	Experiment title:	Experiment number:
	Fuel cell application using proton exchange membrane: micro-SAXS/WAXS studies of the ice formation in electrode-membrane	SC2005
Beamline: ID13	Date of experiment: from: 12/04/06 7h00 to 15/02/03 7h00	Date of report: November 0(
Shifts: 9	Local contact(s): D. Richards	*Received at ESRF:*

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Report:

Experiments SC2005 and SC2006 required the same experimental setup. SC2005, concerning the study of a micro-fuel cell using a micro beam to detect the first stage of the water bubble appearance, was not succesfull, due to strong local beam damage and strong influence by some weak heating on the fuel cell performances. This is why, due to preliminary tests, SC2006 was performed and was more successful.

1. abstract (SC2006)

In this report we will focus on the problem of these water content changes, which occur in perfluorinated membranes and in associated MEA during temperature changes. Upon cooling water saturated perfluorinated membranes at temperatures below 0°C, from NMR results it has been proposed a water desorption mechanism followed by a crystallisation on the membrane surfaces. The aim of this report is to give experimental evidence using micro-X ray diffraction experiments of such mechanism both in membranes and in associated MEA. In this first report, perfluorinated Nafion type membranes will be considered.

2. Experimental

We present mainly data from Nafion 117, purchased from Aldricht but the study was performed also with membrane electrode assembly (MEA) home-made with N117. Nafion 117 membrane is characterised by its equivalent weight 1100 g/eq and its thickness 175 µm in a dry state. The standard procedures were used for the membrane preparation in term of cleaning; the membrane is soaked for 2h in HCl 1M, then for 2h in NaOH 1M. This operation is repeated twice and then the membrane is left for 1h in boiling deionized water.

For bare membrane, rectangular (1mm width, 1cm long) stripes were cut and introduced into a thin quartz capillary (1mm in diameter) as pictured in figure 1, each capillary being sealed at one end. Then, using a syringe, a part of the capillary was filled with water that is used as a natural cap and allows a 100 % of relative humidity around the polymer sample. This capillary is mounted horizontally on a translational stage in order to be scanned with the x-ray beam.

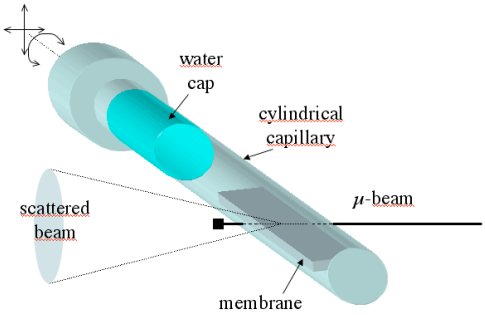


fig. 1: *Scattering geometry with the membrane enclosed in a quartz capillary and layered in the beam in order to scan along the membrane thickness with a x-ray μ-beam.*

These scattering experiments were performed on ID13 microfocus beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The experimental set-up were configured and optimized for our purpose with a standard equipment provided by the beamline (See a sketch in figure 2). A monochromatic x-ray beam (□=0.976) were pre-focalized onto a double Fresnel optics that provides at the sample position a sub-micron beam of about 0.3 μm high and 5 micron large. Before the sample a 5μm pinhole collimator was installed to reduce parasitic scattering from the upstream optics and a ionization chamber to record the incident intensity for transmission measurements. Downstream the sample position, a tiny beamstop, maintained with a metallic wire can be positioned just after the sample to block the direct beam. In order to performed small angle scattering experiment that has been demonstrated that is a suitable technique to quantify the water in ionomer membranes, A 2-D high resolution and time resolved CCD camera was mounted on a translational stage in order to vary the sample to detector distance. For our purpose, this distance was 50 cm. All the sample environment was in air except the optics upstream the collimator.

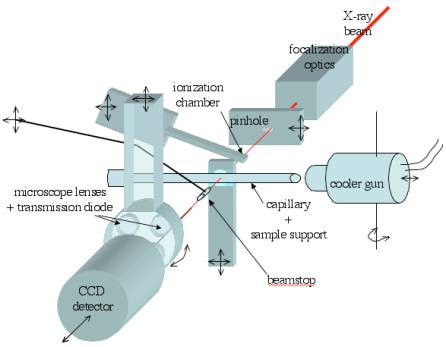


fig 2: *Sketch of the entire scattering set-up on ID13 with the different and main optical elements, translation and rotation stages, sample environment.*

Distortion correction as well as flatfield response were applied before the analysis of the scattering data. Moreover, the scattering being isotropic in the plane of the detector, the 2D spectra were averaged as a function of the azymuthal angle in order to obtain a 1D scattering curve I(q) over a large range of q from small up to large momentum transfer as shown in figure 3 for a swollen piece of Nafion membrane. The characteristic ionomer peak at small angle as well as the amorphous and crystalline scattering peaks at large q value can be observed. The signature of the liquid water, with the correlation peak around 22 nm^{-1}, is also detectable despite the large tail of the second order correlation peak of the crystallites in Nafion.

