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Towards a NMR-Based Method for Characterizing the Degradation of Nafion XL Membranes for PEMFC

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28 The decomposition of the membrane is induced by several factors among which mechanical
29 stress and chemical degradation prevail.

30 The mechanical degradation is initiated by humidity cycling that creates alternating
31 shrinkage/swelling events and a non-uniform stress distribution in the membrane plane. The
32 resulting reduction of the polymer mechanical strength can lead to the formation of cracks
33 and to the final failure of the membrane electrode assembly (MEA) (3-5).

34 The chemical decomposition of the PEM in the MEA is caused by gas crossovers. The
35 electrochemical reactions of these gases cause the formation of free radicals and the attack
36 of the polymer chemical structure, which results in scissions in the main chain and in the side
37 chain and finally to the thinning of the membrane (6, 7).

38 Many studies have focused on PEM chemical degradation and a comprehensive review of
39 the current understanding of the mechanisms in perfluorosulfonic acid (PFSA) membranes
40 was recently published (8). PFSA membranes, such as Nafion, Flemion or Aciplex are today
41 the most widely used fuel cell electrolytes thanks to their good chemical robustness and
42 their high proton conductivity (9). Through the years, efforts have been made to reduce the
43 membrane's ionic resistivity without compromising the mechanical properties. This was
44 made possible by the introduction of chemical stabilizers and mechanical reinforcement. For
45 instance, the Nafion XL is a reinforced membrane composed of two external PFSA layers
46 with stabilizers to reduce chemical attack and a central microporous polytetrafluoroethylene
47 (PTFE)-rich support layer to provide additional mechanical strength and enable the use of
48 thinner ionomer. The central PTFE layer is impregnated with ionomer to provide a
49 continuous conductive pathway across the membrane's thickness.

50 The structure and basic properties of the Nafion XL membrane were investigated by Shi and
51 co-workers (10). The authors examined the effect of reinforcement and pre-treatment and
52 showed that the reinforcement layer alters significantly the dimensional swelling in the
53 plane while it increases swelling in the thickness direction in such a way that the overall
54 water uptake remains similar to that of the non-reinforced analogue membrane. This
55 swelling anisotropy was shown to be important in reducing the swelling-induced fatigue
56 under cycling fuel cell operation. The same conclusions were drawn in the Gore Select
57 reinforced membrane (11). The analysis of the transport properties reveals that the

58 evolution of the through-plane proton conductivity with the relative humidity is similar for
59 both the XL and the unreinforced N212. This demonstrates that the ionic conduction is still
60 very efficient despite the introduction of the central non-conductive PTFE layer.

61 Although chemically stabilized and reinforced membranes represent advanced evolutions of
62 the PFSA copolymer, reinforced membranes stay nevertheless the target of chemical radicals
63 during FC operation. De Moor et al. (12) studied the degradation of reinforced PFSA
64 membrane on the anode and cathode sides by macroscopic thickness measurements. They
65 demonstrated that, in real systems operating conditions, PFSA degrades first at the anode
66 near the hydrogen inlet which enables hydrogen crossover and leads to the degradation at
67 the cathode. Highly degraded areas were also studied and the results showed that the
68 external PFSA layers disappeared almost completely.

69 The understanding of the impact of the combined effect of mechanical and chemical
70 stressors on the membranes properties is thus critical to improve their durability in FC
71 operation.

72 In the present study we aim at measuring several indicators of the Nafion XL properties in
73 the pristine state and after long term FC operation. The object of our analysis is the
74 evolution of the chemical structure and the water properties due to membrane degradation.
75 For this purpose, we use several experimental techniques, each of which capable of
76 delivering complementary information. The chemical structure is probed using ^{19}F -NMR to
77 estimate the global ionic exchange capacity (IEC) and IR spectroscopy in the attenuated total
78 reflectance (ATR) mode to look for chemical heterogeneities at the anode and cathode sides
79 of the aged sample. Information on the different water populations in the composite
80 structure is given by the analysis of the ^1H -NMR spectrum and the global water uptake is
81 measured through the sorption isotherm. Finally, we use pulsed-field gradient (PFG)-NMR to
82 characterize the water mobility and diffusion at the micron scale (13). To this point, our goal
83 is not to study the chemical degradation mechanisms but rather to elaborate an
84 experimental approach able to deliver a set of data indicative of membrane degradation.
85 The collection of structural, sorption and transport data on PEM membranes represents a
86 long and tedious process and necessitates quite a lot of resources (analytical instruments
87 and access to large instruments such as synchrotrons (14, 15)). Since the different data are

88 inter-correlated, we believe that it is possible to gather a set of experimental quantities in a
89 limited amount of time and to define a marker of the membrane degradation based on
90 these data. This paper presents the first steps towards this new approach.

91 **Experimental**

92 *Materials*

93 *Perfluorosulfonated membranes*

94 Two commercial PFSA membranes, Nafion XL and Nafion NR211, were purchased in
95 the protonated (H^+) form from Ion Power Inc.. Both membranes present a similar IEC. Nafion
96 NR211 is a monolayer membrane (nominal thickness 25.4 μm) based on chemically stabilized
97 copolymer of tetrafluoroethylene (TFE) and perfluoro(4-methyl-3,6-dioxoct-7-ene) sulfonyl
98 fluoride (16). Nafion XL is a PFSA based membrane with an additional microporous central
99 PTFE layer. The central reinforcement is impregnated both sides with PFSA. The nominal
100 thicknesses are $\sim 12 \mu m$ for the PTFE layer and $\sim 9 \mu m$ for each external PFSA layer (10, 17) .

