In-situ X-ray diffraction studies of the hydration degree of the polymeric membrane in a fuel cell

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Abstract

One of the factors influencing the performances of polymer electrolyte membrane fuel cells (PEMFCs) is the degree of hydration of their membranes. Up to now, only theoretical calculations of the number of water molecules contained in the membranes or *ex situ* measurements have been carried out. In the present study, we report the first experimental determination of a dehydration process occurring in the polymeric membrane of a fuel cell, observed in real time by *in situ* X-rays of a very high-energy synchrotron radiation.

The wide applicability of fuel cells, as enviromentally-friendly and highly efficient systems for the production of electricity, ranges from stationary power plants, to small portable devices for powering cars[1,2]. Advances have been made recently in hydrogen/oxygen PEMFCs, a leading alternative to internal combustion and diesel engines for transportation[3]. Nevertheless, there are still several technical issues that need to be resolved before fuel cell systems become a commercial reality. One of the main concerns regards water management in PEMFCs, which is essential for maximizing the performance of fuel cell systems[4].

Typically an hydrated polymer membrane of perfluorosulfonic acid (Nafion®) is used as proton conducting electrolyte, the ionic mobility being connected to the water content in the polymer[5,6]. Much effort in the engineering of these devices has been devoted to the determination of the most favourable conditions, such as environmental humidity, working temperature, pressure and stoichiometry of reagents etc., for maximizing the water content of the membrane. Nevertheless, the physical-chemical processes occurring to water inside the electrolyte membrane upon cell working is still under investigation.

Indeed, in a PEMFC, along with the water present in the conducting membrane, more water is produced at the membrane-catalyst interface in the cathodic side and its transportation through the cell is driven by diffusion, pressure gradients and electro-osmotic drag. The overall mechanism is further complicated by the heat generated as a consequence of the exothermic reaction at the cathode that induces evaporation[7]. The need for a deeper understanding of water management upon operating conditions has stimulated a large number of theoretical modelling studies[8-12]. However, due to the large number of factors that need to be taken into account, the results of the calculation are not stringent and a direct experimental method is preferable. Indeed, detecting the amount of water present in the polymer matrix in real working conditions would be extremely important, since this amount may vary, depending on many parameters, such as the pressure exerted on the membrane inside the cell, the electrical current flowing across it, temperature, aging effects etc. The most straightforward technique would be in situ x-ray diffraction, applied in a similar way to that used to study the structural evolution of the battery electrodic materials[13]. However, due to geometric constraints, performing in situ diffraction measurements in fuel cells is extremely difficult and the primary X-ray beam has to cross thick layers of X-ray absorbing materials (thickness of the order of a number of cm). Moreover, such materials are numerous, inhomogeneous and each of them represents a complex composite system. For this reason, the diffraction signal reaching the detector consists of the overlap of the various contributions produced by the single elements crossed by the primary X-ray beam. Furthermore, the diffraction pattern coming from the membrane (nafion + water) is not easy to identify (and process), also because it does not contain sharp peaks but only smooth long period modulations (amorphous and liquid “haloes”) .

In the present study , a solution to the above problems is found by applying a method based on the use of the very high energy X-ray beam and the tools available at the ID15 line of the European Synchrotron Radiation Facility (ESRF) in Grenoble. The results obtained represent the first in situ determination of the (time-dependent) amount of water contained in a Nafion®-like membrane fuel cell.

In order to evaluate the hydration level of a fuel cell polymer electrolyte, a Nafion® Membrane N-117 (Du Pont) was investigated. The membrane was previously treated in acid in order to restore it to the original H^+-form, following Du Pont technical information, and then placed between two Toray™ carbon paper electrode backings (ElectroChem, Inc., estimated surface area 1.13 cm^2). The assembly obtained was constricted between two Teflon cylinders of two electrodes cell made in-house (see Fig. 2a).

To accomplish the in-situ diffraction study, the 87 keV x-ray beam available in the ID15 B beamline at the ESRF was utilized. The use of an image plate (model MAR 345) allows the complete collection of the Debye–Scherrer rings in static conditions (no movements being required during data collection), increasing the counting statistics. Moreover, the high-energy radiation used balances the decrease in resolution due to the large size of the irradiated sample area, which is a consequence of the grazing angle geometry adopted to maximize the signal[14]. Indeed, high energy radiation requires longer sample-to-detector distances, since the angular dispersion of the Debye Scherrer cones is smaller, in this way the ideal Fraunhoffer conditions (infinite distance limit) are recovered.

Before starting the in-situ study, a preliminary test is required to find the height at which the beam passes through the membrane only, in a manner that the diffraction pattern does not contain spurious contributions coming from the other components of the cell (see figures 2a and 2b). In order to do this, a vertical scan of the cell is carried out and the various contributions produced by diffraction on such components, i.e. carbon papers (electrode backings), membrane interfacial regions, can be distinguished. Once the cell is placed in such a way that the membrane can be clearly observed by X-ray diffraction, a sequence of patterns is collected (see figure 3). The analysis of these patterns provides the information needed in order to follow, in situ, the time evolution of the degree of membrane hydration . In the present case, the evolution consists of the spontaneous dehydration process at room temperature.