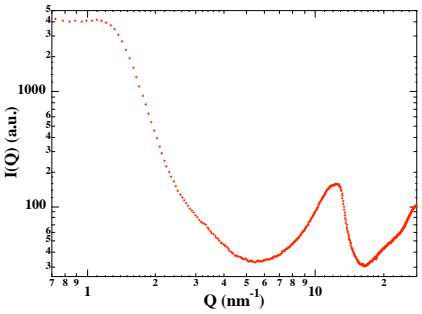


fig. 3: *Typical SA-WAXS curve in log-log plot from a swollen Nafion membrane showing the characteristic ionomer at about 1.1 nm-1, the amorphous and weak crystalline peak around 12 nm-1, the tail of the second order correlation peak arount 25nm-1 as well as the structural peak of the water around 22 nm-1 and that is smeared by the Nafion peak at 25 nm-1.*

Since our experiment is based on a scanning detection, the sample has to be pre-aligned into the μ-beam and a microscope with different magnification lenses mounted on a turret can be inserted between the capillary and the detector in order to place with micron accuracy the membrane, horizontally in the beam, as depicted in figure 1.

The aim of the experiment being to collected data at low temperature between –50°C up to the ambient temperature, a cooling system using nitrogen gas from XXX Cie was used. It allows to produce a laminar, dry and cold gas with a controlled temperature over a distance of less than 1 cm at the output of the gun. This cooler gun was mounting on a rotating support in order to be able to place the output of the gun either as close as possible of the extremity of the capillary along its axis or off-axis when the pre-alignment is applied. Using a thermocouple, we have checked that the temperature

where the membrane is placed and where the beam is shined on, is equal in 1°C range to those imposed by the controller.
The temperature quench from the ambient down to 50 or 70°C is almost instantaneous since we just have to turn the gun from off- to in axis with the capillary. At the opposite, the heating has a relative inertia and several minutes, which depends on the temperature gap, is necessary to achieve the equilibrium. As we will see in the analysis, this effect has some consequences on the water sorption kinetic

3. Results

The main results concerning Nafion membranes are presented in figure 4 and 5:
Figure 4 shows four scattering curves. The first one has been recorded at the ambient temperature and is characteristic of a swollen membrane. The second one was collected once the sample was quenched at -70°C. The ionomer peak characterising the presence of water in the membrane is almost at the same position and the main difference comes from a triangular shape of a scattering peak around 17.8 nm^{-1}, characteristic of amorphous ice in the sample. After the quick decrease in temperature, the water trapped in the membrane was frozen in a disorder state, the time for mobile water molecules to desorb being to short. On the third scattering curve, collected after heating the membrane at -50°C present some sharp Bragg peaks that reveal the presence of ice crystal in the x-ray beam. In parallel we can observe a shift of the ionomer peak to the larger q-value indicating a desorbtion of water molecules from the membrane. Then heating the membrane back to ambient temperature, the fourth scattering curve is also similar to the first one showing that the cycle is reversible.
The different graphs of Figure 5 allow to show that when the water molecules are mobile enough at low temperature, the water is desorbing from the membrane and crystallizes at the surface of the membrane. Indeed, by scanning in and out of the membrane with a micron resolution (fig. 5a), different spectra (fig. 5b and corresponding I(q) that are selected in fig. 5c-f) were recorded showing the ice crystal are apparent only at the surface (fig. 5d) of the membrane and not inside (fig. 5f).

