

Water profile determination in a running PEMFC by small-angle neutron scattering

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Abstract

The water management in an operating polymer electrolyte fuel cell was studied by small-angle neutron scattering (SANS). The experiments were conducted at 80 °C under pressure (1.5 bar) using non-humidified gases and porous gas distributors. The parameters under study were the gas distributor porosity, the membrane thickness, the nature of the electrodes and the gas flow. SANS is shown to be a powerful technique to determine *in situ* the amount of water in the cell, to differentiate the water located within and outside of the membrane and its distribution across the membrane thickness. The data analysis leads to the determination of water concentration profiles across the membrane that could be used to validate mass transfer models. It is shown that a significant current can be extracted with a dry membrane, porous gas distributors and dry gases and that the membrane does not significantly swell whatever the electric load.

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1. Introduction

Proton exchange membrane fuel cells (PEMFC) are considered as a key issue against oil rarefaction and green house gas emissions [1]. However, in addition to high production costs and a lack of reliable components, the development of this technology is hindered by a system and operation complexity. Proton conducting membranes such as Nafion[ ] require minimum water content in order to exhibit a sufficient protonic conductivity [2]. A high water concentration all over across the membrane has then to be maintained under fuel cell operation whatever temperature and current density conditions. During operation, a drag process from the proton, diffusing from the anode to the cathode, disymmetrise the water concentration profile through the membrane; this is called the electro-osmosis effect [3]. Therefore, under stationary electric load, an excess of water accumulates at the cathode while the anode is drying out. Then, these water

molecule movements are partially counterbalanced by water back-diffusion induced by the concentration gradient. This concentration gradient can be reduced using humidified inlet gases especially at the anode. This is part of the water management and its optimization is thus a major challenge for PEMFC applications [4] (Fig. 1).

Mass transport models in operating fuel cells are necessary in order to design and optimize new fuel cell architectures. The number of models has increased dramatically in the past few years introducing an increasing level of complexity from 1D which only takes into account the transport through each layers (gas diffusion layers, active layers and membrane) to 3D which accounts completely for the fuel cell geometry [4,5]. However, the modeling process requires a mathematical description of the transport properties while the microstructure of the main components is far from being clearly elucidated. Thus the mathematical description contains crude approximations [6]. For example, the water diffusion within the membrane is usually approximated by the Fick's law using diffusion coefficients which depend on both the water content and the temperature. These diffusion coefficients also depend on the swelling and

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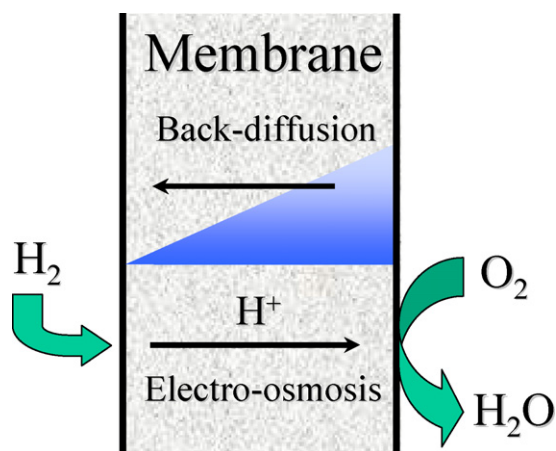


Fig. 1. Illustration of the water management in operating fuel cells. For a given operation condition, a water concentration profile is established as an equilibrium between two main diffusion processes: an electro-osmosis and a back-diffusion effects.

thermal sample history and they are probably strongly influenced by the presence of electrodes stuck on both side of the membrane. Moreover, the membrane swelling process induces some polymer structural modifications and relaxations which are not encountered in a Fickian model [7]. The mass transfer models are usually validated by comparison of simulated experimental polarization curves (cell potential against current density) which allows the adjustment of some fitting parameters but leads to poorly predictive models. An independent determination of the water distribution within the membrane during operation is thus a key issue to validate and improve these complex models. *In situ* impedance spectroscopy is often applied to study the water management. While the electrochemical response is strongly related to the membrane water content of each component, a direct relation between the impedance spectra and the water content is not yet established especially in presence of a non-homogeneous water distribution in the different MEA components [8–10]. Several attempts to experimentally determine the water concentration profiles across the membrane during fuel cell operation have been published [11–13]. Watanabe et al. first suggested the introduction of platinum wires inside a pile of membranes to measure locally the ohmic drops [11]. This technique was then used by Büchi and Scherer to extract the ohmic drops within the membrane close to the anode and to the cathode depending on the electric load [12]. The first water concentration profiles were obtained by neutron absorption [13]. The neutron absorption cross-section is significantly higher for hydrogen atoms compared to carbon, fluorine or any other atoms present in the system [14]. Therefore, the neutron absorption is very sensitive to the water content. However the experimental constraints in these experiments led to operate with very thick membranes (or a pile of membranes) and thus fuel cell conditions not exactly representative of the actual operation. NMR imaging was used to investigate the membrane water content but the spatial resolution is still too low to extract an accurate and determinant water concentration profile across thin membranes [15,16]. Confocal micro-Raman was also success-

