Aging mechanism of Sulfonated poly(aryl ether ketone) (sPAEK) in an hydroperoxide solution and in fuel cell

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ABSTRACT

Ex situ and *in situ* fuel cell degradation of a sPAEK membrane were investigated. Post-mortem analyses of the aged membrane and of the degradation products eluted in water were carried out by NMR, IR, SEC and EDX. *Ex situ* agings were performed in a low concentration H_2O_2 solution (0.07%) without any metallic catalyst. We exemplify that *ex situ* accelerated aging tests in such hydrogen peroxide solution are relevant to the chemical degradation in fuel cell. We have shown that a 500 h fuel cell test at moderate temperature (60 °C) induces significant modifications on the macromolecules such as a 40% molecular weight reduction. Degradation appears heterogeneous and limited to the cathode side. The model compound approach developed in the previous article (Perrot et al. [42]) has allowed the identification of the aging path in fuel cell. Phenolic and carboxylic acid chain ends have been identified as the main products resulting from polymer chain scissions. The *ex situ* lifetime (100 h) of the membrane appears very limited with respect to the *in situ* operating time suggesting that the low H_2O_2 concentration (0.07%) is still much higher than in fuel cell.

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1. Introduction

PEMFC (proton exchange membrane fuel cell) converts the chemical energy of a fuel into electrical energy with a high efficiency. During the last years fuel cell improvements in terms of performances and power densities allowed the unveiling of appealing prototypes for different applications (automotive, portable, back-up power, auxiliary power unit, etc.). For automotive, portable, and residential applications, fuel cells are required to be reliable, inexpensive and durable. Durability targets exceed 5000 h for automotive applications and 40,000 h for stationary applications [1,2]. Therefore component lifetime of hydrogen–air PEMFC has significant implications on the commercial success of these systems.

Among the critical points that make a great impact on the fuel cell durability, the membrane electrode assembly (MEA) stability has been identified as a critical issue. MEA aging results mainly from a partial catalyst dissolution leading to a decrease in the electrode activity and membrane brittleness with formation of pinholes [3].

A common approach for long-term durability studies is to operate a cell or stack for a given period of time, and then disassemble the components for post-mortem examination. This methodology only gives an insight at the point of disassembly and provides no information on how the post-mortem situation arose. Moreover, as long-term fuel cell tests are often performed in very specific conditions (in terms of temperature, gas humidification, nature of the catalyst, gas pressure, etc.), a precise and reliable comparison of the results reported in literature [4–14] on different membranes lifetime does not seem realistic. For example, the localization of the degradation is widely subject to discussion. Some studies suggest that degradation is induced at the anode [4–9] whereas some others conclude that it occurs at the cathode [10–13] or homogeneously through the membrane thickness [14]. In addition, it must be outlined that most of the time operating conditions are not clearly reported while they have a real impact on the electrochemical reactions. This could explain some apparent contradictions.

Durability remains a difficult topic because of the long test time required (i.e. several thousand hours or more), the complexity of failure analysis and the overlapping of failure causes. Additionally, *in situ* non-destructive examination of the membrane electrode assemblies is far from being an easy task.

Two major causes can lead to the membrane aging:

- a mechanical degradation [2,15–22] resulting from swelling and deswelling cycles, pressure variations of reactant gases or even stresses induced by the applied torque during MEA preparation and cell mounting,

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- a chemical degradation [4–6,10,23–34] leading to a significant loss of the material integrity.

However actual mechanisms and factors influencing the degradation such as the membrane thickness or the operating conditions have to be further investigated.

Nafion®, a perfluorosulfonic acid polymer commercialized by DuPont de Nemours, is the most widely used proton conductor in PEMFC. It possesses almost all the physical characteristics required for this use: outstanding conductivity, thermal stability, mechanical strength and chemical stability. However its high price, the environmental risks related to the disposal of a fluorinated material and its limited temperature range of operation, have motivated the research of low cost non-perfluorinated membranes. Numerous studies have already been published on the development of new high performance proton exchange membranes. Most of them deal with polymer synthesis, membrane preparation and the improvement of PEMFC performances. Sulfonated aromatic and heterocyclic proton conductive polymers (poly(imide)s, poly(benzimidazole)s, poly(aryletherketone)s, poly(arylethersulfone)s, etc.) are considered as particularly promising, unsulfonated homologs exhibiting excellent thermal stability, and low sensitivity to oxidation and hydrolysis [3,35]. Surprisingly only few works were devoted to durability studies.

The limited lifetime of alternative membranes in fuel cell is attributed to a chemical degradation. While $HO^\bullet$ and $HO_2^\bullet$ radicals are held responsible for these degradation reactions [32], their initiation mechanism in fuel cell is still under debate. Two main processes are suggested. At the anode [4,9], $HO_2^\bullet$ radicals originate from a $H^\bullet$ recombination with oxygen molecules permeating through the membrane ($H^\bullet$ being induced by the hydrogen reaction on the catalyst surface). At the cathode [13], an incomplete reduction of oxygen (two electrons instead of four electrons) leads to the formation of H_2O_2. The catalytic decomposition of this oxidizing agent then leads to the formation of $HO^\bullet$ and $HO_2^\bullet$ radicals. As an evidence of this mechanism, H_2O_2 has already been detected in the water produced during a fuel cell test performed with Nafion membrane [33].

Fenton's test using a H_2O_2 solution containing a trace amount of Fe^{2+} has become a common ex situ accelerated test for membrane durability. Typical H_2O_2 concentrations are either 3% [36,37] or 30% [38,39] which are much higher than the low amount of H_2O_2 encountered in fuel cell [29,33]. Too high radical concentration can result in additional routes of degradation limiting the membrane lifetime. Therefore, this test is neither predictive nor selective. For example, a sPAEK membrane was found brittle after only few hours in a 3% Fenton reactant while a fuel cell test was conducted for more than a thousand hours [35,40,41]. Moreover, the evaluation of the membrane degradation is very basic. During immersion, membranes are intermittently removed from the solution, and slightly bent to evaluate the immersion time required for the membrane to become brittle. The estimation of the lifetime is only qualitative as the mechanical strength applied to the film is not controlled and reproducible. The use of quantitative mechanical tests, to determine Young's modulus and elongation at break for example, has been carried out as an improvement of this protocol [29,35]. Another way commonly used to evaluate the ex situ degradation is the measurement of weight loss according to the immersion time in the Fenton's medium. Mechanical strength and weight loss are assessed to be representative of the molecular weight evolution due to chain scissions and thus to the extent of degradation. In addition, H_2O_2 concentration quickly decreases during the test mainly due to its catalytic decomposition by metallic cations. Therefore as aging tests are far longer (10–100) than H_2O_2 lifetime, the published values are somewhat questionable.