101 A reinforced membrane which operated in Axane Evopac fuel cell system was also
102 investigated. This system, composed of two stacks of 55 cells, was studied in references (18)
103 and (12). It was operated in the field at a constant current density of 0.26 A/cm² during 12
104 860 hours with approximately 250 start/stop sequences and at an average stack
105 temperature of 60-65 °C. The system was fed at the cathode side with humidified air (60%
106 RH) at a relative pressure of 100 mbar (stoichiometry of 2.5) and at the anode side in dead-
107 end supply mode with pure dry hydrogen at 350 mbar relative pressure (stoichiometry of
108 1.1). The fuel cell stack was shut down due to recurrent low-level voltage faults. The
109 polarization curves measured at the beginning-of-life and at the end-of-life showed a loss of
110 performance in both stacks. The global voltage decay rate was $\sim 3.5 \mu V/h/cell$ and \sim
111 $4.5 \mu V/h/cell$ for the two stacks. The voltage of the cell chosen for the present study
112 decreased slightly from 0.718 to 0.706 V. Based on visual inspection we chose to perform
113 our measurements on a membrane area located near the H₂ inlet and air outlet where the
114 degradation was apparent.

115 *Membrane preparation*

116 The commercial membrane samples were pretreated according to a protocol based
117 on the one established by Xu et al (19, 20). The samples were first boiled in 3 wt. % hydrogen

118 peroxide solution during 1h and rinsed with distilled water to eliminate any organic
119 impurities. They were then soaked 30 minutes at room temperature in nitric acid (10 mol.L⁻¹)
120 ¹), rinsed again with distilled water and boiled in deionized water during 1h. In order to
121 ensure a complete substitution of any ionic sites of the ionomer, the samples were boiled in
122 sulfuric acid (1 mol.L⁻¹) during 1h before boiling during 1h in distilled water to clean the
123 sample. Finally, the samples were dried 24 h in an oven at 60°C.

124 The aged membrane was extracted from the MEA by carefully removing the gas
125 diffusion/electrode layers with a brush soaked in a water/ethanol mixture. It was then rinsed
126 with deionized water, dried at 60°C overnight and rehydrated in deionized water prior to
127 measurement. The sample investigated here (~1 cm x 1 cm) was cut from a specific area
128 near the dry hydrogen inlet and air outlet.

129 *Water Sorption*

130 The water sorption isotherms were measured using a IGASorp (Hiden Isochema, UK)
131 dynamic vapor sorption (DVS) analyzer. The samples were first dried several hours under dry
132 nitrogen at a temperature of 24°C. The water isotherms were recorded at 24°C for a water
133 activity range between 0 and 0.95. The water content λ , characterizing the number of water
134 molecules per sulfonic acid group, is determined from the water uptake $\frac{\Delta m}{m_0}$ using the
135 following relation:

$$\lambda = \frac{n(\text{H}_2\text{O})}{n(\text{SO}_3^-)} = \frac{\Delta m / 18}{\text{IEC} * m_0}$$

136 where IEC is the ion exchange capacity of the considered membrane expressed in eq/g, Δm
137 is the mass variation measured in g, m_0 is the membrane dry weight in g and the molecular
138 weight of water molecule is 18 g/mol.

139 *FTIR-ATR*

140 FTIR-ATR spectra were obtained with a Spectrum One (Perkin Elmer) spectrometer
141 equipped with a DTGS detector and using a single reflection diamond ATR accessory. The
142 spectra were recorded with a wavenumber resolution of 1 cm⁻¹ in the spectral range [650 –
143 4000 cm⁻¹]. The measurements were performed at various locations on the surface of the
144 commercial membrane samples to check the homogeneity of the chemical structure. In the

145 case of the aged sample, the measurements were also performed in various areas of the
146 surface to ensure reproducibility and on both membrane sides to investigate aging
147 heterogeneities.

148 *NMR Spectroscopy*

149 *Solid-state ¹⁹F-NMR*

150 The spectra were measured at 282.37 MHz on a Bruker Avance III 300WB
151 spectrometer equipped with a 2.5 mm X-H/F double-resonance probe. The samples were
152 rolled and packed in a zirconia rotor with Vespel end-caps. All experiments were performed
153 at 24°C using a magic-angle spinning (MAS) rate of 25 kHz. The spectra were recorded using
154 a specific Hahn-echo pulse sequence, which consists in repeating the echo cycle to suppress
155 background signals coming from the probe. The ¹⁹F 90° pulse length was 5 μs and the echo
156 cycle was repeated 5 times during the measurement. 256 scans were recorded and averaged
157 with a recycle delay of 4 s and a dwell time of 3.3 μs.

158 *Liquid-state ¹H-NMR*

159 The experiments were carried out on a Bruker Avance III 600WB spectrometer
160 operating at the Larmor frequency of 600.13 MHz and using a 5 mm Diff30 probe able to
161 deliver a maximum gradient intensity of 1800 G/cm. The spectra were recorded at 24°C
162 using 32–64 scans with a recycle delay of 3 s and a dwell time of 25 μs. The proton 90° pulse
163 width was optimized for each sample. Each sample was first fully immersed in distilled water
164 at room temperature during 60 to 90 minutes. The sample size was approximately 1 x 1 cm
165 for both the pristine and aged XL membranes. Once out of the water, the samples were
166 quickly pressed between two layers of absorbent paper to remove residual water droplets
167 from the surface before being rolled and packed into 5 mm airtight tubes.

