



Evaluating chemical degradation of proton conducting perfluorosulfonic acid ionomers in a Fenton test by solid-state ^{19}F NMR spectroscopy

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ABSTRACT

Chemical degradation and stability of perfluorosulfonic acid (PFSA) ionomers against radical attack were investigated by an (ex situ) Fenton test. Solid-state and solution NMR as well as ATR-FTIR studies were performed on the samples before and after the Fenton reaction. By changing the concentration of the Fenton's solution it is found that the metallic catalyst (Fe^{2+}) is a critical factor which may affect the solid-state NMR results. After adjusting the experimental conditions, i.e., by reducing the Fe^{2+} concentration, it was possible to detect by solid-state ^{19}F NMR spectroscopy the structural changes of the perfluorosulfonic acid ionomers during the ex situ Fenton test.

A comparative study was made on the degradation of Nafion and Hyflon Ion membranes which differ in the length of the side chains. It is shown that the Hyflon Ion membrane with shorter side chains is more stable against side chain attack, most probably because of the absence of an additional tertiary carbon in the side chain. At the same time, there is evidence for enhanced main chain degradation in membranes with unprotected backbone chain ends.

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1. Introduction

Degradation of perfluorosulfonic acid (PFSA) ionomers represents a very important issue in connection with their use as fuel cell membranes, and has been in the focus of many recent articles [1–3]. There are two sources for the degradation, namely redox and acid/base reactions [4,5]. These reactions can cause degradation with different mechanisms, and have therefore a strong impact on the performance and lifetime of these membranes. Chemical degradation based on redox reactions is due to radical attacks [6–14]. This assumption is directly supported by a recent study which proved the formation of HO^\bullet and HOO^\bullet radicals during in situ fuel cell experiments [15].

Inside the fuel cell, radicals can originate from electrochemical and chemical reactions on both the anode and the cathode side [15,16]. Two sources for radical formation are discussed for fuel cells. One is the presence of transition metal cations or heat which can split hydrogen peroxide produced from a two electron oxygen reduction [15,17,18]. The second is the direct reaction of H_2 or O_2

on the surface of the Pt catalyst [16,19–22]. Oxygen crossover from the cathode (at low currents) or hydrogen crossover from the anode (at high currents) might provide the basis for such reactions.

In ex situ degradation tests, the Fenton's solution is the most common method for radical formation, and the Fenton reaction is frequently used for evaluation of the chemical stability of polymer electrolyte membranes. In 1894, Fenton reported that the combination of H_2O_2 and a Ferrous salt, "Fenton's reagent", is an effective oxidant for a wide variety of organic substrates [23]. The produced HO^\bullet and HOO^\bullet radicals in the Fenton reaction can be therefore used for attacking different sites in PFSA ionomers.



Although the situation in a Fenton test does not simulate neither the cathode nor the anode side of the fuel cell, the stability of the polymers against the Fenton's reagent is nevertheless taken as one of the basic tests to evaluate the durability of such electrolyte membranes [6,7,9,24–28]. It is obvious that the presence of a metallic catalyst and a high concentration of hydrogen peroxide provide very drastic conditions which differ from an operating fuel cell, and the membranes become very rigid in a short time at much higher degradation rate. Nevertheless, the Fenton test is considered as a fast and easy evaluation test that is applicable to any kind of mem-

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brane. It provides radicals that can attack the polymer in a similar way as expected in an operating fuel cell. As a primary test prior to real fuel cell tests, the Fenton ex situ test is very practical, and the membranes that can survive the Fenton test with less degradation, typically show also better stability during in situ fuel cell tests. However, it should be emphasised that the results from the ex situ Fenton test not necessarily reflect the behaviour of a fuel cell membrane under operation conditions. For example, hydrocarbon membranes with narrow water channels exhibit reduced gas cross-over in a fuel cell test, and therefore less degradation is expected which, however, is opposite to the experimental observation [16,29].

Recent spectroscopic studies have provided new insights into the structural changes during various degradation tests [4,15,16,30–33]. These studies addressed both in situ degradation and a newly designed ex situ setup which can avoid the use of the traditional Fenton test in order to simulate a situation that is closer to the operating fuel cell condition. Detailed information was obtained by solid-state NMR spectroscopy which provided a clear picture about the structural features and dynamic behaviour prior and after degradation [16,32]. In this context, high-resolution ^{19}F MAS NMR spectroscopy was performed which is a site-selective technique and able to distinguish between the segments in the polymer main and side chains. These studies primarily addressed the polymer side chain segments which exhibited substantial degradation during the various tests. The derived results were in qualitative agreement with independent electron spin resonance (ESR) spectroscopic [15] and mass spectrometric (MS) studies [34].

