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1 **Detailed catalyst layer structure of Proton Exchange Membrane Fuel Cell from contrast**  
2 **variation small-angle neutron scattering**

3  
4 Florian Chabot<sup>a</sup>, Jongmin Lee<sup>a</sup>, Florent Vandenberghe<sup>a</sup>, Laure Guétaz<sup>a</sup>, Gérard Gebel<sup>a</sup>,  
5 Sandrine Lyonnard<sup>c</sup>, Lionel Porcar<sup>b</sup>, Sebastien Rosini<sup>a</sup>, Arnaud Morin<sup>a\*</sup>

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7 <sup>a</sup>Univ. Grenoble Alpes, CEA, Liten, DEHT, 38000 Grenoble, France

8 <sup>b</sup>Institut Max Von Laue-Paul Langevin (ILL), 71 Avenue des Martyrs, 38042 Grenoble,  
9 France

10 <sup>c</sup>Univ. Grenoble Alpes, CEA, CNRS, IRIG, SyMMES, 38000 Grenoble, France

11  
12 \*Email: arnaud.morin@cea.fr

13  
14 Keywords: PEMFC, protonic conductor, ionomer, SANS, catalyst, electrode, water

15  
16 **Abstract :**

17 Despite significant decrease in past decades, the cost of Proton Exchange Membrane Fuel Cell  
18 (PEMFC), largely due to the rare and expensive electro-catalyst made of platinum, restrains its  
19 massive deployment. Therefore, reducing the platinum content in the electrode is the keystone  
20 of intense research efforts to increase catalyst activity or utilisation. Catalyst layer structure,  
21 and especially the water and ionomer distributions, rule the active sites availability for  
22 electrochemical reactions, and thus catalyst utilisation, because of their influence on the  
23 transport of protons and oxygen. However, the rational design of more efficient electrodes faces  
24 the lack of accurate knowledge of its complex nanoporous structure. Specifically, ionomer and  
25 water distribution are very difficult to probe with conventional electron microscopy or X-Ray  
26 techniques. This work provides quantitative information on electrode structure, regarding  
27 ionomer and water distributions thanks to an extensive analysis of Small Angle Neutron  
28 Scattering (SANS) profiles at different relative humidity (RH) and contrast. A 2 to 3 nm thin  
29 ionomer film spreads around the Pt/C catalyst particles while a condensed water layer appears  
30 at the catalyst/ionomer interface depending on the type of carbon support.

## 1 **1. Introduction**

2 Catalyst layers host electrochemical reactions and drive the overall conversion efficiency of  
3 Proton Exchange Membrane Fuel Cell (PEMFC). The best state-of-the-art catalyst layer is a  
4 complex porous nanostructured material (often referred to as electrode) allowing the transport  
5 of gaseous reactants, protons and electrons, as well as heat and water generated during the  
6 electrochemical reactions. It is made of platinum (Pt) nanoparticles (2-5 nm), bearing the electro  
7 catalytic sites supported on carbon particles, of approximate size around 10 to 40 nm, ensuring  
8 the electronic conductivity. These Pt/Carbon catalyst particles agglomerate to create a porous  
9 network, covered by a proton conducting polymer[1] which forms either thin film coating,  
10 typically from 5 to 20 nm[2], either agglomerates larger than 150 nm. The latter partially fills  
11 the pores[3].

12 This proton conducting polymer is also called “ionomer”. Along with water, it plays a crucial  
13 role in the catalyst layer operation by transporting protons between the membrane and the active  
14 sites, a process that directly depends on hydration[4]. However, by filling the pores, the ionomer  
15 decreases reactive gases diffusivity inside the catalyst layer.[5,6] Moreover, by coating the  
16 catalyst, it may act as a barrier for reactants to reach active sites[7–9] and, additionally, it can  
17 specifically adsorb on the active sites, therefore blocking the electrochemical reaction[8]. All  
18 these phenomena can dramatically impact fuel cell operation, especially at the cathode side  
19 where slow Oxygen Reduction Reaction (ORR) kinetics and low oxygen diffusion coefficient  
20 are the two major causes of performance losses[9–11]. Because transport and reaction kinetic  
21 limiting phenomena are coupled, the operation in the catalyst layer is heterogeneous, and the  
22 current is mostly produced by only a small fraction of the catalyst layer volume[12,13]. To  
23 summarize, increasing ionomer content enhances protonic conductivity while decreasing  
24 oxygen diffusivity, thus optimizing its incorporation is critical to improve fuel cell  
25 performances.

26 The state-of-the-art proton conductor used in PEMFC catalyst layers is a perfluorinated sulfonic  
27 acid (PFSA) ionomer. PFSA membranes have been extensively studied in past decades[4,14–  
28 17]. The general chemical structure of PFSA is presented in **Figure S1** in the Supporting  
29 Information. The ionomer is composed of two parts: the perfluorinated hydrophobic polymer  
30 backbone and the pendent side-chains ending with hydrophilic sulfonic acid groups ( $\text{SO}_3^-$ ). As  
31 illustrated in **Figure 1-a**, the combined presence of both highly hydrophobic and hydrophilic  
32 groups leads to nano phase separation between the polymer and the aqueous phase in which  
33 proton transport occurs[18]. The aggregation of polymer backbones induces flat lamella-like

1 structures with an average thickness estimated around 2.7 nm[15] for Nafion<sup>®</sup> membrane. These  
2 lamellae are roughly stacked together in parallel within certain local ordering to form randomly  
3 oriented bundles of hundred of nanometers. It is well known that water uptake, proton  
4 conductivity and oxygen permeability of the ionomer are closely related to its chemical  
5 structure[19]. Specifically, the different PFSA structures are defined through their Equivalent  
6 Weight (EW) as summarized by Kusoglu *et* Weber[18].

7 The behavior and properties of bulk ionomer membranes are well known whereas the role and  
8 state of ionomer inside catalyst layers have been under-evaluated until recently. It has been  
9 demonstrated that ionomer thin films (<50 nm) do not exhibit the same properties as bulk  
10 material[19]. Indeed, the ionomer thin film conductivity and dioxygen permeability are lower  
11 than for membrane[9,19–22] due to the ionomer structural reorganization occurring in the  
12 vicinity of the substrate material described by Woo *et al.*[23], depends on the substrate  
13 material[24]. Even though *ex-situ* characterizations on model flat substrates bring valuable  
14 information on the structure and properties of ionomer thin films, they are most probably not  
15 representative to the actual state in a catalyst layer. Indeed, there are too few *in situ* structural  
16 studies on the ionomer to have a clear understanding of its structure and properties inside the  
17 catalyst layer, especially upon hydration. Thereby, additional *in-situ* characterization are  
18 essential to link the ionomer structure to fuel cell performance. In this objective, several authors  
19 have developed techniques to characterize the ionomer distribution inside catalyst layers by  
20 transmission electron microscopy (TEM) tomography[1] or atomic force microscopy (AFM)[3].

21 Another valuable technique used in the past years to study catalyst layer structure is small angle  
22 scattering (SAS). Myers *et al.*[25] used small angle X-Ray scattering (SAXS) to study the  
23 platinum nanoparticles sizes distribution, taking advantage of the strong interactions between  
24 X-rays and heavy elements. However, it is difficult to extract the ionomer structure from 1D  
25 SAXS profiles because the ionomer contribution to the scattering intensity is very low as  
26 compared to platinum signal. In contrast to X-Rays, neutrons are sensitive to nuclei and the  
27 scattering contribution from platinum is negligible in comparison to carbon and ionomer  
28 contributions. Hence, Small Angle Neutron Scattering (SANS) appears as the best technique to  
29 study the ionomer structure inside catalyst layers. Koizumi *et al.*[26] performed *ex-situ*  
30 characterizations of electrodes by SANS. More recently, Lee *et al.*[27] used SANS to relate  
31 fuel cell operation with the ionomer hydration in a real operating electrode. In addition, Harada  
32 and co-workers used contrast variation to study ionomer adsorption at the catalyst surface  
33 within inks[28,29] and electrodes[30]. However, despite these studies, there is still no

1 straightforward method to unravel the water dependent catalyst layer structure from 1D SANS  
2 profiles due to complex multiscale heterogeneous structures.

3 In this work, we propose 1D SANS profiles analysis highlighting structural information on  
4 catalyst layer, and specifically on the distribution of the ionomer and water, as a function of  
5 relative humidity and using contrast variation. The method was applied to study the influence  
6 of the electrode manufacturing process and the type of carbon support, e.g. Vulcan or High  
7 Specific Area (HSA), on the ionomer structure and water distribution on two electrodes made  
8 from Nafion® (1000 EW) and 50% weight Platinum over Carbon catalyst (Pt/C). The *ex-situ*  
9 method is applicable to a wide range of catalyst layer composition and provides invaluable  
10 insights into nanoscale electrode structure-to-device operation relationship in PEMFC.

