Experimental report 02-01 838_Water management operated at elevated temperature studied in-situ and operando by SAXS

1 Introduction

Reducing human related greenhouse effect is one of the challenges of our modern societies. In this context, efficient ways to convert energy from a non-carbon based fuel into electrical power is essential. Fuel cells represent on of the most promising technologies for automotive and small portable electronics applications. Because of their low operation temperature, high efficiency and moderate cost, Proton Exchange Membrane Fuel cells (PEMFC) are one of the most advanced and promising technologies. A central element of these devices is the ionomer membrane, which acts as a proton conductor while electrically insulating anode and cathode. This material should ideally have low resistance to protonic transfer, as well as excellent resistance to chemical and mechanical stress. Particularly, understanding the organization of this material at a nanometric scale and how it relates to macrosocopic characteristics are of upmost importance. In terms of durability and efficiency, two important aspects have to be understood: i) water distribution as a function of the operating conditions, and ii) aging of the cell, i.e. degradation of the ionomer material due to repeated operation cycles. Aspect i) is linked to efficiency since ionomer proton transport properties are dependent on hydration levels. Aspect ii) is related to fuel cell cost, since degradation ultimately results in membrane failure, which has then to be replaced by a new material. Thus, in-situ measurements of this material are required to design and produce more durable and efficient systems.

Operando characterization of water distribution in PEMFCs have been carried out with numerous techniques including NMR [6], confocal Raman microscopy [12], Small Angle Neutron Scattering (SANS) [8, 13], neutron [10] and X-ray [20] imaging. The global conclusion of these studies is that water distribution in a functioning fuel cell is highly heterogeneous, both in-plane and through-plane. This intrinsic heterogeneity of the functioning fuel cell induces an aging process which in turn is also heterogeneous [4]. Although aging potentially impacts all the materials composing the fuel cell (current collecting plates [22], gas diffusion layers [18], catalyst layers [23] or the ionomer membrane [11]) can suffer from degradation, catastrophic failure of the cell is often a result of membrane failure [3]. In-situ membrane degradation is a result of both chemical corrosion of the polymer, as well as introduction of cation pollutants in the ionic groups. These effects cause changes in the structural integrity of the polymer spanning lengthscales from around 10Å(average distance separating ionic domains) to a few 100Å(size of the polymer bundles). In this context, the large Q-range and high brilliance of SAXS beamlines allows to measure all of these effects in a single measurement, and is thus well adapted for in situ measurements, where structural evolutions can occur in timescales of over 1s [16]. In this document, we report the first attempt at observing in-situ the effects of aging on the large scale organization of the polymer, and how this impacts the swelling properties of the membrane. Since MEA aging is heterogeneous, the membrane was probe at three different representative positions, with a specially designed cell (fig. 6).

2 Materials and Methods

2.1 Fuel cells and experimental conditions

The single serpentine single cells were made of gold coated aluminum. For the X-ray experiment, the metallic gasket was drilled and replaced by x-ray transparent beryllium windows at 3 different

