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# NMR characterization of proton exchange membranes in controlled hygrometry conditions

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## Abstract

NMR methods are highly sensitive to the state of water adsorbed in ionomer membranes for PEM fuel cells and electrolyzers. This study demonstrates the potential of NMR and MRI to reliably and accurately determine a wide range of water parameters such as proton chemical shift, transverse relaxation time, water content, and membrane thickness. Measurements are carried out *in-situ* in membranes in contact with humid air flows that are precisely controlled in terms of flow rate, temperature, and humidity. This precise management of the climatic conditions makes it possible to detect very small variations in the parameters measured, linked to the hydrothermal history of the membrane described in the literature. This history is erased when the membrane is humidity cycled several times. In addition, we demonstrate the use of this MRI imaging method to determine the resistance to water transfer across the membrane/humid air interface under steady-

22 state conditions. Finally, we propose a refinement of the imaging method that reduces acquisition  
23 time by a factor of two, without degrading the 1D water content profile. This improvement gives  
24 us access to the study of transient hydration regimes typical of PEMFC and PEME operation.

25 **Keywords:** PEMFC, PEME, water transfer, NMR, MRI, water profile

## 26        **1. Introduction**

27        Hydrogen has a notable role to play in supporting announced government climate commitments  
28        and to enhance energy security. In 2021 the USA announced a climate goal of cutting emissions  
29        50% below 2005 levels by 2030 while the European Commission proposed to cut greenhouse gas  
30        emissions by at least 55%, also by 2030 [1]. A large number of initiatives aim to advance programs  
31        and projects that accelerate the commercialization and deployment of hydrogen and fuel cell  
32        technologies across all areas of the economy. Ultimately, it seeks to ensure hydrogen's place as a  
33        key enabler in the global clean energy transition. Proton Exchange Membrane Fuel Cells (PEMFC)  
34        and Proton Exchange Membrane Electrolyzers (PEME) are important players in the hydrogen  
35        economy. These systems have now reached a good technological maturity and many commercial  
36        solutions are operational. Research & Development focuses mainly on reducing the costs (*e.g.* by  
37        reducing the amount of catalyst) and increasing the durability of the components (*e.g.* by limiting  
38        the ageing of the membrane/electrode (MEA) assembly) [2, 3]. However, more fundamental  
39        studies are still needed to better understand the limitations induced by the decrease in platinum  
40        content in MEAs, both in terms of operation and aging of the electrodes and the ionomer  
41        membrane. More specifically, a better understanding of the water transport across the  
42        membrane/electrode interface is still required. It is thus necessary to use methods that can probe  
43        the properties of water within the membrane. To this end a number of experimental approaches  
44        have long been developed and used to measure the water profile through the PEM membrane,  
45        either *in-situ*, when the membrane is subjected to controlled temperature and humidity conditions  
46        [4-7], or *in-operando*, when the membrane is in an operational PEMFC [8-11]. Review articles  
47        detail the approaches that have been most productive [12-14]. Among them, nuclear magnetic  
48        resonance (NMR) and magnetic resonance imaging (MRI) have been shown to be effective in

49 studying the distribution and properties of water in the membrane. MRI has been used in particular  
50 to measure 1D water profiles in the membrane thickness with a spatial resolution down to 6  $\mu\text{m}$   
51 per point and an acquisition time of a few minutes per profile. Depending on the protocol used,  
52 the measurements could be performed *in-situ* [7, 15, 16] or *in-operando* [17-19]. In some studies,  
53 dedicated methodologies had to be used in order to adapt the NMR hardware, *i.e.* the radio  
54 frequency (RF) coil, to the 2D geometry of the membrane. The objective was twofold: to increase  
55 the signal-to-noise ratio of the measurement by placing the RF coil ideally with respect to the plane  
56 of the membrane [20] and to allow the measurement even when the carbonated gas diffusion layer  
57 (GDL) is adjacent to the membrane and must therefore be traversed by the RF magnetic field  
58 produced by the coil [16]. The experimental developments also concerned the improvement of the  
59 measurement methods (the so-called “NMR sequences”) in order to measure parameters that are  
60 directly related to the absolute water content of the membrane [15, 20]. In contrast, *in-situ* NMR  
61 studies have so far paid little attention to the precise control of air humidity conditions imposed  
62 on either side of the membrane. This is probably due to the difficulty of maintaining regulated  
63 relative humidity conditions inside the spectrometer. The properties of the membrane however are  
64 very sensitive to variations in water content and so are the NMR parameters that can be accessed  
65 experimentally [21].

66 MRI imaging of the hydration profile across the membrane under unsaturated air conditions, both  
67 in steady state and during transient regimes could provide a good deal of valuable information  
68 regarding both water transfer at the membrane/electrode interface and diffusion properties in the  
69 bulk of the membrane. In this paper we present a device and a methodology capable of finely  
70 measuring the NMR properties of water in proton exchange membranes under controlled  
71 hygrometric conditions. The method, demonstrated on a thick Nafion membrane, allows to

72 measure the NMR properties of the water protons adsorbed in the polymer and the 1D through-  
73 plane water content profile with a good spatial and temporal resolution. We also present a basic  
74 improvement of the measurement sequence in order to accelerate the acquisition and lower the  
75 experimental time to about 2 min 24 seconds / profile, sufficient to have access to the quantitative  
76 evolution of the water distribution during transient hydration or drying regimes.

## 77 2. Materials and methods

### 78 2.1. Experimental setup

#### 79 2.1.1 Humid air generator

80 The global layout of the experimental setup is described in Figure 1. It mainly includes the  
81 measuring cell in which the studied membrane is placed, an air generator with controls relative  
82 humidity (RH), temperature and flow rate, and the NMR spectrometer.

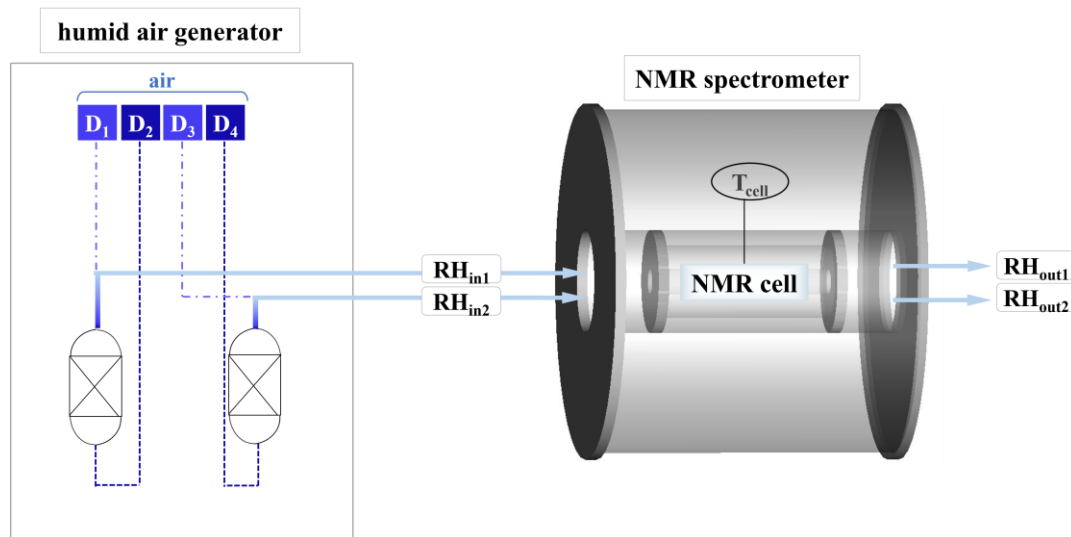


Figure 1. Schematics of the experimental setup.

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84

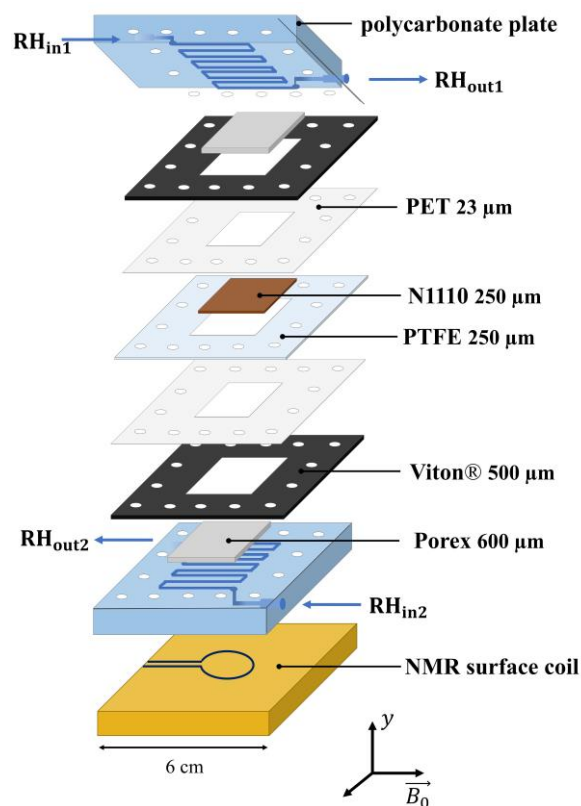


Figure 2. Detailed view of the different layers and materials of the NMR cell.