fully used to determine *in situ* the water concentration profiles using a specially designed polymer cell with a glass window on the top to observe the MEA across its cross-section [17]. The spatial resolution of this technique is sufficient to establish water concentration profiles across the membrane especially with 200- μm thick membranes. The main problem is probably that information only originates from a maximum of several hundreds of micrometers from the membrane end surface. It is then questionable about a possible extrapolation to the entire active area.

Up to now, the most powerful method to quantify the membrane water content in a running fuel cell was shown to be the small-angle neutron scattering (SANS) technique. The SANS Nafion spectra are very sensitive to the water content [18]. They exhibit a scattering maximum (called ionomer peak) whose shape and intensity can be directly correlated to the water content. Moreover, it is possible to use a specially designed fuel cell almost transparent to neutrons in order to insure that most of the SANS signal is due to the membrane contribution. In a previous study [19], the feasibility of such experiments has been demonstrated. It was possible to determine the overall water content of the membrane under operation and to follow its evolution depending on the operating conditions. In addition, it was shown that water concentration profile across the membrane can be extracted using a specific procedure. However, the experiments were conducted at room temperature, with non-optimized electrodes (chemically deposited platinum) and fuel cell design (the gas flow was not forced on the electrodes). The objective of the present study is the determination of the water concentration profiles across the membrane by SANS under fuel cell operation. A new bench and cell hardware were designed to operate at 80 °C and under pressure and to control the gas flow. The experiments were conducted starting from a nearly dry membrane and varying both the current density and the gas (H_2 and O_2) stoichiometry in order to determine the kinetics of swelling in addition to the water concentration profiles at equilibrium under different operating conditions. The effect on the membrane water content of the gas distributor porosity, the membrane thickness and the nature of the electrodes will be also investigated.

2. Experimental

2.1. Membrane electrodes assemblies (MEAs)

Nafion[®] 112, 113.5, 115 and 117 membranes presenting the same ion content but increasing thicknesses (51, 89, 127 and 178 μm , respectively) were purchased from du Pont de Nemours Company. The membranes were first boiled for 2 h in concentrated nitric acid to remove any impurities due to membrane preparation and storage. Two different types of electrodes were used prepared either by direct spray on membrane (Sm) or by hot pressing onto the membrane of Etek[®] electrodes (Etn). In the case of Etn electrodes, the gas diffusion layer has been scraped away in order to keep only the active layer on the membrane and to avoid the strong neutron scattering arising from the carbon fabrics.

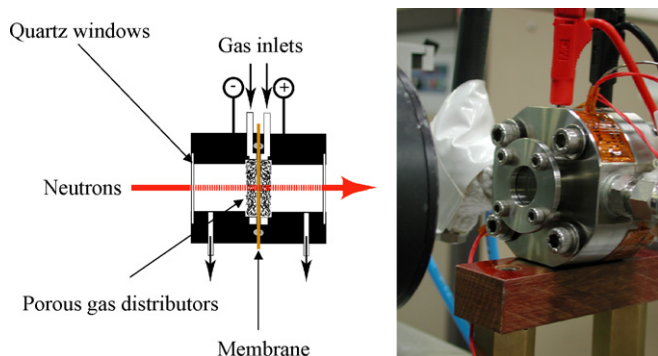


Fig. 2. Fuel cell transparent to neutrons.

2.2. Fuel cell and bench

The specially designed cell is presented in Fig. 2. Quartz windows were used to keep each compartment airtight and to ensure the transparency to neutrons. A second series of quartz windows were added to minimize the water condensation phenomena when operating at 80 °C. The temperature was measured through a thermocouple and adjusted through a temperature controller. A similar cell was built to determine the reference spectra (described in a former section) exactly in the same conditions. The experiments were carried out with two different kinds of porous gas distributors and current collectors. On one hand, we have used a titanium/zirconium alloy (48/52) that was grated and sintered leading to less than 10% of porosity and on the other hand a highly porous steel (>90% porosity). Porous gas distributors were used in place of usual channel gas distributors first to increase the neutron transparency, minimizing the quantity of absorbing and scattering matter in the beam and secondly to be able to run the fuel cell in the absence of gas diffusion layer as the origin of a strong parasitic scattering in this angular of interest. After few hours of operation, the MEAs were renewed in order to avoid any contamination due to metal corrosion. The active area was around 5 cm². The ohmic drops in the cell are rather large which explains that it was difficult to obtain good performances.