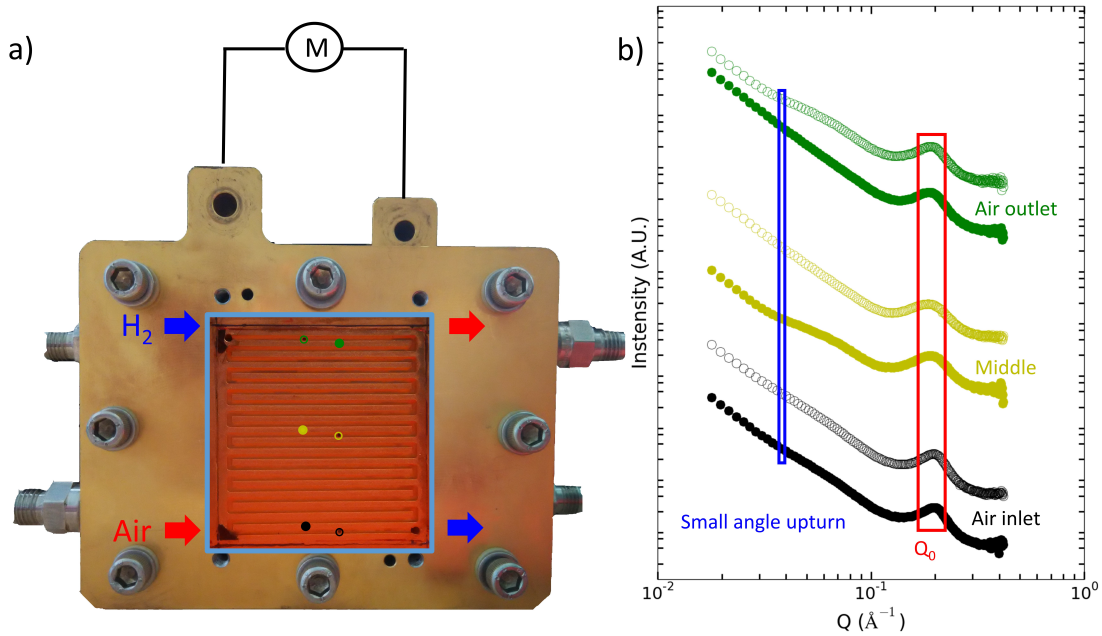


Figure 1 – Experimental principle: a) Photography of the SAXS designed cell, with a picture of the single serpentine gas flow channel in the middle. The colored rectangles highlight the probed zones. b)Example of reference SAXS spectra collected at 80% humidity, with the ionomer peak position Q_0 and small angle scattering upturn highlighted. Filled circles represent measurements made in front of the rib, while open circles were made in front of the channel. The curves are translated in the y-axis for illustration purposes.

representative positions (air inlet, middle, and air outlet), in front of the current collecting rib and the gas flow channel (Fig 6a). This makes a total of 6 different positions that can be probed. In order to not overwhelm the membrane signal by the strongly scattering Gas Diffusion Layer (GDL) and Catalyst Layer (CL), the MEA was stripped of these components at the probed locations.

2.2 Experimental conditions

The single serpentine cell was operated in counter-flow configuration, with H_2 as fuel and air as oxydant Different conditions have been investigated: 80°C_1,5 bars_50 % HR, 90°C_1,2 bars_68/46 % HR, 105°C _1,2 bars_40/26 % HR, 90°C_1,5 bars_70/70 % HR, 105°C_1,85 bars_70/70 % HR.