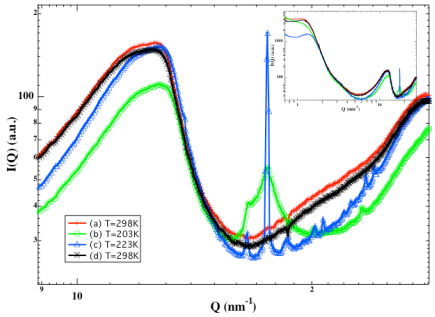
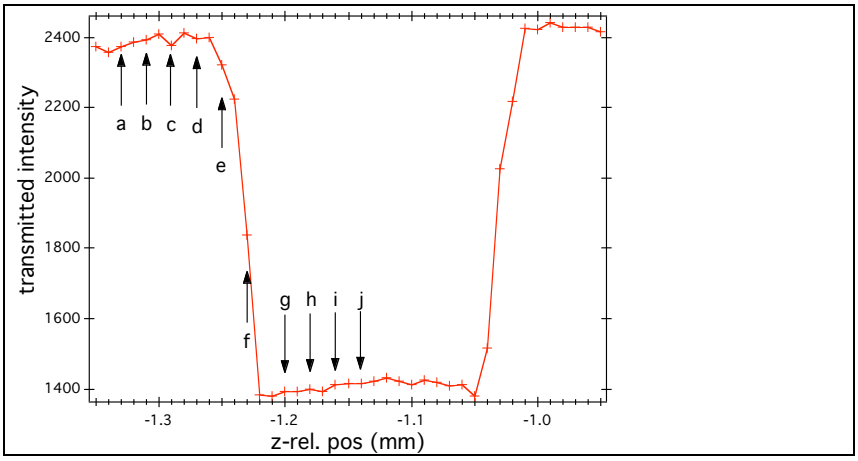


fig. 4: *WAXS spectra collected at the ambient temperature (298 K), at the quenched temperature (203 K) and at two different temperatures (223 and 298 K) during the heating stages. In the insert are presented the corresponding total range of scattering.*



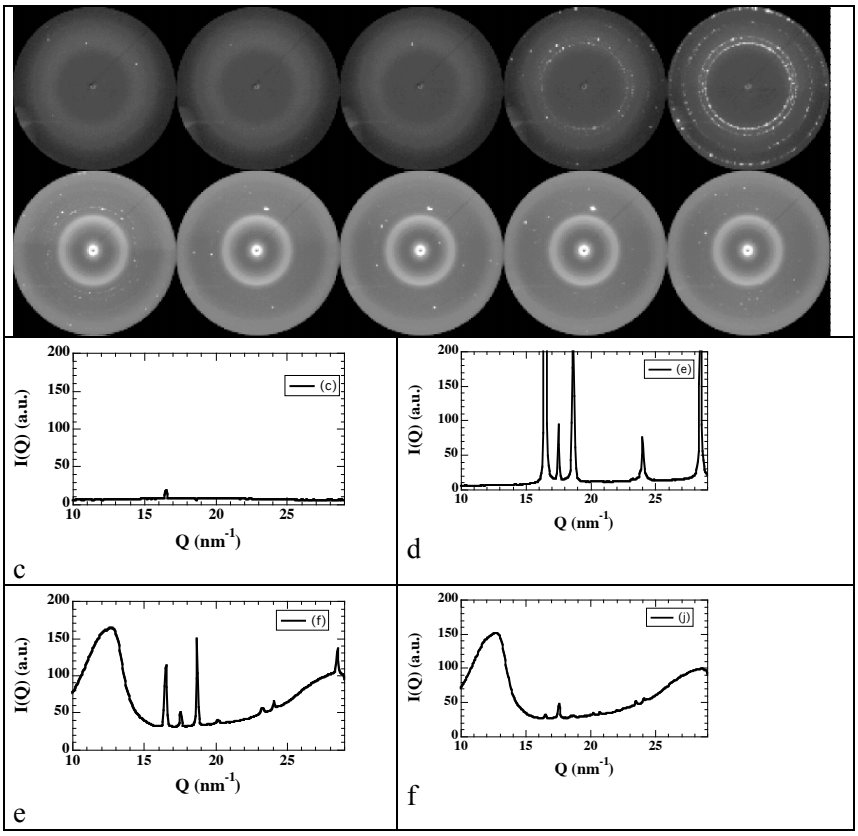


Fig. 5: *a) Transmission curve from a N117 membrane in the capillary, collected at ambient T. The arrows show the different positions for which x-ray scattering spectra were recorded. b) serie of 2D-scattering from the capillary with the beam shining out and in the membrane as depicted by the transmission curve (3a). Fig 3 c-f correspond to scattering plots taken at position c, e, f and j respectively.*

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