Definitively the extracted data cannot be considered as quantitative (lifetime, kinetics, etc.).

A stabilization strategy or design of new molecules requires the knowledge of the degradation path. A better understanding of a membrane degradation process requires a precise identification of the aged products. Indeed, such a strategy should allow the determination of the chemical bonds of the polymer backbone which are prone to degradation. In this perspective, a thorough study of the ex situ aging of a sulfonated aryletherketone model compound in the presence of H_2O_2 has been previously described [42]. Most of the products formed during the aging treatment were isolated and fully characterized. A degradation mechanism was proposed. Ether functions appear much more sensitive to oxidation than the ketone ones. Their degradation leads to polymer chain scissions and to the formation of both carboxylic acid and phenol chain ends. Chain scission results from the addition of a hydroxyl radical on the aromatic rings (primary product of degradation), followed by oxidation. In the present work, the objective is to demonstrate that aging tests performed on membrane result in the same chemical modifications observed for the model compound and are representative of the fuel cell degradation, which to the best of our knowledge has never been demonstrated. Suitable off-line experiments are necessary to perform extensive aging tests on different membranes in order to identify the best technical solution (material, stabilization, used conditions, etc.). Both ex situ and in situ aging treatments were performed. Different physical and chemical analyses were conducted to identify the nature of the polymer chain ends, the molecular weight evolution and the localization of the degradation process during ex situ and fuel cell tests.

2. Experimental

2.1. Materials

2.1.1. Sulfonated poly(aryletherketone) (sPAEK) synthesis

N-methyl pyrrolidinone (NMP), dimethyl sulfoxide (DMSO), potassium carbonate (K_2CO_3) and toluene were used as received. 4,4′-hexafluoroisopropylidene diphenol (Bisphenol AF) and 4,4′-difluorobenzophenone were, respectively, purified by sublimation and by crystallization from a petroleum ether/ethyl acetate mixture. 4,4′-difluoro-3,3′-disodium sulfonate benzophenone was prepared according to the procedure described by Wang [43].

Typically, in a 100 ml three necked round bottom flask equipped with a nitrogen inlet, a mechanical stirrer and a dean stark trap, 5.0607 g of 4,4′-hexafluoroisopropylidene diphenol (1.5×10^{-2} mol), 2.9108 g of K_2CO_3 (2.1×10^{-2} mol), 1.734 g of 4,4′-difluorobenzophenone (7.1×10^{-3} mol) and 3 g (7.1×10^{-3} mol) of 4,4′-difluoro-3,3′-disodium sulfonate benzophenone were refluxed 2 h in a mixture of 39 ml of DMSO and 11 ml of toluene. The water released during the bisphenate formation was stripped off by azeotropic distillation with toluene. The temperature was then increased up to 160 °C in order to complete the polymerization (10 h). After cooling, the polymer was precipitated into methanol. The fiber-like polymer was chopped into pieces and then collected by filtration, washed with methanol and dried under vacuum at 80 °C. The chemical structure of this polymer is presented in Scheme 1.

IR valence vibrations (cm^{-1}): 3500–3100 (O–H); 1652 (C=O); 1600, 1585, 1480 and 1490 (C=C); 1206 (Ar–O–Ar); 1176 (C–F); 1098, 1020 and 930 (O=S=O). Absorptions at 1492 and 1470 cm^{-1} as well as at 1414 and 1402 cm^{-1} are associated with the 1,3,4-trisubstituted aromatic skeletal vibrations. ^1H NMR (400 MHz, 50 °C, DMSO-d_6): δ (ppm) 7.06 (H_{A2}); 7.15 (H_{B2}); 7.22 (H_{C2}); 7.22 (H_{D2}); 7.4 (H_{B3}); 7.43 (H_{D3}); 7.74 (H_{A3}); 7.82 (H_{C3}); 8.26 (H_{A5}). ^{13}C NMR (400 MHz, 50 °C, DMSO-d_6): δ (ppm) 64.1 ($C_{C\alpha}$); 119.1

Scheme 1. Synthesis of sPAEK.
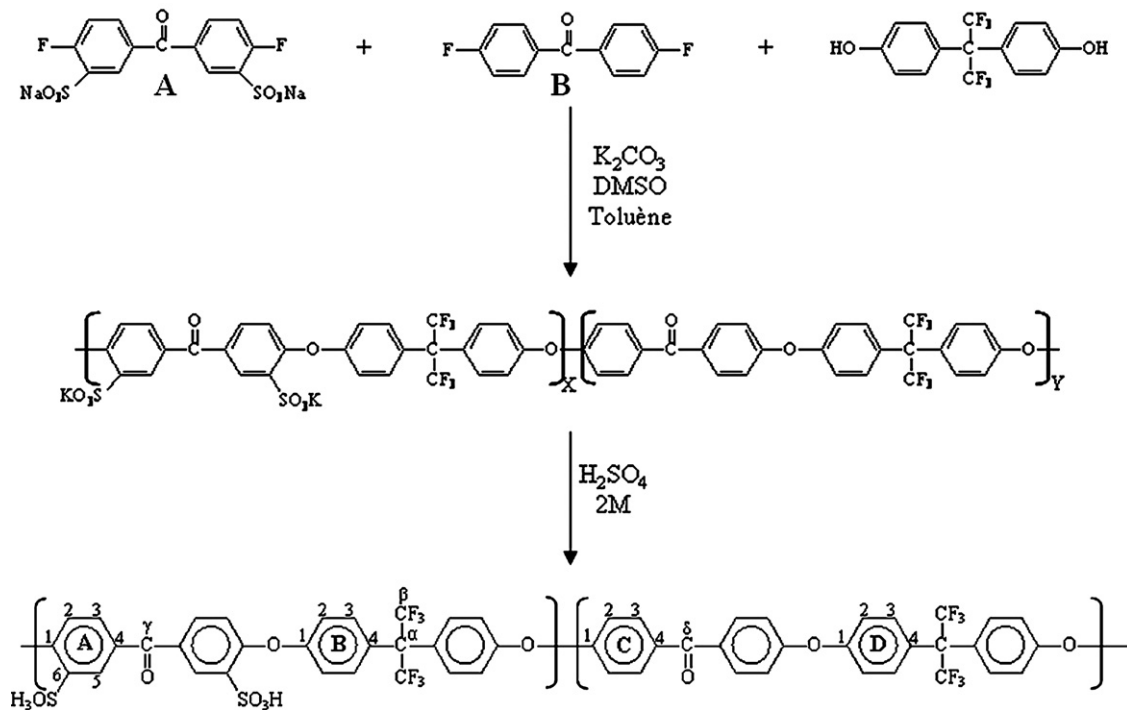
(C_{C2}); 119.7 ($C_{B2 \text{ or } D2}$); 119.8 ($C_{B2 \text{ or } D2}$); 120.5 (C_{A2}); 124.8 ($C_{C\beta}$); 127.5 (C_{B4}); 128.5 (C_{D4}); 131.2 (C_{A5}); 132.0 (C_{B3}); 132.4 (C_{D3}); 132.8 ($C_{A3 \text{ and } C3}$); 133.4 (C_{C4}); 139.7 ($C_{A4 \text{ or } A6}$); 140 ($C_{A4 \text{ or } A6}$); 157 ($C_{A1, B1 \text{ or } D1}$); 158.1 ($C_{A1, B1 \text{ or } D1}$); 158.3 ($C_{A1, B1 \text{ or } D1}$); 160.1 ($C_{C1}$); 193.9 ($C_{C\gamma \text{ and } C\delta}$).