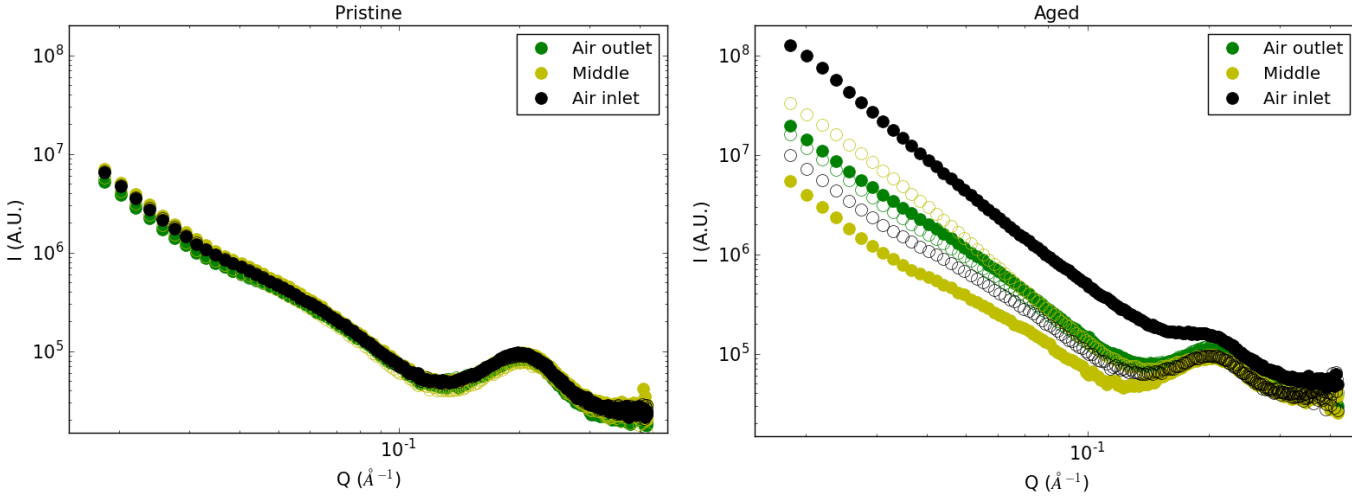
2.3 SAXS

SAXS data were collected on the D2AM/BM2 beamline at the ESRF (Grenoble, France). After radial integration and empty cell subtraction, scattering angles were converted to wavevector transfer Q by using a calibrated scattering pattern (BeAg standard). The ionomer peak and the small angle scattering upturn were determined by using the procedure of Maccarini et al.: the data was fitted with a sum of 2 gaussian functions (one for the ionomer peak and one for the matrix peak) and a background. The Q_0 value was extracted from the position of the gaussian corresponding to the ionomer peak. The small angle scattering upturn is determined by the intensity at a fixed Q-value of Q = 0.04 $Å^{-1}$. The MEA consisted of a Nafion XL membrane and two home-made gas diffusion electrodes made of Gas Diffusion Layer from SGL Sigracet 24BC with PtRu/C at the Anode and PtCo/C at the cathode. Two similar MEA have been studied in two different cells with exactly the same design. The first MEA have been characterised after break-in at 80°C_1,5 bars_50 % HR for 16 hours. The second one has been aged at 90°C_1,2 bars_68/46 % HR during roughly 700 hours after break-in, and then characterised by SAXS.

3 Results and Discussion

3.1 'Ex-situ' aging characterization

Quantification of aging effects on swelling properties of the membrane was carried out by measuring SAXS spectra for each MEA position at imposed relative humidity conditions. Spectra taken at a particular relative humidity value for aged and pristine membrane is shown in fig. 2. While the pristine membrane is highly homogeneous, spectacular differences are observed for the aged sample, highlighting heterogeneous aging. This result is in accordance with previously published ex-situ data, where it was observed that the most significant effects of aging were observed at the air inlet [15]. This is due to operating conditions (counter-flow gas delivery and high temperature), which create a water concentration gradient within the cell during operation [17]. This causes the regions far from the air outlet to encounter greater amounts of liquid water, especially in front of the current collecting ribs [5] causing a slow polymer backbone relaxation observed in kinetic experiments [9, 1].



(a) (b)

Figure 2 – SAXS spectra for all three positions in front of a channel (open symbols) or in front of a rib (closed symbols) for a pristine (a) and an aged (b) membrane.Recorded at 90°C_1,2 bars_68/46 % HR

To quantify the effects of aging, we follow the approach taken in Maccarini et al. [15], which consists of extracting two parameters from the data in a 'model free approach'. The first parameter is the d-spacing, which is obtained from the position of the ionomer peak, is a marker of the microscopic swelling properties of the membrane at a small scale [19, 21]). The second parameter is the intensity at low Q (ILQ) reflecting the large scale organization of the polymer. The values of these 2 parameters at different hydration levels (50,60,70,80,90,100 % relative humidity) are shown in figure 3. Substantial differences are observed in the absolute value of these parameters which are shifted both in d-spacing and ILQ with the position, reflecting the heterogeneous nature of in-situ membrane aging. Interestingly, systematic discrepancies between ribs and channels are observed, and they increase when we get further away from the air inlet, being minimal near the air outlet. Indeed, it has been shown that i) liquid water tends to accumulate under the current collecting ribs [5] and ii) the grtadient in water content in an operating cell goes from the air inlet (most hydrated) to the air outlet (less hydrated) [17]. Hence these two parameters reflect the water distribution in the operating cell, meaning that water distribution could be a driving force in membrane degradation. We also observe a linear relationship between the value of the d-spacing and the intensity at low Q, showing that microscopic swelling impacts the long range organization of the polymer. Interestingly, at high humidity conditions, the d-spacing shows a dramatic increase at the air air inlet rib. This overswelling effect, which has been onserved ex-situ membranes aged in a stack [15], is substantially different than hygrothermal aging, which causes a slight decrease