168 *PGF-NMR*

169 The water self-diffusion coefficients were measured using a stimulated-echo
170 sequence (PGSTE) with unipolar gradients and calculated from a plot of the observed signal
171 attenuation as a function of the applied gradient strength g . The experiments were
172 performed with a pulse time $\delta = 1.0 - 1.6$ ms, a diffusion delay $\Delta = 5 - 10$ ms and a gradient
173 strength 20 - 700 G/cm. The water self-diffusion coefficient D_s was obtained from a fit of the

174 experimental data using the Stejskal – Tanner equation (21). The error on diffusion
175 measurements is estimated to be on the order of 5%, the main source of errors being the
176 gradient calibration and the control of both temperature and water content.

177 *NMR relaxation*

178 The ^1H spin-lattice relaxation times (T_1) were measured at 24°C using the inversion-
179 recovery pulse sequence. 8 scans were recorded with a recycle delay of 2 or 3 s (depending
180 on the sample) and a dwell time of 25 μs . The relaxation time T_1 was determined by fitting
181 the experimental evolution of the signal attenuation as a function of the relaxation delay τ
182 using single or bi-exponential functions, depending on the situation (see Results).

183 **Results**

184 *Water populations and mobility.*

185 Figure 1-a presents a set of ^1H -NMR measurements on the water saturated Nafion XL
186 membrane. The static spectrum shows two resonances lines. The chemical shift of the most
187 intense component at 4.69 ppm corresponds approximately to that observed in non-
188 reinforced hydrated PFSA membranes at equivalent temperature and water content: Nafion
189 NR211 (6.20 ppm), Gore 800 (5.83 ppm at 98% RH) (22).

190 In unreinforced Nafion, water is known to exist in different states (23-26), namely non-
191 freezing water, bound freezing water and free water. Although dielectric relaxation
192 spectroscopy is able to describe different responses relative to these populations, the
193 spectral resolution of proton NMR performed at room temperature is not high enough to
194 detect them directly. Because the exchange time between these populations is fast
195 compared to the NMR time scale (ms) they all appear at about the same chemical shift and
196 the proton spectrum is composed of a single component.

197 The second resonance observed at 6.40 ppm is much weaker than the main component. The
198 higher chemical shift indicates a deshielding of the water protons and thus less electron
199 density around them. This could come from a denser hydrogen bond network and/or a
200 different local environment for the water in the central layer. Given the complex
201 microstructure of the porous PTFE layer (see for example Fig. 10 of Reference (10)) and the
202 pore size [10 nm - 1 μm] some of the water adsorbed in the reinforcement is presumably in

203 a confined state with water-ionomer interactions that are different in the central layer than
204 in the two external layers. These interactions would result in stronger hydrogen bonds and
205 lead, on average, to a higher NMR chemical shift.

206 The ratio of the area of the two lines corresponds in principle to the ratio of the two water
207 populations. In the water-saturated Nafion XL, the measured ratio is approximately 3.4 %.
208 Given the relative thickness of the central layer $l/L = 0.33$ in the water saturated state (10)
209 and the high porosity of the PTFE matrix, it is likely that only a fraction of the water adsorbed
210 in the central layer contributes to this second peak.

211 The longitudinal NMR relaxation time T_1 is indicative of the proton molecular translational
212 and rotational dynamics at a time scale corresponding to the inverse NMR frequency (~ 1 ns
213 at a NMR frequency of 600 MHz). Figure 1-b presents the T_1 measurements for the two
214 water populations. The longitudinal relaxation is mono-exponential for population 1, with a
215 relatively short relaxation time (18.9 ms). Interestingly, the NMR relaxation of the second
216 water population presents a bi-exponential behavior with one-time constant equivalent to
217 that of population 1 and a second, much longer, indicative of water with a faster dynamic.

218 This complex behavior proves that two water populations contribute to the low amplitude
219 resonance line of the ^1H spectrum (populations 2.1 and 2.2). The PFG-NMR diffusion
220 experiments help to clarify the situation. Figure 1-c presents the raw spectra, recorded at
221 different magnetic field gradient values. The data clearly show that the two resonances are
222 attenuated in the course of the experiment, thus proving that populations 1 and 2
223 correspond to water diffusing at the time scale of the measurement (several ms). The
224 calculated area of the peaks is plotted on Figure 1-d versus the magnetic field gradient and
225 the experimental points are fitted using the Stejskal – Tanner equation. Water from
226 population 1 presents a simple behavior and the single exponential fit gives a diffusion
227 coefficient of 2.32×10^{-10} m²/s. This value corresponds to what is usually measured in the
228 unreinforced water-saturated Nafion (13, 20, 27-30). As already observed in the relaxation
229 data, the behavior of population 2 is more complex and the fit to the data must be made
230 with two exponential components. Again two water populations are detected. Population
231 2.1 diffuses with a diffusion coefficient which is about half the value of population 1. This is
232 coherent with the two similar relaxation times, the lower value of the diffusion coefficient

233 being due to confinement in the porous PTFE. Population 2.2 is diffusing very fast, its
234 diffusion coefficient being approximately one third of the coefficient of bulk water at the
235 same temperature ($0.77 \times 10^{-9} \text{ m}^2/\text{s}$ versus $2.30 \times 10^{-9} \text{ m}^2/\text{s}$). The high diffusion coefficient
236 and the long relaxation time are indicative of a water population which is relatively free to
237 move. Thus, it is possible to assign it to a small amount of free water which may exist at the
238 interface between the ionomer and the PTFE reinforcement or present in voids spaces that
239 were not filled with PFSA during the casting of the membrane.

