Experimental report

20/04/2018

Proposal:	**1-04-133**	**Council:**	4/2017

Title: Probing water content in electrodeof proton exchange membrane fuel cell during operation using Small Angle Neutron Scattering

Research area: Engineering

This proposal is a new proposal

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Samples: carbon (C) + proton conducting ionomer (C, F, S, O) in fuel cell

Instrument	Requested days	Allocated days	From	To
D22	3	2	22/03/2018	24/03/2018

Abstract:

The Proton exchange membrane fuel cell (PEMFC) is an electrochemical converter which produces electricity and heat from hydrogen and oxygen, with water as the only by product. It is a promising, but still expensive, technology. The need of improvement is still important and equally important is the need of understanding. The active layer (AL) of the PEMFC is probably the most critical component of this technology, but also the least understood. In particular, the water content in the proton conducting ionomer and in the pores of this material are largely unknown, despite the fact that it has a strong influence on the performance and durability. Thus, it is currently a subject at the forefront of the research. This proposal aims to quantifying the amount of water in both phases within the AL simultaneously and operando using Small Angle Neutron Scattering (SANS), since no other technic can provide such information. This requires a dedicated cell whose constraints have been identified, a small beam and consequently high neutron flux along with an efficient spectrometer. The crucial information will allow to raise bottlenecks to go toward the design more efficient electrodes.

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1 Experiment Principle

A polymer electrolyte membrane (PEM) fuel cell generates electricity by converting chemical energy of hydrogen and oxygen. The fuel cell is considered as a main powertrain for electrified vehicles due to zero-pollutant-emission, high power density, and versatile performance. At the heart of these systems lies the membrane electrode assembly (MEA), composed of an ionomer membrane encased between two catalyst layers and gas diffusion layers. The catalyst layer (CL) is a porous structure that contains carbon nanoparticles (electron pathway), perflourinated ionomer (proton pathway), and platinum catalyst. The electrochemical reactions can take place only where electrons, protons and gas are delivered to the catalyst. The accumulation of product liquid water in the CL results in flooding which limits the accessibility of the gas to the active sites. On the contrary, the ionomer (e.g. Nafion) can conduct protons only when it is hydrated. Hence, it is critical to the fuel cell performance to balance the amount of water in the CL. Our group has recently published several papers on through-plane SANS on operating fuel cells [2, 3], where the water quantity is thus averaged over the different components (CL and membrane). The goal of this experiment was to record in-plane data with a small beam (30 micron width), in order to discriminate these materials.

2 Preliminary results

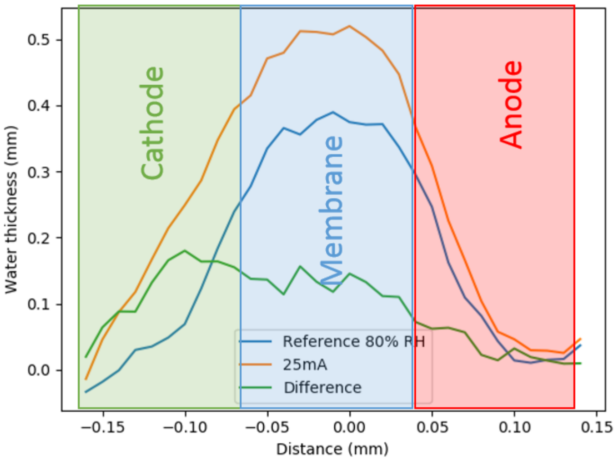

Figure 1: Water thickness calculated with the transmissions scans as a function of the position in the MEA. The difference represents the operating cell subtracted from the reference state

The suitability of the technique was first assessed by performing a transmission scan along the plane, in order to identify the different materials seen by the neutron beam. Furthermore, by normalizing the transmission to that of a dry sample, we can directly calculate an equivalent water thickness [3]. Figure 1 shows the aforementioned water thickness along the MEA for a reference state and an operating state, i.e. when current is drawn from the cell. We can clearly see, by subtracting the reference and operating curves that water is being produced at the cathode, as expected.

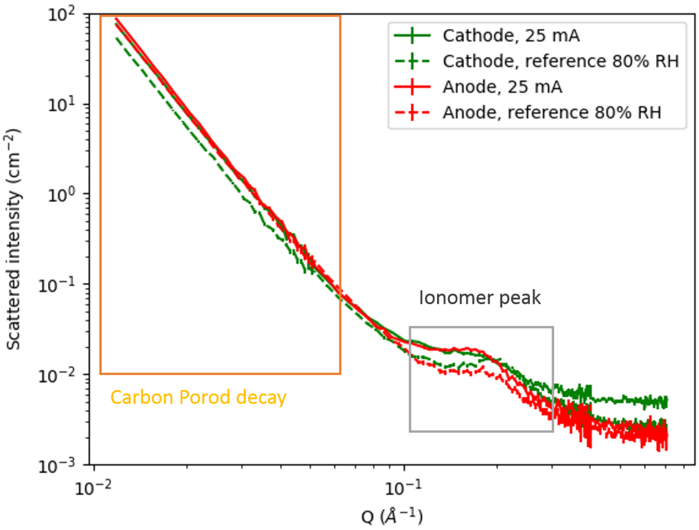

Figure 2: Intensity as a function of Q at the cathode (green) and anode (red), for the reference (broken lines) and operating (full lines) cell.

