Experimental report

14/09/2023

Proposal: 9-12-673 **Council:** 10/2022

Title: Influence of the solvent and ionomer types on the fuel cell electrodestructure and its water uptake

Research area: Materials

This proposal is a new proposal

Main proposer: Arnaud MORIN

Experimental team: Arnaud MORIN
Pierre TOUDRET
Marie HEITZMANN
Gerard GEBEL
Benoit GOUZE
Jean Francois BLACHOT

Local contacts: Lionel PORCAR

Samples: Carbon + platinum + Perfluorosulfonated ionomer

Instrument	Requested days	Allocated days	From	To
D22	3	2	25/06/2023	27/06/2023

Abstract:

Proton exchange membrane fuel cell (PEMFC) is a conversion devices that uses the chemical energy of the dioxygen and dihydrogen to produce electricity, heat, with water as a by-product. The main component of the individual cells composing the PEMFC is the Membrane Electrode Assembly (MEA) that is made of a proton conducting polymer electrolyte membrane sandwiched between two electrodes. The electrodes are key and critical components in PEMFC, in terms of cost, performance and durability, as they are the places of the electrochemical reactions. The electrodes are made of platinum (Pt) nanoparticles (~3 nm) supported on electrically conductive mesoporous (high surface area) carbon particles (~40 nm) which are bound in a proton conducting polymer, the ionomer. The proposed experiment aims at systematically investigating the effect of solvent, catalyst and ionomer types on the electrode nanostructure and more precisely on the distribution and swelling behaviour of the ionomer in the electrode with SANS. This will help for a better understanding of the influence of the fabrication process on the structure and dispersion of the ionomer in the electrode, and finally on the performance.

Investigation of Ionomer nanostructure, dispersion and swelling behaviour inside fuel cell electrode by SANS: influence of the solvent and the ionomer structure

The aim of the experiment was to investigate the impact of the composition and the fabrication process on PEMFC electrode structure. The electrode is a critical component, which rules the whole PEMFC operation. The electrode is porous and is made of catalyst particles bound by a proton conducting polymer, the ionomer. Catalyst particles are made of platinum nanoparticles (2-5 nm) supported on carbon nanoparticles (30-50 nm). The ionomer is composed by a hydrophobic fluoric backbone (PTFE type polymer) and hydrophilic side chains containing sulfonic acid groups that uptakes water as relative humidity increases. Ionomer can be in the form of thin film (2-20 nm) on the surface of the catalyst particles or aggregates (>50 nm) within the pores.

The electrode is obtained by drying after coating with an ink consisting of a dispersion of catalyst and ionomer in a solvent. The performance of the electrode depends on its composition (type and content of ionomer and catalyst) and on the manufacturing parameters, such as the type of solvent, mixing and drying processes. In particular, the ionomer dispersion influences the electrode performance. In fact, the ionomer plays a crucial role for the proton conduction in the catalyst layer by controlling the water distribution and thus the percolation path in the catalyst layer. In order to better understand the relationship between composition, manufacturing parameters and electrode structures, 23 samples were tested. Three different types of ionomer and catalyst were tested. Different solvents, ionomer contents, mixing and printing processes were used to prepare the samples.

Small Angle Neutron Scattering (SANS) measurements were performed on powders scratched from the electrode and equilibrated at different relative humidity. The Q ranges explored in this experiment probe structures from the nanometer to several hundred nanometers, so the characteristic size probed is much smaller than that of the powder particles. A homemade titanium test cell was developed to control the temperature and humidity of the sample.

The test cell is presented in Figure 1 and is 33 mm thick. The test cell allows the equilibration of 5 samples in humidity and temperature by sending a flow of humidified N_2 in it. The sample container of the cell is a 250 µm thick cylinder with a diameter of 3 mm for a volume of 1.8 mm^3. The temperature of the cell was maintained below ambient temperature at 18°C using a thermostat-controlled bath. The cell temperature was measured during the experiment at several positions as shown in Figure 1.

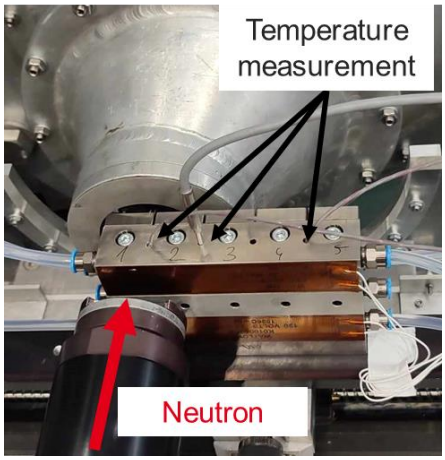

Figure 1: SANS cell on the experimental setup at the D22 beamline

The gas flow, temperature and humidity was controlled by a home-made test bench. The gas sent to the cell was N_2 with a flow of 60 L/h at atmospheric pressure. Several relative humidity were tested in this experiment: 0, 70, 80, 95 % RH with H_2O and 95%RH with D_2O. The gas humidification was calculated in order to obtain the targeted relative humidity at the cell temperature. The D_2O condition was used to match the contrast of catalyst particles. Samples were maintain under gas flow at the desired condition for 25 min before performing a SANS measurement to guaranty sample equilibration.