11

## 12 **2. Experimental**

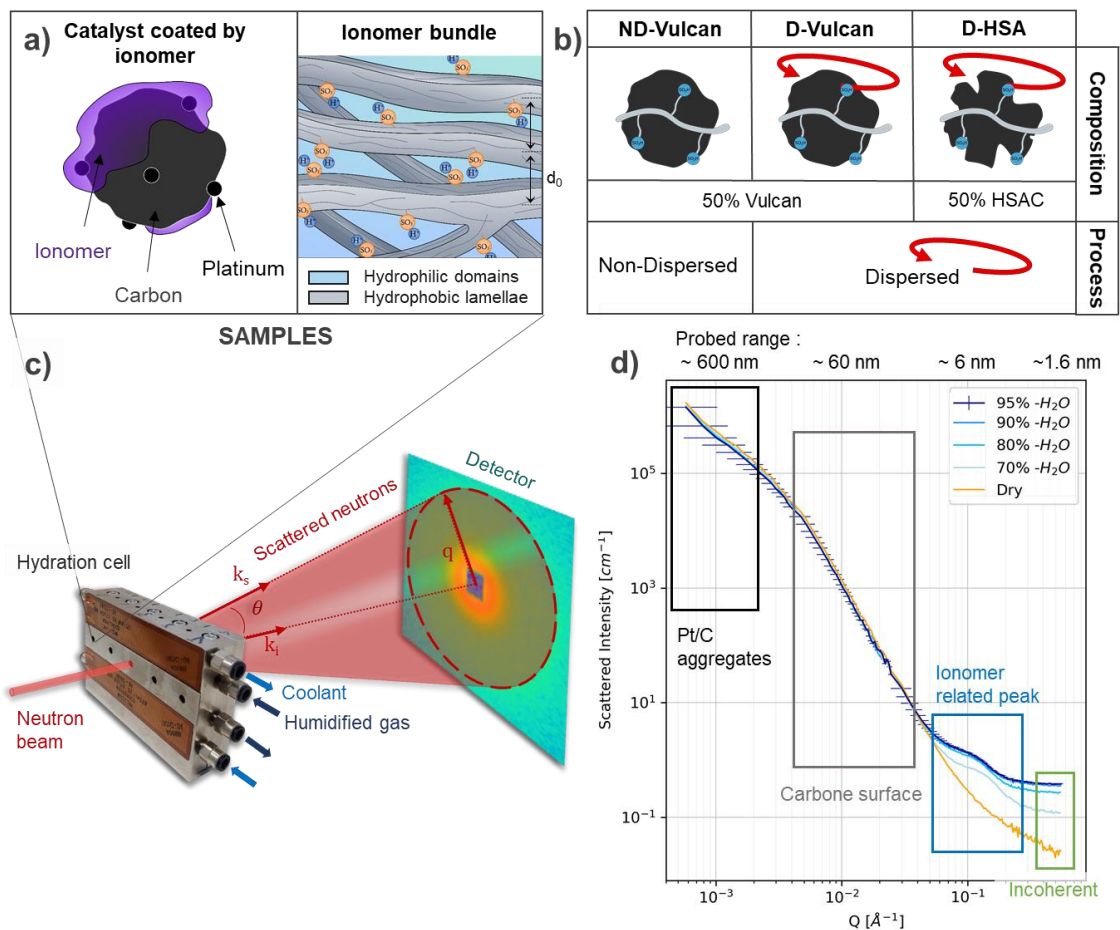
### 13 **2.1. Samples specifications**

14 Three types of electrodes were manufactured in order to study the influence of the dispersion  
15 process and the type of carbon support on the structure of the catalyst layer, and more  
16 specifically, the ionomer dispersion, structure and swelling behavior. Electrodes did not operate,  
17 thus they should be either cathode or anode.

18 ND- Vulcan (ND for Non Dispersed): the ink was prepared using 50% weight platinum  
19 supported on Vulcan carbon (TEC10V50E from Tanaka) with Nafion® D2020  
20 (EW = 1000 g.molSO<sub>3</sub><sup>-1</sup>) dispersion provided by Dupont DeNemours. The ink dry content was  
21 17% weight. Water is added first on the catalyst powder, then the ionomer dispersion and finally  
22 pure ethanol. Ionomer dispersion solvent is a water/2-propanol mixture (20/75%). The ink was  
23 then left twenty-four hours under magnetic stirring. Then, it was deposited onto a PTFE  
24 substrate using bar coating. Finally, Membrane Electrode Assembly (MEA) was obtained by  
25 hot pressing electrode on N115 membrane at 160°C and 2 MPa for 10 minutes.

26 D- Vulcan (D for Dispersed): the ink was prepared with TEC10V50E and Nafion D2020. In  
27 order to improve the ionomer dispersion compared to the previous ink (ND- Vulcan), the  
28 catalyst was first dispersed into a mixture of Diacetone Alcohol (DAA) and ultrapure water.  
29 Then, the Nafion dispersion was added. The catalyst ink was mixed before and after ionomer  
30 addition with a planetary mixer (Kurabo). Next, the ink was stirred with milling balls onto a  
31 roller mixer for 24 hours, before being sprayed onto a PTFE sheet. The ink dry matter content  
32 was 2% weight.

1 D- HSA - supplied: MEA was manufactured and provided by Toyota Motor Europe (TME) in  
2 the frame of the European project Further-FC[31]. The ink was prepared from Nafion D2020  
3 and TEC10E50E catalyst from Tanaka, which is a catalyst with 50% weight platinum supported  
4 on High Specific Area (HSA) carbon. Catalyst powder was dispersed into ultrapure water and  
5 then mixed with a planetary mixer. Next, the ink was mixed again after adding Nafion and DAA.  
6 The dry matter content was 10% weight. The catalyst layer was prepared by bar coating a PTFE  
7 substrate and then transferred by hot pressing on a NC700 membrane from Dupont DeNemours.  
8 **Table S1** gives more details on samples composition and manufacturing. Schemes on **Figure**  
9 **1-b** represents main samples features. Two main characteristics differentiate the electrodes: first,  
10 the improved dispersion process used for “Dispersed (D)” catalyst inks, represented by the red  
11 arrow, and second, the type of carbon support that is represented by a smooth sphere for Vulcan  
12 and by a spherical particle with a rough surface for the HSA nanoporous particles. In the  
13 following, those schemes will be used in figures as a guide to distinguish electrodes called  
14 ND- Vulcan (Non-dispersed), D- Vulcan (Dispersed) and D- HSA (Dispersed). Thus, in the  
15 following, on the one hand, comparison of D- Vulcan and ND- Vulcan electrodes exhibits  
16 structural evolutions induced by the manufacturing process, while, on the other hand, D- Vulcan  
17 and D- HSA electrodes comparison shows the carbon support key role for the electrode  
18 structure.



1  
 2 **Figure 1.** a) Schematic representation of structures probed with SANS; electrode building block  
 3 made from Pt/Carbon aggregates covered with thin ionomer films; Ionomer bundles present in  
 4 bulk membrane or in the large aggregates ( $\sim 150$  nm) with nano phase separation between  
 5 hydrophobic and hydrophilic domains. b) Main characteristics of the three electrodes studied  
 6 with their associated schemes representing the type of carbon support, the ionomer and the use  
 7 of improved dispersion process (red arrow). c) Illustration of the experimental set-up for in-situ  
 8 acquisition of 1D SANS profiles of catalyst layers and membranes.  $\vec{k}_i$  being the neutrons  
 9 incident wave vector,  $\vec{k}_s$  the scattered neutrons wave vector and  $\vec{q}$  the scattering vector. d) 1D  
 10 SANS profiles of ND- Vulcan electrode for several relative humidity and characteristic sizes of  
 11 probed structures. Measurements errors on intensity and angles ( $Q$ ) are represented only on the  
 12 first SANS profile.

## 13 2.2. SANS Technique

14 Small angle neutron scattering (SANS) probes structures with characteristic sizes from the  
 15 nanometer to the micron. Collimated neutrons beam scatters at specific angles values after  
 16 interacting with a sample. Scattered neutrons intensity is proportional to the volume fraction of

1 particles within the sample and to the contrast factor between the particle and the surrounding  
 2 medium, squared. Contrast factor is the difference between two materials in Scattering Length  
 3 Density (SLD), which is an intrinsic property. In the present case, the SLD of the flowing gas  
 4 was controlled by the level of deuteration present in the water solvent controlling the gas  
 5 humidity. As presented in **Figure 1-c**, a flat 2D detector collects scattered neutrons intensities  
 6 at a defined distance from the sample. Then, for isotropic materials, azimuthal scattered  
 7 intensities averaging leads to 1D SANS profile. It is a plot of the average scattered intensity as  
 8 a function of the modulus of the scattering vector  $q$  (in  $\text{\AA}^{-1}$ ) related to the scattering angle  $\theta$  and  
 9  $\lambda$  the incident neutrons wavelength in  $\text{\AA}$  through Equation 1.

$$10 \quad q = \frac{4\pi \cdot \sin(\theta/2)}{\lambda} \quad (1)$$

11 **Figure 1- d** presents typical 1D SANS profiles from ND- Vulcan electrode for different relative  
 12 humidity conditions. In our experimental configuration, 1D SANS profiles probe structures  
 13 ranging from almost 1 nm to roughly 500 nm and exhibit four significantly distinct regions that  
 14 give different structural information as presented by the **Table 1**. As shown by the calculated  
 15 probed range on the top y-axis of the plot, large structures scatter at low  $q$  values whereas small  
 16 ones scatter at high  $q$  values. In our samples, the platinum volume fraction is estimated to be  
 17 around 4% and its scattering length density ( $\rho = 6.3 \cdot 10^{-6} \text{\AA}^{-2}$ ) is close to the SLD of carbon ( $\rho$   
 18  $= 6.7 \cdot 10^{-6} \text{\AA}^{-2}$ ). Thus, we consider the platinum contribution to the SANS profile cannot be  
 19 distinguished from that of carbon, and is even negligible. For SANS experiments on powder  
 20 (as the catalyst layer), the solvent is the air hydrated either with  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$ .