Further information can be obtained by analyzing the scattering curves taken at the cathode and anode sides: the catalyst layer is a 2 phase component with carbon and ionomer in dispersed phases, so the inclusion of water should modify the shape of the scattering curve via contrast modifications and/or modification of the nanostructure. More precisely, the CL scattering curves can be broken down in two regions (fig 2): the small angle region, dominated by a steep Q^{-4} Porod decay due the Carbon interface and a large Q region dominated by the ionomer peak consequent to the nanostructuration of water within the PEM matrix. These features can allow us in principle to elucidate the whereabouts of the electrochemically produced water at the cathode. Visually we see that when current is drawn, this ionomer peak shifts to lower Q values both in cathode and anode, which means that the ionomer phase is swelling, i.e. water is entering the matrix. For the Q^{-4} Porod decay, only the cathode side sees an increase in intensity when current is drawn. This could mean that part of the electrochemically produced water is entering the carbon interface.

The amount of water in the ionomer matrix is usually expressed as an average number of water molecules per sulfonic acid group, which can be obtained by assuming a lamellar swelling behavior typically observed for Nafion [1]. This quantity is shown in fig. 3a. We observe a 2-fold increase in the average number of water molecules in the cathode when the cell is operated, versus a 40% increase in the anode. This means that part of the electrochemically produced water at the cathode is captured by the ionomer. Quantification of the amount of water at the carbon interface can be

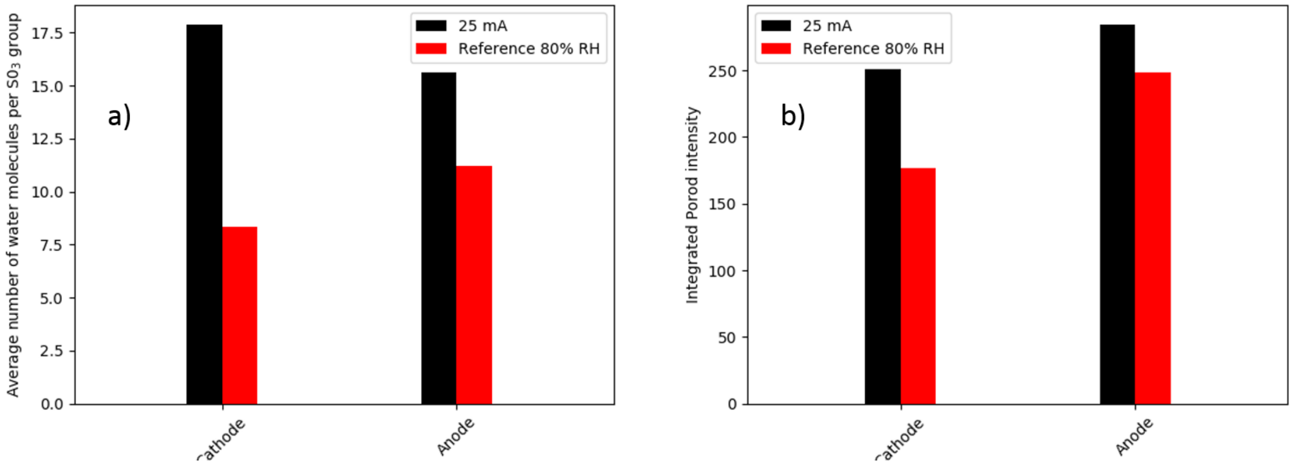

Figure 3: a) Average number of water molecules per sulfonic acid group and b) Porod integrated intensity, for the cathode and anode in the reference and operating cells

obtained by integrating the intensities in the Porod region of the scattering profiles, in the 0.01-0.04 Å^{-1} range. Water interaction at the carbon surface should in theory shift the value of this parameter by raising the carbon interface contrast. We observe a 40% increase of the Porod integral at the cathode when drawing current from the cell, while the anode sees a slight increase of 15%. This could mean that at least part of the produced water could be interacting with the carbon interface in the cathode.

In summary, this experiment allowed us to characterize the water content across the MEA. We observed, as expected an increase in the overall water content when the cell was operated, with an accumulation at the cathode side where it is electrochemically produced. Part of the produced water molecules were captured by the ionomer in the CLs, while some were most likely adsorbed at the carbon interface, specifically at the cathode. Further analysis should allow us to precisely quantify the amount of water captured by the carbon and the ionomer, which could allow us to understand the basic mechanisms of water management in the CL.

References

[1] Gérard Gebel. Structural evolution of water swollen perfluorosulfonated ionomers from dry membrane to solution. *Polymer*, 41(15):5829–5838, 2000.

[2] N Martinez, Z Peng, A Morin, L Porcar, G Gebel, and S Lyonnard. Real time monitoring of water distribution in an operando fuel cell during transient states. *Journal of Power Sources*, 365:230–234, 2017.

[3] A Morin, G Gebel, L Porcar, Z Peng, N Martinez, A Guillermo, and S Lyonnard. Quantitative multi-scale operando diagnosis of water localization inside a fuel cell. *Journal of The Electrochemical Society*, 164(2):F9–F21, 2017.