240 Figure 2 presents ^1H -NMR data measured in the water-saturated reinforced membrane
241 extracted from the aged MEA after 12,860 hours of operation. The proton spectrum shows
242 two resonance lines (Figure 2-a). Population 1 resonates at a lower field than in the pristine
243 membrane ($\delta H = 4.07 \text{ ppm}$ versus 4.69 ppm) while the chemical shift of population 2
244 remains approximately the same. Furthermore, the relative area of the two resonances
245 increases significantly after FC operation ($\sim 7\%$ of the total water content versus 3.4%).
246 These two observations are consecutive of changes that occurred in the membrane's
247 microstructure during FC operation. They could either indicate a decrease of the quantity of
248 ionomer in the external layers and/or a partial loss of the membrane sorption properties. In
249 Figure 2-b the diffusion data show the corresponding changes in the diffusion properties for
250 the two water populations.

251 In coherence with the proton spectrum, the diffusion coefficient of population 1 is lower in
252 the aged membrane. Again, this is indicative of less water content and/or changes in the
253 diffusion pathways in the PFSA structure. The water sorption isotherm presented in Figure 3
254 can help to understand these observations. In the Nafion PFSA, the water sorption behavior
255 is one of the most important phenomenon affecting its structural and transport properties.
256 This complex curve is highly non-linear as a result of complex interactions between the
257 water, the hydrophilic ionic sites and the hydrophobic matrix. It is often described as a
258 three-steps process (9): the ionization of the sulfonic acid groups at very low water activity
259 (a_w), the formation of multiple solvation shells in an interconnected water network at
260 intermediate water activity and, finally, the growth and the increase in the connectivity of
261 the hydrophilic domains by adding bulk-like water at high hydration levels. The first step
262 involves strong interactions caused by hydrogen bonds and can be described by the
263 Langmuir adsorption process. The second step corresponds to the dissolution of water in the

264 polymer phase and can be modelled by the Henry's linear equation (31, 32). The final upturn
265 of the isotherm at higher water activities is linked to the macroscopic swelling of the
266 membrane and thus is controlled by the membrane's mechanical properties (9).

267 The experimental isotherms of Figure 3 show that the maximum water uptake is much lower
268 in the aged membrane than in the pristine sample. This is mostly due to the partial loss of
269 the Langmuir contribution ($a_w < 0.1$) and the reduction of the Henry's slope (shown in bold
270 lines for $0.15 < a_w < 0.65$), which can be linked to a decrease in the hydrophilic character of
271 the membrane and a loss of ionic groups due to the scission of polymer chains. Interestingly,
272 the final upturn at high a_w was not impacted after operation, which means that even if
273 structural changes are induced by long term operation, they don't seem to alter the polymer
274 matrix's resistance.

275 *Chemical structure analyses*

276 *¹⁹F-NMR spectroscopy*

277 The chemical structure of the PFSA polymer can be characterized by ¹⁹F-NMR spectroscopy
278 (Figure 4). The chemical shifts of the pristine XL reinforced membrane are assigned and
279 identified in Figure 4 on the basis of Chen and Schmidt-Rohr's investigation (33). This
280 assignment is characteristic of the long side chain (LSC) – PFSA ionomer as well as the PTFE
281 signature outlined by a higher intensity ratio $I_{(CF_2)_n \text{ at } -117\text{ppm}} / I_X$ compared to the Nafion
282 NR211 monolayer. PFSA membranes can be characterized through the IEC parameter
283 measured from the ¹⁹F NMR spectra. Indeed, the IEC is related to the number of moles of
284 TFE n per mole of comonomer unit by:

$$\text{IEC} = \frac{1000}{100 \times n + M}$$

285 where M corresponds to the molecular weight of vinyl ether monomer ($M = 444 \text{ g.mol}^{-1}$) and
286 n can be calculated thanks to the resonance peak area $I_{CF_3+OCF_2}$ and $I_{CF_2+(CF_2)_n}$ with a
287 theoretical relationship deduced from the chemical structure of the LSC – PFSA ionomer.
288 This relationship was also previously validated by solid-state ¹⁹F NMR on PFSA membranes
289 (17).

290 In the case of reinforced membranes, the IEC does not correspond only to the PFSA ionomer
291 since the resonance peak area at -117 ppm inevitably takes into account the NMR signal of
292 the PTFE reinforcement. Without knowing the proportion of PTFE per unit of PFSA, it is not
293 possible to separate the $(CF_2)_n$ PFSA from the PTFE signals. Therefore, the IEC measured in
294 the case of reinforced membranes corresponds to a “global IEC” (IEC_g) of the tri-layer
295 membrane (17). Even though NMR does not directly provide the IEC of the LSC – PFSA, the
296 IEC_g allows us to estimate the degree of chemical degradation in a comparative study after
297 FC operation. The experimental measurement of the IEC of NR211 and IEC_g of XL membranes
298 are in agreement with, respectively, the supplier data sheet and literature values (17), as
299 indicated on Figure 4.

300 After 12,860 hours of FC operation, the spectrum shows a similar structure with the
301 same resonance peaks and chemical shifts (Figure 4) but with lower normalized intensities
302 associated to the $-OCF_2 / -CF_3$ (-73 ppm) and SCF_2 (-112 ppm) groups. These variations
303 point out a change in the chemical structure related to side chain groups which seems to
304 correspond to a partial loss of side chains. The chemical degradation by side chains loss has
305 already been observed for monolayer PFSA in previous ex-situ and in-situ studies (7, 8, 34-
306 36). The decrease of the IEC_g from 0.87 to 0.83 indicates here that the global IEC is only
307 slightly impacted by FC operation.

