Experimental report :

We obtained 6 shifts for the experiment devoted to the water management in membranes for fuel cells performed on the ID13 microfocus beamline. This experiment was divided in two main parts: the first analysis of the in situ analysis of the membrane water content under mechanical stress and the study of water desorption at low temperatures depenping on the nature of the ionomer membrane and its initial water content.

In fuel cells, the membrane-electrode assemblies are stacked between current collectors in which a 1mm serpentine is designed for gas distribution. In order to avoid gas leaks and to minimise the contact ohmic losses, a mechanical constraint is applied on the membrane. This constraint can be at the origin of physical degradations during long term operation. The main goal is thus to determine the level of acceptable constraints on the membrane and validate the mechanical models. Due to the shape of the gas distributors the constraint distribution will not be homogeneous. Moreover, the membrane conductivity is directly linked to its swelling state. It is thus of primary importance to determine its water content as a function of the mechanical load especially for the water management models. A specific cell reproducing the local geometry of the gas distributors with alternating 1 mm ribs and channels was built. The mechanical load was controlled using calibrated springs. The cell was introduced in a box to control the humidity with kapton windows to insure transparency to x-rays. Different series of experiments were conducted with dry and water swollen membranes was mounted in the cell and equilibrated at 100%RH with 1, 5, 10, 15 MPa as mechanical load. Finally, a kinetic of swelling was measured for constrained and non-constrained membranes. A 87cm sample-to detector distance was chosen to observe clearly the ionomer peak position which is directly related to the membrane water content. The main results are: (i) the membrane water swelling is not affected for 1 MPa whatever the initial state, (ii) the water content under the ribs decreases as the mechanical load increases; (iii) for large mechanical constraints applied on swollen membranes the membrane microstructure becomes anisotropic and the anisotropy increases with the mechanical load and (iv) unexpectedly, the spectra recorded with the membrane in front of the channel also becomes anisotropic despite the absence of direct mechanical constraint. This last result can be understood because of the membrane swelling which induces some constraints (see figure). Finally, we have followed a swelling kinetic for a membrane under mechanical load equilibrated at room humidity and placed in the presence of a water tank. Surprisingly kinetics observed in the channel and below the ribs were very similar. However, additional experiments on the sorption kinetics in water vapour phases have shown the limiting process is the sorption at the interface. These results have been presented in the PhD manuscript of Nassim Ottmani defended in December 2009 and an article based on these results should be submitted as soon as possible.

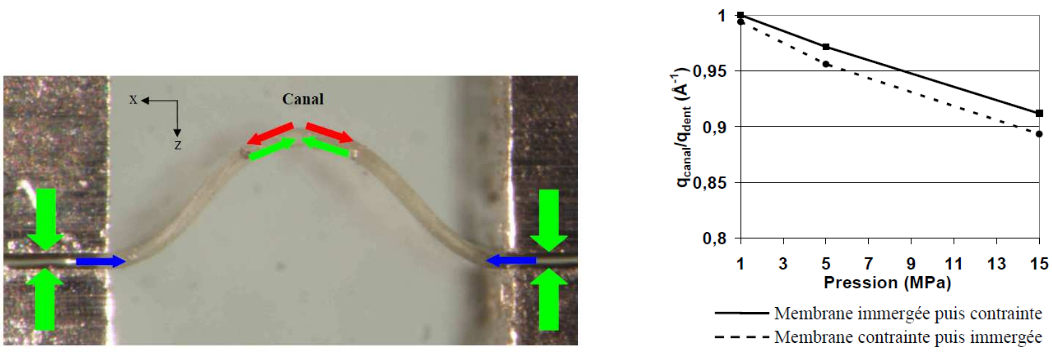

Figure : membrane in the cell and evolution of the ionomer peak as a function of the mechanical constraint revealing a lower water content under the rib for a constraint larger than 1MPa.

The second series of experiments were devoted to the study of the water desorption in ionomer membranes at low temperatures. In a previous work, we have shown that there is no ice formation within a Nafion membrane equilibrated in liquid water when the temperature is decreased below 0°C. We have shown that a water sorption occurs and that the ice is formed on the membrane surface. Similar experiments were performed in the laboratory using NMR in order to quantify the desorption process. The objective of this second run of experiments was the study of sulfonated polymide membrane which does not exhibit desorption by NMR and the microfocus X-ray experiments confirmed the absence of ice formation neither within the membrane nor at the membrane surface. The second main objective of these experiments were the study of the desorption process depending on the initial water content. NMR experiments have also suggested the absence of water desorption below a threshold and the microfocus X-ray experiments confirmed the absence of ice formation neither within the membrane nor at the membrane surface. The membrane water content can be increased continuously up to membrane dissolution equilibrating the membrane in liquid water at different temperatures up to 250°C. Highly swollen membranes were prepared and studied in order to correlate the ice formation within the membrane and the size of the ionic domains. We have evidenced ice formation within the membrane when swollen in water at 150°C while no ice as observed for a swelling at 125°C.