The fuel cell experiments were conducted under electric load with amperometric control using pure oxygen and under a pressure of 1.5 bar for both compartments. The current densities were increased step by step from 50 mA to 1.1 A. The current density was changed when both the fuel cell perfor-

mance was stable and a series of three successive SANS spectra was found to be identical. At the beginning of the experiment the membranes equilibrated at room humidity were dehydrated *in situ* by the flow of dry gases. When the temperature was increased up to 80 °C, it was very difficult to start the experiments since it was almost impossible to extract any significant current densities. A starting procedure was applied to the system in order to keep minimum water content in the membrane involving an electric load of 50 mA during the temperature equilibration.

2.3. Techniques

Small-angle neutron scattering experiments were performed on the PAXE spectrometer of the Laboratoire Léon Brillouin (Orphée reactor, Saclay, France). The incident wavelength was $\lambda = 5 \text{ \AA}$ and the sample-to-detector distance was 1.5 m leading to $0.02 < q (\text{\AA}^{-1}) < 0.4$ as q -range where q is the transfer momentum normalized amplitude ($q = 4\pi \sin \theta / \lambda$) and 2θ is the scattering angle. During fuel cell operation, a spectrum was recorded each 10 min in order to get a good signal over noise ratio. Usual corrections for background subtraction and intensity normalization were applied to the data to account the detector response and the empty cell contribution and to normalize the scattered intensities [14]. Radially averaged data were analyzed since the 2D collected scattering data were isotropic. The membrane pre-treatment remove the orientation induced by the membrane preparation. The neutron beam was circular with a diameter of 0.7 cm.

The reference spectra were recorded in a second and identical cell connected to a reservoir containing different saturated ionic solutions to vary the relative humidity within the cell. SANS spectra were recorded until equilibrium was reached leading to a series of at least three identical successive spectra. Typical equilibration time varied from 2 to 5 h.

3. Principle of the method

A series of reference spectra were recorded for membranes equilibrated with different vapor pressures and immersed in water at different temperatures. In order to obtain representative references, the references were measured in the same cell used for the fuel cell experiment and the identical MEAs. The SANS spectra used as reference obtained for the Nafion[®] 1135

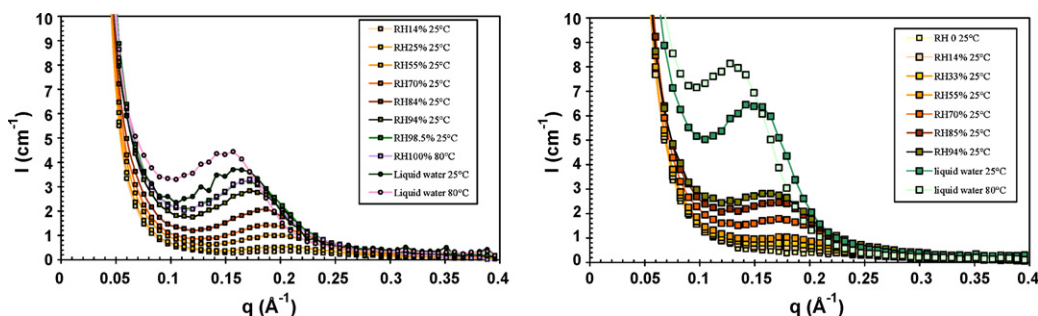


Fig. 3. Reference SANS spectra obtained for Nafion 1135 at various water content from almost dry membrane (RH = 11%) to a membrane equilibrated in water at 80 °C for two different types of electrodes: spray on membranes (left) and hot-pressed Etek electrodes (right).

membrane with spray on membrane (Sm) and hot-pressed (Etn) electrodes are presented in Fig. 3, respectively.

The water content corresponding to each reference spectrum was deduced from the ionomer peak position by comparison with the same experiments conducted on neat membranes and sorption isotherms on the same membranes [18,20]. We have preferred not to use directly sorption isotherms on MEAs since in this case we could not differentiate between the water contained in the membrane and in the active layers.

The SANS spectra recorded for the running fuel cell were fitted as a linear combination of the reference spectra corresponding to defined water contents [18] weighted as a fraction of membrane thickness [19,21]. Plotting these fitting coefficients as a function of the corresponding water content for each defined layers allows the reconstruction of a water concentration profile through the membrane. It is worth noting that this procedure does not allow the determination of the relative position of each layer in the profile. Therefore, we have to assume that this profile is monotonic. This is obviously true in our experiments conducted under stationary operating conditions, starting from almost dry membranes and using dry gases. In such conditions, only water molecules produced by the electrochemical reaction at the cathode are present in the system. This water then diffuses through the membrane creating a more or less pronounced profile. The spatial resolution is thus defined by the number of reference spectra which present significant differences as water content increases (9 to 10 spectra covering the entire humidity range appear as an optimum). Indeed, the SANS spectra are very sensitive to the membrane water content (Fig. 3) and the shape of the profiles cannot be significantly modified keeping the same fit quality.

