A fuel cell is an electrochemical system producing a DC current from two half chemical reactions: an \( \text{H}_2 \) (the fuel) oxidation at the anode and the reduction of \( \text{O}_2 \) at the cathode as indicated in figure 1a. Proton exchange membrane fuel cell (PEMFC) is a cell using a proton conducting polymeric membrane as a solid electrolyte separating both electrodes (and so both gases) and allowing the proton conduction between the anode and the cathode. These membranes require a minimum of water content to exhibit a sufficient conductivity and this water has to be controlled whatever the temperature and current density conditions during the cell operation. Then, the management of the water around the cell and more especially between both electrodes is a major challenge for PEMFC applications. When the cell is operating, water is produced at the cathode. Therefore, under stationary conditions and depending on the current density, an excess of water accumulates at the cathode and has to be removed. Nevertheless, it exists always a water concentration profile across the membrane, which is partially counterbalanced by water back-diffusion and reinforced by water electro-osmosis (see Fig. 1b). This concentration profile can also be reduced using humidified inlet gases especially at the anode.

Several attempts to experimentally determine these profiles during fuel cell operation have been published. However the experimental constraints [1-4] lead to operate in conditions, which were not representative of the actual fuel cell operation. The determination of the water concentration profile across the Nafion \(^1\) membrane and under fuel cell operation can be achieved using small-angle neutron scattering (SANS) technique. Indeed, both the shape and the level of scattered intensities of Nafion spectra are very sensitive to the water content. Moreover, it is possible to use a specially designed fuel cell which is almost transparent to neutrons and allows mainly the observation of the membrane contribution to the SANS spectra. In a previous study, we have demonstrated the feasibility of such experiments but with some poor fuel cell performances due to i) electrodes which were not appropriate (chemically deposited platinum) ii) a cell design which did not allow an optimized gas flow on the membrane and iii) a control of the cell temperature which were nonexistent. In the present study, a new bench and a new cell were designed (see Fig. 2) to operate at 80°C and under pressure, to control the gas flow, and to measure the gas outlet humidities.

Figure 2. Porous gas distributors and current collectors are either in a titanium/zirconium alloy (48/52) which was grated and sintered or in highly porous steel (90% porosity). Quartz windows were to insure each compartment to be airtight and the transparency to neutrons. The temperature was measured through a thermocouple and adjusted through a temperature controller. Two different types of electrodes were used either a spray (Sm) or a hot pressed Etek\(^\text{®}\) electrode (Etn) on membrane. In the case of Etn electrodes the diffusion layer has been torn away in order to deposit the active layer on the membrane and to avoid the strong scattering of the carbon tissue.

\(^1\) Nafion\(^\text{®}\) is a perfluorinated membranes purchased from du Pont de Nemours Company
The experiments (see an example in Fig. 3a) were performed starting from a nearly dry membrane and varying both the current density and the gas stoichiometry in order to determine the kinetics of swelling in addition to the water concentration profiles. Following the different scattering profiles shown in Fig. 3, the membrane was first dried by a flow of dry gases and increasing the temperature up to 80°C. The current density was then increased by step after at least the stabilization of the fuel cell performance and of the SANS spectra (typical steps of current were between 1 and 2 hours). The analysis in term of water concentration profiles is presented in figure 3b.

![Figure 3. Series of SANS spectra (left) obtained from a Nafion 115 membrane using highly porous gas distributors. The membrane is first dried and then the current density is increased from 0 to 1A/cm². Example of a series of experimental data extracted from left. Each curve were fitted (inset) and the corresponding profiles (% of water into the membrane as a function of thickness) are presented (right) for different current densities.](image)

It was shown that it is possible to determine the overall water content of the membrane under operation and to follow its evolution depending on the operating conditions fitting the data using a linear combination of referenced spectra (obtained from membranes at given humidity and placed in similar support and temperature conditions).

The performances and the stability of the fuel cell (polarization curves not shown here) were very good which suggests that the membrane has not to be completely water swollen as it is usually believed. Others experiments indicate that the fuel cell can run with a nearly dry membrane but the operating parameters such as the gas flow, the humidification or the temperature becomes crucial.

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