85

86 The humid air generator can produce two separated flows of humid air with flow rates in the range  
 87  $[0.05 - 1 \text{ Nl/min}]$ ,  $RH = [0 - 95 \text{ \%}]$  and  $T = [15 - 30^\circ\text{C}]$ . Each stream is generated by mixing  
 88 known volumes of dry and fully saturated air. The relative volumes are calculated based on the  
 89 desired flow rate and the temperature of the measuring cell, determined with a thermocouple  
 90 placed as closed as possible to the front of the NMR spectrometer. The relative humidity of the  
 91 streams at the inlet ( $RH_{in1}, RH_{in2}$ ) and outlet ( $RH_{out1}, RH_{out2}$ ) of the cell are recorded using four  
 92 VAISALA HMP7 Relative Humidity and Temperature Probes. The probes are heated to prevent  
 93 water condensation and allow the measurement in a wide range of RH values, with an accuracy up  
 94 to  $\pm 0.8 \text{ \% RH}$  (value given by the manufacturer [22]). As the stray field of the NMR spectrometer

95 propagates far from the magnet, the air generator should be placed at a distance of about 2 – 3 m  
96 from it. The air inlet and outlet tubings are wrapped with heating cords and insulated with foam to  
97 avoid water condensation. The temperature of the cords is regulated at 65°C.

### 98 **2.1.2 NMR cell**

99 The measuring cell (Figure 2) must be able to supply a membrane with humid air on both sides in  
100 a homogeneous way. The materials must also be compatible with the presence of strong magnetic  
101 fields and not interfere with the NMR measurement. The humid air is fed into polycarbonate (PC)  
102 plates with serpentine channels 1 mm wide and 0.8 mm deep. The two air streams flow in  
103 countercurrent. The membrane sample ( $2.7 \times 2.7 \text{ cm}^2$ ) is placed in the center of a PTFE layer  
104 which thickness is approximately the same as the nominal thickness of the membrane (250  $\mu\text{m}$ )  
105 and between two 23  $\mu\text{m}$  thick polyethylene terephthalate (PET) layers to prevent air leakage. Gas  
106 diffusion layers (GDL) homogenize the distribution of air coming from the bipolar plates. They  
107 are composed of 600  $\mu\text{m}$  thick Porex<sup>®</sup> sheets ( $2.7 \times 2.7 \text{ cm}^2$ ) placed in the center of 500  $\mu\text{m}$   
108 Viton<sup>™</sup> seals. Porex<sup>®</sup> is a polyethylene-based porous media used in filtration and ventilation  
109 applications. The pore size is in the range 40 – 100  $\mu\text{m}$ . The whole cell is clamped with nylon  
110 screws on the plate on which is engraved the radio frequency surface coil used to perform the  
111 NMR measurement (see next paragraph).

### 112 **2.2. NMR and MRI protocols**

113 The NMR experiments are performed on a Bruker BioSpec 24/40 spectrometer operating at the  
114 proton Larmor frequency of 100.36 MHz. The system is equipped with a 6 cm ID magnetic field  
115 gradient system (BGAs) producing a maximum intensity of 1 T/m. The NMR probe is a custom-  
116 built single turn 1 mm wide copper strip loop printed on CuFlon<sup>®</sup> (Polyflon Company). The  
117 internal and external diameters are 1.8 cm and 2.0 cm respectively. This coil is used for both



118 radiofrequency emission and NMR signal reception. More details about its design are given in a  
119 previous publication [7]. This kind of two-dimensional probe is suitable for the characterization of  
120 thin films [23]. The sensitivity is best when the plane of the object (the membrane) is placed at a  
121 distance equal to half the coil radius. Since the thickness of the N1110 membrane is small  
122 compared to the coil radius, there is no need to apply a correction due to the negligible  
123 inhomogeneity of the RF field in the depth of the membrane.

124 The different layers of materials were chosen so that they did not produce an NMR signal (Viton,  
125 PTFE) or the produced signal was very different from that of the water signal in the membrane.  
126 This is the case for hydrocarbon plastics such as Porex<sup>®</sup>, PET and PC, which produce a solid-like  
127 proton NMR signal (with very short NMR relaxation times  $T_2$ ) that contributes to the NMR  
128 spectrum only in the baseline. Note that this background signal also contains the contribution of  
129 all the plastics surrounding the RF coil (such as the PMMA frame that supports the RF coil plate).  
130 The proton spectra were obtained by performing the Fourier transform of the FID temporal signal  
131 obtained after the application of a 23  $\mu s$ -long  $90^\circ$  RF pulse. The relaxation time  $T_2$  was determined  
132 by fitting the time evolution of the spin-echo amplitude during a CPMG sequence [24] by a single  
133 exponential function. The echo time was  $TE = 2 ms$ . The through-plane water profiles were  
134 measured using the 1D spin-echo single-point imaging sequence (SE-SPI) introduced by Ouriadov  
135 and coworkers for the NMR characterization of thin films, including a Nafion membrane [20]. The  
136 temporal sequence is depicted in Figure 3. The combination of the two RF pulses  $90^\circ - 180^\circ$  at  
137 times  $t = 0$  and  $t = TE/2$  produces a spin echo signal which is recorded at time  $t = TE$ . The  
138 through-plane spatial coordinate  $y$  is encoded in a one-dimensional reciprocal space by the variable  
139  $k_y = \gamma \cdot g_y \cdot t_{enc}$ , where  $\gamma$  is the proton gyromagnetic ratio,  $g_y$  is the amplitude of the magnetic  
140 field gradient and  $t_{enc}$  is the encoding time, *i.e.* the time during which the field gradient is turned

141 on. The acquisition of an NMR intensity profile containing  $N_p$  points consists in recording the spin  
 142 echo intensity at  $t = TE$  for each value of the magnetic field gradient in the interval  
 143  $[-g_{max}; +g_{max}]$  divided into  $N_p$  values. The repetition time  $TR$  separating the acquisition of two  
 144 consecutive points in the reciprocal space is parameterized by the longitudinal relaxation time  $T_1$   
 145 and must verify  $TR \sim [3 - 5] \times T_1$  to ensure the return to equilibrium of the nuclear  
 146 magnetization between two experiments. The complex signal intensity is written:

$$S(k_y) = \int S(y) \exp[i2\pi k_y \cdot y] dy \quad \text{Eq. 1}$$

147 where  $S(y)$  is the spatial NMR intensity profile, determined from Fourier transformation. The  
 148 intensity profile is related to the water concentration profile  $\lambda(y)$  by:

$$S(y) = K \cdot \lambda(y) \exp\left[\frac{-TE}{T_2(\lambda)}\right] \left(1 - \exp\left[\frac{-TR}{T_1(\lambda)}\right]\right) \quad \text{Eq. 2}$$

149 where  $K$  is a constant and the relaxation times  $T_1(\lambda)$  and  $T_2(\lambda)$  are functions of the water content.  
 150 When the repetition time  $TR$  is sufficiently large, the NMR intensity is only weighted by the  
 151 transverse relaxation term:

$$S(y) = K' \cdot \lambda(y) \exp\left[\frac{-TE}{T_2(\lambda)}\right] \quad \text{Eq. 3}$$

152 Under this condition, when the membrane is in thermodynamic equilibrium and is exposed to two  
 153 humid air flows with the same relative humidity on both sides, the water content profile can be  
 154 inferred from the intensity profile using a calibration procedure. The water sorption isotherm,  
 155 measured at the same temperature using a dynamic vapor sorption analyzer (IGAsorp from Hiden  
 156 Isochema, Warrington, England), provides the relationship between relative humidity and water  
 157 content [The measurement is shown Figure SI1 of the Supplementary Information].

158

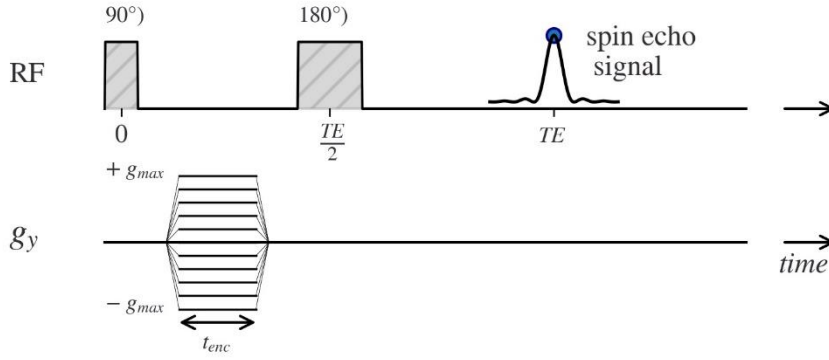


Figure 3. Timeline showing the main events that take place during the SE-SPI sequence.