2.1.2. Membrane preparation

sPAEK membranes (thickness = 50 μm) were prepared by casting a 20 wt% polymer solution in NMP onto a clean glass plate. After solvent evaporation (1 night at 50 °C, 1 h at 80 °C, 1 h at 120 °C, 1 h at 180 °C), membranes were peeled of by immersion in water. The acid form of the sulfonic groups was obtained by treating the membranes in 2 mol l^{-1} H$_2$SO$_4$ for 4 h at room temperature. The resulting membranes were thoroughly washed with deionized water and dried under vacuum at 80 °C.

2.2. Aging conditions

2.2.1. Ex situ aging

Ex situ experiments were performed in a H$_2$O$_2$ solution at a concentration of 0.07 vol% and 80 °C. At this temperature HO· and HOO· radicals are induced through a homolytic decomposition of H$_2$O$_2$. For these experiments the decomposition is not photo-assisted (to avoid a photo-degradation of the polymer) or catalysed through metallic species like in Fenton reaction (to avoid ionic exchange with the member). A low concentration was used to avoid additional routes of degradation. Membrane was removed from this aging medium after a complete decomposition of H$_2$O$_2$ (100 h) and washed with water to remove any residue. In order to collect eluted products in water, washing water was collected and added to the aging medium for lyophilisation. This range of hydroperoxide concentration is based on previous work performed on sulfonated polyimide membrane.

2.2.2. Fuel cell tests

The membrane was directly sandwiched between two electrodes (not hot pressed) into a 25 cm^2 single cell test fixture in order to perform the single cell test experiments. Commercial ELAT-DS gas diffusion electrodes supplied by E-TEK with a platinum loading of 0.5 mg cm^{-2} and impregnated with Nafion® following our own standard spraying procedure were used. Before mounted into the cell, the membranes were humidified by immersion into water (few minutes) at ambient temperature. Excess of water onto their surfaces was then removed. The monopolar plates of the 25 cm^2 single cell test fixture were made of impregnated graphite with machined single serpentine channel. The stress applied on the MEA was about 3 MPa. It was controlled by choosing an appropriate type of gasket and by adjusting the tightening torque of the 6 screws of the cell. The homemade fuel cell test bench allows to control cell temperature and current density as well as gas flow, pressure and relative humidity both at the cathode and anode sides.

The *in situ* ageing tests were performed at 60 °C. Dry hydrogen and oxygen, absolute pressure of 3 bar, were applied at the anode and cathode sides, respectively. The gas flows were controlled by mass flow controllers in order to have a stoichiometry of 1.2 and 2, for hydrogen and oxygen, respectively. The cell was first heated up to 40 °C before increasing the current density up to 400 mA cm^{-2} by steps of 40 mA cm^{-2} every minute. In parallel, the temperature was increased up to 60 °C. The current density was fixed at 400 mA cm^{-2} and the voltage variation was recorded. The excellent stability of the performance indicates a correct membrane hydratation without gas humidification.

The water produced during the fuel cell test was collected and freeze-dried. The aged membrane was separated from the electrodes for post-mortem analyses.

2.3. Characterization methods

Sulfur content across the membrane thickness was determined by energy dispersive X-ray analysis (EDX) using a Jeol SM840 scanning electron microscope (SEM), as described earlier [44].

Molecular weights were determined by Size Exclusion Chromatography (SEC). N,N-dimethylformamide containing 0.05 mol l^{-1} lithium bromide was used as eluent. 1 wt% poly-
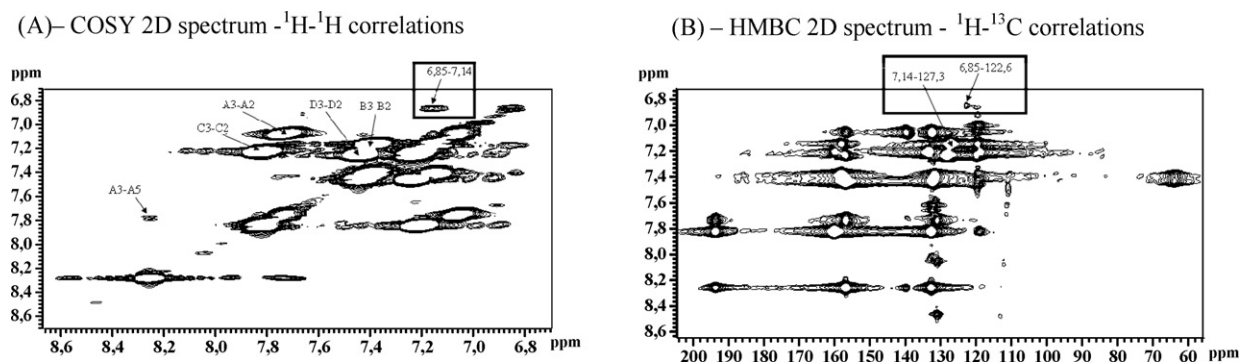
(A)– COSY 2D spectrum -^{1}H-^{1}H correlations   (B) – HMBC 2D spectrum - ^{1}H-^{13}C correlations

Fig. 1. COSY and HMBC NMR 2D spectra of sPAEK: (A) COSY 2D spectrum—^{1}H–^{1}H correlations; (B) HMBC 2D spectrum—^{1}H–^{13}C correlations.

mer solutions were analysed at 70 °C, using a Waters 510 apparatus equipped with two columns (PL Gel Mixed-D) calibrated with polystyrene standards and coupled to a Waters 410 refractometer.