21 **Table 1.** Description of information obtained from a SANS profile of catalyst layer at  
 22 different  $q$  ranges.

$q$ range [ $\text{\AA}^{-1}$ ]	Materials and structures probed
$q < 5 \cdot 10^{-3}$	Profiles give information on the large Pt/Carbon catalyst aggregates structure.
$5 \cdot 10^{-3} < q < 5 \cdot 10^{-2}$	The intensity decreases as a $q^{-n}$ function, with $n$ a value around 4 related to the carbon surface and its roughness.
$1 \cdot 10^{-1} < q < 2 \cdot 10^{-1}$	Profiles of hydrated catalyst layers exhibit a peak of a well-defined structure of few nanometers, which is related to ionomer.
$q > 3.5 \cdot 10^{-1}$	Scattered intensity mainly comes from the incoherent scattering that depends on the sample composition. Due to high incoherent scattering of hydrogen atoms, intensity gives information on the total hydration level of the sample.

23



1 In the following, SANS profiles are corrected from the incoherent scattering. Incoherent  
 2 scattering intensity is measured at  $0,4 \text{ \AA}^{-1}$  and subtracted to the scattering intensity on the whole  
 3 Q range. Hence, SANS profiles evolution with relative humidity or contrast variation would be  
 4 related to sample structure.

5

### 6 **2.3. SANS Setup**

7 SANS experiments[32,33] were performed at the beamline D22[34] of the Institut Laue-  
 8 Langevin (ILL). The catalyst layer was recovered by gently scratching catalyst layer deposit  
 9 with a surgical blade. We checked by electronic microscopy that the surface of the membrane  
 10 was not scratched and that only catalyst layer was collected. However, it is difficult to recover  
 11 the whole catalyst layer thickness, a thin layer remains on the membrane surface. The recovered  
 12 powder was then loaded in a titanium cell without any additional treatment to avoid any  
 13 modification of the nanostructured catalyst layer. The cell, presented in **Figure 1-c**, was  
 14 designed specifically for SANS measurements. It allows to control the temperature and relative  
 15 humidity for five samples in parallel by  $\text{N}_2$  flushing with dew point monitored and controlled  
 16 by a homemade bench. Cell compartments diameter and depth are respectively 3 mm and  
 17  $200\mu\text{m}$ . **Table 2** presents the several SANS configurations used in order to record profiles with  
 18 good resolution when needed and good statistic in a broad q range from  $5.10^{-1}$  to  $5.10^{-4} \text{ \AA}^{-1}$   
 19 characterizing structures ranging from 1 nm to  $1 \mu\text{m}$ . The beam diameter is 3 mm.

20 **Table 2.** Experimental configurations used for 1D SANS profiles acquisition of the three  
 21 electrodes studied.

Configuration	ND- Vulcan electrode		D- Vulcan & ND- HSA electrodes		
	1 <sup>st</sup>	2 <sup>nd</sup>	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>
Wavelength [ $\text{\AA}$ ]	5	5	6	6	11
Sample to Collimator Distance [m]	2	17.6	2.8	17.6	17.6
Sample to Detector Distance [m]	2.8	17.6	3.1	17.6	17.6
Counting Time [min]	2	5	5	5	5

22

### 23 **2.4. SANS correction and reduction**

24 Grasp Software[35] developed by the ILL was used for data correction and reduction as  
 25 presented by Hammouda[36]. Data with were merged between configuration and analyzed. As  
 26 the sample is a powder, the quantity of material inside the 6 mm x  $200 \mu\text{m}$  cavity cannot be

1 determined with accuracy, such that average sample thickness is not really known. As a result,  
 2 profiles cannot be normalized by the material thickness value, which is set to 200  $\mu\text{m}$   
 3 corresponding to the depth of the cavity in which the sample is loaded. Since the total quantity  
 4 of material is not controlled in each cell, the overall scattered intensity differs from one sample  
 5 to another. In order to get rid of the difference in material amount between samples, the  
 6 invariant  $Q_v$  in  $\text{\AA}^{-4}$  for each dry sample was computed following Equation 2. Its value is directly  
 7 proportional to components volume fractions[36].

$$8 \quad Q_v = \frac{1}{2\pi^2} \int_{-\infty}^{+\infty} I(q)q^2 \cdot dq \quad (2)$$

9 Experimentally, the invariant is computed over the  $q$  range of the profiles, so at least on three  
 10 orders of magnitude. Hence, it is assumed that it gives a good approximation of the theoretical  
 11 invariant. Finally, each 1D SANS profile intensities were multiplied by the ratio of their dry  
 12 invariant over one dry sample chosen arbitrary as a reference.

### 13 **2.5. SANS profiles simulation**

14 In the following, ideal core shell sphere models are used to simulate SANS profiles from the  
 15 catalyst layer primary particles. Authors have already used those models to study the  
 16 catalyst/ionomer interaction in catalysts inks[37,38]. Simulation and fitting of experimental  
 17 data were realized with SASView Software[39]. Equation 3 presents the form factor  $P(q)$  in  
 18  $\text{cm}^{-1}$  for a simple core shell model[40] that could be extended to several shells.

$$19 \quad P(q) = \frac{\varphi}{V} \cdot F^2(q) + \textit{background} \quad (3)$$

20 Where,

$$21 \quad F(q) = \frac{3}{V_{s1}} \cdot [ 3V_c(\rho_c - \rho_1) \frac{\sin(q \cdot r_c) - q \cdot r_c \cos(q \cdot r_c)}{(q \cdot r_c)^3} \\ 22 \quad + \sum_1^s 3V_s(\rho_s - \rho_{s+1}) \frac{\sin(q \cdot r_s) - q \cdot r_s \cos(q \cdot r_s)}{(q \cdot r_s)^3} ] \quad (4)$$

23 With  $c$  standing for the core (carbon particle) and  $s$  for the number of shells. Thus,  $r_s$  is the sum  
 24 of the core radius,  $r_c$ , and the shell thickness.  $\varphi$  being the scale factor,  $V$  the volume ( $\text{\AA}^3$ ),  $\rho$  the  
 25 scattering length density ( $\text{\AA}^{-2}$ ) and  $r$  the radius ( $\text{\AA}$ ).  
 26

### 27 **2.6. Transmission electronic microscopy**

28 In order to image the ionomer distribution within the two CLs, the MEA cross-section were  
 29 analyzed by transmission electron microscopy (TEM). For these analyses, the MEA samples

1 were embedded in epoxy resin and thin slices of around 100 nm thick were cut by  
2 ultramicrotomy and deposited on a copper TEM grid. Observations were performed on a FEI-  
3 Themis microscope operated at 200 kV and equipped with probe corrector and X-EDS  
4 spectrometer composed of 4 SiliconDrift Detectors. The fluorine EDS elemental map were  
5 recorded on the two samples using the same experimental conditions (beam intensity, pixel size,  
6 acquisition time) in order to expose the sample to the same electron dose[41].

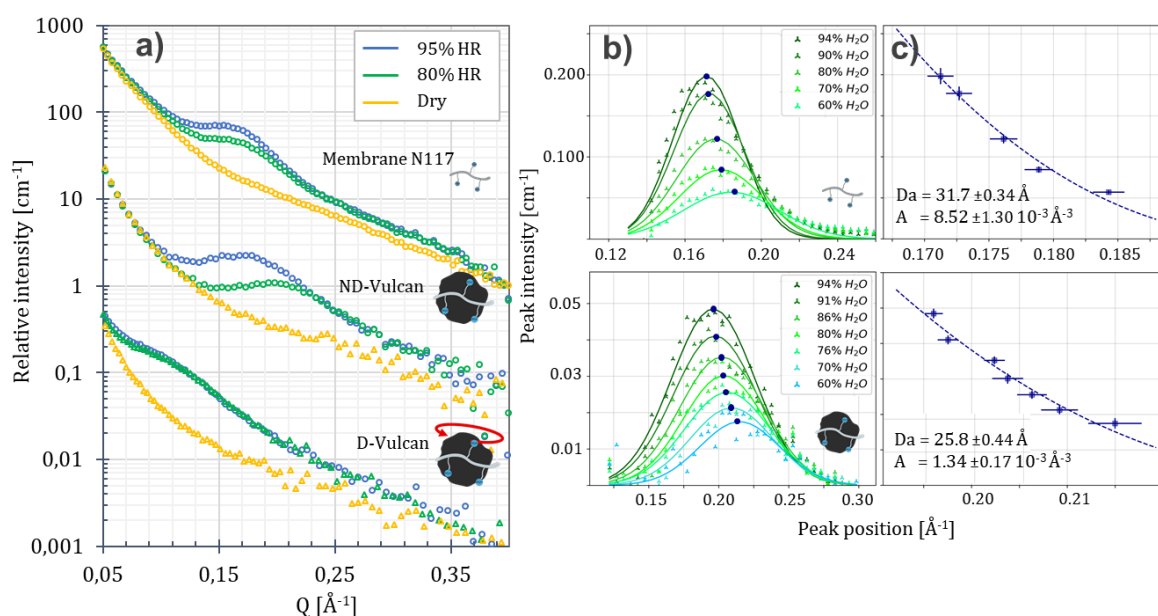
### 7 **3. Results and discussion**

#### 8 **3.1. Impact of manufacturing process on ionomer structure in catalyst layer**

9 Electrodes profiles presented in **Figure 1-d** show a characteristic peak around  $0.17 \text{ \AA}^{-1}$  once the  
10 catalyst layer is hydrated. This location corresponds to a characteristic size of the structure  
11 probed that is around 4 nanometers. However, even if it roughly corresponds to the diameter of  
12 the Pt nanoparticles, this peak could not result from the platinum particles because of their  
13 negligible contribution to the total scattered intensity. Moreover, the observed peak appears  
14 only upon hydration, increase in intensity and shift to lower  $q$  values when increasing the  
15 relative humidity. This trend is characteristics of swelling structures. Now, as discussed in the  
16 introduction, ionomer phase separation appears as its water content increases with relative  
17 humidity, which leads to the so called ionomer peak[4,14,15,42] for the bulk material in the  
18 exact same  $q$  range. Therefore, one can confidently assume that this peak results from the  
19 ionomer inside the catalyst layer, which forms either aggregates ( $\sim 150 \text{ nm}$ ) or thin films  
20 (5- 15 nm).

