Experimental report

12/09/2023

Proposal: 1-04-243 **Council:** 10/2022

Title: Influence of the operating conditions on the electrode nanostructure and ionomer distribution in PEMFC under Operation

Research area: Other...

This proposal is a new proposal

Main proposer: Arnaud MORIN

Experimental team: Arnaud MORIN
Pierre TOUDRET
Gerard GEBEL
Benoit GOUZE

Local contacts: Lionel PORCAR

Samples: Nafion+C+Pt
Fuel cell with Platinum and carbon, with perfluorosulfonic acid ionomer

Instrument	Requested days	Allocated days	From	To
D22	3	3	22/06/2023	25/06/2023

Abstract:

Being the place of the electrochemical reactions, the electrodes, made of Pt/C catalyst and a proton conducting ionomer, play a crucial role in PEMFC. Research and progress are still needed on this component to face the major challenges that are the cost, performance and durability, and finally, for large-scale commercialisation of PEMFC. We recently developped and validated a setup and specially designed cell to perform SANS measurements on the electrode under operation conditions. The proposed experiment aims at characterizing operando the effect of the working parameters (temperature, relative humidity, total pressure, partials pressures of oxygen, current density) simultaneously on the electrode performance, as well as its nanostructure and hydration, and more precisely on the influence of water content on ionomer nanostructure.

Influence of Operating Conditions on Electrode Nanostructure and Ionomer Distribution in Proton Exchange Membrane Fuel Cell (PEMFC) under Operation

The aim of this experiment, labelled 1-04-243, is to characterise electrodes and membrane nanostructures of a proton exchange membrane fuel cell under varying operating conditions. Emphasis is placed on the understanding of the correlation between the cell performances and the water/ionomer behaviour as conditions such as humidity, temperature, pressure and current density evolve.

The “sample” in this experiment is a specially designed operational fuel cell with an active surface area of only 1mm wide and 10mm long. Like a classic fuel cell system, ours can be described as a five parts assembly with a central Nafion membrane, electrodes deposited on each sides of the membrane, and porous gas diffusion layers pressed on each electrode. Airtightness between the membrane and the cell body is ensured by titanium seals, chosen to be neutron transparent as the electrodes are expected to be behind them, then, the total thickness of the sample and holder is 3mm.
Physical and electrochemical performances of the selected fuel cell for the experiment were previously tested to ensure reliability throughout the shift.

Fuel cell experimental conditions controls are fully remoted using home-made MICEAU 2 bench on one hand, designed for fuel cell testing by CEA it controls operating temperature, gas supply type and pressure, and with Bio-Logic potentiostat on the over hand to manage electrochemical conditions and characterisations.

The first 12 hours were dedicated to the preparation of the experiment: sample mounting in the beamline enclosure (see figure1), bench installation and preparation, gas supply connection (H_2, D_2, N_2, O_2), safety checks, communication test between instruments, neutron beam and detector alignment,… The final configuration for SANS measurement is set as 8m distance from detector, 6 angstrom neutron wavelength, with a q range from 0.005 to 0.6 $Å^{-1}$. Beam stop is not required.

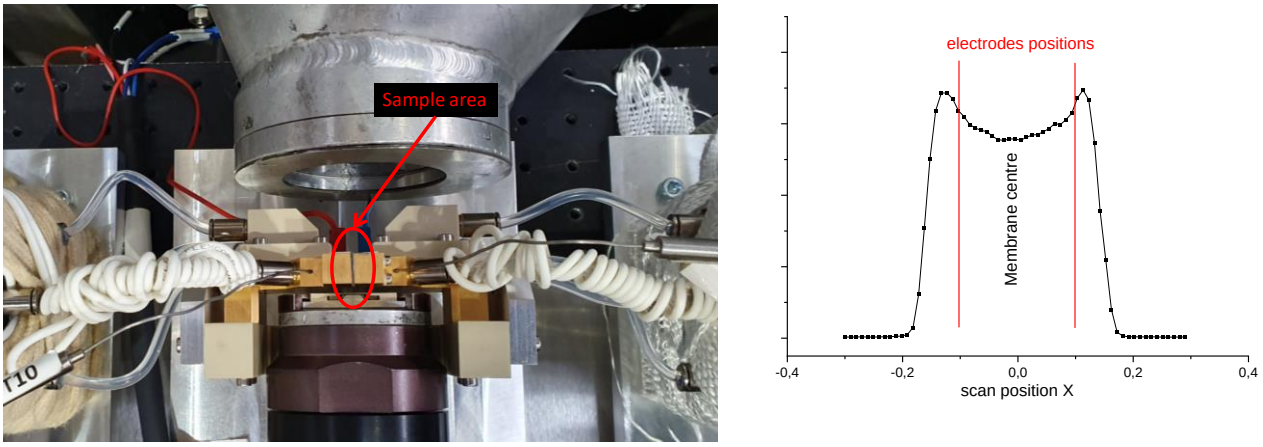

Figure 1: Fuel cell and its holder mounted on D22 beamline, "sample" area highlighted by red circle (left) and example of a transmission scan on X position (right)

Using a narrowed neutron beam of 15 µm in width and 8 mm in height, we expect to observe each component independently (electrodes and membrane) while scanning along X axis. Membrane centre is set on position 0 based on the minimum in transmitted intensity and SANS diagram preliminary observation, electrodes position are expected around position 0.1 according to the cell geometry and observed intensity on the scan.

Due to its nature, the changing conditions and previous experience, we knew that despite the holder rigidity, the sample might move during the experiment. In order to maintain consistency in the probed area, a transmission scan on X position is always performed after a change in operating conditions or long waiting times. Then an automated calculation is used to find the membrane centre as the minimum in the scan curve for a defined range, and the 0 position is reset before each acquisition (example given on figure 1).

