Experimental report

17/09/2018

Proposal:	**1-04-141**	**Council:**	4/2018

Title: Operando invsetigation of water content in PGM-free electrode of fuelcell using Small Angle Neutron Scattering

Research area: Engineering

This proposal is a new proposal

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Local contacts:	Lionel PORCAR

Samples: Electrode membrane assembly (carbon + ionomer + catalyst)

Instrument	Requested days	Allocated days	From	To
D22	5	4	13/06/2018	17/06/2018

Abstract:

As an alternative to platinum group metal (PGM) catalyst, our collaborator developed PGM-free catalyst based on Fe-N-C for fuel cell applications. However, the performance of the PGM-free catalyst is sensitive to the water content in the electrode compared to the conventional PGM catalyst. In the proposed study, we will quantify the water content in the PGM-free electrode in an operating fuel cell using small angle neutron scattering (SANS) technique. The hydration state of the proton conducting ionomer will be measured by observing the position of the peak (Q~0.1 and 0.25 A-1), and the liquid water content within the pores of the electrode will be measured by monitoring the incoherent scattering level. This experiment must be performed at a high neutron flux beamline such as the D22 where high detectability of water can be achieved. The outcome of this study will be essential to the development of high performance reliable PGM-free catalyst.

1-04-141: Operando investigation of water content in PGM-free electrode of fuel cell using Small Angle Neutron Scattering

Scientific Context

The proton exchange membrane fuel cell (PEMFC) generates clean electricity from hydrogen and oxygen. The fuel cell is an alternative to a combustion engine for power generation in automotive and stationary applications. However, the commercialization of PEMFC is bounded by the use of expensive platinum group metal (PGM) catalyst in the electrodes. Thus, the development of cost-effective catalyst for oxygen reduction reaction (ORR) is essential for accomplishing the hydrogen society.

In the cathode electrode, water is produced as a result of electrochemical reactions. The water is absorbed by the proton conducting polymer (ionomer), which modifies the molecular structure of the ionomer. It also accumulates in the pore of the cathode electrode causing oxygen transport limitation. The presence of water in the electrode has direct impacts on the performance of the fuel cell.

Objective

The objective of the proposed research is to quantify the liquid water in the electrode which will contribute to identifying the failure mechanisms of the PGM-free catalyst and improving its reliability. To accomplish this objective, customized fuel cells incorporating these two types of the electrodes have been investigated by operando SANS technique in simultaneous to electrochemical characterization (Figure 1).

Use of Beamtime

We installed a custom miniature fuel cell with an active area of 0.1 cm × 1 cm and the test bench on the D22 beamline (Figure 2). A 15 µm slit with adjustable thickness was used to obtain a beam with the desired dimension. The distance between the cell and the beam was about a few mm. Taking into account the divergence, the size of the beam in the middle of the sample was around 30 µm. This takes us about 8 to 9 hours to install the setup and align the cell.

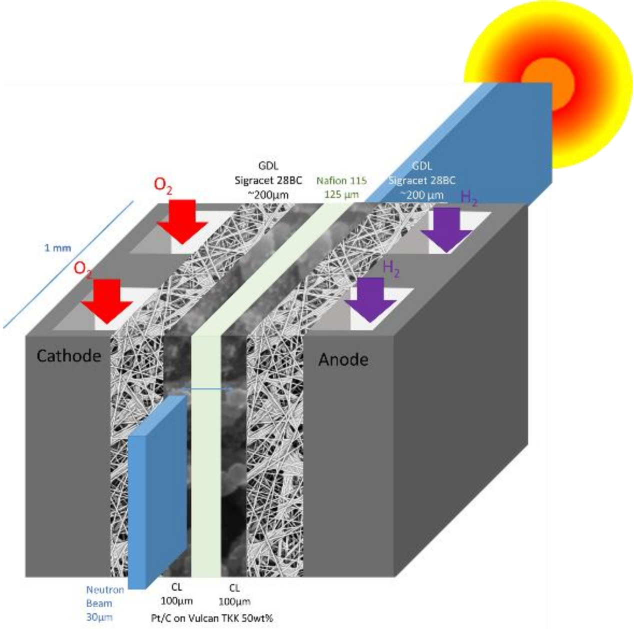

Figure 1. Schematic principle of the method of quantification of water content in catalyst layer of an operating proton exchange membrane fuel cell using SANS