159

160 The pixel size  $\Delta y$  is determined by the maximum amplitude of the field gradient  $g_{max}$  according

161 to:

$$\Delta y = \frac{\pi}{\gamma \cdot g_{max} \cdot t_{enc}} \quad \text{Eq. 4}$$

162 The resolution limit (related to the minimum value of  $\Delta y$ ) is therefore theoretically determined by

163 the maximum value of the field gradient that can be produced by the gradient coils. In reality, this

164 limit, extensively examined by Gravina and Cory [25], is limited by the mean square displacement

165 of the water molecules during the echo time (TE), which is about  $\Delta y_{min} = \sqrt{2D_s TE} \cong 4 \mu m$  for

166  $TE = 15 ms$  and  $D_s = 5.10^{-10} m^2/s$ , the approximate value of the water self-diffusion

167 coefficient at  $25^\circ C$  in a water saturated Nafion membrane [21]. Unlike frequency encoding

168 methods, SPI techniques use a phase encoding scheme. This method is preferred for imaging water

169 in ionomer membranes because it is insensitive to imaging artifacts resulting from the dependence

170 of NMR chemical shift on membrane water content (as observed on Figure 7). In this study the

171 hydration profiles were measured using an encoding time  $t_{enc} = 3 ms$ , a maximum gradient

172 strength  $g_{max} = 0.375 T/m$ , 128 encoding steps,  $TE = 7.5 ms$  and  $TR = 500 ms$ . The spatial

173 “resolution” is  $\Delta y = 9.776 \mu\text{m}/\text{point}$  and the field of view  $FOV = 1.251 \text{ mm}$ . Finally, it should  
174 be mentioned that the measurements of the hydration profiles are performed after carefully  
175 aligning the plane of the membrane orthogonal to the direction of the imaging gradient (y). The  
176 alignment procedure, described in reference [7], is critical in order to obtain profiles with square  
177 edges. The thickness of the membrane measured on the profiles is deduced from the variation of  
178 the NMR intensity when crossing the interface between the outside and the inside of the material.  
179 The inflection point is considered as the edge of the membrane and is obtained numerically by the  
180 determination of the maximum and minimum of the second derivative of the thickness with respect  
181 to the distance.

### 182 **3. Results**

#### 183 *3.1 Performance of the humid air generator*

184 The performance of the humid air generator was evaluated under the same conditions as in the  
185 experiments that are described later (paragraph 3.2), i.e. with the same air flow rate ( $30 \text{ NL}/\text{h} =$   
186  $500 \text{ mL}/\text{min}$ ) and temperature ( $T = 23.4 \pm 0.2^\circ\text{C}$ ). The polymer membrane was replaced for the  
187 performance test by an impermeable PET layer so that the gas outlets were directly connected to  
188 the inlets and no water flow passed through the membrane plane. The air humidity was varied in  
189 the range [10% – 95%] in 3 hours long step. Since the cell's clamping screws are made of nylon,  
190 the air tightness of the cell was checked by immersing it in water. The test was repeated several  
191 times and no air bubbles were observed. An example of the measurements is shown in Figure 4,  
192 where the relative humidity of two air streams, at the inlet and outlet of the cell, are plotted as a  
193 function of time. The accuracy of the relative humidity is shown in Figure 5(a), while the standard  
194 deviation is plotted in Figure 5(b).

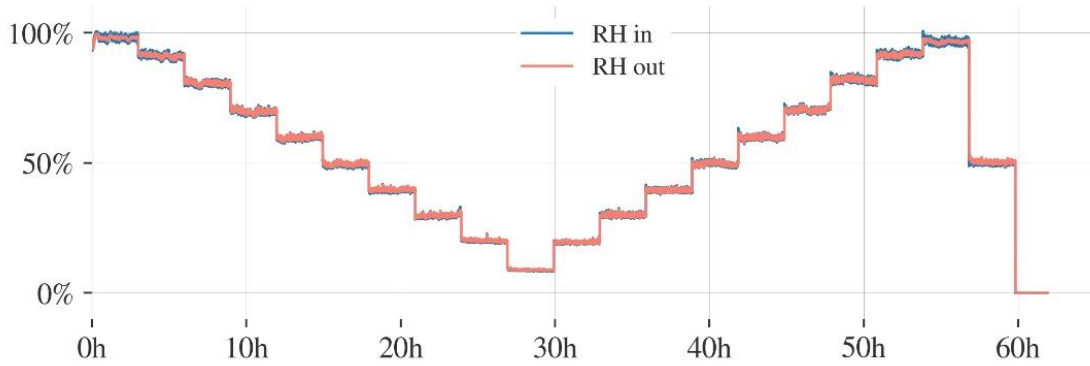


Figure 4. Performance test of the humid gas generator. Relative humidity of the cell inlet and outlet gases as a function of time.

195

196 The overall tests show that:

197 - The system is able to generate and maintain humid airflow over the entire relative humidity  
 198 range;

199 - Humidity stability is greater at low *RH* than at high *RH*;

200 - The measured values correspond to the setpoints with very good accuracy over the entire  
 201 range;

202 - The deviation relative to the setpoint ( $\frac{RH_{measured} - RH_{setpoint}}{RH_{setpoint}} \times 100$ ) does not exceed 5%,

203 except when the humidity is very low, typically below 15% *RH* where it can reach 15%

204 at most ( $15 \pm 2.25$  %*RH*).

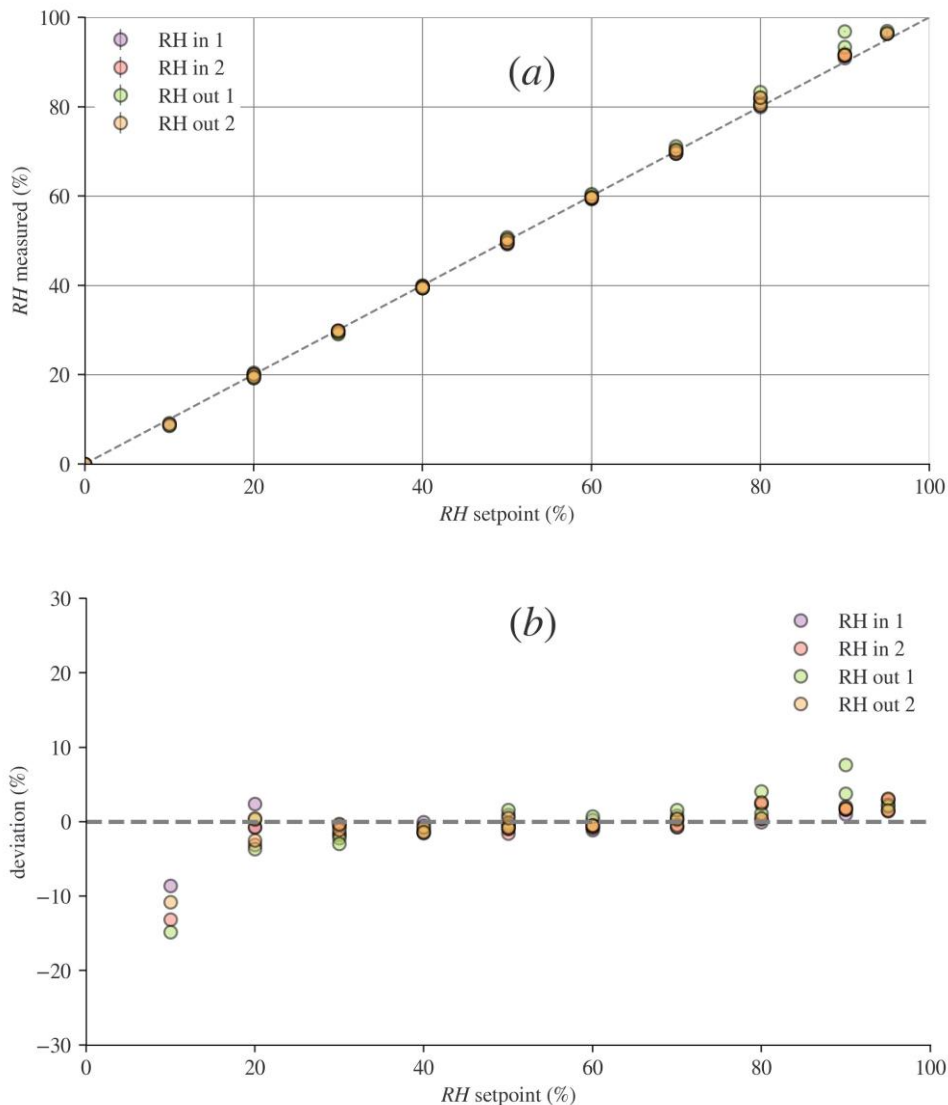


Figure 5. a) Accuracy of the humid air generator: RH measured as a function of the setpoint. b) Deviation in percent of the generated RH from the setpoint.

