nanoparticle (NP) spatial distribution and ionomer distribution. For this purpose, we are developing 3D characterization techniques applied to the PEMFC electrodes, such as electron tomography and 3D FIB-SEM.

### Methods

The studied cathode electrode was prepared using TEC10E50E catalyst from Tanaka that is 50 wt % loading of Pt deposited on high-specific area carbon (HSAC), and Nafion D2020 as the electrode ionomer. The Pt loading of the electrode is 0.2 mgPtcm<sup>-2</sup> and the ionomer/carbon ratio is 0.8.

The electrode was analyzed using electron tomography and 3D FIB-SEM.

### Results

As a first step, electron tomography analyses were performed on the Pt/HSAC powder to determine the distribution of Pt NPs which can be located either on the carbon surface (outer NPs) or inside the carbon porosity (inner NPs)[1-2]. Our strategy is to record tilt image series by using two annular detectors: i) a high angle annular detector avoiding Pt NP diffraction contrast for the 3D image reconstruction of Pt NPs (without diffraction artifact) and ii) a lower angle annular detector that enhances carbon contrast for the 3D image reconstruction of the carbon phase. These two segmented images were then combined (Figure 1), allowing the calculation of the NP size histogram but also of the volume and the surface area of the two NP populations (inner and outer NPs).

On the second step, the porosity of the electrode was analyzed by 3D FIB/SEM. A volume of around 10 X 10 x 5 µm<sup>3</sup> was imaged with a cubic voxel size of 5 × 5 × 5 nm<sup>3</sup>. The solid phase

(carbon, Pt NPs and ionomer) segmentation was based on a composite image created from two electron detectors (secondary and backscattered electrons) and using a machine learning software. Quantitative data such as the total porosity and the pore size distribution were extracted from this volume. Figure 2a shows a 2D slice of this segmented volume where the solid phase is in black and the porosity in white.

In order to analyze the electrode porosity with a higher spatial resolution, electron tomography experiment was also performed on a 150 nm thick slice of the electrode cut by ultramicrotomy after being embedded in an epoxy resin. The tilt image series were recorded with a pixel size of 0.5 nm and a field of view of  $2 \times 2 \mu\text{m}^2$ . The 2D slice of the reconstructed volume (Figure 2b) shows that the largest solid agglomerates detected on the 3D FIB/SEM image can be identified as an agglomeration of numerous carbon particles. The challenge now is to quantify the porosity created between these carbon particles, which cannot be detected by 3D FIB-SEM.

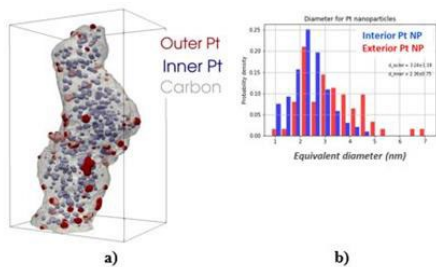
Finally, the distribution of the ionomer was analyzed within the electrode similarly to [3]. For this analysis, a 150 nm slice of the electrode was cut by cryo-ultramicrotomy without embedding in epoxy resin as described in [4]. TEM images show that the ionomer is not homogeneously distributed on the surface of the entire carbon particles but is often observed in the concave surface created between the carbon particles (Figure 3). These observations suggest a ionomer distribution in agreement with the heterogeneous ionomer coating model proposed by Inoue et al. [5]. We also suggest that a part of the ionomer could be localized in the small pores located inside the large carbon agglomerates described in the previous paragraph. This could explain why the ionomer is so difficult to detect on TEM images.

#### Conclusion

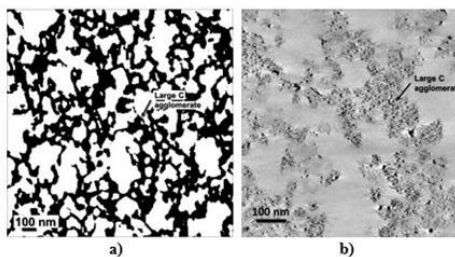
The different 3D electron microscopy techniques make it possible to obtain information on the distribution of the different components of the PEMFC electrode. This 3D description of the electrode can then be incorporated into recent models that calculate electrochemical performance as a function of microstructural parameters, in an attempt to identify the key parameters that limit cell performance. Similar studies are also being carried out on aged electrodes after the fuel cell operation.

This work has been done in the frame of the FURTHER-FC project. 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.

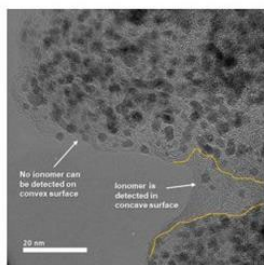
**Graphic:**



**Figure 1:** a) 3D view of the Pt/HSAC powder obtained from electron tomography experiment and after segmentation (C in grey, inner Pt NPs in blue and outer Pt NPs in red). The parallelepiped is 80 x 80 x 110 nm<sup>3</sup>. b) Histograms of the two population Pt NP size



**Figure 2:** Electrode 2D slices extracted from a) segmented volume obtained by 3D FIB/SEM and b) from reconstructed 3D image obtained from electron tomography experiment.



**Figure 3:** HRTEM image showing that the ionomer is not homogeneously distributed on the surface of the entire carbon particles but is often observed in the concave surface created between the carbon particles.

**Keywords:**

PEMFC, Electrode, e-tomography, 3D FIB-SEM

**Reference:**

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