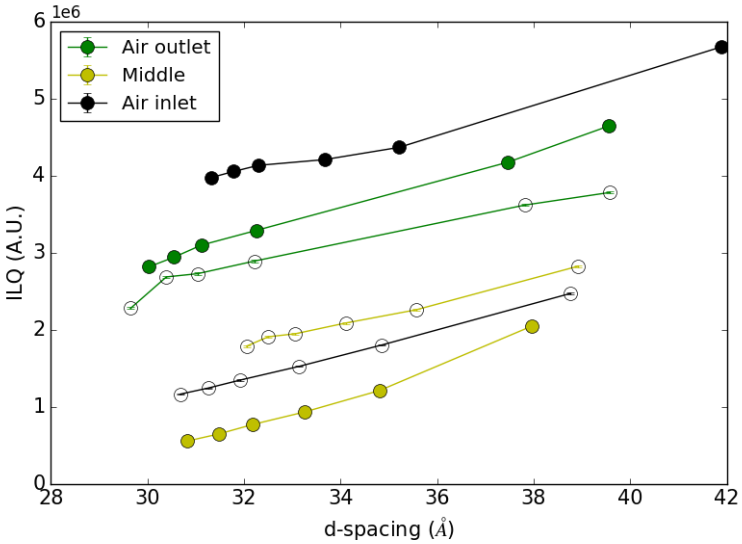


Figure 3 – Intensity at low Q (ILQ) as a function of d-spacing. The filled circles rebresent current collecting ribs, the open symbols gas flow channels.

in microscopic swelling [2] or cationic pollution, which tends to hinder swelling properties both microscopically [14] and macroscopically [7].

3.2 In-situ measurements

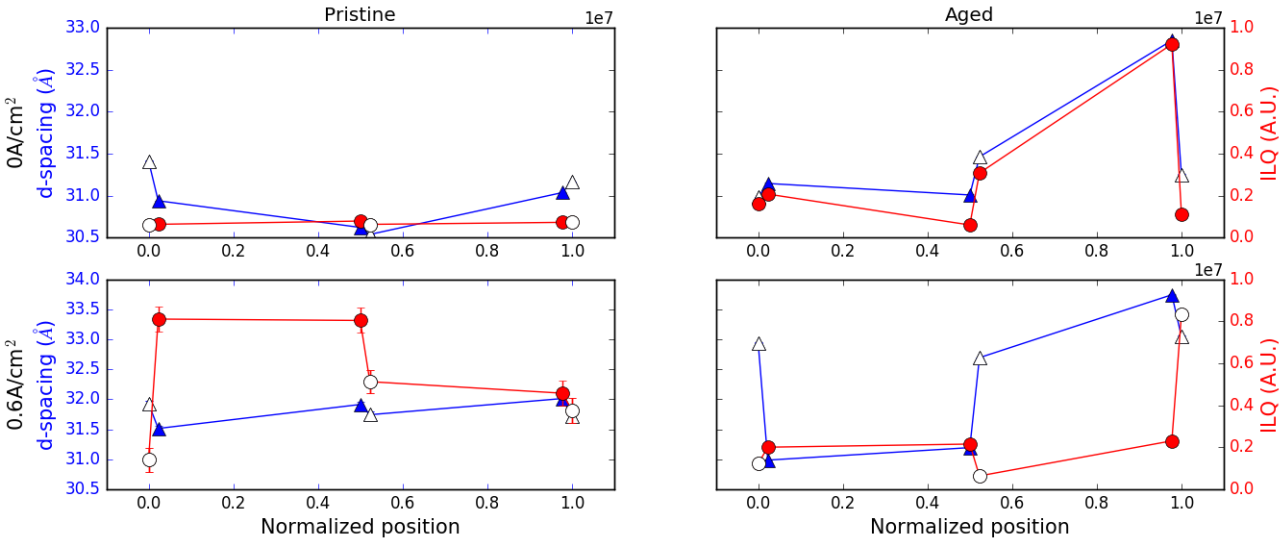


Figure 4 – d-spacing (blue triangles) and Intensity at low Q (red circles) at OCV (top), and 0.6 A/cm^2 (bottom) as a function of the position (0 being the air outlet, 1 the air inlet), for the pristine (left) and aged (right) membranes. Hollow symbols represent channels, full symbols ribs.