308

309 *FTIR-ATR spectroscopy*

310 The FTIR investigation was carried out in order to measure exclusively the chemical
311 degradation of the ionomer part of the reinforced membrane. The ATR mode was used to
312 characterize the PFSA outer layers on both sides of the reinforced membrane and in
313 different areas to ensure reproducibility. The data are plotted in the $4000-650\text{ cm}^{-1}$
314 frequency range on Figure 5-a. The spectra were normalized to the asymmetric CF_2
315 stretching mode (1145 cm^{-1}). As expected, they exhibit the characteristic signal of the LSC –
316 PFSA type ionomer. The assignment is detailed in Table 1 based on literature (37-40). All
317 studies agree on the absorption bands assignment except for the peak located at $\sim 980\text{ cm}^{-1}$
318 whose attribution is still open to discussion. Some authors (39, 41, 42) attributed this peak
319 to the stretching mode of C–O–C group close to the main chain while others assigned it to CF
320 stretching mode of the $CF_2-CF(CF_3)-$ group (38, 43). The cathode and anode side spectra

321 measured after FC operation are plotted on Figure 5, and compared to the pristine XL
322 membrane. In Figure 5-b, after FC operation we observe a significant decrease of the S–O
323 and C–O–C stretching bands intensities as well as a small decrease of the absorption band at
324 $\sim 980\text{ cm}^{-1}$. The decrease of these characteristic bands confirms that the chemical
325 degradation corresponds to a partial loss of the side chains. As plotted in the insert Figure 5-
326 a, two new bands were detected on aged samples in the range of 2850 to 3000 cm^{-1}
327 attributed to symmetric and asymmetric CH stretching modes corresponding to C-H
328 vibration band already observed and identified as chemical degradation observed after
329 ageing (34, 44, 45). Furthermore, FTIR data highlights decrease of O-H signal relative to liquid
330 water (4000-2500 cm^{-1}) in membrane after fuel cell operation. This confirms the water
331 sorption loss measured by DVS. Figure 5-a and Figure 5-b also show a large similitude in the
332 spectra measured on the anode and cathode sides, showing a similar degradation on both
333 sides on the membrane.

334 A specific area of the sample, where the PFSA external layers have partially disappear, was
335 also probed. The spectra corresponding to the anode and cathode sides are plotted on
336 Figure 5. A drastic decrease is observed in the characteristic PFSA signals as well as an
337 intensity drop of the S–O stretching / C–O–C stretching / band at $\sim 980\text{ cm}^{-1}$ and a
338 sharpening of the CF_2 stretching signals (1210 and 1145 cm^{-1}). These spectra thus present
339 the characteristic features of PTFE with a small presence of S–O stretching / C–O–C
340 stretching bands. In this degraded area the PFSA layers are thus almost completely lost, in
341 coherence with what is visually observed.

342 **Discussion**

343 The multi-techniques characterization shows that the reinforced PFSA membrane undergoes
344 a modification of its chemical structure during FC operation, which significantly impacts its
345 sorption and transport properties.

346 The fluorine NMR and FTIR spectroscopies provide experimental clues for a chemical
347 degradation of the PFSA ionomer by side chain scission (on ether groups or/and carbon-
348 sulfur bond). This results in a partial loss of the ionic sulfonic groups and a decrease of the
349 maximum water uptake as observed on the sorption isotherm and through the intensity
350 ratio of the two resonance lines in the proton NMR spectrum. In addition, the proton NMR

351 analysis suggests that the sorption properties of the outer layers (whose water contributes
352 the most to component 1) are predominantly affected since the NMR signature assigned to
353 water in the central layer is not significantly changed after FC operation. The mechanical
354 cohesion of the polymeric matrix, however, is not altered since the final upturn of the
355 sorption isotherm is not modified. This is confirmed by the NMR relaxation and diffusion
356 measurements which show that the adsorbed water does not present a free water behavior
357 as it would be in a porous-like structure with less mechanical cohesion and less water
358 confinement.

359 *Contribution of the used experimental techniques to the characterization of membrane aging*

360 • The evolution of the chemical structure in PFSA ionomers is often investigated using
361 ^{19}F -NMR spectroscopy since the IEC can be quantitatively measured. In the case of
362 reinforced membranes, the IEC determination is made difficult using this method because of
363 the contribution of the PTFE in the central layer. Thus, without the precise knowledge of the
364 relative PTFE content in the central layer and in the outer layers, the signature of the
365 chemical degradation appears only qualitatively on the raw NMR spectrum. Therefore, the
366 FTIR analysis is more relevant even though it is not easily quantitative. Moreover, FTIR is a
367 local probe of the chemical structure, while ^{19}F -NMR only provides averaged information. It
368 allows the investigation of both sides of the membrane exposed to anode and cathode
369 electrodes. One can thus probe possible differences between both sides and heterogeneities
370 in the plane.

371 • ^1H -NMR appears to be a fast and efficient technique to investigate the different
372 water populations, in the external layers and in the ionomer dispersed in the PTFE
373 reinforcement. The relative areas and the difference in NMR chemical shift of the two
374 resonance lines can be used as indexes to quickly quantify the water content. As aging is
375 seen to impact the sorption properties of the external layers, these two parameters can be
376 defined as indicators of the aging condition of the membrane.