21 **Figure 2-a** presents recorded 1D SANS profiles of a Nafion membrane N117 (1100 EW ) from  
22 a previous paper[43] and shows the bulk ionomer behaviour upon hydration. When increasing  
23 the relative humidity from 80% to 95% the ionomer peak shifts to lower  $q$  and its intensity  
24 increases. This is a footprint of ionomer swelling, where the average characteristic size of  
25 hydrophilic domains increases with the relative humidity. Indeed, the ionomer peak comes from  
26 Bragg diffraction of the periodical organization between hydrophilic and hydrophobic domains.  
27 This nanophase separation structure is represented in **Figure 1-a**. Peak position ( $Q_0$ ) is directly  
28 related to the average lamellae inter distance ( $d_0$ ) through the Bragg Equation,  $d_0 = 2\pi/Q_0$ [36].  
29 Through SAXS study on membrane ionomer, Kreuer *et al.*[14] showed that ionomer peaks  
30 positions from membrane shift to higher  $q$  values when decreasing the equivalent weight. They  
31 showed also that polymer lamellae average thickness decreases with ionomer equivalent weight  
32 from  $27 \text{ \AA}$  for a 1100 EW membrane to  $24 \text{ \AA}$  for a Dow 858 EW membrane. Thus, short side

1 chains ionomers have larger hydrophilic domains and exhibit higher water uptake than 1000  
 2 and 1100 EW ionomers.  
 3 Looking at **Figure 2-a**, it is interesting to notice that peaks from membrane N117 and  
 4 ND- Vulcan electrode are close in shape and in position. Thus, the ionomer in bulk membrane  
 5 and in the catalyst layer have certainly very similar structure. According to several  
 6 works[9,19,20,24], thin film structure (<50 nm) differs from bulk material and depends on the  
 7 substrate material on which ionomer is coated. Therefore, it seems that the ionomer peak from  
 8 ND- Vulcan electrode results rather from aggregates with a characteristic size larger than  
 9 50 nanometers having the same structure and behavior as the bulk membrane ionomer. Profiles  
 10 on **Figure 2-a** are corrected from the incoherent scattering as discussed in section 2.2.



11  
 12 **Figure 2.** a) Effect of manufacturing process on the ionomer nanostructure contained in catalyst  
 13 layers. 1D SANS profiles from Nafion N117 membrane is adapted with permission[43].  
 14 Copyright 2022, IOP Publishing. ND- Vulcan and D- Vulcan electrodes profiles obtained under  
 15 dry conditions, 80% and 95% relative humidity. Profiles intensity were multiplied by a factor  
 16 10<sup>2</sup> or 10<sup>4</sup> to visually compare profiles from different samples, y-axis is then in relative intensity.  
 17 Profiles intensity are corrected from incoherent scattering. b) Evolution of the ionomer peak  
 18 with relative humidity for the N117 membrane and the ND- Vulcan electrode and their fitted  
 19 Gaussian curves. c) Fit of peaks intensities and positions at several relative humidity with the  
 20 ideal lamella law model gives the swelling law parameter of the ionomer.  $D_a$  is the average  
 21 thickness of hydrophobic lamella and  $A$  is a scale factor.

1 In order to obtain the ionomer swelling law, several authors[4,15] used Small Angle Scattering  
 2 (SAS) and isotherm sorption curves to relate lamellae inter-spacing distances and water volume  
 3 fraction or average number of water molecules per sulfonic group ( $\lambda$ ). Hence, Gebel[4] showed  
 4 that ionomer hydration follows an ideal lamella structure swelling behavior in the range of water  
 5 content that corresponds to our study. Ideal lamellae are infinitely long structures in comparison  
 6 to their thickness. Here, the ionomer sorption curve inside the catalyst layer cannot be measured  
 7 *in-situ*. Indeed, because of the interaction between ionomer and catalyst[44], the water uptake  
 8 of the catalyst layer for a given relative humidity condition is not the simple sum of the water  
 9 uptake of the catalyst and of the ionomer.

10 Based on SAS studies of membranes, the ideal lamella structure behavior of the ionomer will  
 11 be used in order to obtain swelling laws from the extracted peaks positions and intensities at  
 12 several relative humidity. This was done with the ND- Vulcan electrode as peaks seem close in  
 13 shape and in position to the membrane ionomer peaks. Diffraction pattern from an ideal lamella  
 14 structure follow Equation 5, as presented by Ryiong-Joon Roe[45].

$$15 \quad I(q) \propto |F(q)|^2 \cdot z \left( \frac{dq}{2\pi} \right) \quad \text{with} \quad |F(q)|^2 = (\Delta\rho)^2 \cdot \frac{4}{q^2} \sin^2 \left( \frac{D_a q}{2} \right) \quad (5)$$

16 With z equals 1 when the Bragg condition is fulfilled, which corresponds to the maximum peak  
 17 intensity position. Hence, at the peak maximum position ( $Q_0$ ), Equation 6 defines the  
 18 relationship between intensity (I) and position,  $D_a$  being the average thickness of the  
 19 hydrophobic lamellae of polymer in the ionomer. Fitting experimental data with Equation 6  
 20 would give the ionomer swelling law that is unique for each ionomer structure.

$$21 \quad I(Q_0) = \frac{A}{Q_0^2} \sin^2 \left( \frac{D_a Q_0}{2} \right) \quad (6)$$

22 A term gathers contrast factor and scale unit. Subtraction of the incoherent scattering and the  
 23 carbon surface slope to the 1D SANS profile allows extracting the ionomer peaks from SANS  
 24 profiles (see the Supporting Information subsection 2.1 for details). **Figure 2-b** presents the  
 25 extracted peaks fitted with Gaussians functions for several relative humidity conditions, from  
 26 60% to 94% relative humidity for the ND- Vulcan electrode and the Nafion N117 Membrane.  
 27 Evolutions of peaks intensity and position with hydration are fitted with the ideal lamella  
 28 structure model defined in Equation 6 and are presented in **Figure 2-c**. Then, polymer lamella  
 29 average size ( $D_a$ ) are extracted from fitted curves while their average inter distances are directly  
 30 related to peaks position through the Bragg law ( $d_0 = 2\pi/Q_0$ ). The hydrophilic domains  
 31 characteristic sizes ( $th_{water}$ ) is the difference between  $d_0$  and  $D_a$  ( $th_{ionomer}$ ). Ionomer water

1 uptake strongly depends on the ionomer equivalent weight. In order to compare results obtained  
 2 with the Nafion 1000 EW to a short side chain ionomer, we performed the same analysis on an  
 3 electrode made with the same process and composition as ND- Vulcan electrode, but with  
 4 Aquivion™ (835 EW) instead of Nafion. Details on lamella swelling law are given in  
 5 subsection 2.2 in the Supporting Information. Peaks intensity and position are summarized in  
 6 **Table S2** of the Supporting Information for the N117 Membrane, the ND- Vulcan Nafion  
 7 electrode and the ND-Vulcan Aquivion electrode while **Figure S3** presents results on the  
 8 Aquivion ND- Vulcan electrode. Results are in close agreement with literature on bulk ionomer  
 9 structure. At a given relative humidity condition, extracted peaks positions shift to higher  $q$   
 10 when decreasing the equivalent weight from N117 membrane,  $0.17 \text{ \AA}^{-1}$  (1100 EW), to Nafion  
 11 ND- Vulcan electrode,  $0.20 \text{ \AA}^{-1}$  (1000 EW) until Aquivion ND- Vulcan electrode,  $0.21 \text{ \AA}^{-1}$   
 12 (835 EW). From ionomers swelling laws, the estimated lamellae thickness decreases with  
 13 ionomer equivalent weight from  $32 \text{ \AA}$  for N115 (1100 EW), to  $26 \text{ \AA}$  for Nafion (1000 EW) in  
 14 electrode, down to  $22 \text{ \AA}$  for Aquivion (835 EW) in electrode. Thus, at 94% relative humidity,  
 15 the hydrophilic domains inside Nafion and Aquivion ionomers are respectively  $6.3$  and  $7.8 \text{ \AA}$   
 16 thick in average.

$$17 \quad \%wt = \frac{th_{water}}{th_{water} + \frac{\rho_{ionomer}}{\rho_{water}} \cdot th_{ionomer}} \quad (7)$$

18 Following the Equation 7, we retrieved an ionomer weight water uptake of 20% and 26%,  
 19 respectively, which are close from the water sorption measurement performed on Nafion  
 20 coating (1000 EW). Indeed, isotherm sorption curve presented on **Figure S4** shows a weight  
 21 water uptake of 25% for Nafion (1000 EW) at 95% relative humidity.

