Experimental report

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Proposal: **9-12-595** **Council:** 10/2019

Title: Nanostructure of ionomer in fuel cell electrodes by SANS

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: Catalyst layer : C + Pt + Nafion (C9HF17O5S)

Instrument	Requested days	Allocated days	From	To
D22	4	4	14/09/2020 19/02/2021	15/09/2020 22/02/2021

Abstract:

A polymer electrolyte membrane (PEM) fuel cell is an energy conversion device that is expected to replace internal combustion engines. One of the technical barriers for the wide commercialization of PEM fuel cells is their durability, in particular at the level of the electrode, which is made of platinum based catalyst nanoparticles supported onto carbon embeded in proton conducting polymer named ionomer. The degradation of ionomer during operation was postulated. However, this was not correlated to fuel cell performances and, overall, the ageing mechanisms are largely unknown.

The proposed experiment aims at using SANS to evaluate the impact of aging on the nanostructure of the ionomer in the electrodes as well as its swelling ability as a function of water activity or Relative Humidity (RH). To assess the mostly unknown degradation mechanisms, we plan to systematically evaluate the impact of key parameters: the SANS measurements will be conducted ex-situ on a series of electrodes prepared using different composition and aged following distinct aging protocols. The gained knowledge will allow us to give recommendation in order to improve PEMFC performance and durability.

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1. Experiment principle

A Proton Exchange Membrane Fuel Cell, usually called PEMFC, is an electrochemical device that converts hydrogen and oxygen chemical energy into electricity. As a performant, flexible and non-greenhouse-emissive technology, The PEMFC is seen as one of the main solution to promote electrical vehicles. At the fuel cell heart, the energy conversion is made from the Membrane Electrode Assembly (MEA), which is composed by a proton conducting membrane encased between two electrodes and gas diffusive layers. Electrode is a multiple purposes material. It must ease the transport of humidified gas reactants while driving electrons and protons through the electrode to the active sites where it produces heat and water. Facing numerous requirements, developed electrode are specifically complex. Its structural base is a cluster of porous carbon support that conducts electrons and develops an important specific surface where platinum particles disperse and create active sites allowing reactions. This typical structure is covered by a heterogeneous dispersion of ionomer enhancing the protonic conduction through the catalyst layer.

Ionomer nanostructure is easily revealed by SANS measurements as shown in previous work from G. Gebel[1] on the bulk material. However, its characterisation inside electrode is also a critical work to understand and improve the catalyst layer and fuel cell operation. Therefore our research group works on the characterisation of the ionomer contains in the catalyst layer. We have recently studied the ionomer structure of an operating fuel cell on D22[2]. For this experiment, we have planned a comprehensive study of the ionomer structure.

2. Results

We had multiples goals for this experiment. Firstly, we aimed to study the interaction between ionomer and its surrounding (carbon and platinum particles). Secondly, we studied the whole structure of different catalyst layer. Finally, we wanted to see how operation and degradations might affect the ionomer and electrode structure. In this scope, we realised twenty-five electrodes samples at CEA Grenoble. Each samples were characterised electrochemically before and after various processing. Then, we used a homemade bench and a specific cell to control the samples temperature and humidity while recording SANS spectrums on D22. Spectrums were recorded at three distances in order to study electrode structure ranging from 500 nm to 1 nm:

- 5 Å – 2 m
- 5 Å – 8 m
- 11.5 Å – 17,6 m

In addition, three solvents were used to modify the contrast factor: H_2O (-0,56.10-6 Å^{-2}) to reveals the ionomer structure and its swelling with hydration, D_2O (-6,36.10-6 Å^{-2}) to match the carbon support and a mix matching the ionomer scattering length density (4,2.10-6 Å^{-2}).

To further present measurements done for this experiment, the Figure 1 exhibit typical electrodes spectrums at different hydrations and its different contributions. From left to right, spectrums show three regions. At low Q, the carbon interface intensity, which is close from a Q^{-4} slope under 6.10^{-3} Å^{-1}. At higher Q, around 0.1-0.2 Å, the ionomer phase separation due to water uptake leads to a peak intensity around 0.1-0.2 Å, which may be extracted and analysed independently as shown by Morin et al. [3]. At the highest Q, the prevailing intensity comes from the incoherent scattering, which is mostly due to the sample water content.

From spectrums, we are able to extract the ionomer peak by subtracting the incoherent and the Q^{-4} slope of the carbon interface as presented in the Figure 1. This peak is a Gaussian curve with its parameters reflecting the ionomer nanostructure. Peak position and intensity reflects the size and the quantity of the hydrophilic domains that conduct protons throughout the ionomer.