377 • Water mobility is related to both the water content and the microstructure of the
378 polymer matrix. The simultaneous determination of the membrane's water content from the
379 proton spectrum and of the water diffusion coefficient from PFG-NMR experiments
380 represents efficient means of quantifying the changes in the structure-transport relationship
381 due to aging.

382 • The complex nature of the small water signal at lower field in the proton NMR
383 spectrum was revealed by the NMR relaxation and diffusion measurements. We saw that at
384 least two water populations contributed to this peak. To supplement the information
385 obtained from the 1D spectrum, more advanced techniques can be used (46). Relaxation-
386 diffusion 2D spectra for instance can give interesting correlations between the molecular
387 rotational dynamics and the nanosecond time scale and the long-range diffusion (millisecond
388 time scale and micrometer length scale). Such experiments will be performed in a near
389 future to elucidate with more details the nature of this peak. Exchange experiments should
390 also provide information about the exchange time between the different water reservoirs.

391 • In the present experiments, the presence of a small quantity of highly mobile water
392 in the central reinforcement or at the interface reinforcement/external layers is detected in
393 both the pristine and aged membranes. Our ability to detect free water, either in the
394 external layers or at the interface with the mechanical reinforcement can be very useful in
395 order to characterize the membrane's degradation. When the microstructure is modified
396 due to the scission of polymer chains, the confinement of the water molecules is less
397 pronounced as the matrix's resistance to swelling is lowered: this could effectively result in
398 more bulk-like water and a higher mobility. The detection of more free water in the
399 membrane's structure can thus become an indicator of its mechanical degradation.

400 **Conclusion**

401 We performed an experimental study of some of the important properties of PFSA
402 reinforced membranes before and after long-term operation (12,860 hours) in a fuel cell.
403 Our objective was to demonstrate that a small quantity of fast measurements can bring
404 relevant information on the impact of FC operation on these properties. To our knowledge
405 this is the first time that proton NMR is used to study the different water states and their
406 dynamics in the Nafion XL membrane.

407 From our measurements we conclude that:

408 • The PFSA reinforced membrane, although chemically and mechanically reinforced,
409 endures chemical degradations leading to a decrease of its sorption capacity. This is due to
410 the partial loss of the ionic sulfonic groups caused by side-chain scissions. The mechanical

411 integrity of the membrane is not severely impacted and the adsorbed water does not lose its
412 confinement.

413 • Proton NMR is powerful to detect the different water states in this membrane as the
414 water present in the central reinforcement gives a NMR signature distinct from the one
415 present in the outer layers. The relative area of the two resonances gives indications on the
416 water fraction in the two locations. In aged reinforced membranes, this measurement can
417 thus serve as a marker to quantify the degree of degradation.

418 • The relaxation and diffusion data give insights on the water dynamics at the
419 nanoseconds and microseconds, respectively. We observe that water in the external layers
420 of the pristine Nafion XL behaves as in the unreinforced Nafion. The second signal is more
421 complex and two distinct populations exist with very different dynamics. A small proportion
422 of it is highly mobile while the rest presents a signature similar to that of the water in the
423 external layers. In the aged sample, the majority of the water (component 1) is less mobile
424 because of lower water content. More detailed measurements are needed at this stage to
425 elucidate the exact nature of these components. More specifically it will be relevant to
426 perform correlation experiments in order to study the exchange between the different
427 water reservoirs.

428 Based on our findings, we think that it is possible to use proton NMR and FTIR to quickly
429 characterize the degradation state of PFSA reinforced membranes. More experiments are
430 being performed in our institution in order to study the evolution of the NMR parameters as
431 a function of the hydration in the pristine membrane. The set of data will be use as a
432 calibration of the reference properties.

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435 the CRM2/NMR methodology groups (<http://crm2.univ-lorraine.fr/lab/fr/research/rmn/>),
436 the H2E project for providing the membrane samples after FC operation and Axane fuel cell
437 systems.