In the fitting procedure, another parameter corresponding to a constant background (namely incoherent scattering mainly due to the proton of water molecules) was used. Since the level of incoherent scattering which originates from the water contained within the membrane is already encountered in the reference spectra, this additional incoherent background is due to water accumulation in the cell either at the membrane surface, in the gas distributors or in the quartz windows.

4. Results and discussion

The first noticeable and unexpected result is the important differences in the peak position and intensity observed for the two different types of electrodes equilibrated in the same conditions

(Fig. 3). These differences reveal different water content due to differences MEA fabrication procedures and perhaps in surface properties. The Nafion membrane swelling properties are known to be very sensitive to the thermal history especially on acidic form [2,22]. On one hand, the hot pressing procedure involves a thermal treatment at 140 °C which can induce structural reorganization. On the other hand, the spraying method involves a solvent containing at least 50% of ethanol which is known as a good swelling agent of Nafion membranes. In addition, the swelling kinetics are rather different, namely the swelling equilibrium was reached in less than 1 h for the electrode sprayed on the membrane while several hours were necessary for the hot-pressed Etn electrode. The equilibrium was supposed to be reached when three successive spectra recorded after at least 1 h were exactly superimposable. The presence of electrodes strongly modifies the swelling properties probably due to a modification of the membrane electrode interface by the preparation processes. As a consequence, the use of diffusion coefficients measured on neat membrane in mass transfer models is thus somewhat questionable especially in the case of very thin membranes such as Nafion 112 and 111.

In the previous set of experiments [19] we have shown that it was not possible start the fuel cell experiment at room temperature with a membrane dried at 120 °C overnight in an oven. Therefore, the membranes were equilibrated at room humidity before being mounted in the cell. It appeared that it was not possible to start the fuel cell when the temperature of the cell was equilibrated directly at 80 °C in the presence of dry gases flow. The membrane resistance is too large to produce a significant current density. The small quantity water produced by the electrochemical reaction is then quickly evaporated and cannot be incorporated within the membrane in the absence of hydrophobic diffusion layer. A starting procedure was developed increasing simultaneously the cell temperature and the current density by steps in order to avoid a complete membrane drying. When the final temperature was reached, the current density was decreased in order to control membrane drying using neutrons. According to the neutron spectra, it is almost impossible to differentiate between the low water content which allow the fuel cell starting and the completely dry membrane (see for example the first SANS spectrum in Fig. 4).

A first series of experiments was carried out using a hot-pressed MEA based on Nafion 115 and sintered Ti–Zr alloy porous gas distributors and current collectors presenting a low porosity (<10%). The first spectra are recorded just after the

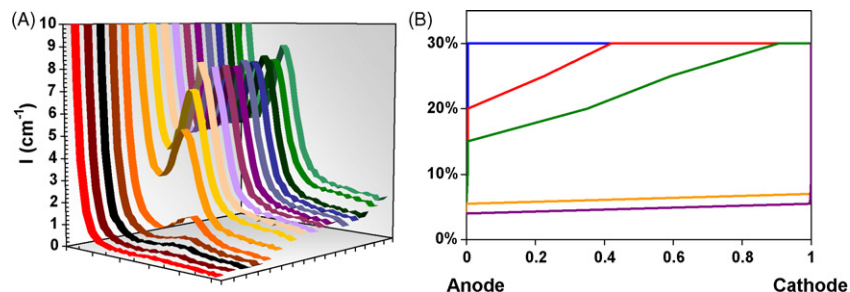


Fig. 4. (A) Series of SANS spectra recorded every 10 min obtained from a Nafion 115 membrane using a low porosity sintered gas distributor. (B) Water concentration profiles across the membrane expressed in water volume fraction during the swelling process (right).

operating temperature was reached ($80\text{ }^{\circ}\text{C}$) and the SANS spectra clearly indicate that the membrane is almost completely dry despite a low production of water by the electrochemical reaction under 50 mA during the starting procedure. The electric load is then increased to 0.5 A . The membrane swells relatively rapidly up to the maximum value and the level of intensity and the ionomer peak position corresponds to a completely swollen membrane. The SANS spectra then do not evaluate when the current is further increased to 1 A indicating that the maximum water content is reached (five last spectra in Fig. 4A). The water concentration profiles across the membrane were determined by fitting the spectra during the membrane swelling (Fig. 4B). The profiles confirm that the maximum membrane swelling is reached in a little bit more than 20 min. At the end of the experiments, the flooding of the cell was observed directly through the glass windows by the presence of liquid water on the gas distributors. This phenomenon was mainly due to the low porosity of the gas distributor “trapping” the water by capillarity. The presence of liquid water directly in contact with the membrane surface explains such a very fast swelling process. The cell flooding is also observable on the SANS spectra since an incoherent scattering arises when the membrane is fully swollen and increases continuously. Its intensity close to 2 cm^{-1} corresponds to an equivalent film of liquid water of 2 mm . Simultaneously the direct beam transmission decreases significantly. Let's remember that 1-mm thick water layer absorb roughly 50% of the neutrons at this wavelength.