22 Based on ionomer peak evolution with hydration and sorption measurements, results showed  
 23 that ionomer contained in ND- Vulcan electrode and bulk ionomer are similar: they have a close  
 24 nanostructure and swelling law. It was said in the introduction that ionomer inside the catalyst  
 25 layer disperses as thin film or as aggregates. Results on ND- Vulcan electrode suggest that  
 26 ionomer peak results from diffraction inside aggregates, which are bulk like material with  
 27 numerous ordered nanophase separation. On the other hand, looking at scattering profiles of  
 28 D- Vulcan electrode on **Figure 2-a**, one can see that peaks positions and shapes are dramatically  
 29 different. Both electrodes were made with the exact same composition but with a different  
 30 manufacturing process. There is no doubt that peaks on the profiles of D- Vulcan electrode  
 31 result from ionomer but it is not an ionomer peak resulting from diffraction of ionomer bundles.  
 32 Indeed, assuming that the peak observed on D- Vulcan electrode results from diffraction and

1 considering 26 Å thick lamellae, we estimate that ionomer should have 62% weight water  
2 uptake at 94 % relative humidity. Such an excessive water uptake has never been observed on  
3 bulk Nafion in this range of temperature and humidity conditions. This is an evidence showing  
4 that the peak related to the ionomer structure from D- Vulcan electrode does not result from  
5 bulk ionomer aggregates but from another ionomer structure, which is probably an ionomer thin  
6 film spread around the catalyst. This assumption has been checked by Transmission Electronic  
7 Microscopy. Elemental Fluorine EDS mapping presented in section 5 of the Supporting  
8 Information confirms that ionomer forms large aggregates of several hundreds of nanometers  
9 inside the D- HSA electrode. At the opposite, fluorine mapping on a well-dispersed electrode  
10 shows a homogeneous ionomer distribution at the carbon surface.

### 11 **3.2. Ionomer thin film structure and water distribution inside the electrode**

12 We will simulate 1D SANS profiles of ideal structures in order to study the ionomer structure  
13 and its distribution inside D- Vulcan and D- HSA electrodes. In the literature, microscopy  
14 studies[1,46] show that despite its relative high roughness, carbon primary particles can be  
15 considered as sphere-like structures covered by an ionomer layer with a dry polymer film  
16 thickness of 2 to 3 nm thick according to Park *et al.*[46] Koizumi *et al.*[47] have used a simple  
17 core shell model in order to analyze their SANS profiles on the q range that probes carbon  
18 primary particles. Their electrode was hydrated with a solvent having the same SLD as the  
19 ionomer in order to merge the ionomer and the water scattering contributions. Thus, they could  
20 not resolve the water location. However, several works on ionomer thin film[2,24] showed that  
21 condensed water appears at the Pt/ionomer interface. Ueda *et al.*[2] shown the presence of a 3  
22 Å thick water film between a reconstructed Nafion thin film (400 Å thick) over a flat platinum  
23 surface using Grazing Incident Small Angle Neutron Scattering (GISANS). Besides, sorption  
24 isotherms measurements performed on carbons (HSA and Vulcan) showed that water uptake  
25 by carbon increases with relative humidity (Sorption isotherm of **Figure S5**). Those results  
26 shows that carbon rough surface must adsorb water even without ionomer. In addition, sorption  
27 isotherms of catalyst made with the same carbons support revealed that catalyst uptake even  
28 more water (Sorption isotherm of **Figure S6**). This behavior is probably due to the hydrophilic  
29 nature of platinum.

30 Taking into account the results previously published, our scattering profiles were then fitted  
31 with different models of core shell structures presented in **Figure 3-a**. In the first one, named  
32 “hydrated ionomer model”, the spheres of carbon are covered with a hydrated ionomer film  
33 with variable thickness and SLD, depending on its hydration. Indeed, SLD of the hydrated

1 ionomer is supposed to decrease with water uptake, considering their respective SLD  
2  $4.2 \cdot 10^{-6} \text{ \AA}^{-2}$  and  $-0.56 \cdot 10^{-6} \text{ \AA}^{-2}$ . In the second model, named “inner water layer model”, the  
3 carbon spheres are covered by a first layer of pure water surrounding by a second layer of dry  
4 ionomer, that do not uptake water. The last one, named “porous carbon surface” considers that  
5 water may fill carbon surface pores creating an outer carbon layer of variable thickness and  
6 SLD, this particle is then covered by a pure water layer and a dry ionomer shell. Nevertheless,  
7 our models are supposed to depict the organisation of the Pt/C and ionomer interface, even if  
8 we consider only a single type of interface because of the small contribution of Platinum to  
9 scattering profiles. At the  $q$  range where correlation appears, SANS intensity probes the electrode  
10 structure at the scale of few nanometers. Models are then used to fit correlation peak and to  
11 study the water and ionomer shells at the catalyst surface. Since, at this  $q$  range, scattering  
12 intensity results from neutrons interferences on few nanometres, apparition of the correlation  
13 peak does not require primary carbon particles to be fully covered by water and ionomer.  
14 Indeed, carbon particles sizes are much larger, around 20 to 50 nm of diameter, than the  
15 structure scale probed at this  $q$  range. Correlation peaks result from shells structures present  
16 locally at the carbon surface but which is not necessary homogeneously dispersed.

17 At the  $q$  range where correlation peak appears, shape and size of carbon particle does not affect  
18 strongly the position of the correlation peak since profiles intensity probes shells organization  
19 and sizes at the carbon surface, which are very small compared to carbon particles diameter.  
20 However, models require a carbon particles average size that is known from literature. Padgett  
21 *et al.*[48] studied Vulcan carbon and showed that, in average, primary particles radius are  
22 around  $135 \text{ \AA}$ . In fact, Vulcan particles split in two populations with different diameter 10-20  
23 nm and 25-40 nm. HSA carbon presents also distinct primary particles types, one with 15-35  
24 nm diameters and a larger one with 20-40 nm that appears partially hollowed. We include in  
25 our model some polydispersity in the size of the carbon nanoparticles and in the thicknesses of  
26 the ionomer and water shells. Details on models parameters are presented in the subsection 4  
27 of the Supporting Information.

28 Before fitting the correlation peak, incoherent scattering intensity was measured at  $0,4 \text{ \AA}^{-1}$  and  
29 subtracted to SANS profiles intensity. As shown by Equation 3 and 4, the form factor  $P(q)$  of  
30 ideal smooth core shells structures decreases as a  $q^{-4}$  function. Hence, correlation peaks  
31 observed due to constructive interferences of shells scattering contributions will be amplified  
32 by plotting  $I(q) \cdot q^4$  versus  $q$  for ideal smooth core-shell structures. On experimental profiles,  
33 slopes observed between  $8 \cdot 10^{-3}$  and  $5 \cdot 10^{-2} \text{ \AA}^{-2}$  decreases as a  $q^{-n}$  function with a  $n$  comprise



1 between 3 and 4. Experimental profiles were then plotted as  $I(q) \cdot q^n$  versus  $q$  to reveal correlation  
2 peaks. Resulting profiles were then fitted on the  $q$  range corresponding to the correlation peak  
3 ( $0.07\text{-}0.5 \text{ \AA}^{-1}$ ) with the core shells form factors of ideal smooth core shells structure multiplied  
4 by  $q^4$ . Profiles from D- Vulcan and D- HSA and their fits are presented on **Figure 3-a** and  
5 **Figure 3-b** respectively. The “hydrated ionomer model” does not fit with experimental data for  
6 D- Vulcan and D- HSA electrode. It does not reproduce the experimental correlation peak as  
7 shown by the dash grey line plot that is the best fit obtained. Experimental peaks on profiles of  
8 D- Vulcan and D- HSA electrodes can only be reproduced with core multishell models  
9 considering a condensed water layer between the Pt/C catalyst and the ionomer. Then, extracted  
10 water and ionomer shells thicknesses using the “inner water layer model” are shown on **Figure**  
11 **3-d** as a function of relative humidity for D- Vulcan. Parameters extracted from fitting process  
12 are presented in **Table S3** of the Supporting Information. The thickness of the condensed water  
13 increases with relative humidity. The ionomer film thickness is estimated to be around  $21 \text{ \AA}$   
14 and it does not seem to absorb water since its SLD does not decrease below  $4.2 \cdot 10^{-6} \text{ \AA}^{-2}$ , which  
15 is the dry ionomer SLD. Indeed, with water uptake, the hydrated ionomer SLD would decrease  
16 toward  $-0.56 \cdot 10^{-6} \text{ \AA}^{-2}$  ( $\text{H}_2\text{O}$  SLD) depending on the volume of water uptake. It is important to  
17 understand that those results do not suggest that ionomer covers the whole carbon support  
18 surface. Indeed, at the  $q$  range of the correlation peak, neutrons scattering probes scales sizes  
19 of few nanometers and not the whole carbon particles. Thus, each fraction of carbon surface  
20 covered by water and ionomer would contribute to the correlation peak even if the carbon  
21 particle is not fully covered by water and ionomer. Core-shells models fitting shows then the  
22 average structure of water and ionomer layers over the volume sample.