205

### 206 3.2 In-situ NMR measurements of membrane properties

207 The experiments discussed in this section were conducted by sending a stream of wet air  
 208 equilibrated at different relative humidity into the measuring cell containing the membrane sample.  
 209 The whole range of humidity was tested, from 10% to 90% RH at a temperature of 24°C, with  
 210 steps lasting three hours each. Five humidity cycles, called in the following "step sequences", are

211 discussed. The temporal variation of the step sequences is described in Figure 6. The total duration  
212 of the experiments was 108 hours. Each side of the membrane was exposed to an identical gas  
213 flow rate and relative humidity condition throughout all the described experiments. The NMR  
214 spectrum,  $T_2$  transverse NMR relaxation time and water content profile were measured five times  
215 at each step. At the end of the steps, all the NMR parameters are stabilized which allows to consider  
216 that the membrane has reached a state of equilibrium with the humid air.

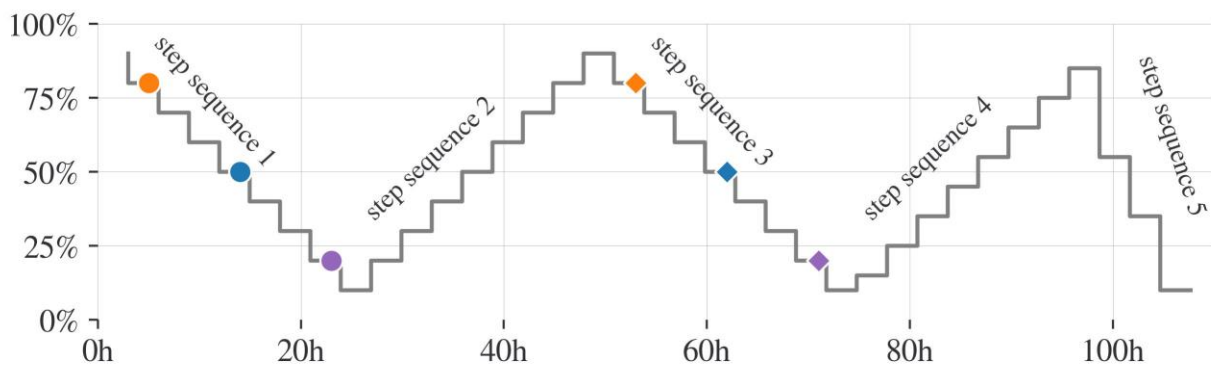


Figure 6. Temporal evolution of the air relative humidity (RH) during the five step sequences.

217

218 The proton NMR spectra measured during step sequence 2 are shown in Figure 7. They are  
219 composed of a single resonance line, as described in the literature [26, 27]. The different  
220 populations of protons are in a fast exchange regime relative to the time scale of NMR  
221 measurement which makes them indistinguishable [28]. The resonance line is centered at about  
222 12 ppm in the driest membrane and shifts to low chemical shifts as the amount of water increases.  
223 This shift reflects the loss of confinement of water molecules and the dilution of the charges as  
224 water content increases. The evolution as a function of hydration is fast at low water content  $\lambda$  and  
225 moderate after [29], so that the evolution is  $\sim$  linear for  $RH > 10\%$  (this can be seen later in the

226 document on Figure 10(a)). The bump observed on the right side of the spectra is a "solid" NMR  
227 signal produced by all proton-containing layers in the cell (PET, PC, Viton).

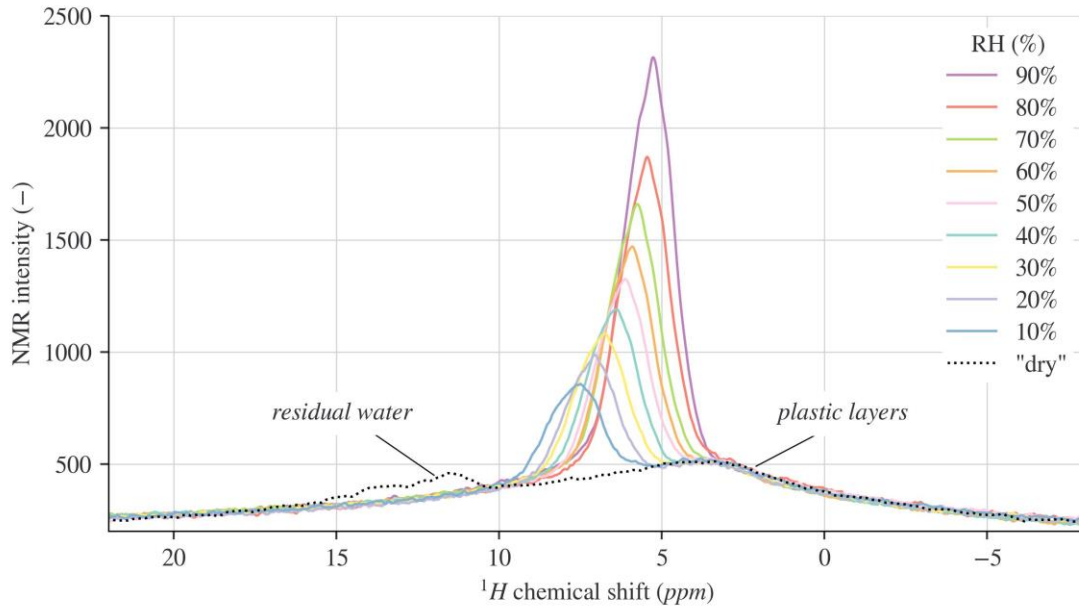


Figure 7. Evolution of the proton NMR spectrum as a function of equilibrium RH. The data were collected during step sequence 2 at the end of each humidity step.

228

229 The “dry” membrane was exposed to a flow of dry air for three hours. Therefore, the residual  
230 hydration is close to one molecule of water per ionic  $SO_3H$  site (three protons) [21, 28, 30]. As the  
231 chemical shift strongly depends on the water content, its determination can be seen as a good  
232 method to evaluate  $\lambda$  in a reliable and fast way. As the spectral resolution of the measurement is  
233 very high ( $0.003\text{ ppm} = 0.3\text{ Hz}$  in the case of our measurements), the accuracy of the  
234 measurement can in theory be very good if accurate calibration is available. The perfluorosulfonic  
235 acid (PFSA) ionomer membranes have quite remarkable behaviors and are extremely sensitive to  
236 the thermal and hydric history. In particular, many studies demonstrate the influence of  
237 hydrothermal conditions on the mechanical, sorption and diffusion properties of water [31, 32].



238 The evaluation of the chemical shift is therefore a good way to characterize the effect of these  
239 environmental conditions. The chemical shift, the  $T_2$  relaxation time and the 1D water content  
240 profile were systematically measured during the five different step sequences (Figure 8). The zoom  
241 on the right part of the figure corresponds to the evolution of each of the parameters during the  
242 first step sequence between 10 *h* and 20 *h*. The NMR intensity and the thickness of the membrane  
243 are clearly stabilized at the end of each humidity step (note that if the error on the thickness is  
244 evaluated at  $\pm 1$  point then it is quite important ( $\pm \sim 10 \mu m$ ) relatively to the thickness variation  
245 between two steps). The chemical shift and the relaxation time have slightly less stabilized values  
246 at the end of the humidity steps. The chemical shift, as we have seen, has an excellent sensitivity  
247 and its determination is very accurate, while the determination of the transverse relaxation time  
248 relies on an exponential function fitting, which is less reliable and leads to less accuracy.