The following experiments were conducted using high porosity stainless steel gas distributors (porosity $>90\%$). The gas pressure (1.5 bar) and the gas feed stoichiometry were kept constant during the experiments (2 for hydrogen and 3.5 for oxygen). An example is shown in Fig. 5. The six first spectra correspond to the membrane drying out increasing the temperature up to $80\text{ }^{\circ}\text{C}$ under no electric load. At the end, the SANS spectrum reveals that the membrane is not completely dry since the intensity of the ionomer peak remains significant. The next spectrum was recorded under 0.04 A in order to stabilize the water content. The electric load was then increased step by step after stabilization of the fuel cell performance. After two spectra recorded under 0.1 A , the electric load was settled to 0.16 A and eight spectra were recorded each 10 min during the swelling process. After 80 min, the evolution of the SANS spectra appears limited indicating a stabilization of the swelling process. The electric was increased by step of 0.1 A again from 0.2 to 1.1 A with an equilibration time of at least $1/2\text{ h}$ per step.

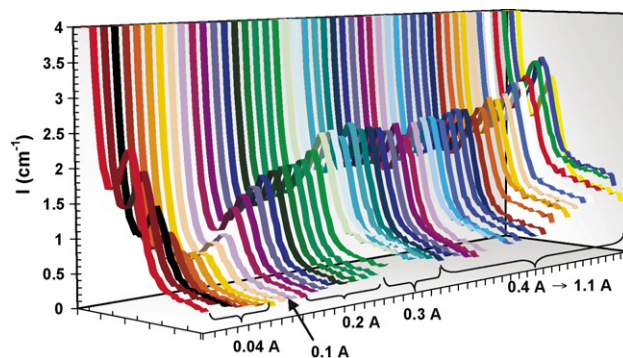


Fig. 5. Series of SANS spectra obtained from a Nafion 117 membrane using highly porous gas distributors. The membrane is first dried and then the current density is increased step by step from 0 to 1.1 A . The duration of the overall experiment is around 7 h.

The analysis in term of water concentration profiles is presented in Fig. 6 focusing on the swelling process. A shift of the ionomer peak is clearly visible up to an electric load of 0.2 A . For larger values, the spectra modifications are negligible except a strong increase of the incoherent scattering background attributable to an excess of liquid water. The water concentration profiles mainly corresponds to relatively dry membranes whatever the current density which explains that the fuel cell performances were relatively poor (Fig. 7). The absence of complete membrane swelling is mainly due to the fact that the experiments were conducted at constant gas stoichiometry using dry gases. The flow of dry gas was thus increased linearly with the electric load removing most of the water produced by the electrochemical reaction.

The next two series of experiments were conducted varying the gas feed stoichiometry. The stoichiometry was first increased to 2.5 for hydrogen and 4.5 for oxygen. In this case, the same behavior is observed at the beginning of the experiment namely at low current densities (Fig. 8). When the current density is increased, the SANS spectra reveal that the membrane is drying out (decrease of the intensity). The performance of the fuel cell then decreases (Fig. 7). It could be surprising that the drying effect is more pronounced for higher current densities where more water is produced but the experiments are performed at constant gas stoichiometry. Therefore, the absolute value of the gas flow is continuously increased as current density is increased. The water concentration profiles were determined and corresponds for almost all the SANS spectra to a

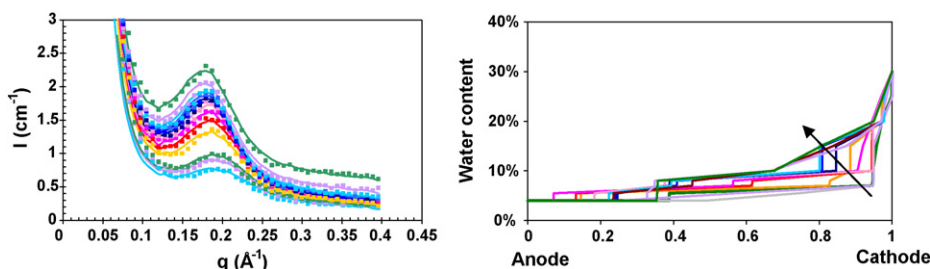


Fig. 6. SANS spectra recorded at different electric load (lowest spectrum at 0.04 A , two next ones at 0.1 A , seven following ones at 0.16 A and the two last ones at 0.2 and 0.3 A). Each curve has been fitted (left) and the corresponding profiles are presented (right). The arrow indicates the profile evolution with time.