Infrared spectra were recorded in transmission mode with a Nicolet Magna System 750 on thin films to obtain macroscopic information. Thin films (<10 μm thick) were obtained by casting a polymer solution in THF onto ZnSe plates. Surface analyses were performed by attenuated total reflection (ATR) with a diamond crystal ATR attachment. Spectra were obtained using 32 scans and a 2 cm^{-1} resolution.

High-resolution liquid NMR spectroscopy was carried out with a Varian Unity 400 spectrometer operating at a resonance frequency of 399.960 MHz for ^{1}H and 100.58 MHz for ^{13}C NMR analyses. All spectra were done at 50 °C (better resolution). Deuterated dimethyl sulfoxide (DMSO-d_6) and tetramethylsilane (TMS) were, respectively, used as solvent and chemical shift reference. For 2D spectra, a COSY sequence was chosen for ^{1}H–^{1}H correlations and heteronuclear multiple bond-correlation sequence (HMBC) for ^{1}H–^{13}C correlations.

3. Results and discussion

3.1. Virgin material characterization

As observed in Scheme 1, sulfonated poly(aryletherketone) (sPAEK) was synthesized by aromatic nucleophilic substitution between 4,4′-difluoro-3,3′-disodium sulfonate benzophenone, Bisphenol AF and 4-4′-difluorobenzophenone, in a polar aprotic solvent, as described earlier by Xing et al. [37]. High molecular weight polymer was obtained, with a $\overline{M_n}$ of 35.4 kg mol^{-1} and a $\overline{M_w}$ of 74.3 kg mol^{-1}, enabling the elaboration of tough membranes. A high ionic exchange capacity of 1.6 mequiv. H$^+$ g^{-1} was obtained.

Structural characterization of the polymer (by IR and NMR 1D and 2D) is in good agreement with the expected structure and results published by Xing et al. [37].

Based on COSY and HMBC 2D spectra (Fig. 1), phenol end-groups were identified by specific chemical shifts reported in Table 1.

The stability of sPEAK membrane under hydrothermal conditions has been evaluated. No chemical modification was detected up to 1500 h at 130 °C.

3.2. Aged materials characterization

Ex situ aging experiments were performed on sPAEK membranes, at 80 °C in 0.07 vol% H$_2$O$_2$ aqueous solutions as described previously in Section 2.2. Both the *ex situ* aged membrane and the "eluted species" were characterized.

In situ aging was carried out during a long-term fuel cell test (500 h, 60 °C). The cell voltage increased with temperature at the beginning of the test and reached a value of approximately 660 mV after 50 h (Fig. 2). Then, the voltage decreased slowly to reach 640 mV after 500 h when the test stopped due to an unpredictable membrane breakdown. Indeed, this slow evolution of the voltage did not give a clear evidence of strong degradation and the end of the test was characterized by a sharp drop of the voltage. The membrane was separated from the electrodes for post-mortem analyses.

Although the water formed during the test was collected and freeze-dried, no reliable characterization could be performed because of the scarce amount of isolated material. Therefore, elution of oligomers or organic species coming from the chemical degradation is not significant.

For both *ex situ* and *in situ* experiments, aged membranes (initially tough) became brittle, suggesting some structural modifications of the polymer. Physico-chemical characterizations (SEC,

Table 1
NMR chemical shifts of phenolic end-groups.

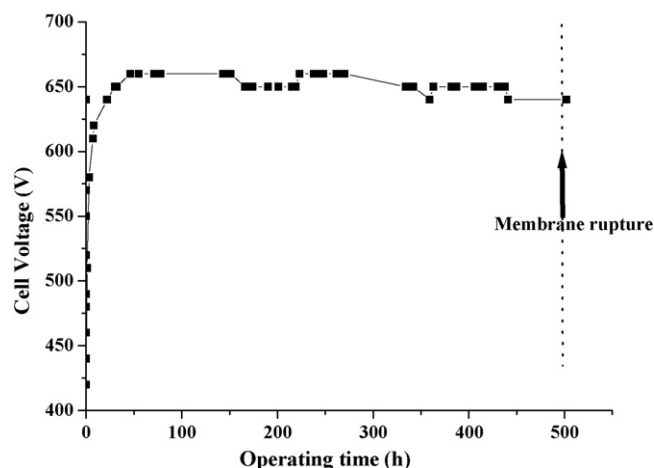| Proton H/carbon C	δ (ppm)
H2	7.14
H3	6.85
C2	127.3
C3	122.9

Fig. 2. Cell voltage evolution during the fuel cell test (*in situ* ageing).

Table 2
sPAEK molecular weights.

Material	$\overline{M_n}$ (10^3 g mol^{-1})	$\overline{M_w}$ (10^3 g mol^{-1})	IP
Virgin sPAEK	35.4	74.3	2.1
Ex situ aged sPAEK[a]	17.3	36.7	2.12
Eluted species during *ex situ* experiments[a]	10.2	21.4	2.1
In situ aged sPAEK as removed from the bench test[b]	20.3	51.1	2.52

[a] 0.07 vol% H_2O_2—100 h at 80 °C.

[b] 500 h at 60 °C.

IR, EDX and NMR) were performed on the different materials (aged membranes, "eluted and extracted species").

3.2.1. SEC

Molecular weights ($\overline{M_n}$ and $\overline{M_w}$) determined by SEC analysis are reported in Table 2. As expected by the loss of the membrane mechanical strength, aging treatments lead to a significant decrease in the initial polymer molecular weight. Moreover, an extensive degradation process during the *ex situ* experiment results in the formation of water-soluble oligomers corresponding to the "eluted species".

3.2.2. IR

IR spectra of *ex situ* aged membrane and "eluted species" are reported in Fig. 3. No significant modification can be evidenced comparing IR spectra of the aged and virgin sPAEK membranes. More interesting is the apparition of a shoulder at 1714 cm^{-1} on the "eluted species" spectrum. Indeed, this new band suggests the formation of new products containing carbonyl groups, clearly identified since they are quite different from the ketone groups absorbing at 1659 cm^{-1}. Between 3700 and 3000 cm^{-1}, the eluted products spectrum reveals a stronger absorption band than the virgin material one. This absorption band is associated to O–H vibrations resulting from OH groups on the backbone (SO_3H, COOH, OH, etc.).