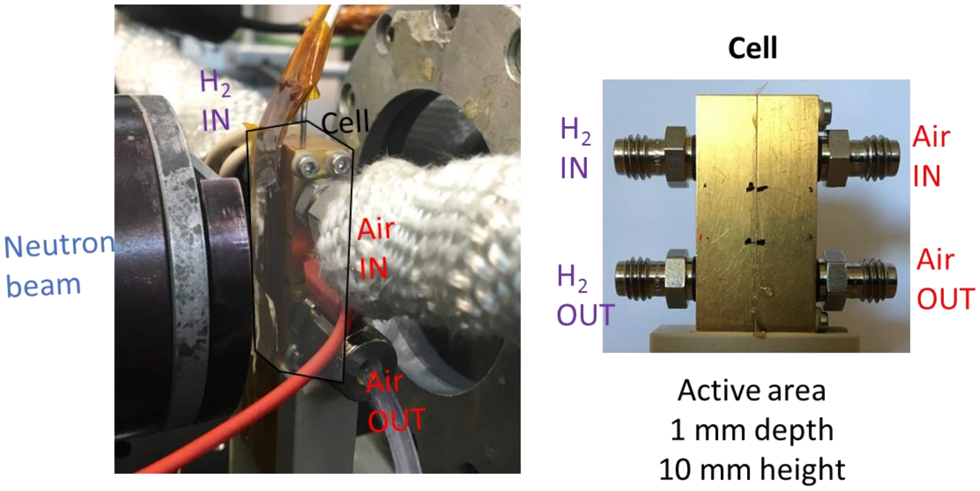

Figure 2. (Left) Single cell on D22 beamline. (Right) Face view of the single cell. The total width of the gilded parts of the cell is 20 mm.

The whole 250 µm thick membrane electrode assembly must be scanned by step of 5 microns to record the transmission and find the positions of interest (each electrode and the membrane). This represents 50 steps. The scan is lasting about 5 minutes. We recorded the spectra at three sample-detector distances, ~1.2, ~2 and 5 m to probe a Q range between 2x10^{-2} and 0.6 A^{-1}. Each spectra takes about 3 minutes.

We recorded the reference spectra under N$_2$ at 30°C at different RH: 0, 70, 80, 90, 100%. This has been done with H$_2$ and D$_2$. We also recorded spectra under operation with H$_2$O and H$_2$ at 30°C and 60°C.

We successfully demonstrate the possibility to extract the water content in the proton conducting polymer during operation (Figure 3), which is the first time that such information is available.

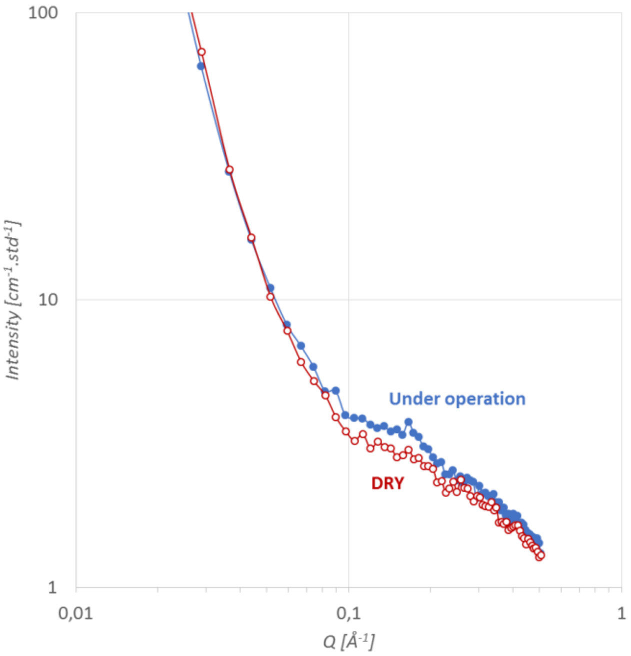

Figure 3. SANS spectra of the catalyst layer in dry state and under operation. The ionomer peak related to the nanostructure of the ionomer within the catalyst layer appears due to the hydrophilic/hydrophobic nanophase separation.

In addition, we recorded spectra on sample of electrode ex-situ in quartz cell with H$_2$O and D$_2$O. This took us about 4 days total to conduct these experiments (Figure 4).