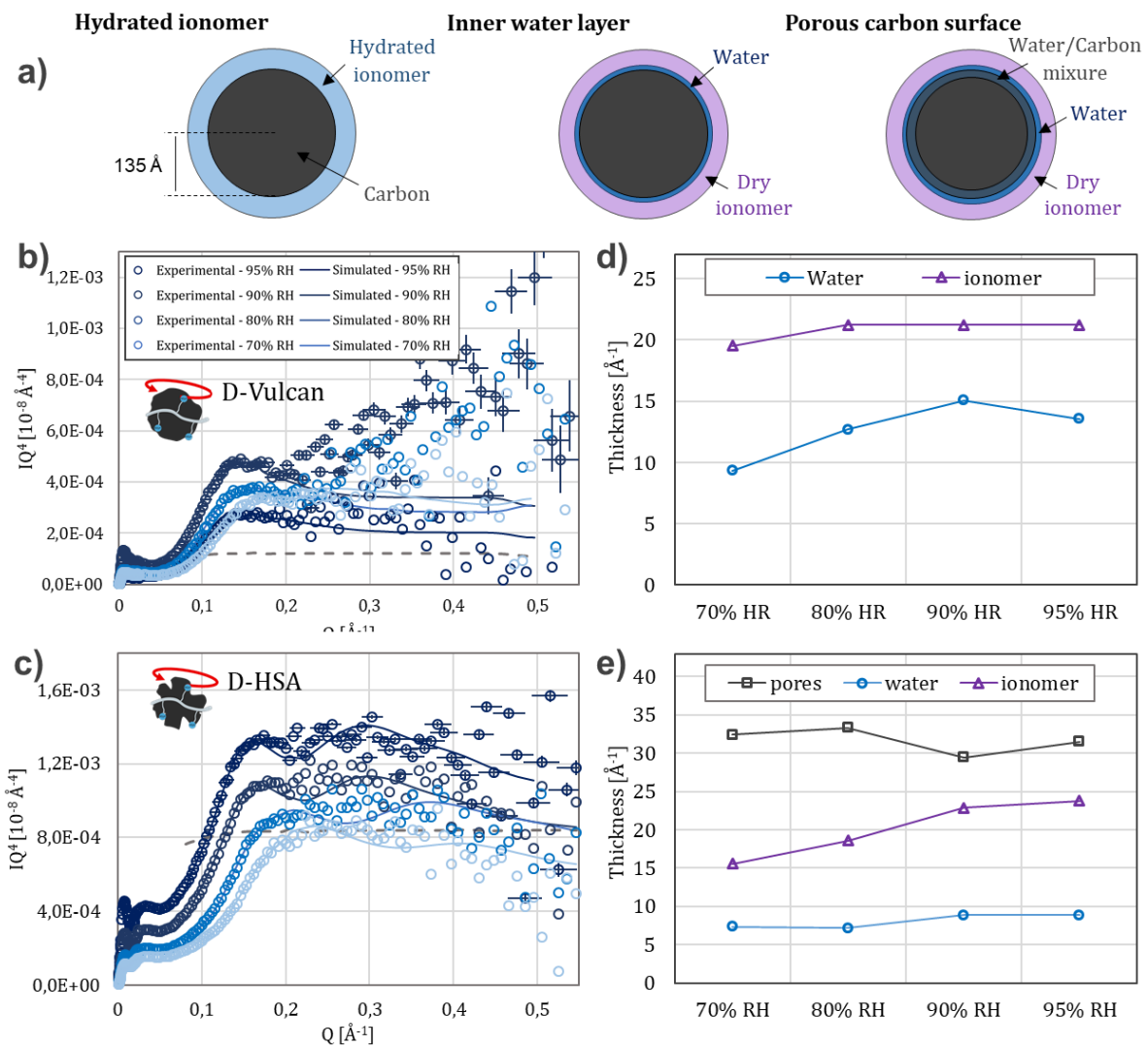
23 The same analysis with the “inner water layer model” was performed on D- HSA electrode and  
24 fitting of experimental curves are presented on **Figure S8** of the Supporting Information while  
25 **Table S4** summarizes fitted parameters. Using this “inner water layer model”, the water film  
26 thickness estimated around  $5 \text{ \AA}$  for D- HSA electrode was much lower than for D- Vulcan  
27 electrode. Now, we know from water sorption measurements, presented in **Figure S7** of the  
28 Supporting Information, that D- HSA electrode water uptake is more important than D- Vulcan.  
29 The literature shows that High Specific Area (HSA) carbon support has a large amount of meso  
30 pores, which constitutes more than 50% of its specific surface area[49]. This pores can be filled  
31 by water because of capillary condensation that explains the larger water uptake of HSA carbon  
32 compared to Vulcan carbon as shown by Pt/C catalysts isotherms presented in **Figure S6** of the  
33 Supporting Information. Therefore, the “inner water layer” model does not depict properly the

1 D- HSA electrode because it does not take into account surface meso porosity and strongly  
2 underestimates the water content.

3 Then, we have to consider that water filling those pores changes the SLD over a certain  
4 thickness of the outermost carbon layer. In order to fit properly the data one have to use the  
5 “porous carbon surface” model. Fitting profiles of D- HSA electrode gives the parameters  
6 values presented on **Figure 3-e**, which are summarized in **Table S5** of the Supporting  
7 Information. Ionomer film thickness seems to increase with hydration from 16 to 24 Å while it  
8 remains apparently dry ( $SLD = 4.2 \cdot 10^{-6} \text{ \AA}^{-2}$ ). This could be explained by the deformation of the  
9 ionomer film upon catalyst hydration when pores are progressively filled with water pushing  
10 out some of ionomer that cover the porous structure on the surface. The pure water film at the  
11 catalyst/ionomer interface is estimated around 8 Å while the depth of meso pores filled with  
12 water is about 32 Å with an SLD of  $3.7 \cdot 10^{-6} \text{ \AA}^{-2}$  at 95% relative humidity. Hence, if surface  
13 meso porosity is fully filled with H<sub>2</sub>O at 95% relative humidity, then pores represent 42% in  
14 volume of the carbon outmost layer. Thanks to these results, we can compute the volume of  
15 water contained at the carbon particles surface. Then considering the volume of carbon particles  
16 and the volume of the several layers, we may retrieve the overall water volume  
17 fraction ( $V_{\text{water}}/V_{\text{total}}$ ), which is 17% and 23% for D- Vulcan and D- HSA electrodes,  
18 respectively. Water sorption isotherms give a water volume content of 12% and 25% for  
19 D- Vulcan and D- HSA electrodes. Sorption and SANS measurement are close for D- Vulcan  
20 and D- HSA electrode, thus the full amount of water seems to be located at the Pt/C catalyst  
21 surface.

22 In addition, it is interesting to notice that the thickness of the ionomer shell spread over is very  
23 close for Vulcan and HSA carbon supports, respectively 21 and 24 Å at 95% RH, and is smaller  
24 than the average thickness of 27 Å for hydrophobic lamellae in Nafion 1100 EW membrane.  
25 However, Loppinet *et* Gebel[50,51] studied ionomer dispersion in different media by SAXS,  
26 considering hydrophobic domains were rodlikes structures (instead of lamellae). They estimate  
27 that in average, hydrophobic domains radius were between 17 to 25 Å, which corresponds to  
28 the dry ionomer shell thicknesses measured in this study. Therefore, this explains the fact that  
29 water is not located inside the ionomer but at the interface between Pt/C catalyst and ionomer.  
30 The 34 Å of the total ionomer and water shell thickness retrieved on D- HSA electrode at 95%  
31 relative humidity is thinner than the 50 Å found by Koizumi *et al.*[26] by SANS because they  
32 did not take into account the scattering contribution of the porous carbon surface. In addition,  
33 water film thickness retrieved at the Pt/C catalyst is thicker than estimated by Ueda *et al.*[2] on

1 a reconstructed Nafion thin film (400 Å thick) over platinum. However, thin film study on  
 2 smooth substrate may not reproduce what happens in electrode, since the water uptake at the  
 3 substrate/ionomer interface is an interplay between, material hydrophilicity and  
 4 substrate/ionomer interaction. Therefore, SANS characterisation afford new additional  
 5 information on the water and ionomer distribution in catalyst layer and revealed that ionomer  
 6 thin film and bulk ionomer structures are drastically different. Indeed, in the electrode, ionomer  
 7 film thickness is in the order of bundle aggregates thicknesses and a water layer appears at the  
 8 Pt/C catalyst and ionomer interface.



9  
 10 **Figure 3.** a) Schemes of three models used to reproduce the local structure of the electrodes  
 11 and more precisely the catalyst, water and ionomer organisation at the nanometer scale.  
 12 b) Experimental profiles from D- Vulcan and their fitted curves resulting from “inner water  
 13 layer” model. Dash grey line is the best-fitted curve obtain with “hydrated ionomer” model.  
 14 Error bar are only reproduced on one scattering profile for clarity. c) Experimental profiles from

1 D- HSA and their fitted curves resulting from “porous carbon layer” model. Dash grey line is  
2 the best-fitted curve obtain with “hydrated ionomer” model. d) Evolution of water and ionomer  
3 shells thicknesses with relative humidity. Parameters obtained from “inner water layer” model  
4 fitting. Error bars attributed to covariance of fitted parameters are within markers thicknesses  
5 e) Estimation of carbon meso pores depth and evolution of ionomer and water shells thicknesses  
6 with hydration. Parameters obtained from “porous carbon surface” model fitting. Error bars  
7 attributed to covariance of fitted parameters are within markers thicknesses.