During our first set of parameters, membrane and cathode SANS diagrams were systematically acquired for 1200 seconds; the cathode acquisition time was later set to 3600 seconds for better counting statistics. Moreover, 3 to 6 consecutive 300 seconds measurements were performed on the cathode during parameters equilibration prior to longer acquisitions. A few acquisition on anode side (1200 seconds) were also made, but quickly abandoned in order to optimise our dedicated time. By the end of our shift, almost 24 hours were spent on sample acquisitions. The rest of the time was allocated to equilibration between conditions, from 45min to 2h depending on the gap between conditions, which included four relative humidity (0, 60, 80, 95%) for each set of parameters as reference (no current, 30°C), ambient temperature (30°C, current 20 and 50mA, pressure 1 and 1.5bar), high temperature (70°C, current 40 and 80mA, pressure 1 and 1.5bar).

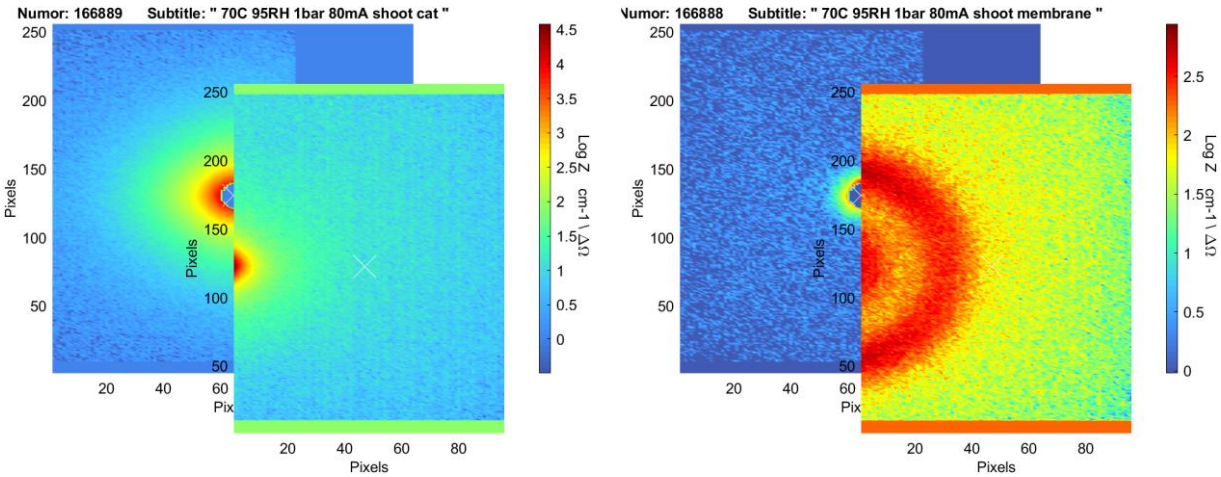

Figure 2: SANS 2D plate of the cathode (left) and anode (right) functioning at 80mA and 70°C under 95% relative humidity, 1bar pressure

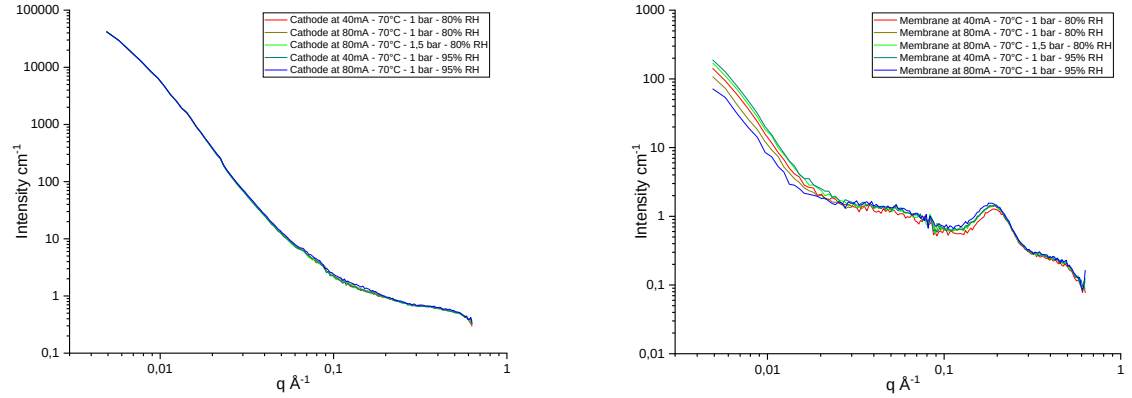

Figure 3: Integrated 1D SANS diagrams of cathode (left) and membrane (right) at 70°C under several relatives humidity

Each set of parameters was conclude by a contrast matching acquisition using D2 and D2O instead of H2 and H2O in order to minimise the carbon scattering contribution and enhance the ionomer one. Figure 2 shows example of obtained 2D scattering data among 78 acquisitions and 27 set of conditions.

As expected, a first look on the integrated data (figure 3) of the membrane clearly show the swelling of the ionomer peak as the relative humidity increase. Combined with the electrochemical data acquired in parallel, we should be able to determine the dependence of water uptake in the membrane following the operating conditions.

However, an unexpected, and unpleasant, surprise is the very weak, or non-existent, evolution on the cathode SANS plots. Some further treatment on the data (clean holder subtractions, good covering between the two detectors) could still be tried in order to assure if these results should be treated further or not, but it is already noted that this behaviour was not expected.