Concerning IR characterization of the *in situ* aged membrane, ATR experiments were particularly attractive as they enabled a surface analysis (with a penetration depth of few microns). It is thus possible to differentiate the chemical modifications that occur on both sides of the aged membrane (respectively corresponding to the anode and cathode sides of the MEA). Spectra are reported in Fig. 4, as well as the spectrum of the virgin membrane. Whereas no significant difference appears between the membrane reference
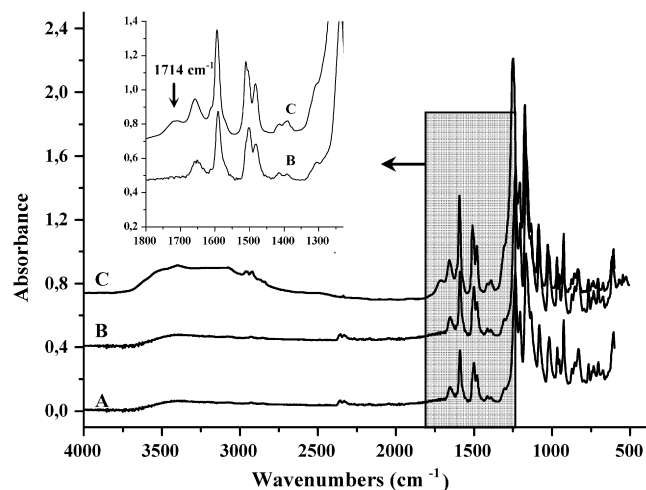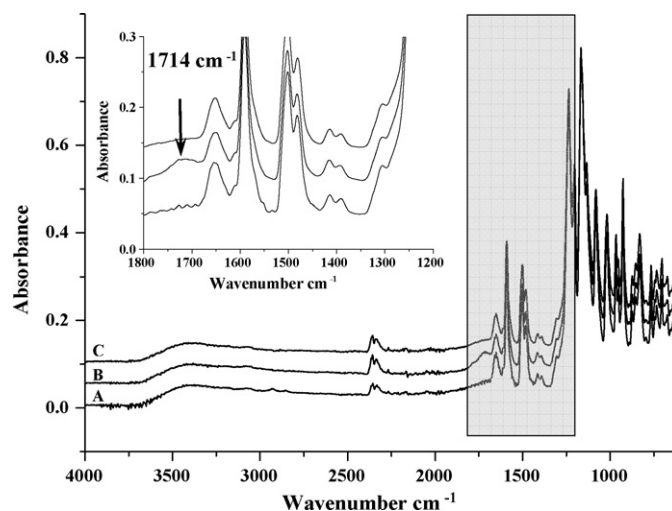

Fig. 4. ATR-IR spectra after an *in situ* aging treatment (500 h at 60 °C in a fuel cell): cathode side (B) and anode side (C), compared to the virgin membrane (A).

and the anode side of the aged membrane, a shoulder at 1714 cm^{-1} is visible on the cathode side spectrum.

From these results we can understand that during both *ex situ* and *in situ* aging treatments, sPAEK has been oxidized to some extent. In the case of a fuel cell test, such a phenomenon mainly occurs at the cathode side of the MEA.
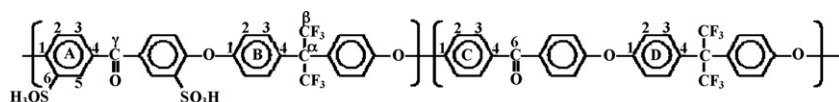
3.2.3. EDX analysis

Sulfur content across the membrane thickness was determined by EDX on the *ex situ* and *in situ* aged membranes. From these analyses, the distribution of the sulfonic groups can be considered as homogeneous over the membrane thickness. It must be outlined that an *in situ* aging does not induce any modification of the sulfonic content nor its distribution. This observation confirms that no species were eluted from the membrane. At the opposite, an *ex situ* aging induces a decrease of the sulfonic content due to at least to the elution of sulfonated oligomers (water-soluble).

3.2.4. NMR

NMR analysis of *in situ* aged membrane does not reveal any significant modification compared with the virgin membrane. However, IR analysis performed on this sample has shown that the membrane degradation was heterogeneous. Therefore, one can consider that the degradation products are diluted into the polymer matrix and not in sufficient amount to be observed in these conditions. To improve the resolution of NMR analysis, and thus the detection of modifications induced on the backbone, oligomers resulting from chain scissions were removed from the membrane by a hot water treatment at 100 °C (60 h) of the *in situ* aged membrane. Indeed, at 100 °C the membrane swells allowing oligomers to diffuse into the water. Products collected from this hot water treatment will be labelled "extracted" species whereas the eluted species into the aging medium of an *ex situ* test are called "eluted" species.

^{1}H NMR spectra of the virgin polymer as well as those of all aged samples (*ex situ* aged membrane, "eluted" (*ex situ*) and "extracted" (*in situ*) species) are reported in Fig. 5. Whatever the aging treatment, no fundamental change in the polymer backbone can be evidenced. However, some new species (noted * in Fig. 5), which seem to have the same nature in all cases, are produced during these experiments. As chemical modifications are quite similar on aged membrane, "eluted" and "extracted" species, extensive analyses were performed on the two lyophilised last fractions. High-resolution NMR spectra were recorded.

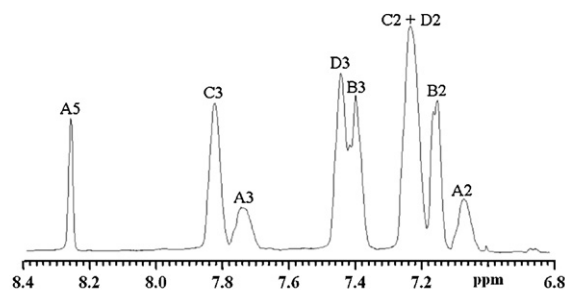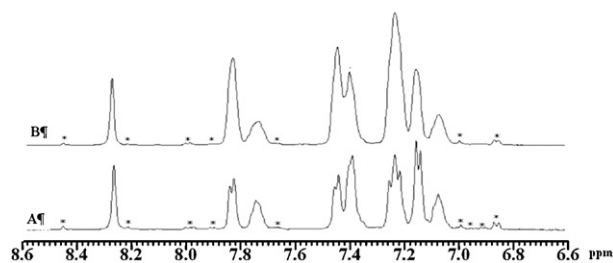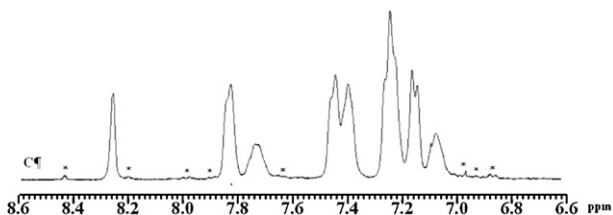**Fig. 3.** FTIR spectra after an *ex situ* aging treatment (H_2O_2 0.07 vol%—100 h at 80 °C). (A) Virgin membrane; (B) aged membrane; (C) eluted species.