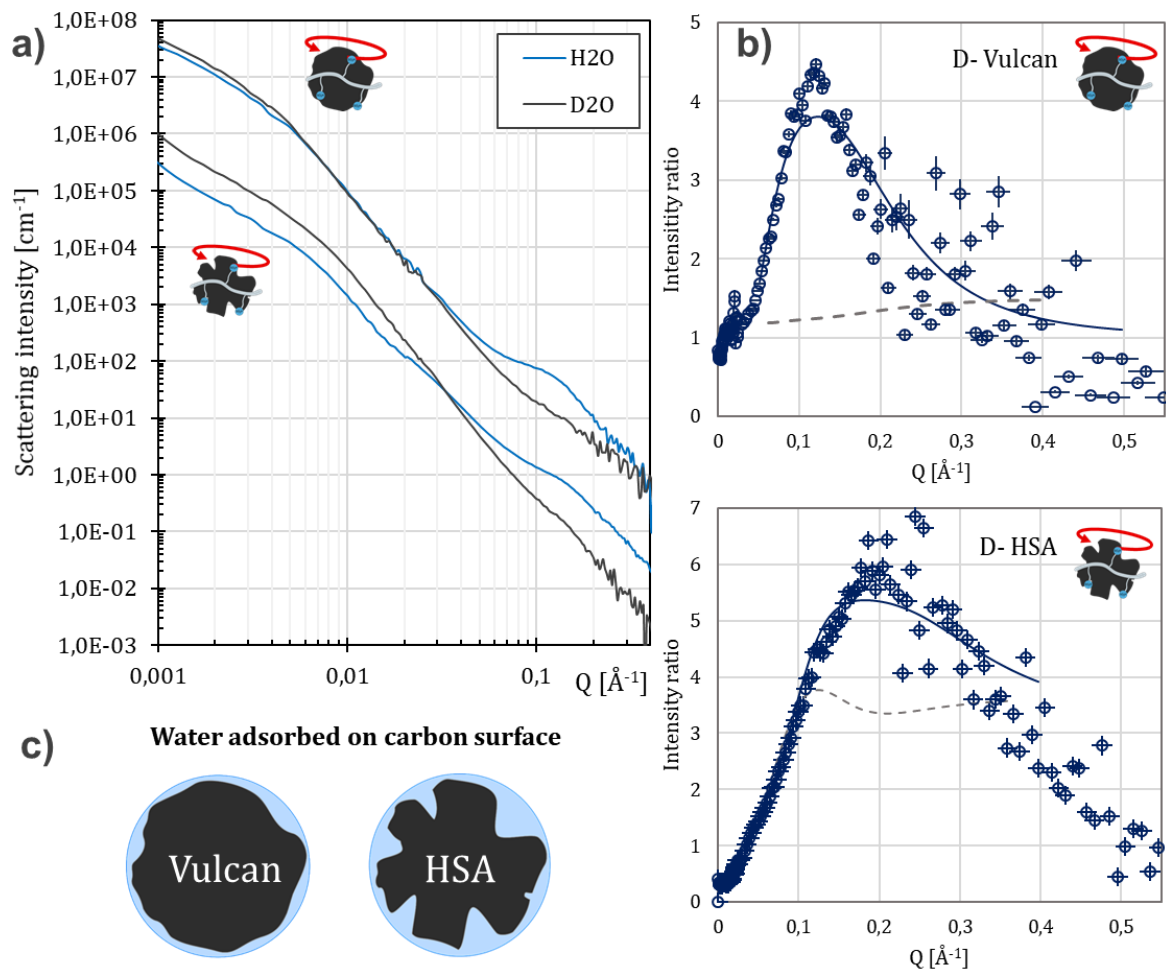
8 To summarize, from the actual knowledge of carbon and electrode structures, we analysed 1D  
9 SANS profiles with two different core-shells form factor models to depict the catalyst, water  
10 and ionomer organization at the nanometer scale with two different types of carbon, either  
11 Vulcan or HSA in the electrode. We highlight that a thin ionomer film of about 20 Å in thickness  
12 cover the catalyst and does not seem to swell significantly increasing the relative humidity. This  
13 means that, for well dispersed electrodes and for the probed ionomer over carbon weight ratio  
14 (I/C) that ranges between 0.67 and 0.8, the ionomer is nearly totally in the form of a thin film  
15 coating at least partially the surface of the Carbon particles. There is no significant contribution  
16 of scattering due to ionomer aggregates on the SANS profiles. This does not imply necessarily  
17 that the whole carbon surface is covered homogeneously and totally by the ionomer. We gave  
18 an averaged value for the ionomer film thickness, but there is a polydispersity in thickness of  
19 the film, as mentioned above. On the SANS profiles, the intensity of the peak due to the film  
20 covering the carbon increases with the ionomer coverage. In addition, there is a thin water film  
21 between the Pt/C catalyst and the ionomer even below 100%RH. Its thickness is about 10 Å  
22 and is larger than what has been reported at the interface between Pt and ionomer on flat model  
23 substrates. It implies that there is also water at the carbon/ionomer interface. In addition, our  
24 results strongly suggest the presence of water inside the HSA carbon surface porosity. Further  
25 analysis of SANS profiles in the lower q range will confirm those results.

26

### 27 **3.4. Validating core shell models with contrast variation**

28 In this section will use the unique advantage of neutrons to perform contrast variation in order  
29 to study the organization of water and ionomer at the nanometer scale of the catalyst . Neutrons  
30 interaction with light or heavy water is dramatically different and thus, Scattering Lengths  
31 Densities (SLD) of water H<sub>2</sub>O ( $-0.56 \cdot 10^{-6} \text{ \AA}^{-2}$ ) and heavy water D<sub>2</sub>O ( $6.34 \cdot 10^{-6} \text{ \AA}^{-2}$ ) are  
32 significantly different. In addition, the SLD of H<sub>2</sub>O and D<sub>2</sub>O are close to air ( $0 \text{ \AA}^{-2}$ ) and carbon  
33 ( $6.7 \cdot 10^{-6} \text{ \AA}^{-2}$ ) respectively allowing to mask a material contribution to the overall profile.

1 Hence, with H<sub>2</sub>O hydration, air and water contribution are merged together while with D<sub>2</sub>O  
2 hydration, it is the water and the carbon contribution that are merged together in the resulting  
3 SANS scattering profile. We therefore perform scattering experiments on the same samples but  
4 having the surrounding media (air) saturated by H<sub>2</sub>O and D<sub>2</sub>O. Doing so, only the scattering  
5 length density of the solvent varies while the catalyst particles are not affected. Obtaining a  
6 second contrast within the same state of dispersion and structure will give further confidence  
7 on the fine details. **Figure 4 -a** presents experimental profiles obtained from D- Vulcan and  
8 D- HSA electrodes. Electrodes hydrated with H<sub>2</sub>O have a larger incoherent than those with  
9 D<sub>2</sub>O. Both profiles exhibit same evolutions with contrast variation. Two main features are  
10 observed with D<sub>2</sub>O hydration, the correlation peak disappearance, and the decrease of the  
11 intensity slope between 0.02 Å<sup>-1</sup> and 0.06 Å<sup>-1</sup>. The variation of the intensity observed at the  
12 lowest q values between H<sub>2</sub>O and D<sub>2</sub>O profiles highlights this slope evolution. Core shell  
13 models used in subsection 3.2 should be able to reproduce profiles evolutions induced by  
14 contrast variation. Therefore, we have plotted the ratio of experimental profiles under H<sub>2</sub>O and  
15 D<sub>2</sub>O hydration at 95% relative humidity. In this way, the structure factor of the carbon  
16 contribution is erased and the correlation peak is fully revealed. Curves were then fitted with  
17 the ratio of the form factors using “inner water layer” model for D- Vulcan profile and “porous  
18 carbon surface” model for D- HSA. Again, experimental profiles cannot be reproduced by the  
19 model when considering that the ionomer film is hydrated (dash grey line). However, there are  
20 well fitted by their respective models and give results in close agreement with those obtain in  
21 subsection 3.2. At 95% relative humidity, the estimation of the ionomer shell thickness is 25.3  
22 Å (±0.177 Å) on D- Vulcan and 19.3 Å (±0.306 Å) on D- HSA while meso porosity are  
23 estimated at 29.9 Å (±1.68 Å) than previously. Full details are given in subsection 4.3 in the  
24 Supporting Information while **Table S6** and **Table S7** present fitted parameters from D- Vulcan  
25 and D- HSA electrodes. Finally, results from this contrast variation analysis strengthen our  
26 previous conclusion on the structure of carbon primary particles inside both catalysts layers.



1  
 2 **Figure 4.** a) 1D SANS profiles evolution with contrast variation of D- Vulcan and D- HSA  
 3 electrodes. Electrodes hydrated with H<sub>2</sub>O and D<sub>2</sub>O at 95% RH. H<sub>2</sub>O profiles intensities are  
 4 subtracted from incoherent scattering. b) Ratio of H<sub>2</sub>O profile over D<sub>2</sub>O profile highlights the  
 5 correlation peak for D- Vulcan and D- HSA. Experimental ratio fitted with ratio of core shells  
 6 models using the “inner water layer” model for D- Vulcan and the “porous carbon layer” model  
 7 for D- HSA. Dash grey lines are the best fit obtained considering a shell made from hydrated  
 8 ionomer instead of water and ionomer layers. c) Schemes of adsorbed water at the surface of  
 9 Vulcan and HSA carbon supports with water filling HSA carbon meso porosity.