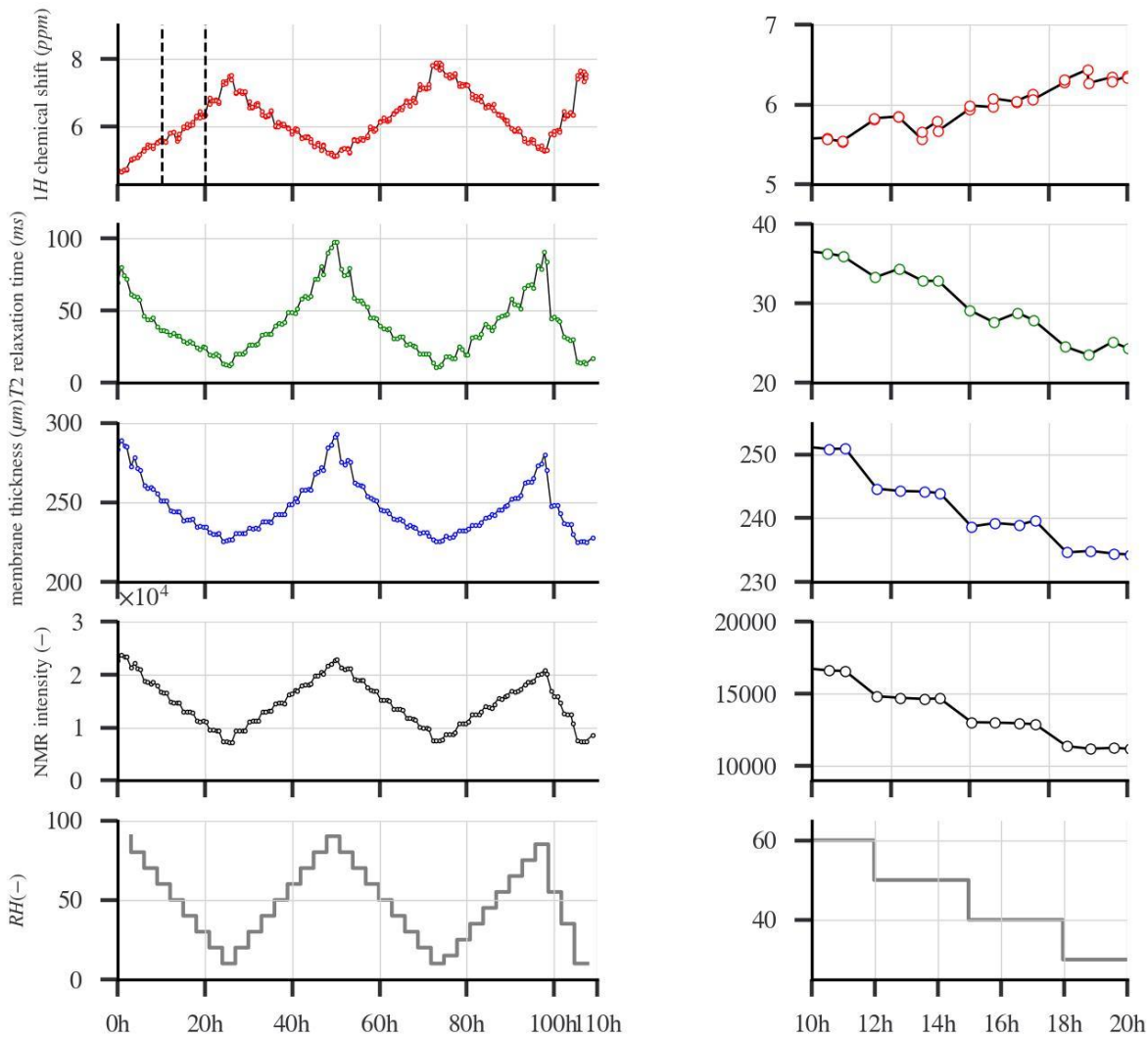


Figure 8. Evolution of  $^1\text{H}$  chemical shift,  $T_2$  relaxation time, NMR intensity and membrane thickness as a function of time during the five step-sequences. The experiments are repeated four to five times at each RH step. The right column shows a zoom in the period 10–20h during the first step-sequence.

249

250 Figure 9 shows the proton NMR spectra collected at the same RH values (20%, 50% and 80%)

251 during step sequence 1 and 3 (the times at which the measurements were performed are shown on

252 the timeline of Figure 6 using the same color codes). It can be seen that the resonance line

253 systematically shifts towards the high chemical shifts during the second dehydration sequence.

254 The initial state of the membrane at the beginning of sequence 1 corresponds to a fully hydrated

255 state, i.e. the sample has been soaked in water before being installed in the NMR cell. Water  
256 adsorption in liquid phase is known to induce a strong swelling of the membrane and to modify its  
257 mechanical properties: the swollen structure is softer and the water is very mobile. After a humidity  
258 cycle, the state of the water is different for the same RH values: after passing through a low  
259 humidity hydration stage, the polymer membrane is more rigid, the sorption capacity is slightly  
260 reduced and the water is less mobile at a given relative humidity. The effect of the hydration history  
261 of the membrane is therefore precisely detectable by measuring the NMR spectrum of water  
262 protons.

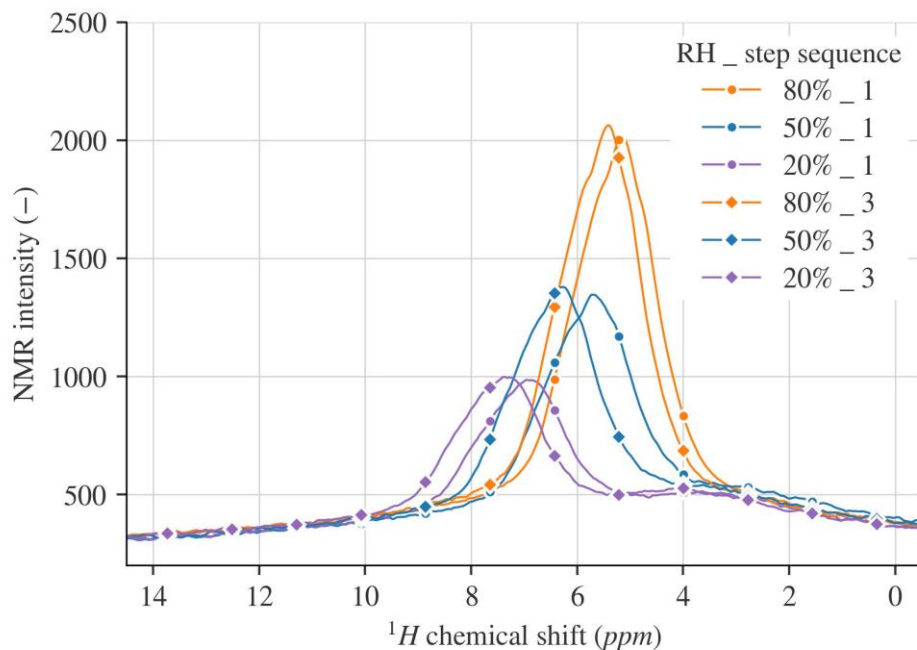


Figure 9. Comparison of NMR spectra measured at the same RH values during different step-sequences.

263  
264 As the relative humidity of the air in contact with the membrane is further cycled, the chemical  
265 shift reaches a stable value, as shown in Figure 10(a) where this parameter is plotted for all step-  
266 sequence. The same observation can be deduced from the evolution of the transverse relaxation

267 time  $T_2$  for the different step sequences (Figure 10(b)). The  $T_2$  time, which also depends strongly  
268 on the membrane water content (the variation is almost an order of magnitude), varies by about  
269 25% at  $RH = 90\%$  between the first and the second step sequence. The effect is more visible for  
270 higher relative humidities, but in all cases the parameter reaches a plateau value when the gas  
271 humidity has been cycled several times. The NMR relaxation times  $T_1$  and  $T_2$  are markers of the  
272 water molecular dynamics in the membrane and are known to be dependent on temperature and  
273 hydration [33, 34]. The absolute value of the relaxation times is much lower than that measured  
274 on free water because of the confinement effects of water interacting with the internal surfaces of  
275 the pores in the microstructure of the membrane [35]. Paramagnetic interactions can also  
276 contribute strongly to the relaxation of the proton nuclear magnetization in samples containing  
277 impurities of metal cations such as sodium, copper or manganese [33, 36] which is frequently the  
278 case for membranes that have not undergone a specific washing protocol. The balance between the  
279 two effects is difficult to evaluate and the increase or decrease of  $T_2$  values with water content can  
280 be observed in some cases due to subtle dilution effects during sorption that can lead to a change  
281 in the nature of the driving interaction between nuclear spins [37]. In the present study, the short  
282  $T_2$  times and their increase during humidity cycles in parallel with a decrease in the amount of  
283 water (Figure 10(c)) tend to prove that paramagnetic impurities are present in the membrane  
284 samples and are responsible for most of the nuclear relaxation. Regardless of the precise origin of  
285 the relaxation,  $T_2$  reaches a plateau value at the end of the cycles, which corroborates the  
286 observations made on the chemical shift, and demonstrates a stabilization of the microstructure  
287 and mechanical properties of the membrane.