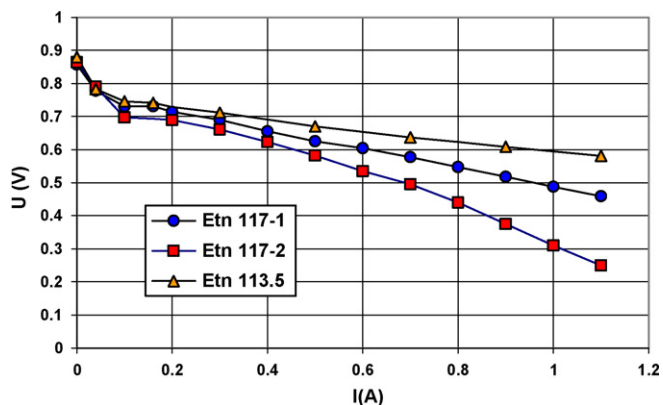


Fig. 7. Polarization curves determined during the SANS experiments. The active area was estimated to be around 5 cm^2 . The MEA were prepared by hot pressing of Etek electrodes on Nafion 117 and 113.5. The Etn 117-1 and Etn 117-2 experiments were conducted with $\text{H}_2 = 2/\text{O}_2 = 3.5$ and $\text{H}_2 = 2.5/\text{O}_2 = 4.5$, respectively, as gas feed stoichiometry.

completely dry membrane except a thin layer (5% of the total thickness) at the cathode. The data treatment also indicates that there is no additional incoherent background (absence of extra water). An experiment has been also performed at lower gas flow (stoichiometry 1.5 for H_2 and 2 for O_2) in order to favor the membrane swelling but the experiment was rapidly stopped due to cell flooding. This is probably due to water condensation on the quartz windows which are poor thermal conductors.

The experiments were reproduced varying the membrane thickness with Nafion 113.5, 115 and 117 (membrane thickness 89, 127 and $178 \mu\text{m}$, respectively). MEAs based on hot-pressed Etek electrodes were prepared using the same procedure. Intermediate gas feed stoichiometry was used in order to attempt avoiding the membrane drying or the cell flooding. As expected a decrease of the membrane thickness leads better fuel cell performances. The analysis of the water concentration profiles reveals similar swelling behavior whatever the membrane thickness. The evolution of the profiles increasing the electric load mainly corresponds to those presented in Fig. 6. The membranes are almost dry on the anode side due to the combined effect of electro-osmosis and water desorption by hydrogen. The evolution of the incoherent background as a function of

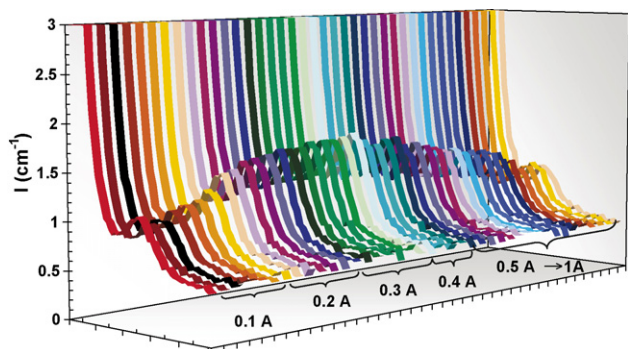


Fig. 8. Series of SANS spectra of a Nafion 117 recorded every 10 min during cell operation under high gas flow. The electric load is increased from 0.1 to 1 A (gas feed stoichiometry $\text{H}_2 = 2.5/\text{O}_2 = 4.5$). The first spectrum is recorded during temperature equilibration.

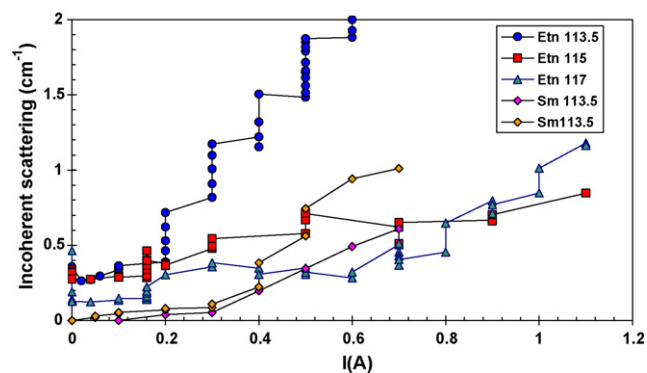


Fig. 9. Incoherent scattering as a function of the electric load for different membranes and electrodes.

the electric load is presented for the different experiments in Fig. 9.