For SANS measurements the neutron beam wave length was tuned to 6 Å. The collimation with an aperture of 40 mm of diameter at 5.6 m. The sample aperture has a diameter of 3 mm. The two 2D detectors used was placed at 1.4 m from the sample at 5.6 m. The SANS set up allows to obtain a Q range between $1x10^{-2}$ and $5x10^{-1}$ $Å^{-1}$. SANS measurements were performed with an acquisition time of 15 minutes. Around the 26 hours of shift was spent on sample acquisition. The rest of the time was allocated to equilibration of samples or change the samples of the cell.

The integrated data of the reference electrode of this study are shown in Figure 2. 1D SANS profiles of all electrodes tested have similar shapes. The slope observed in the Q range below $8x10^{-2}$ $Å^{-1}$ is due to the surface roughness of the catalyst particles. The correlation peak observed at a Q range between $8x10^{-2}$ $Å^{-1}$ and $3x10^{-1}$ $Å^{-1}$ is related to the ionomer and water contribution in the 1D SANS profile of the electrode. At Q range higher than $3.5x10^{-1}$ $Å^{-1}$ the scattered intensity comes mainly from incoherent. Further data processing will allow extracting information about ionomer structure in the catalyst layer.

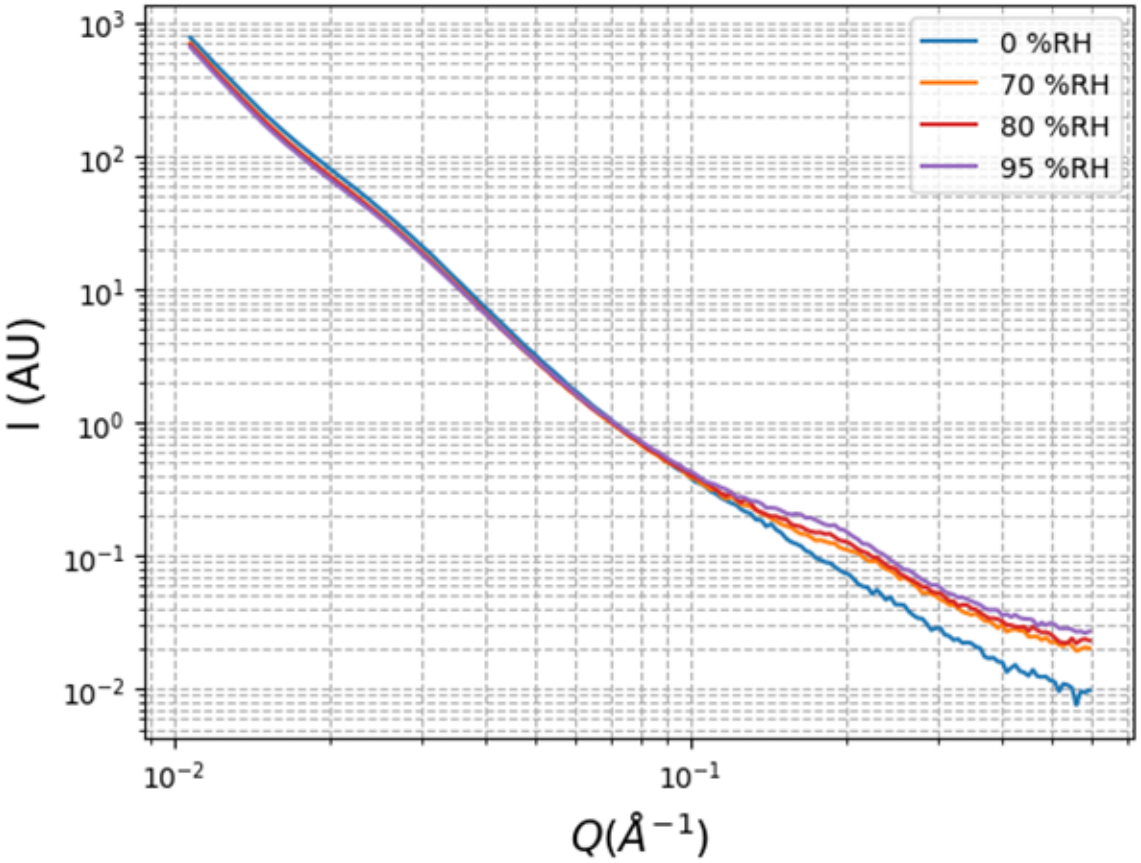

Figure 2: 1D SANS profiles of the reference electrode equilibrated at different relative humidity with H_2O