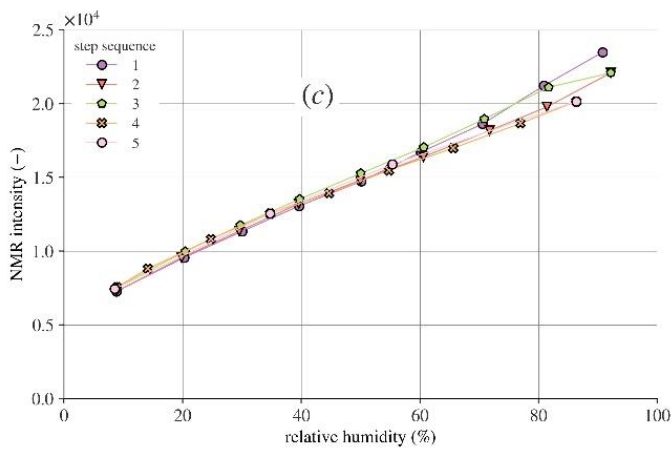
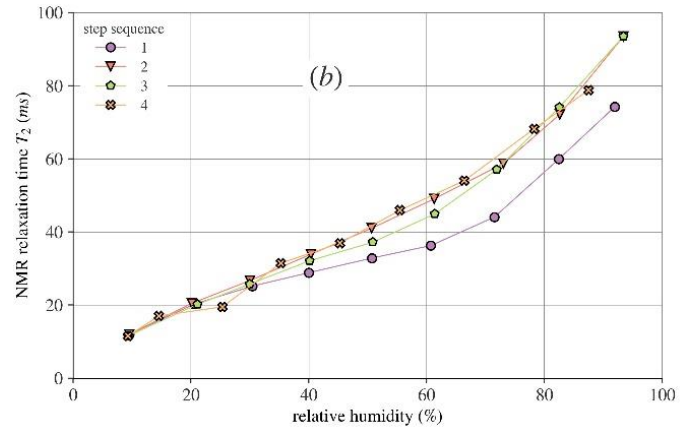
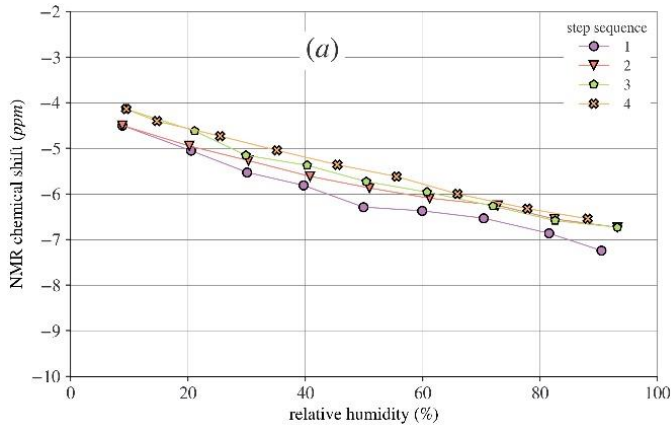
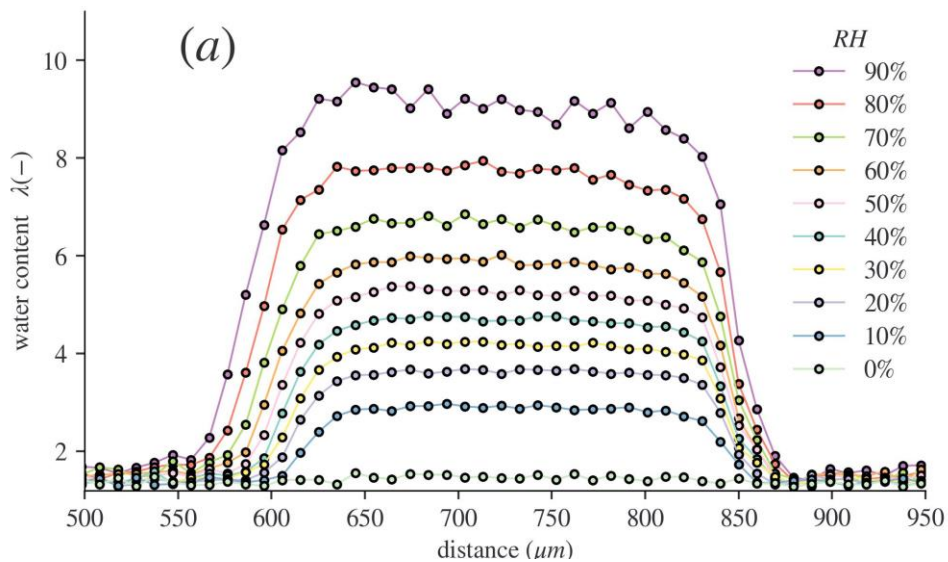


Figure 10. Evolution of the proton chemical shift (a), NMR  $T_2$  relaxation time (b) and NMR intensity (c) measured at equilibrium at the end of each humidity step during the five step sequences.

288

289 The through-plane water content profiles measured at equilibrium during step sequence 3  
 290 are shown in Figure 11(a). The profiles are logically square because the moisture content of the  
 291 air in contact with the membrane is the same on each side. Despite the rigorous alignment  
 292 procedure, the edges are not very steep, the transition from the outside to the inside of the  
 293 membrane being about four points wide. The main reason for this is the lack of flatness of the  
 294 membrane on the detection surface of the NMR probe ( $\sim 4 \text{ cm}^2$ ). Another reason is a possible  
 295 variation in the chemical composition of the membrane at the interface. It is indeed known that the  
 296 sulfonated sites of Nafion are less concentrated there [38]: the water content of the membrane  
 297 would then be less important over a short distance near the interface. This effect, even if it is

298 supposed to be measurable, should not propagate over a large distance: less than a few microns in  
299 any case. The water content ( $\lambda$ ) plotted on the profiles was obtained from a calibration of the NMR  
300 intensity measured in the membrane at equilibrium with humid air (see Eq3) and the Nafion N1110  
301 sorption isotherm (Figure SI1). The calibration curve is shown in Figure SI2 of the Supplementary  
302 materials. The variation in membrane thickness extracted from the profiles is shown in Figure  
303 11(b). Like the NMR intensity, the shape of the curves is analogous to that of the sorption curve,  
304 with the thickness of the membrane varying approximately linearly with its water content  
305 (isotropic swelling). The error in thickness determination (at most +/- 1 point) is significant, so the  
306 difference between the curves for the different step sequences is less marked than it is in the case  
307 of NMR intensity (Figure 10(c)).



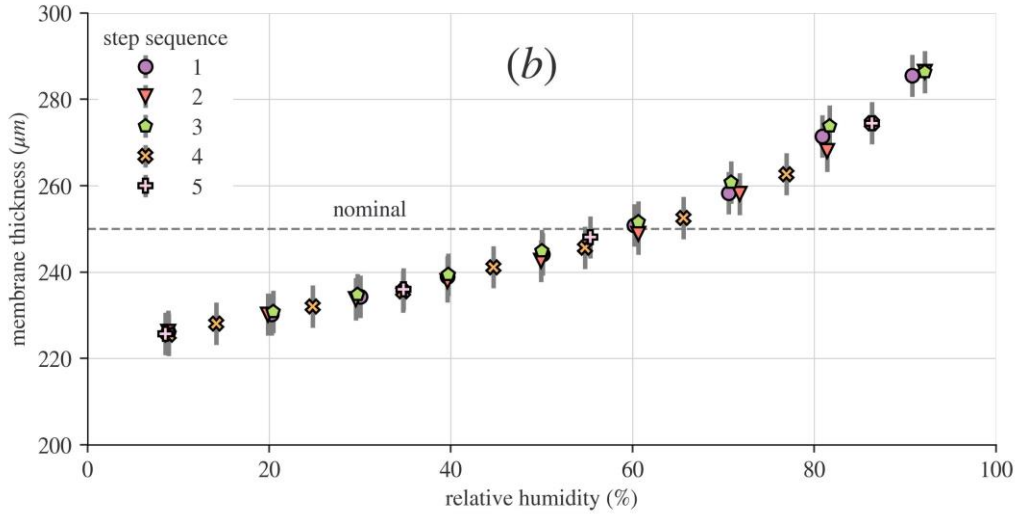
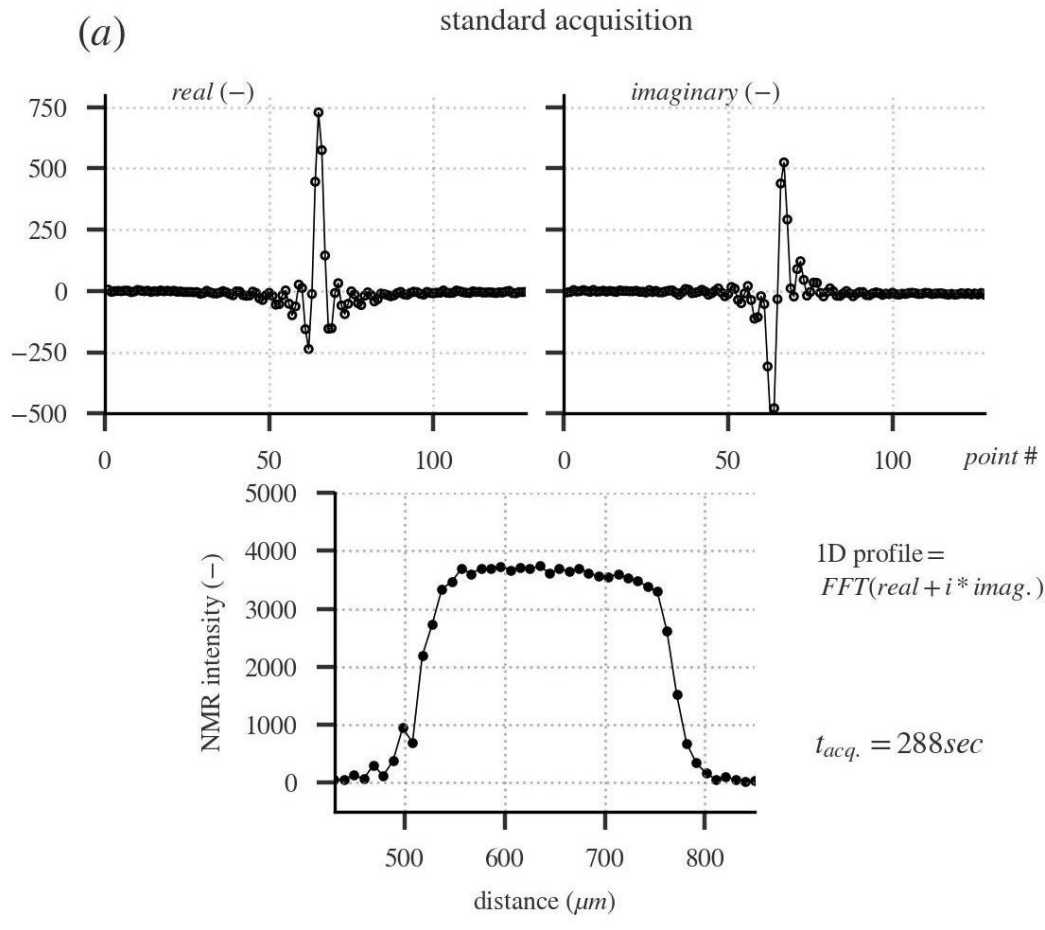


Figure 11. (a): through-plane water profiles in N1110 membranes at equilibrium with two streams of RH-controlled humid air. (b): Evolution of the membrane thickness as a function of relative humidity for the different step sequences. The nominal thickness of the membrane ( $250 \mu\text{m}$ ) is indicated with a dashed line.