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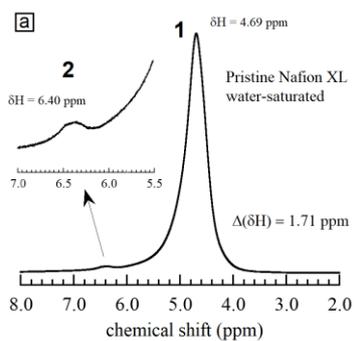
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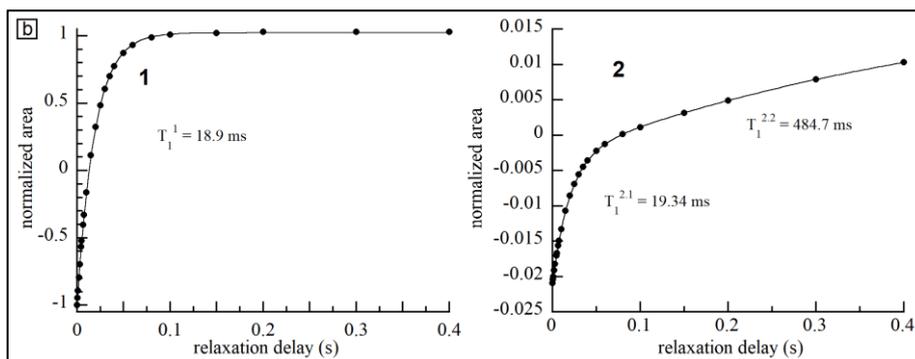
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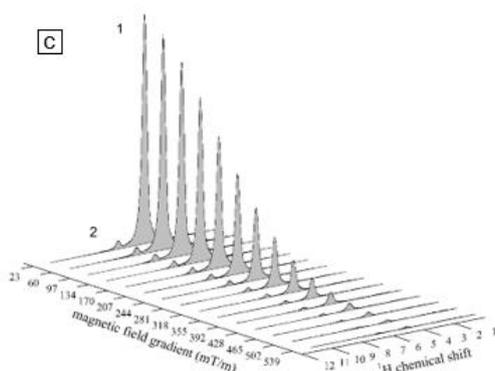
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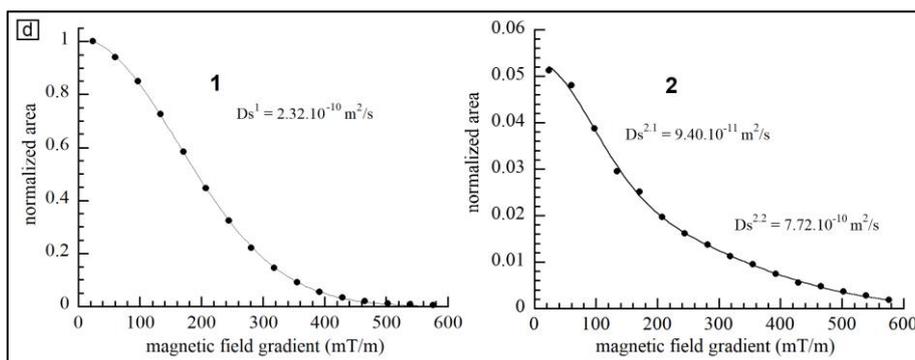
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522 **Figure 1. $^1\text{H-NMR}$ experiments in the water-saturated Nafion XL reinforced membrane (600 MHz).**
 523 **a- Static $^1\text{H-NMR}$ spectrum. b- T_1 relaxation experiments. c- Raw water diffusion data. d- Fitted**
 524 **diffusion data.**

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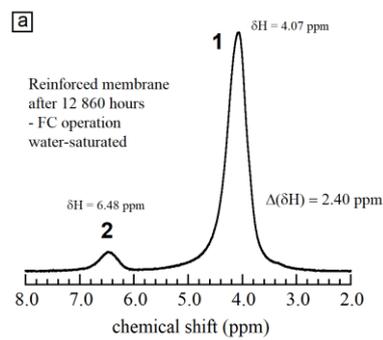
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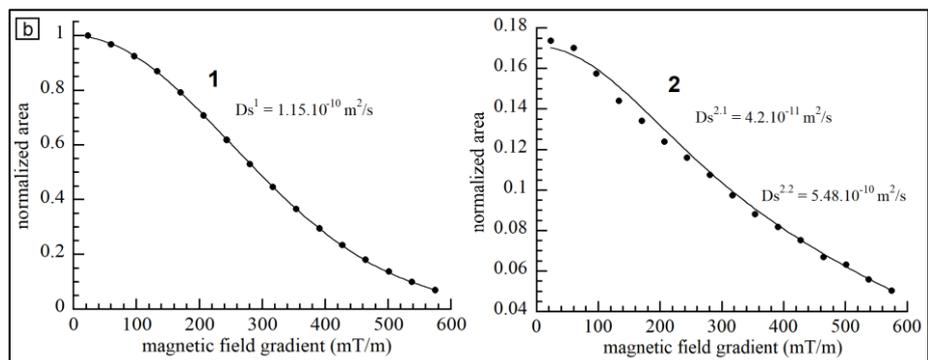
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533 **Figure 2. ¹H-NMR experiments in the water-saturated reinforced membrane after long-term FC**
534 **operation. a- Static ¹H-NMR spectrum. b- Diffusion data.**

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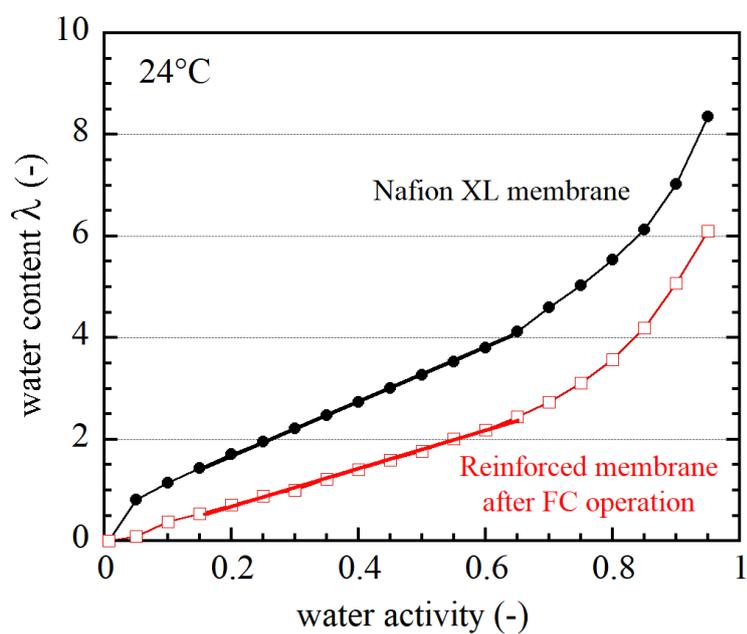
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549 *Figure 3. Water sorption isotherms at 24°C of Nafion XL reinforced membrane and reinforced*
550 *membrane after long-term FC operation.*