### 10 3.5 Using contrast variation to reveal the carbon support structure

11 On **Figure 4-a**, important differences are observed from one electrode to another pointing out  
 12 the structure evolutions induced by the carbon supports used; either Vulcan or High Surface  
 13 Area (HSA) carbon supports. Then, contrast variation is used to reveal structural differences  
 14 between the two electrodes. Since SLDs of air and H<sub>2</sub>O are very close, these carbon particles

1 will scatter neutrons similarly when dispersed in water or in air. Therefore, once hydrated with  
2 H<sub>2</sub>O, 1D SANS profiles probe specifically the carbon particles. According to Porod law[52],  
3 the slope observed with H<sub>2</sub>O profiles between 0.02 Å<sup>-1</sup> and 0.06 Å<sup>-1</sup> characterizes the carbon  
4 surface roughness. Ideal smooth spheres would present a slope decreasing as a q<sup>-4</sup> function  
5 while smaller power values between 3 and 4 characterize rougher surfaces. Profiles intensity  
6 from D- Vulcan electrode decreases as a q<sup>-3.9</sup> function while it does as a q<sup>-3.1</sup> for D- HSA  
7 electrode. This is in accordance with the higher roughness of HSA carbon compared to Vulcan.  
8 Then, replacing H<sub>2</sub>O with D<sub>2</sub>O increases the water SLD close to the carbon SLD value  
9 (6.34.10<sup>-6</sup> Å<sup>-2</sup> for D<sub>2</sub>O against 6.5.10<sup>-6</sup> Å<sup>-2</sup> for carbon). Thus, carbon and D<sub>2</sub>O, having similar  
10 SLDs, would scatter as the same material. Looking at D- Vulcan electrode profiles on the  
11 **Figure 4-b**, using D<sub>2</sub>O for sample hydration instead of H<sub>2</sub>O has little effect on the slope which  
12 means that adsorbed water at the carbon surface does not change its apparent roughness.  
13 However, the D- HSA electrode profile slope increases from q<sup>-3.1</sup> with H<sub>2</sub>O hydration to q<sup>-3.9</sup>  
14 with D<sub>2</sub>O as if the surface of carbon becomes smoother due to the presence of D<sub>2</sub>O. This can  
15 be ascribed to the incorporation of water inside the surface meso pores of the carbon as  
16 represented on **Figure 4- c**. Profiles recorded from catalyst alone, 50% weight Pt over HSA  
17 carbon, are presented on **Figure S9-a** of the Supporting Information. They showed the same  
18 increase of slopes with D<sub>2</sub>O hydration suggesting that carbon surface meso pores are filled with  
19 D<sub>2</sub>O even without ionomer. Those results confirm the presence of meso pores at the HSA  
20 carbon support surface, which are filled by water through capillary condensation and are  
21 responsible for the high water uptake of D- HSA electrode. Our study shows that a water thin  
22 film appears between the Pt/C catalyst and the ionomer film. SANS profiles were also recorded  
23 on a sample made only with HSA carbon and ionomer (without platinum), which are presented  
24 on **Figure S9-b** of the Supplement Information. SANS profile of the sample hydrated at  
25 95%RH shows a correlation peak around 0.12 Å<sup>-1</sup>. Therefore, even if there is no platinum,  
26 ionomer disperses as a thin film at the carbon surface and a water layer appears again between  
27 ionomer and carbon. All those results shows that ionomer disperses at the Pt/C catalyst surface  
28 and that a water layer appears both at the carbon/ionomer and platinum/ionomer interfaces.  
29 Slopes inflexions at lower q values, around 0.005 Å<sup>-1</sup> give information on carbon network  
30 structure. Below the inflexion location, scattered intensity characterizes the primary particles  
31 while above it characterizes the catalyst layer aggregates. On **Figure 4-a**, inflexion appears at  
32 higher q values for the D- Vulcan catalyst layer (4.10<sup>-3</sup> Å<sup>-1</sup>) than for D- HSA (6.10<sup>-3</sup> Å). The  
33 upturn position is related to the volume average of particles characteristic sizes over the entire

1 electrode volume illuminated by the beam. Therefore, carbon particles mean diameter appears  
2 20% larger for Vulcan carbon. In addition, below  $4.10^{-3} \text{ \AA}^{-1}$ , differences in experimental profiles  
3 slopes witness that the structure of catalyst layer aggregates are radically different from one  
4 electrode to another.

#### 8 **4. Conclusion**

9 In this paper, we propose a detailed method to characterize the structure of the catalyst layer in  
10 a large range of length scales from nm to hundreds of nm through an analysis method of 1D  
11 Small Angle Neutron (SANS) profiles with contrast variation. Catalyst layers differing in  
12 composition, either in types of ionomer or carbon support, but also in fabrication process. It  
13 shows how powerful the SANS is to get information on the structure of the catalyst layer. This  
14 is the only method that could offer such quantitative and detailed information on water  
15 distribution and ionomer structure.

16 The analysis of the 1D SANS profiles in a wide  $q$  range with contrast variation reveals the  
17 presence of ionomer as aggregates or as thin film coating the Pt/C catalyst depending on the  
18 manufacturing process. When stacked in the pores of the catalyst layer, the size of the ionomers  
19 aggregates appears to be larger than 50 nm up to several hundreds of nanometers. Their  
20 structure and swelling behavior are very similar to that of the bulk ionomer in the membrane .  
21 However, once ionomer disperses as thin film, 1D SANS profiles exhibit a drastically different  
22 feature with a correlation peak whose shape and position depend on the relative humidity. All  
23 the profiles obtained with the different catalyst layer compositions can be fitted with a form  
24 factor of a core multi-shell model allowing extracting information on the ionomer thin film  
25 thickness and water location and content. To summarize, a 20 to 30  $\text{ \AA}$  thick ionomer shell coats  
26 the Pt/C catalyst made from Vulcan or High Surface Area Carbon (HSAC) support. For both  
27 catalyst, condensed water appeared at the ionomer/catalyst interface, even under 100% relative  
28 humidity. However, there are differences between smooth spherical particles from Vulcan and  
29 the rough and porous spherical particles from HAS carbon. In the case of HSA carbon support,  
30 the volume of condensed water at the carbon/ionomer interface is larger than for Vulcan carbon  
31 support because water fills the HSA carbon meso pores due to capillary condensation.

32 SANS method paves the way toward a more refined understanding of the structure/properties  
33 relationship of the electrode. It shows how the structure of the carbon support of the Pt/C



1 catalyst influences the ionomer and the water dispersions, and it can explain why the HSAC  
2 offers better performance. Indeed, these conclusions drawn from ex-situ measurements can  
3 most probably be extrapolated to what happens during PEMFC operation with water being  
4 primarily located in the pores of the carbon and at the Pt/C catalyst/ionomer interface before  
5 filling larger pores.

6  
7 Furthermore, the same SANS profile analysis can be applied to various catalyst layers used in  
8 fuel cells or electrolyzers (PEME, AEMFC, AEME, DMFC...) that used nanoscale structured  
9 electrodes. Thus, this work provides to the scientific community original tool and crucial  
10 information to understand the fuel cell operation that are not accessible through other methods  
11 than SANS.

## 12 **Supporting Information**

13 Details on the manufacturing process and composition of the electrodes, details on the SANS  
14 models, analyses and results of the models, water vapor sorption isotherms, STEM imaging of  
15 the ionomer in the electrodes.

## 16 **Corresponding author**

17 Arnaud MORIN, CEA - Liten

18 [arnaud.morin@cea.fr](mailto:arnaud.morin@cea.fr)

## 19 **Author Contribution**

20 The manuscript was written through contributions of all authors. All authors have given  
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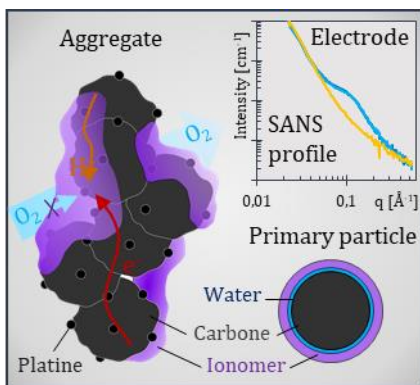
13

1 **Detailed catalyst layer structure of Proton Exchange Membrane Fuel Cell from contrast**  
2 **variation small-angle neutron scattering**

3

4 PEMFC catalyst layer operation is closely related to its nanoscale structure and its water uptake,  
5 which were revealed by Small Angle Neutron Scattering (SANS). 1D SANS profiles analysis  
6 allowed to probe catalyst layer structure, revealing the ionomer distribution (as aggregates or  
7 as thin film), the water uptake and its location. This study revealed that condensed water  
8 accumulates at the carbon/ionomer interface or inside porous particles depending on the type  
9 of carbon support used.

10



11

12 **Figure.** Complex heterogeneous structure of catalyst layer probed by SANS. Scheme of the  
13 critical role of the ionomer distribution on catalyst layer operation at the aggregates scale. 1D  
14 SANS profile from electrode and the associated scheme of the primary particle structure  
15 revealed by profiles analysis.

16

17