The incoherent scattering corresponds to the water molecules which are seen by the neutron beam and which are not within the membrane. However, the exact location (on the electrodes, within the porous gas distributors or condensation of the quartz windows) is not possible. For example, the experiments conducted with the Etn 113.5 MEA indicate a large cell flooding since the incoherent background continuously diverges. Despite the presence of a large amount of liquid water in the cell, the SANS data indicate that the membrane remains nearly dry and the water concentration profile are not significantly influenced. This is probably due to the combined effect of the absence of hydrophobic gas diffusion layers which could limit water evaporation, of the use of dry gases and the cell geometry in which the dry gases are forced on the active areas. For the other experiments, its value increases significantly for an electric load equal or larger than 0.3 A. Two series of experiments were then conducted with electrodes prepared by spraying the catalytic ink directly on the Nafion 113.5 membrane (Sm electrodes). Once again, the water concentration profiles are similar to those obtained with hot-pressed MEAs suggesting that the water management is not strongly influenced by the nature of

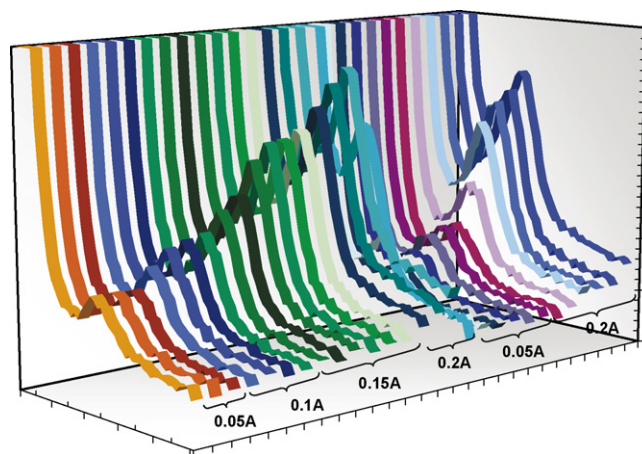


Fig. 10. SANS spectra recorded every 10 min under fuel cell operation at different currents with a MEA based on Nafion 113.5 membrane and electrolytic ink deposited by spray.

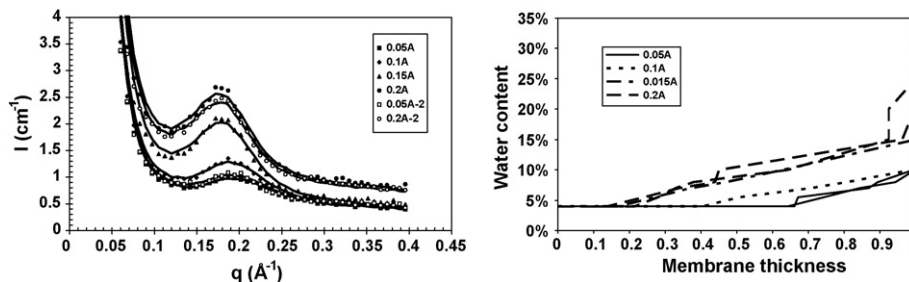


Fig. 11. SANS spectra and corresponding water concentration profiles (cathode side on the right) for different electric load at equilibrium.

the electrodes. In other words, it is mainly related to electro-osmosis and diffusion processes within the bulk material rather than being controlled by the sorption and desorption processes at the interfaces.

The last experiment was performed with a Nafion 113.55 membrane varying the electric load in order to verify the reversibility and the reproducibility of the membrane swelling process. The electric load was voluntarily limited to 0.2 A to avoid the cell flooding which becomes significant for electric load equal to 0.3 A. The main objective is to avoid the presence of excess of liquid water within the cell which could modify the membrane behavior during operation. The three first spectra recorded at 0.05 A are identical after 1 h of operation which suggests that swelling equilibrium is reached. The electric load was then increased successively to 0.1, 0.15 and 0.2 A. In the three cases, the SANS spectra reveal that equilibrium is reached after roughly 1 h. At 0.2 A, the incoherent background increases and the electric load was decreased to 0.05 A keeping constant the gas flow during 10 min to remove the excess of water. After 1 h, the SANS spectra are identical to the one observed at the beginning of the experiments. The electric load was then increased again to 0.2 A and the intensity and the shape of the ionomer peak, and the incoherent background are found identical to the data previously obtained (Fig. 10).

These results indicate that the swelling behavior within the cell is relatively reproducible, does not depend on the swelling history and require 1 h of equilibration. Both the SANS spectra at equilibrium for different current densities and the corresponding water concentration profiles are presented in Fig. 11. The membrane swelling is limited to low current densities (up to 0.15 A) as shown by the increase in intensity of the ionomer peak and its shift toward small angles. For values larger than 0.15 A, the spectra and consequently the water concentration profiles do not change except an increase of the incoherent background.