Fig. 5. ^{1}H spectra in DMSO-d_6 at a concentration of 3.75% (in weight)/50 °C. *Ex situ* aged materials (H$_2$O$_2$ 0.07%/80 °C/100 h): membrane (A) and eluted species (B). *In situ* aged material (500 h/60 °C): hot water extracted products (C).

In order to elucidate the chemical structure of the products formed during the aging treatments, 2D NMR analysis was carried out on the "eluted" and "extracted" samples (Fig. 6).

Due to the complexity of these spectra and to the presence of overlapping signals, a complete assignment of the different species was not possible. However, five different chain ends were rigorously identified. Their structure and NMR chemical shifts are reported in Table 3.

From these analyses, we understand that phenol and carboxylic acid end-groups are formed during *ex situ* aging. These results are in good agreement with those reported earlier [42].

A COSY ^{1}H–^{1}H analysis of the "extracted" species during an *in situ* experiment corroborates the former results. In this case, different chain ends (CE1, CE2 and CE5) have been identified and the presence of phenol end-groups such as CE3 and CE4 were established. However, ^{13}C–^{1}H HMBC analysis would have been necessary to undoubtedly define the structure. Unfortunately, insufficient amount of material was available to perform such an analysis. It must be outlined that two differences are observed between *ex situ* (Fig. 6A) and *in situ* (Fig. 7) agings: the proton at 7.23 ppm is only detected for the *ex situ* aging whereas protons at 6.93 and 7.38 ppm are only present for the *in situ* aging. However, degradation products associated to these later spots have not been identified yet.
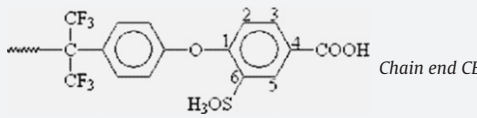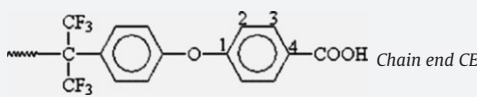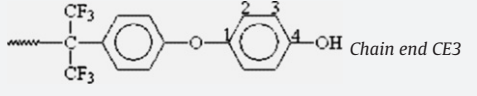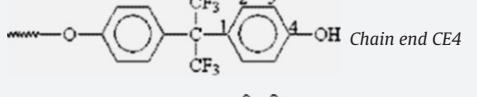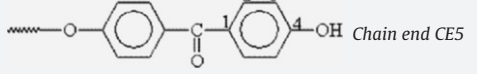
4. Discussion

Only few chemical modifications are revealed by NMR and IR analyses whereas polymer degradation generates a large number of different species and the mechanical properties are strongly affected. As a consequence it is very difficult to identify the aging mechanism. In a previous study, the degradation path of a model compound, tailored to be representative of a sPAEK repeat unit, in H$_2$O$_2$ solutions has been elucidated (Fig. 8).

The main degradation process results from the addition of a HO$^\bullet$ radical on the non-sulfonated aromatic ring [42]. Then the phenolic group oxidation leads to successive chain scissions with a preferential consumption of the terminal units. On the basis of this mechanistic and molecular approach, we suspect an oxidability of the terminal units as the driving force of sPAEK degradation. Although the degradation products differ from the monomers, this mechanism can be considered as analogous to an "unzipping" process (Scheme 2).

Chemical modifications in H$_2$O$_2$ of sPAEK macromolecules analysed by NMR reveal mainly the formation of new chain ends. This is consistent with a polymer molecular weight decrease. Based on NMR analyses, phenolic and carboxylic acid chain ends (EC1–5) for both *in situ* and *ex situ* agings was observed. The identification of these chain ends confirms the aging path established from the

Table 3
Chain ends identified on freeze-dried eluted products during an *ex situ* aging.

Structure	Proton assignments		Carbon assignments	
	H	δ (ppm)	C	δ (ppm)
Chain end CE1			C1	156.9
			C2	–
	H_2	6.97	C3	132.3
	H_3	7.89	C4	126.4
			C5	131.3
	H_5	8.44	C6	140.0
			COOH	167.1
Chain end CE2			C1	160.2
	H_2	7.14	C2	119.7
	H_3	7.97	C3	133.9
			C4	127.5
			COOH	167.1
Chain end CE3			C1	158.7
	H_2	7.14	C2	119.7
	H_3	6.85	C3	115.9
			C4	–
Chain end CE4			C1	–
	H_2	7.14	C2	127.5
	H_3	6.85	C3	122.9
			C4	–
Chain end CE5			C1	128.6
	H_2	7.64	C2	130.8
	H_3	6.93	C3	–
			C4	158.7

–: not clearly identified peaks.

model compound study. According to this process, chain ends EC6 to EC8 (Table 4) are expected. However, they were not detected. One might suspect that the kinetics of oxidation is faster than the kinetics of formation.

In the same way, chain ends issued from the addition of a hydroxyl radical on the aromatic end-group were not detected (EC6) whereas this addition product has been identified as respon-

sible of the model compound degradation (Fig. 8). A combination of several factors may be responsible for these observations. First, this chain end is a primary degradation product very sensitive to oxidation. Consequently, it is expected to be consumed as fast as it is produced and then it cannot accumulate in a sufficient amount to be detected. Second, as originated from the modification of few chain ends (already a minor component in the bulk polymer), its concentration cannot be significant. Third, virgin sPAEK macromolecules should present only 50% of phenolic chain ends according to the polycondensation reaction in equimolar conditions. Their oxidation should be faster than the hydroxy radical addition process on the other 50% chain ends (fluorine type). For the same reasons, it was not expected to observe EC7 and EC8 chain ends. In addition, the hydrophilic character of these groups leads to an aqueous environment which favors the radical attack of OH•.