Quantification of the structural effects of aging in situ was evaluated by measuring both the d-spacing and ILQ as a function of the relative position without and with current (fig 4). At OCV, since no current is drawn from the cell, these two parameters behave exactly like a situation where the membrane is equilibrated at an equivalent relative humidity: similarly to observation made in reference spectra, the pristine membrane is homogeneous, in contrast to it's aged counterpart which presents large heterogeneities, especially near the air inlet. We also observe a scaling of the ILQ with the d-spacing due to the effect of humidity on the polymer large scale organization, as

described in the previous section.
When current is drawn from the cell, the overall effect on ionomer hydration is minimal for both aged and pristine membranes, as the d-spacing does not dramatically change, although small differences are observed. Nevertheless, a slight shift towards higher values with current is observed in both cases, which is in agreement with measured in-situ SANS data [17].
The small angle upturn, on the other hand, encounters spectacular changes in both cases. In the pristine membrane, we observe that current tends to segregate ribs from channels, as well as. Interestingly, it is much more marked for the small angle upturn, for both aged and pristine cases. Interestingly, the application of current does not drastically change the swelling properties of the membrane in the aged situation, which could mean that unlike the pristine case, swelling behavior is here driven by the history of the membrane, not the application of current. In contrast to the pristine case, The ILQ shows a very peculiar behavior: indeed, the scaling property with membrane hydration is broken, as we observe a discrepancy between since the ILQ values follow the opposite trend of the d-spacing, thus breaking the relationship between ILQ and d-spacing. This peculiar behavior is thus a signature of the effect of proton transport through an aged ionomer large scale organization.
Since ILQ is dependent on the d-spacing (and in turn, to local hydration conditions [17, 16]), it is difficult, to separate the effect of current on the large scale organization of the polymer from in-plane hydration inhomogeneities. In order to overcome this issue, we further propose a normalized ILQ, which can be obtained by dividing the measured ILQ by a reference ILQ. This reference value can simply be obtained by transforming the measured d-spacing into an ILQ reference by exploiting the linear relationship between ILQ and d-spacing that is measured in the reference curves (fig. 3).

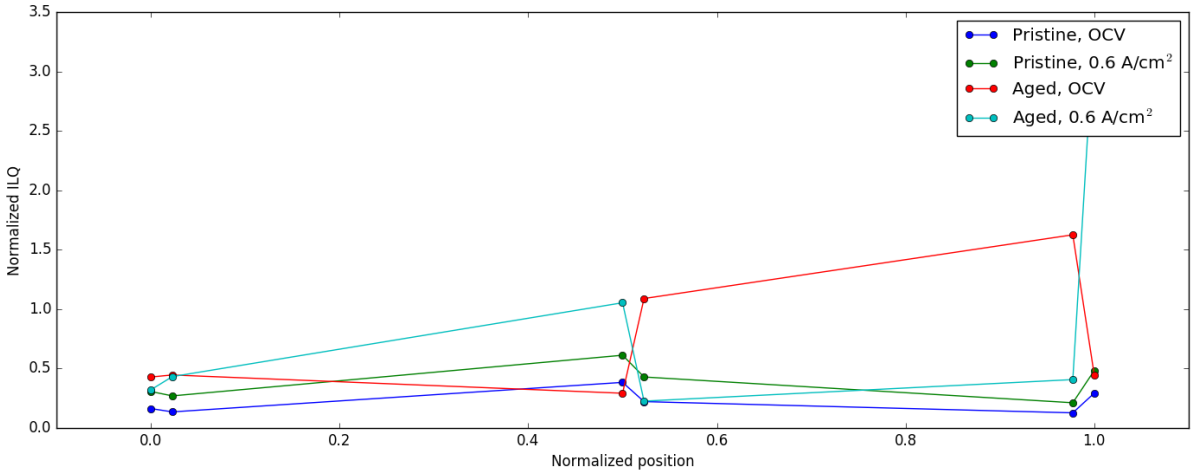


Figure 5 – Normalized ILQs

4 Kinetics

We have been able to record the evolution of the ionomer peak position and small angle upturn during change in current with a time resolution of 5s (fig.5). We have shown that the membrane reacts within less than one minute. The water content increases in the membrane when current goes from 0 to 0.1 A/cm^2.

References

[1] G Alberti, R Narducci, and M Sganappa. Effects of hydrothermal/thermal treatments on the water-uptake of nafion membranes and relations with changes of conformation, counter-elastic force and tensile modulus of the matrix. *Journal of Power Sources*, 178(2):575–583, 2008.