### 308 3.3 Reduce acquisition time with partial acquisition

309 The motivation for using partial Fourier image reconstruction is the possibility of  
 310 completing acquisition in roughly half the time of a normal profile. We used the most basic partial  
 311 acquisition scheme which consists in acquiring only some of the 128 phase-encode steps without  
 312 sacrificing spatial resolution. We tested different options (25% acceleration, 30% acceleration,  
 313 etc..) and we finally chose to acquire only half of the points (50% acceleration) by removing the  
 314 first 40 gradient steps (32%) and the last 24 (18%). An example of this procedure is shown Figure  
 315 12.





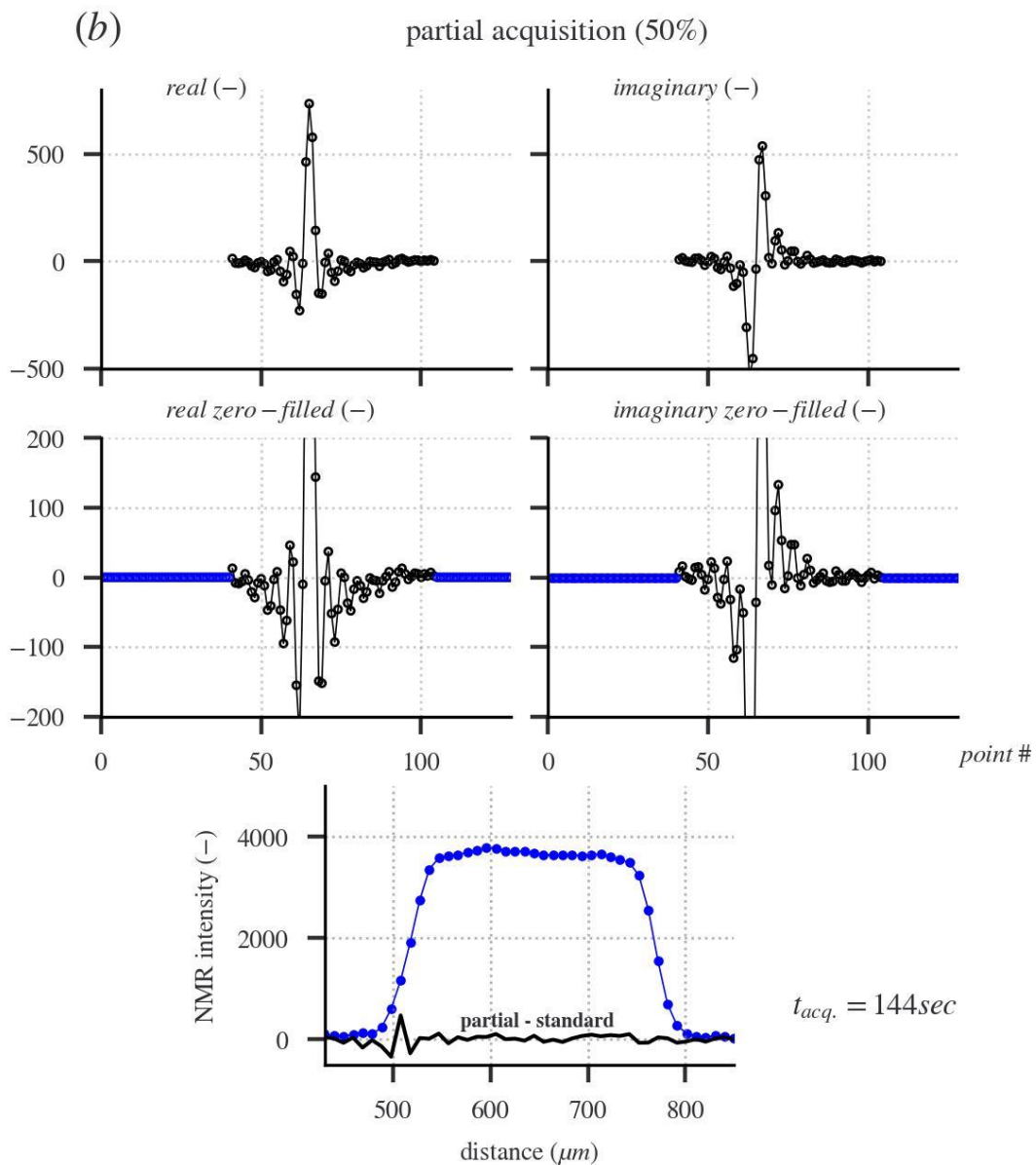


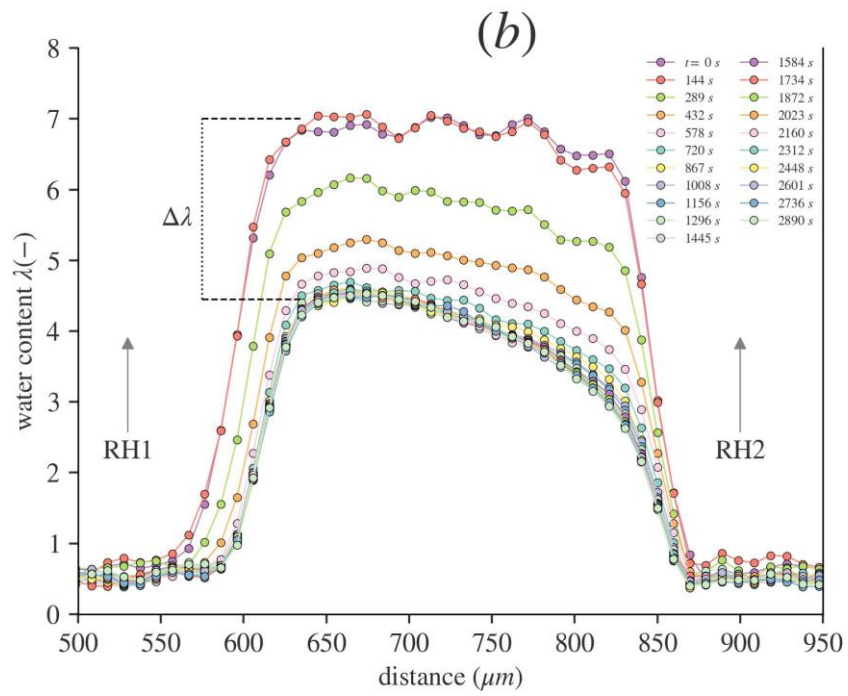
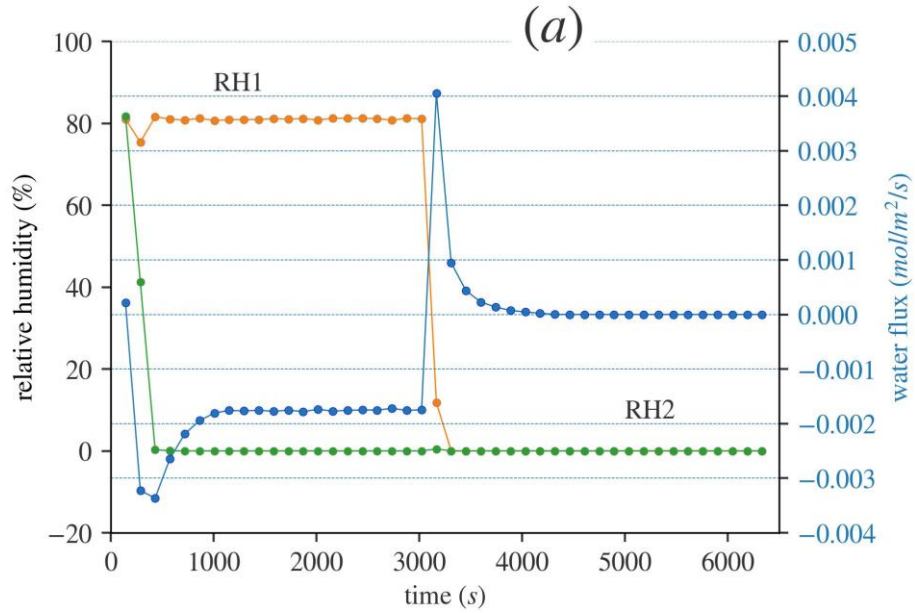
Figure 12. (a) Real and imaginary parts of the NMR signal during standard measurement of the water profile in the membranes. The profile is obtained by fast Fourier transform of these signals. (b) Partial acquisition performed on the same membrane a few moments after the first measurement. The first 40 points and the last 24 points were not recorded. Acquisition time is reduced by 50%. The data were then zero-filled (zoom and blue dots) before Fourier transformation to obtain the water profile.