5. Conclusion

A fuel cell based on porous gas distributors was studied by SANS under operation and the analysis of the spectra using reference spectra allows the *in situ* determination of both the water content and of the water concentration profile depending on the operating parameters. The three main results are, first, the influence of the structure of electrodes on the swelling properties of the membrane in terms of kinetic of swelling and of the membrane structure. However, these changes in

swelling properties are shown to induce only minor effects on the water management under fuel cell operation. Second, the operation of fuel cell with highly porous gas distributors and in the absence of gas diffusion layers generates an excess of liquid water even at very low current densities (50 mA cm^{-2}) while the membrane remain almost dry. At the contrary, with low porosity gas distributors, the water produced cannot be efficiently removed and the condensation within the gas distributor in contact of the membrane induce a complete swelling whatever the operating conditions. Finally, using high porosity gas distributors and dry gases, a significant concentration profile can be obtained, and the fuel cell can be operated with an almost dry membrane. By adjusting, the gas flow rates and the current density it is possible to modulate slightly the membrane water content and subsequently the fuel cell performances.

The main problem of this technique was the use of both dry membranes and dry gases which strongly limits the fuel cell performance. The main interest is to produce some water concentration profiles that could be used to validate the mass transfer models. A necessary improvement of the technique is the development of fuel cell with channel gas distributors transparent to neutrons and operating with state of art MEAs studied on a swollen state and leading to state of art performance. This work is now under progress.

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References

- [1] W. Vielstich, A. Lamm, H. Gasteiger, in: W. Vielstich, A. Lamm, H. Gasteiger (Eds.), Handbook of Fuel Cells: Fundamentals, Technology, Applications, John Wiley, 2004.
- [2] T.A. Zawodzinski, C. Derouin, S. Radzinski, R.J. Sherman, V.T. Smith, T.E. Springer, S. Gottesfeld, J. Electrochem. Soc. 140 (1993) 1041.
- [3] B.S. Pivovar, Polymer 47 (2006) 4194.
- [4] C.-Y. Wang, Chem. Rev. 104 (2004) 4727.
- [5] A.Z. Weber, J. Newman, Chem. Rev. 104 (2004) 4679.
- [6] K.D. Kreuer, S.J. Paddison, E. Spohr, M. Schuster, Chem. Rev. 104 (2004) 4637.
- [7] D. Rivin, C.E. Kendrick, P.W. Gibson, N.S. Schneider, Polymer 42 (2001) 623.

- [8] T.J.P. Freire, E.R. Gonzalez, J. Electroanal. Chem. 503 (2001) 57.
- [9] Y. Bultel, K. Wiezell, F. Jaouen, P. Ozil, G. Lindbergh, Electrochim. Acta 51 (2005) 474.
- [10] A. Schmitz, M. Tranitz, S. Eccarius, A. Weil, C. Hebling, J. Power Sources 154 (2006) 437.
- [11] M. Watanabe, H. Igarashi, H. Uchida, F. Hirasawa, J. Electroanal. Chem. 399 (1995) 239.
- [12] F.N. Büchi, G.G. Scherer, J. Electrochem. Soc. 148 (2001) A183.
- [13] R.J. Bellows, M.Y. Lin, M. Arif, A.K. Thompson, D. Jacobson, J. Electrochem. Soc. 146 (1999) 1099.
- [14] P. Lindner, T. Zemb, in: P. Lindner, T. Zemb (Eds.), Neutron, X-rays and Light Scattering: Introduction to an Investigate Tool for Colloidal and Polymeric Systems, Elsevier, North Holland, 1991.
- [15] K.W. Fiendel, L.P.-A. LaRocque, D. Starke, S.H. Bergens, R.E. Wasylshen, J. Am. Chem. Soc. 126 (2004) 11436.
- [16] S. Tsushima, K. Teranishi, S. Hirai, Electrochem. Solid-State Lett. 7 (2004) A269.
- [17] H. Matic, A. Lundblad, G. Lindbergh, P. Jacobsson, Electrochem. Solid State Lett. 8 (2005) A5.
- [18] B. Dreyfus, G. Gebel, P. Aldebert, M. Pineri, M. Escoubes, M. Thomas, J. Phys. Fr. 51 (1990) 1341.
- [19] R. Mosdale, G. Gebel, M. Pineri, J. Membr. Sci. 118 (1996) 269.
- [20] L. Rubatat, A.-L. Rollet, G. Gebel, O. Diat, Macromolecules 35 (2002) 4050.
- [21] M. Thomas, M. Escoubes, M. Pineri, J. Membr. Sci. 46 (1989) 57.
- [22] A.-L. Rollet, G. Gebel, J.-P. Simonin, P. Turq, J. Polym. Sci.: Polym. Phys. 39 (2001) 548.