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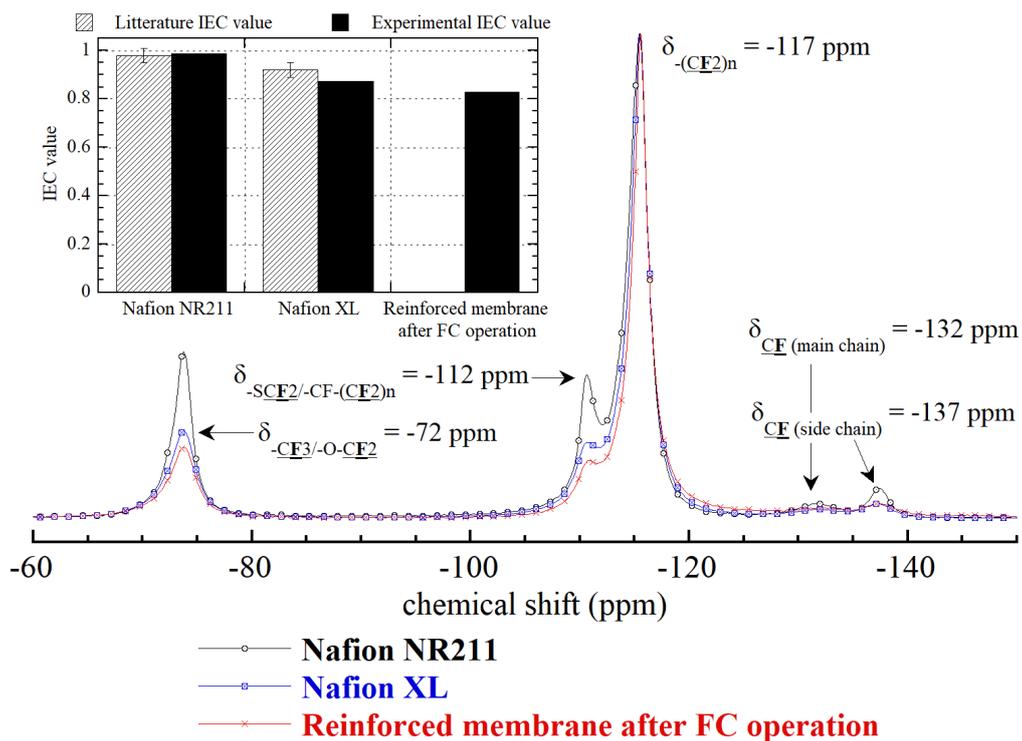
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564 *Figure 4. ¹⁹F-NMR spectra of Nafion NR211, Nafion XL reinforced membrane and reinforced*
565 *membrane after FC operation. The bars compare the measured IEC of NR211 and XL membranes to*
566 *the literature values (10, 16, 17) and the IEC of reinforced membrane after FC operation.*

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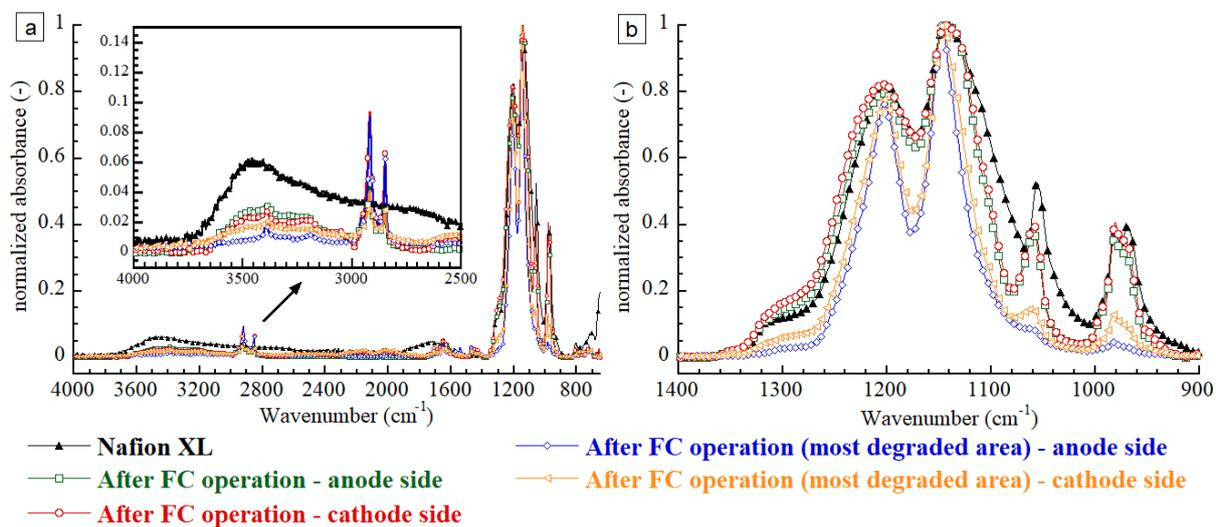
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584 *Figure 5. ATR-IR spectra of Nafion XL reinforced membrane compared to reinforced membrane*
585 *after FC operation in the range (a) 4000-650 cm^{-1} and (b) 1400-900 cm^{-1} .*

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Table 1. Assignment of the IR bands of the LSC – PFSA based on literature (37-40)

Absorption band location (cm^{-1})	Assignment
~ 3450	O-H stretching
~ 1210	CF ₂ stretching, asymmetric
~ 1145	CF ₂ stretching, symmetric
~ 1055-1060	S-O stretching, symmetric
~ 980	C-O-C (close to backbone) stretching, symmetric (39, 41, 42)
	C-F stretching (-CF ₂ -CF(CF ₃)-group) (38, 43)
~ 970	C-O-C stretching, symmetric

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