317 Figure 12(a) shows the "standard" measurement (duration: 288 seconds), during which all 128  
318 points are acquired. The 1D membrane hydration profile is obtained by Fast Fourier Transform  
319 from the real and imaginary NMR signals. It can be clearly seen that the majority of the signals  
320 are located in the center, and that the edges contain little information. After the partial acquisition  
321 of the experiment in Figure 12(b) (duration: 144 seconds) the 1D Fourier space was zero-filled  
322 during postprocessing. The quality of resulting profile obtained after Fourier transform is not  
323 deteriorated and is almost indistinguishable from the reference profile. The difference profile  
324 between the results of the two acquisitions shows just a small discrepancy near the left interface  
325 of the membrane where the reference profile shows an artifact. It is obvious that the partial  
326 acquisition strategy falls down when the 50% acceleration is concentrated on the first (or last) 64  
327 points because in this case the most important part of the information, concentrated in the center  
328 of the Fourier line, is not acquired. The resulting profile is then largely distorted (Figure SI3 of the  
329 Supplementary Information).

#### 330 **4. Perspectives: record transient hydration profiles, study interfacial water transfer** 331 **and determine the evolution of the diffusion coefficient**

332 By using the partial acquisition approach, it is possible to make the acquisition time of the  
333 water profiles compatible with a time-resolved study of the water transfers that take place during  
334 transient regimes when the humidity of the air in contact with the membrane varies from one value  
335 to another. Results of such an experiment are presented on Figure 13. In this experiment, the  
336 membrane is initially at equilibrium with two streams of humid air at 80% RH. The air humidity  
337 is then suddenly switched from 80% to 0% on one side of the sample. The water content profiles  
338 and the water flux through the membrane are recorded as a function of time (Figure 13(b)). A  
339 steady state is reached after  $\sim 2500s$  when the water profile and flux have stabilized. Then, the

340 air humidity is switched from 80% to 0% on the second side of the membrane and the profiles are  
 341 observed for another  $\sim 3000$ s period of time.



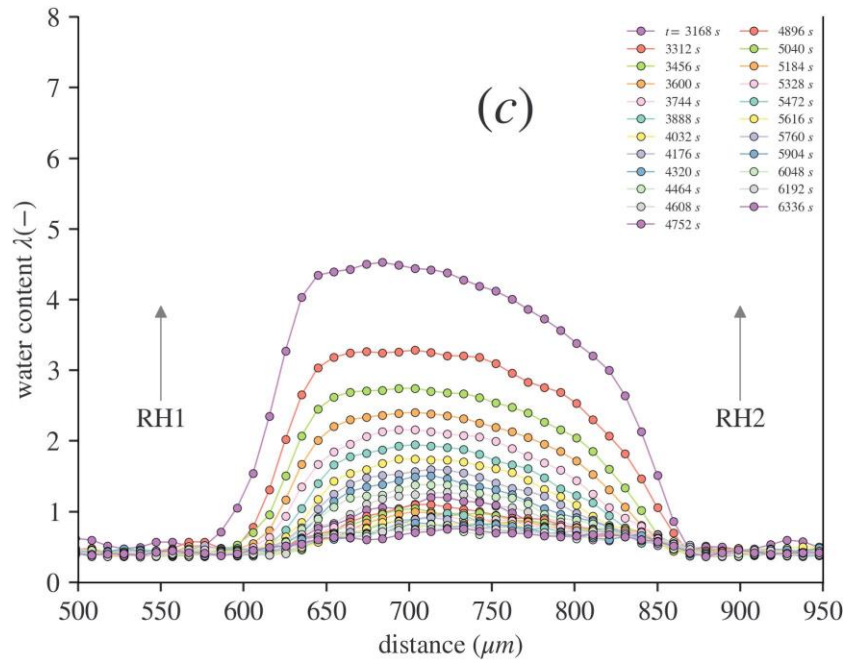


Figure 13. Time-resolved experiment. (a) Time variation of air relative humidity in contact with both sides of the membrane. In blue color (second axis): evolution of the water flux through the membrane. (b) Water profiles measured as a function of time following the initial switch of air humidity on one side of the sample (RH2) from 80% to 0%. (c) Water profiles measured as a function of time after switching the air humidity on the second side of the sample (RH1) from 80% to 0%.

342

343 During transient regimes water redistribution in the membrane is limited by the transport of water  
 344 across the membrane/vapor interface. In the literature, the interfacial resistance to water transport  
 345 across Nafion membranes has been characterized using water permeation measurements [36, 39,  
 346 40] and the results demonstrated that there is a competition between interfacial water transport and  
 347 water diffusion in the bulk of the membrane. Both effects depend on water content, and the  
 348 resistance due to diffusion scales linearly with the membrane thickness so that permeation  
 349 experiments have to be repeated multiple times by varying membrane thicknesses. This approach  
 350 is time-consuming. The method discussed here measures the water content of the membrane at the

351 membrane/vapor phase interfaces by means of MRI and the water flux through the membrane by  
352 means of the four RH probes. At steady state the interfacial resistance  $R_{int}$  can be evaluated using  
353 the following relationship between the driving force  $\Delta\lambda$  (the difference between the water content  
354 at the interface and the water content at equilibrium, see Figure 13(b)) and the water flux  $\varphi$  :

$$R_{int} = C_{SO3H} \frac{\Delta\lambda}{\varphi} \quad \text{Eq. 5}$$

355 where  $C_{SO3H}$  is the concentration in sulfonate ions in the membrane in mole/ $m^3$  [41].

356 The water profile and the flux measured at  $t = 2890$  s enable us to estimate an interface resistance  
357 approximately equal to  $2.6 \cdot 10^6$  m/s, in full agreement with literature data [36, 38, 39, 41]. Using  
358 this procedure, it is possible to determine the evolution of interface resistance as a function of the  
359 air humidity to which the membrane is exposed.

360 Furthermore, as the measured steady states water profiles are not linear, the water diffusion  
361 coefficient is consequently a function of the membrane water content. The hydration dependence  
362 of the water diffusion coefficient in Nafion has been widely debated in the literature, and no clear  
363 consensus has yet emerged. As noted by Kosoglu and Weber, the difficulty comes from the nature  
364 of diffusion process in PFSA membranes, which is strongly dependent on the type of the  
365 measurement and the transport mechanisms it probes and become more complex over larger  
366 concentration gradients and time scales [38]. Using our experimental method and a suitable model  
367 of diffusive transport in the membrane, the shape of the water profiles and their evolution over  
368 time in response to changes in air humidity can be used to determine this concentration  
369 dependence. All these prospects are currently under study in our laboratory.

370

371

## 372 **Conclusion**

373 The important physicochemical parameters of PFSA membranes used in fuel cells and  
374 electrolyzers are highly dependent on the state of the water in the polymer: the water content, its  
375 dynamics, its interactions with the pores in the microstructure. Nuclear magnetic resonance is a  
376 proton-selective method that is extremely sensitive to the state of water in such complex structures.  
377 The method discussed in this study enables precise *in-situ* measurement of NMR parameters such  
378 as the proton chemical shift and the transverse relaxation times in a reliable and reproducible way  
379 in a membrane exposed to well controlled climatic conditions. This control allows us to detect  
380 very small variations in the water state linked to the hygrothermal history of the membrane.  
381 Measurements show that this history is erased by repeated cycling of air humidity in contact with  
382 the membrane. 1D MRI measurements through the membrane allow us to follow the evolution of  
383 the material's thickness, and precise calibration allows us to quantitatively determine the hydration  
384 profile in terms of the hydration number  $\lambda$ . Finally, a simple-to-implement partial acquisition  
385 refinement substantially reduces 1D image acquisition time without sacrificing quality. This opens  
386 the door to faster measurements that can be used to study transient phenomena at the  
387 membrane/moist air interfaces, when gas humidity setpoints vary at the edges of the membrane.  
388 All the prospects opened up by this study are potentially applicable to fuel cell and electrolyzer  
389 applications.

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392 n° 19247 ALPE: "Advanced Low-Platinum hierarchical Electrocatalysts for low-T fuel cells".

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