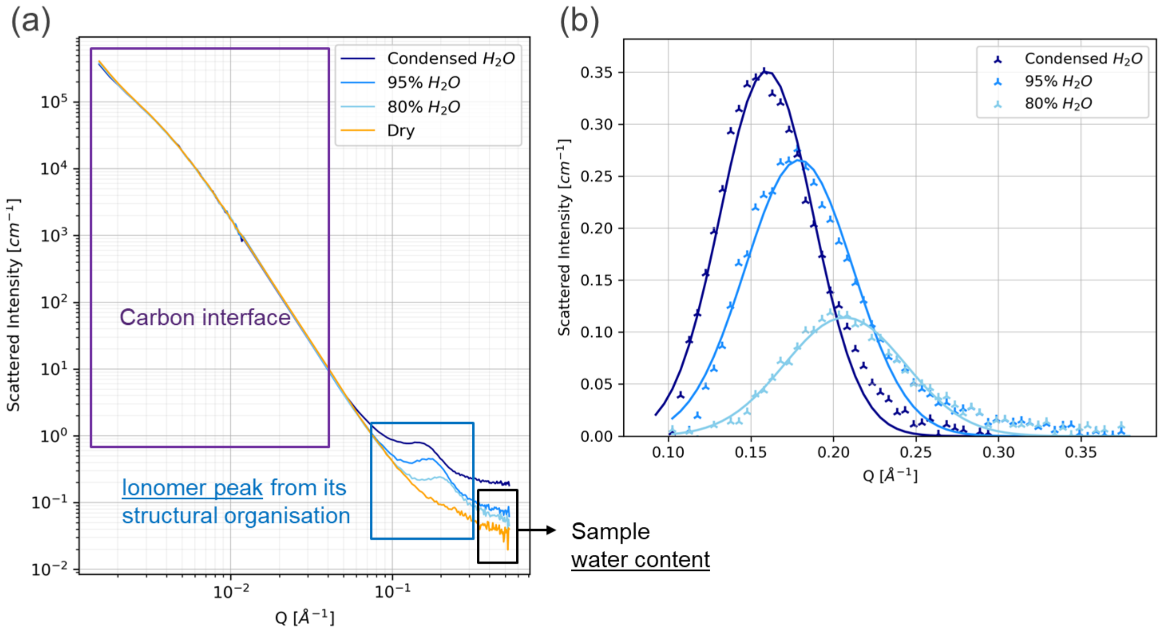

Figure 1: (a) Plotted intensity versus Q for electrodes spectrums obtained at four levels of hydration. (b) Plotted of the extracted ionomer peak intensity versus Q (markers) and fitted Gaussian (lines).

Through this experimental approach, we have studied every expected samples and obtained numerous results on the response of ionomer to conditions, on the ionomer interaction with carbon and platinum and on the operation effect over the whole catalyst layer structure. Thus, we have showed the effect of fuel cell break-in over the ionomer behaviour, which swells more after this process. We also demonstrate, passing through condensate gas conditions or higher conditions temperature alters its swelling behaviour enduringly. Furthermore, studying the ionomer dispersion inside the catalyst layer, we have revealed its strong attraction with platinum nanoparticles. At the opposite, we have exhibited its poor affinity with the carbon support. This carbon support was also studied by contrast variation as nanoparticles dispersion. From this, we retrieved the typical carbon scattering length density of 6,6.10-6 $Å^{-2}$ and a scattering slope close from a fractal sample.

3. Following objectives

As mentioned, we got several results in the previous two days campaigns and we are looking for the following BeamTime to support these results. Specifically, we expect to validate the electrode structure evolutions observed after decay processing by using commercial membrane electrode assembly. Moreover, while we demonstrate ionomer interaction is stronger for platinum than for carbon, we aim to link the ionomer dispersion inside the catalyst layer with the platinum proportion. Thus, we asked for supplementary BeamTime that we obtained from 19th to 22nd of February. We plan to characterize 7 samples for the degradation study and 9 for the ionomer distribution. In both studies, we will record spectrums at 5 relative humidity conditions to obtain the ionomer swelling law and test 3 H_2O/ D_2O proportions to modify the contrast factor. Finally to extend our study on the carbon support structure we will study 3 types of carbon in dispersion, each one will be diluted in 5 solvents with different scattering length density.