SEC analyses (Table 2) reveal that H_2O_2 leads to a significant decrease in the molecular weight of the macromolecules (namely 50%). According to Scott [45] the polydispersity index could be used to define which process is implied (random and non-random chain scissions). However, this parameter cannot be used for these exper-
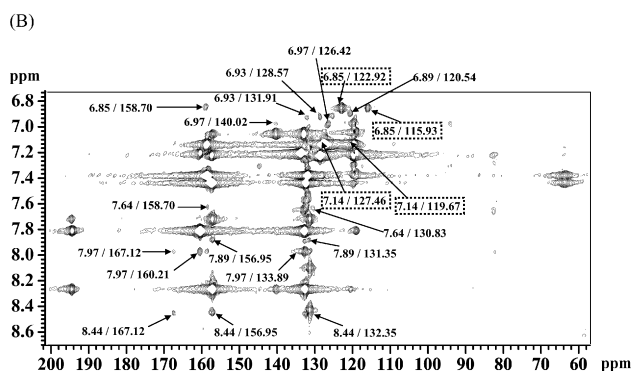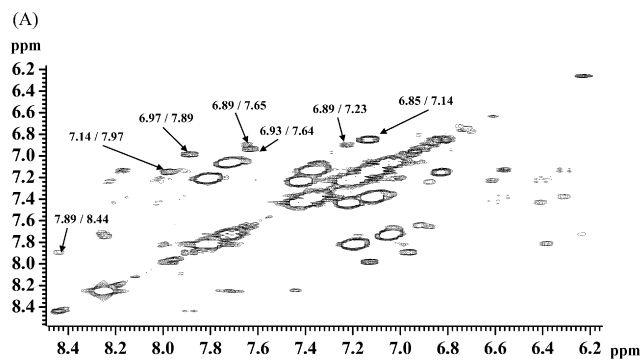

Fig. 6. NMR 2D spectra of the eluted species during an *ex situ* aging test: (A) COSY 2D spectrum—^{1}H–^{1}H correlations; (B) HMBC 2D spectrum—^{1}H–^{13}C correlations.
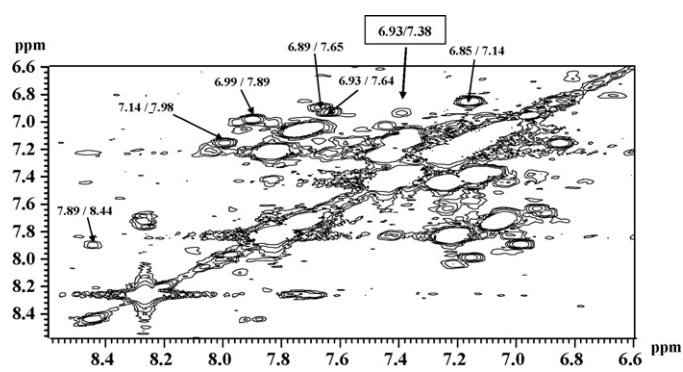

Fig. 7. 2D COSY spectrum (^{1}H–^{1}H correlations) of species "extracted" from *in situ* aged membrane.
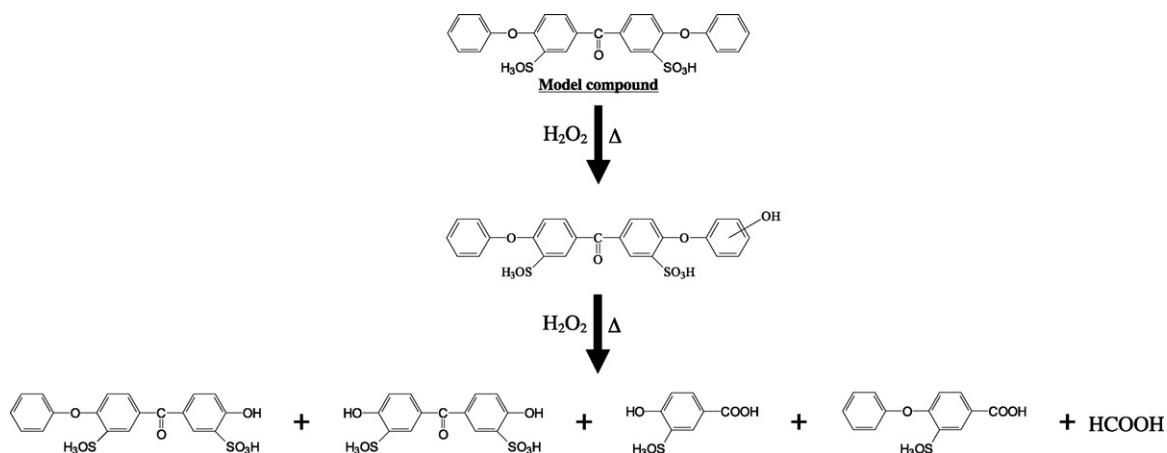
Fig. 8. Aging mechanism of a model compound representative of a sPAEK repeat unit [42].

iments as oligomers issued from chain scissions can diffuse through the membrane into the aging medium. They become more accessible to radical attack compared to the ones embedded in the polymer matrix. As a consequence, molecular weight of eluted products is significantly lower than the aged membranes one.

While *ex situ* aged materials (membrane and eluted products) have similar NMR spectra, their infrared signature is quite different. No oxidized products were detected for the aged membrane whereas an IR absorption band between 1800 and 1700 cm^{-1} with a maximum located at 1714 cm^{-1} was observed on the eluted products spectrum. This large absorption band is characteristic of carboxylated products. As previously pointed out, chain scissions lead to the formation of carboxylic and phenolic groups. Random chain scissions should allow an accumulation of these species contrary to the "unzipping" phenomenon. In addition, an "unzipping" process generates phenolic molecules which are turned into carboxylated products by oxidation. These small molecules exhibit a high mobility and their diffusion from the membrane to the aging medium is favored. It explains why oxidized products observed by IR at 1714 cm^{-1} are present more significantly in the eluted fraction.
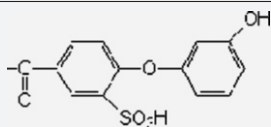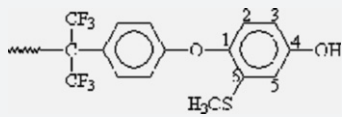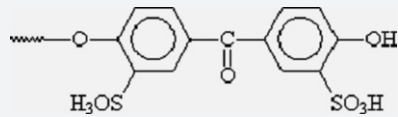
The analogy between degradation path of a sPAEK model compound and the corresponding macromolecule is thus relevant in *ex situ* conditions. The next step of the approach is the comparison between *in situ* and *ex situ* fuel cell tests. SEC analyses exhibit a significant molecular weight decrease after a 500 h fuel cell test of the order of 40%. IR analysis reveals a heterogeneous degradation of the material since carboxylated products are detected on the cathode side whereas no modification is observed on the anode side. This observation is in agreement with previously published works [11,12,28]. As sPAEK degradation results from an oxidation process we must keep in mind that it could be enhanced by the presence of oxygen at the cathode side. As a consequence, a strong effect of the operating conditions (gas stoichiometry and composition, potential difference between the electrodes) is expected and will be investigated in further work.