The main changes in the diffraction pattern are localized between the q-values 0.5 and 5 $Å^{-1}$. They correspond with the progressive increase of the main peak height (at 1.1 $Å^{-1}$) accompanied by a decrease of the intensity in the 1.5-2.5 $Å^{-1}$ q-range, where the initial secondary maximum gets progressively flatter before finally becoming a minimum.

In Fig. 4, the first (initial (a)) and last (final (b)) patterns of the sequence are shown together with pattern (c), representing a pure water sample and with the result of data processing (d). It can be noticed that the profile of the latter curve overlaps that of the final pattern. This means that, after proper data correction[15], the pattern of the fully hydrated membrane can be obtained by normalizing a weighted composition of the pattern produced by the fully de-hydrated membrane at the end of the process (namely pure Nafion®) with the pattern produced by a pure liquid water sample.

This method applied to the first and the last patterns can also be applied to each pattern of the sequence, which represents an intermediate stage of the dehydration process, providing the amount of water contained in the membrane at that stage. The graph in figure 5 is obtained by plotting the values of the water content calculated in this way,. It describes an exponential decay, as can be seen more clearly in the insert, in which a semi log scale is used. The hydration percentage is reported on the vertical axis, having assumed that the water uptake of the fully hydrated Nafion® is 38 %, according to the data supplied by Du Pont (see *www.dupont.com*)

Indeed, the above method is able to detect the relative variation, rather than the absolute values of the water content. However, once the initial amount of water is known, a precise determination of its changes can be obtained. The time constant (i.e. the time at which the water is reduced to 1/e of its initial value) of the dehydration process under investigation can be calculated in a straightforward manner by fitting the data in fig. 5, and is $\tau = (25.5 \pm 0.4)$ min.

This numerical value cannot be considered to be representative of the general dehydration process, since it depends on many of the characteristics of the system under investigation, such as the membrane thickness, its active surface, temperature, environmental humidity, cell geometry etc. Nevertheless, this is a demonstration of the feasibility of in-situ measurements to detect the time evolution of the water content in a fuel cell membrane.

Indeed, once this test cell is substituted with an operating cell, which is currently under construction, it will be possible to observe the time change of the PEM water content in real working conditions.

In conclusion, we report the first determination of the (time-dependent) amount of water contained in a Nafion® membrane of a fuel cell. The method that is utilized is based on the use of the very high energy X-ray beam available at ESRF and on the capability of distinguishing and, then, extracting and analysing the diffraction signal coming from the membrane. In this way, the characteristics of the spontaneous dehydration process of a membrane were observed in real time. The results demonstrate that the proposed technique can be successfully used to measure the degree of hydration of the membrane and, therefore, to correlate it with its transportation properties and with overall cell performances.

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Figure Captions

Figure 1

The set-up used at the ESRF ID15 beamline.

Figure 2

A vertical scan of the cell allows the separation of the various contributions produced by the single elements (carbon paper in red, membrane in blue, interfacial regions in black)

Figure 3

Time resolved measurements of the dehydration process of the cell membrane at room temperature.

Figure 4

The pattern of the hydrated membrane can be reproduced by composing the pattern of fully dehydrated membrane with that of pure water.

Figure 5

The amount of water present in the membrane at intermediate stages of the dehydration process can be obtaining by processing the pattern collected at that stage together with those of the pure Nafion-like membrane and pure water.

Figure 1.

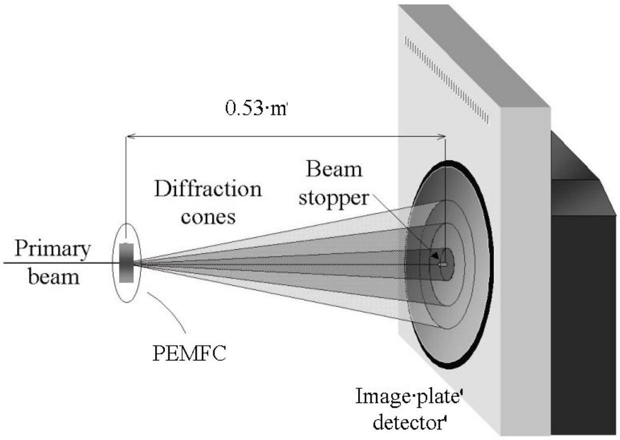

0.53 m
Diffraction cones
Beam stopper
Primary beam
PEMFC
Image plate detector

Figure 2.