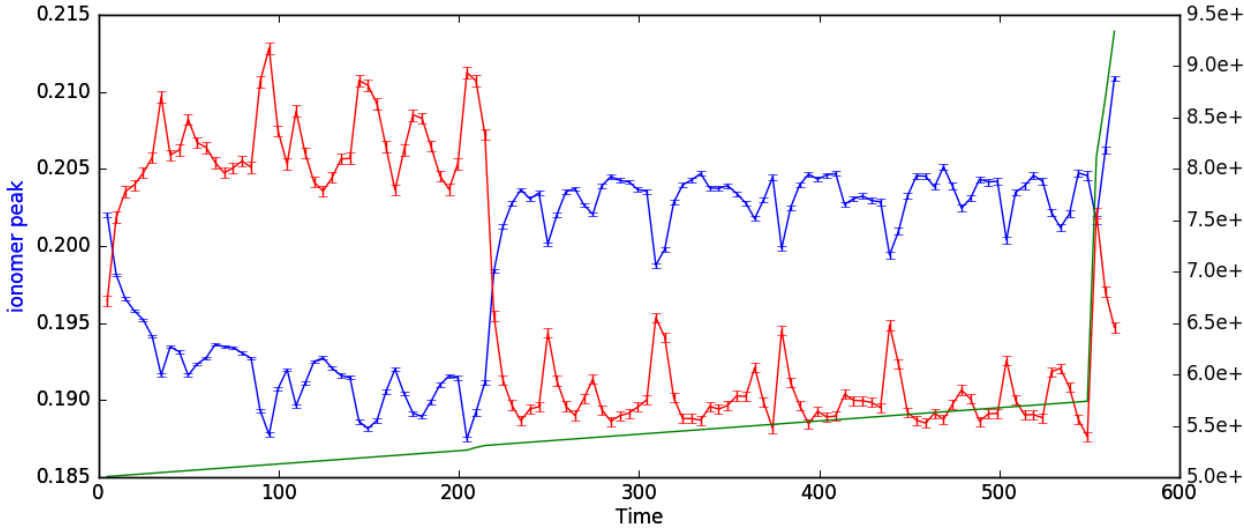


Figure 6 – Evolution of ionomer peak position and small angle scattering upturn during change in current from 0 to 0.1 A/cm^2

[2] Floraine M Collette, Francette Thominette, Hakima Mendil-Jakani, and Gérard Gebel. Structure and transport properties of solution-cast nafion® membranes subjected to hygrothermal aging. *Journal of membrane science*, 435:242–252, 2013.

[3] G De Moor, C Bas, N Charvin, E Moukheiber, F Niepceron, N Breilly, J André, E Rossinot, E Claude, ND Albérola, et al. Understanding membrane failure in pemfc: comparison of diagnostic tools at different observation scales. *Fuel Cells*, 12(3):356–364, 2012.

[4] Laetitia Dubau, Luis Castanheira, Frédéric Maillard, Marian Chatenet, Olivier Lottin, Gaël Maranzana, Jérôme Dillet, Adrien Lamibrac, Jean-Christophe Perrin, Eddy Moukheiber, et al. A review of pem fuel cell durability: materials degradation, local heterogeneities of aging and possible mitigation strategies. *Wiley Interdisciplinary Reviews: Energy and Environment*, 3(6):540–560, 2014.

[5] Joseph D Fairweather, Dusan Spernjak, Adam Z Weber, David Harvey, Silvia Wessel, Daniel S Hussey, David L Jacobson, Kateryna Artyushkova, Rangachary Mukundan, and Rodney L Borup. Effects of cathode corrosion on through-plane water transport in proton exchange membrane fuel cells. *Journal of The Electrochemical Society*, 160(9):F980–F993, 2013.

[6] Kirk W Feindel, Logan P-A LaRocque, Dieter Starke, Steven H Bergens, and Roderick E Wasylishen. In situ observations of water production and distribution in an operating h2/o2 pem fuel cell assembly using 1h nmr microscopy. *Journal of the American Chemical Society*, 126(37):11436–11437, 2004.

[7] Gerard Gebel, Pierre Aldebert, and Michel Pineri. Structure and related properties of solution-cast perfluorosulfonated ionomer films. *Macromolecules*, 20(6):1425–1428, 1987.