The EDX analysis revealed that the sulfur profiles do not change as aging proceeds indicating that no elution of sulfonated oligomers occurs. This conclusion is confirmed by the absence of degradation products in the water collected during the *in situ* test. However some degradation products can be extracted from aged membrane by a hot water post-treatment. Chemical modifications on these

[1]

[2]
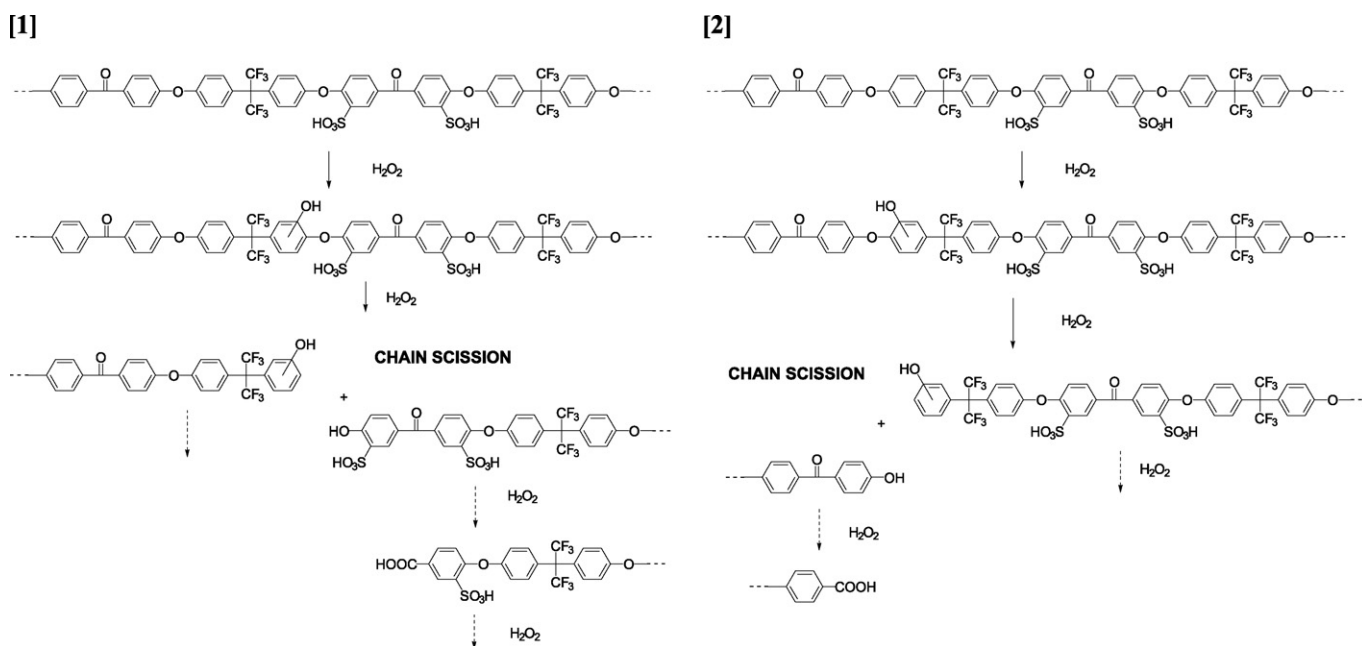
Scheme 2. Aging path of sPEAK membrane (1—hydrophilic unit and 2—hydrophobic unit).

Table 4
Terminal chain ends not detected on *ex situ* aged materials.

End chain EC6	End chain EC7	End chain EC8

trapped species, as detected by NMR and IR analyses, appear quite similar for both *in situ* and *ex situ* agings since the same phenolic and carboxylic terminal chain ends are detected.

It must be outlined that significant membrane modifications (presence of carboxylic species, membrane brittleness, molar weight decrease) were detected whatever the aging conditions. One can assess that the oxidability of the phenolic chain ends resulting from the synthesis is the driving force of the degradation. Their oxidation leads to chain scission, and consequently to an unzipping phenomenon.

5. Conclusion

High ionic exchange capacity sulfonated poly(aryletherketone)s were synthesized by direct polycondensation of a sulfonated monomer. Tough membranes were obtained from these polymers. *Ex situ* tests in the presence of H_2O_2 (0.07 vol% at 80 °C) as well as *in situ* fuel cell tests (500 h at 60 °C) were performed on these membranes. In all cases, the resulting material is brittle due to a polymer chain length reduction, as confirmed by molecular weight measurements (SEC).

"Aged membranes", "eluted species" and "extracted species" isolated after the aging experiments were analysed by different techniques (IR, NMR, SEM EDX). A qualitative IR analysis suggests the presence of oxidized products. Namely, carboxylated valence vibrations ($1714\,cm^{-1}$) appeared for both *ex situ* and *in situ* experiments. However, in the case of fuel cell tests, ATR results show that the chemical modifications are heterogeneous and mainly occur on the cathode side. EDX analyses were consistent with a homogeneous repartition of the sulfonic groups across the membrane thickness, and with no elution of any sulfonated species during the fuel cell test. Finally, an extended analysis of the polymer chain ends was performed by NMR 1D and 2D (COSY ^1H–^1H correlation and HMBC ^{13}C–^1H correlations). The presence of phenol and carboxylic end-groups was clearly established. These results are in good agreement with those reported earlier on a model compound [42].

Finally, it is important to outline three main points:

- Chemical agreement between the *ex situ* and *in situ* tests shows that H_2O_2 is a powerful tool to evaluate the durability of ionomer membranes used in fuel cell. This *ex situ* aging test offers a way to determine the aging mechanism which could give us a way to test the potential of new materials as electrolytes.
- The aging process on a well-defined model compound can be representative of the complex phenomena which occur on a macromolecular structure both in *ex situ* or *in situ* experiments. Such a result opens new perspectives for a reliable evaluation of different membranes chemical stability for fuel cell applications.
- The H_2O_2 concentration generally used (3%) is too high to be relevant to a fuel cell test. Indeed, we have shown that after 100 h

of degradation in a 0.07% H_2O_2 solution, the extent of degradation of the membrane is significantly more important than after 500 h in fuel cell. This H_2O_2 concentration which is already 40 times lower than the generally used value should be reduced a bit to have a good estimation of the lifetime. Moreover, the use of too concentrated solutions could involve additional degradation routes and misleading conclusions.

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