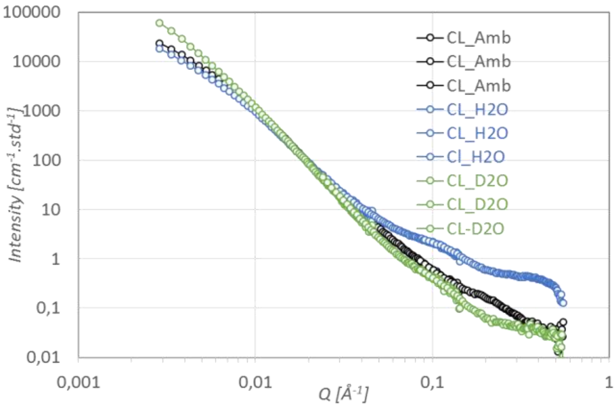

Figure 4. Ex-situ spectra of the catalyst layer equilibrated at ambient, in H_2O and in D_2O

However, we faced two issues related to the beam and sample environment which prevent us to accomplish all the program which was planned (Figure 5). These issues have been identified and discussed with the local contact of D22 (Lionel Porcar). First, thermal fluctuations in the sample environment between days and nights induced oscillations in the position of the beam with regard to the sample. This is a critical aspect because of the size of the sample and of the beam in the range of tens of microns. This obliged us to scan the fuel cell along a distance much larger than the size of the region of interest to be sure to probe the electrode. Thus, a lot of time has been loosed to extract relevant data. Second, the width of the adjustable slit used to tune the size of the beam unexpectedly changed in an uncontrolled manner during the experiment because of the thermal expansion induced by the warming of the cell located at only few mm. The decrease in width has been estimated to be around 30%. This has been verified with a microscope at the end of the experiment. This happens before recording the spectra during operation with D_2O. This makes the quantitative analysis of the intensity of spectra recorded before the last modification in width of the slit impossible. Indeed, the intensity of the direct beam used to estimate the transmission of the sample, and thus the absolute intensity, has been measured only at the end of the experiment. Analyzing the shape and the position of the scattering spectra already gives valuable and expected results, but we did demonstrate with ex-situ experiments that relevant information on the catalyst layer structure can be extracted from contrast variation between H_2O and D_2O.

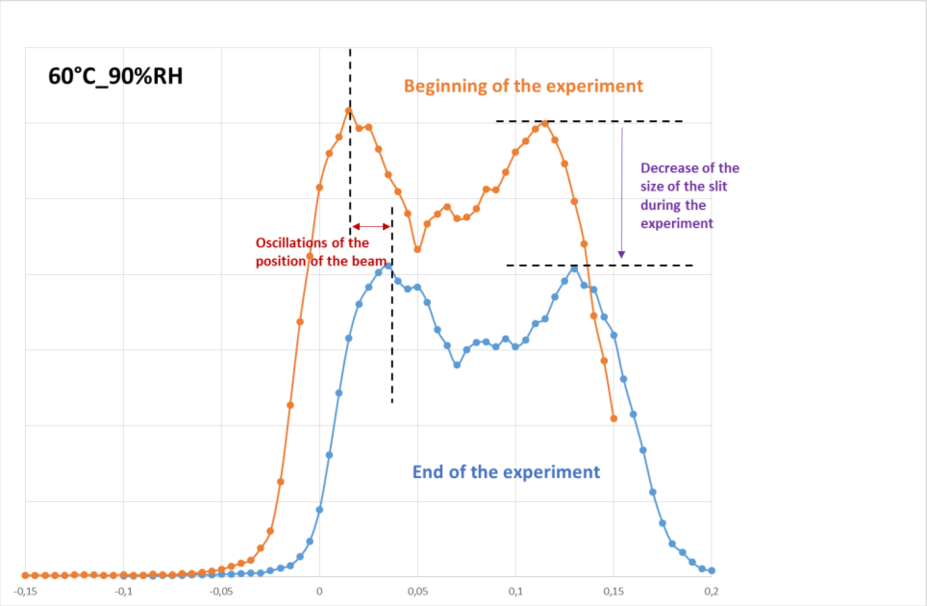

Figure 5. Intensity of the transmitted beam as a function of sample position in a given condition (60°C 90%RH) showing the shift of the position of the beam and the decrease in intensity due to the reduction of the size of the slit.