[8] Gérard Gebel, Olivier Diat, Sylvie Escribano, and Renaut Mosdale. Water profile determination in a running pemfc by small-angle neutron scattering. *Journal of Power Sources*, 179(1):132–139, 2008.

[9] Gérard Gebel, Sandrine Lyonnard, Hakima Mendil-Jakani, and Arnaud Morin. The kinetics of water sorption in nafion membranes: a small-angle neutron scattering study. *Journal of Physics: Condensed Matter*, 23(23):234107, 2011.

[10] AB Geiger, A Tsukada, E Lehmann, P Vontobel, A Wokaun, and GG Scherer. In situ investigation of two-phase flow patterns in flow fields of pefcs using neutron radiography. *Fuel Cells*, 2(2):92–98, 2002.

[11] J Healy, C Hayden, T Xie, K Olson, R Waldo, M Brundage, H Gasteiger, and J Abbott. Aspects of the chemical degradation of pfsa ionomers used in pem fuel cells. *Fuel cells*, 5(2):302–308, 2005.

[12] P Huguet, A Morin, G Gebel, S Deabate, AK Sutor, and Z Peng. In situ analysis of water management in operating fuel cells by confocal raman spectroscopy. *Electrochemistry Communications*, 13(5):418–422, 2011.

[13] H Iwase, S Koizumi, H Iikura, M Matsubayashi, D Yamaguchi, Y Maekawa, and T Hashimoto. A combined method of small-angle neutron scattering and neutron radiography to visualize water in an operating fuel cell over a wide length scale from nano to millimeter. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 605(1):95–98, 2009.

[14] Benoit Loppinet, Gérard Gebel, and Claudine E Williams. Small-angle scattering study of perfluorosulfonated ionomer solutions. *The Journal of Physical Chemistry B*, 101(10):1884–1892, 1997.

[15] Marco Maccarini, Sandrine Lyonnard, Arnaud Morin, Jean Francois Blachot, Emanuela Di Cola, Govind Prajapati, Michael Reynolds, and Gérard Gebel. Submicrometer 3d structural evidence of fuel cell membrane heterogeneous degradation. *ACS Macro Letters*, 3(8):778–783, 2014.

[16] N Martinez, Z Peng, A Morin, L Porcar, G Gebel, and S Lyonnard. Real time monitoring of water distribution in an operando fuel cell during transient states. *Journal of Power Sources*, 365:230–234, 2017.

[17] A Morin, G Gebel, L Porcar, Z Peng, N Martinez, A Guillermo, and S Lyonnard. Quantitative multi-scale operando diagnosis of water localization inside a fuel cell. *Journal of The Electrochemical Society*, 164(2):F9–F21, 2017.

[18] Carl A Reiser, Lawrence Bregoli, Timothy W Patterson, S Yi Jung, J Deliang Yang, Mike L Perry, and Thomas D Jarvi. A reverse-current decay mechanism for fuel cells. *Electrochemical and Solid-State Letters*, 8(6):A273–A276, 2005.

[19] Laurent Rubatat, Anne Laure Rollet, Gérard Gebel, and Olivier Diat. Evidence of elongated polymeric aggregates in nafion. *Macromolecules*, 35(10):4050–4055, 2002.

[20] Takashi Sasabe, Shohji Tsushima, and Shuichiro Hirai. In-situ visualization of liquid water in an operating pemfc by soft x-ray radiography. *International Journal of Hydrogen Energy*, 35(20):11119–11128, 2010.

[21] Klaus Schmidt-Rohr and Qiang Chen. Parallel cylindrical water nanochannels in nafion fuel-cell membranes. *Nature materials*, 7(1):75–83, 2008.

[22] H Tawfik, Y Hung, and D Mahajan. Metal bipolar plates for pem fuel cell—a review. *Journal of Power Sources*, 163(2):755–767, 2007.

[23] Shengsheng Zhang, Xiao-Zi Yuan, Jason Ng Cheng Hin, Haijiang Wang, K Andreas Friedrich, and Mathias Schulze. A review of platinum-based catalyst layer degradation in proton exchange membrane fuel cells. *Journal of Power Sources*, 194(2):588–600, 2009.