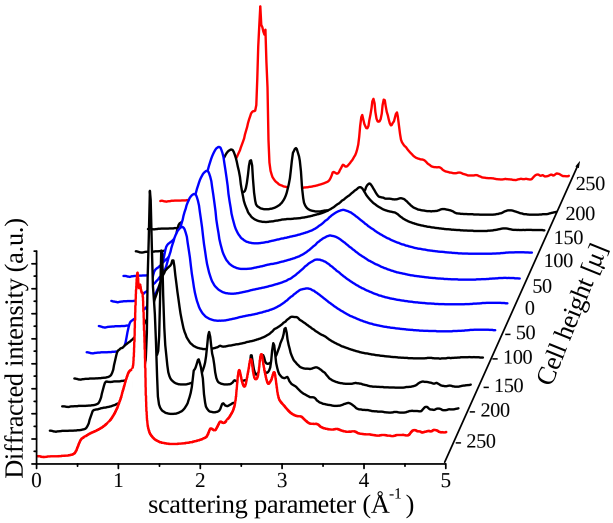

Diffracted intensity (a.u.)
scattering parameter (Å^{-1})
0
1
2
3
4
5
Cell height [μ]
250
200
150
100
50
0
- 50
- 100
- 150
- 200
- 250

Figure 3.

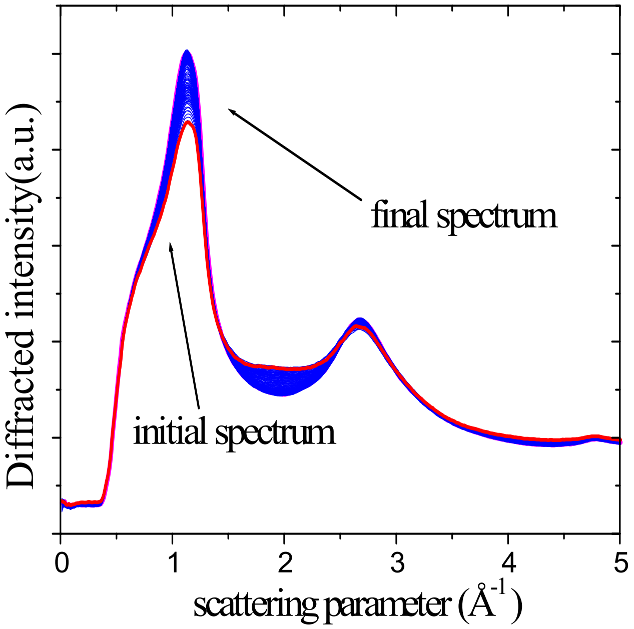

Diffracted intensity(a.u.)
final spectrum
initial spectrum
0
1
2
3
4
5
scattering parameter (Å^{-1})

Figure 4.

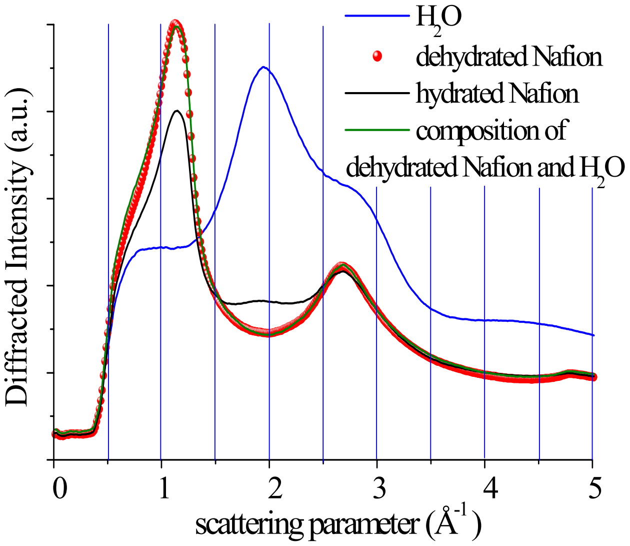
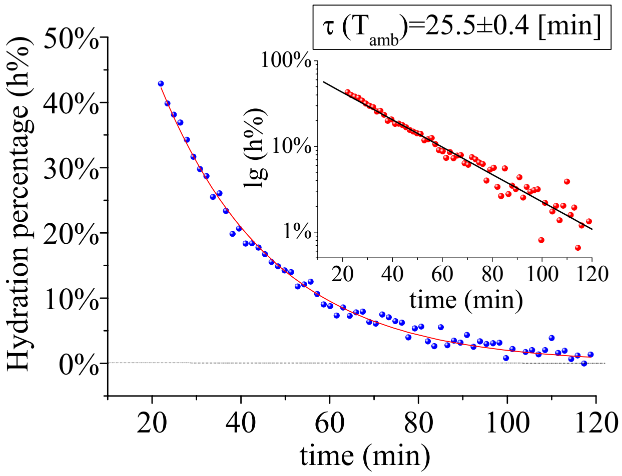

H_2O
dehydrated Nafion
hydrated Nafion
composition of dehydrated Nafion and H_2O
Diffracted Intensity (a.u.)
0
1
2
3
4
5
scattering parameter ($Å^{-1}$)

Figure 5.


τ (T_amb)=25.5±0.4 [min]
Hydration percentage (h%)
50%
40%
30%
20%
10%
0%
20
40
60
80
100
120
time (min)
100%
10%
1%
lg (h%)
20
40
60
80
100
120
time (min)