So far, only one solid-state NMR study has been reported dealing with the Fenton test applied to Nafion membranes [12]. In this former work, the membranes were treated in a 0.1 molar solution of $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ (and other metallic salts), and subsequently in a 30 w/w% solution of hydrogen peroxide. As a general result, the emission of fluoride and sulfate was found to increase with the duration of the Fenton test. Nevertheless, the experimental solid-state ^{19}F NMR spectra remained practically unchanged and independent of the exposure time of the membranes to the Fenton's solution [12]. In addition, a substantial line broadening was observed for the treated membranes.

In order to understand the discrepancies in this former work, we underwent a systematic study of the Fenton reaction in PFSA ionomers. In particular, the influence of the Fe^{2+} concentration on the spectral broadening was examined. For the optimized test conditions, ex situ degradation studies for two types of PFSA ionomers with different side chain lengths were performed. The present work primarily relies on solid-state ^{19}F NMR spectroscopy which is completed by ATR-FTIR and solution NMR investigations on selected samples.

2. Experimental

2.1. Sample preparation and degradation test

2.1.1. Membrane pre-treating

Pieces (size: 6 cm \times 9 cm) of Nafion 112, Nafion 117 (received from Hydro2Power SRL) and Hyflon Ion E87 (received from Solvay Solexis S.p.A.) were washed in H_2O_2 (3 v/v%) at 80 °C for 1 h, and were rinsed in deionized water for another hour at 80 °C. After this procedure, the membranes were completely transparent. To exchange all metal ions by protons, the membranes were exposed to a solution of HNO_3 (5 w/w%) at 80 °C for 4 h. The membranes were then rinsed in deionized water at 80 °C. The water was renewed after each hour for at least four times. In the last step, the membranes were kept in deionized water at room temperature overnight.

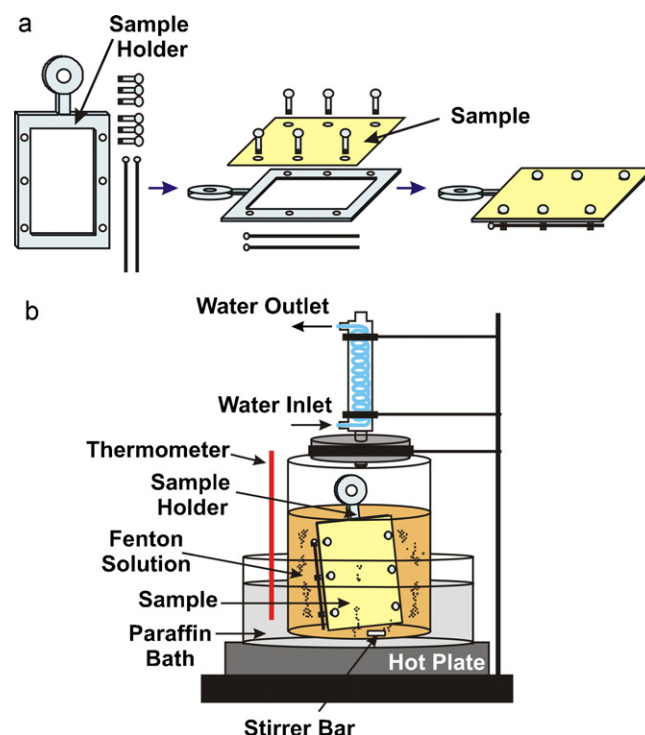


Fig. 1. Ex situ Fenton test. (a) Membrane preparation and (b) setup of Fenton test.

2.1.2. Preparing the membranes and the Fenton test

PFSA ionomers are normally floating on the water surface or Fenton solution, and therefore the samples do not possess a homogeneous surface after the test, but are deformed and rolled. This is a serious problem for any quantitative study because the different parts of the membrane do not exhibit the same rate of degradation, and a repetition of the evaluation test on the same material may provide different results. To overcome this problem, the membrane should be kept completely flat inside the Fenton solution. Moreover, to have a reliable catalyst concentration in a Fenton reaction, any metallic accessories should be avoided.

In this work, a glass frame has been used to keep the membrane inside the solution (Fig. 1a). The membrane was laid on a glass frame with some holes in the corners. The same holes were made in the membrane at the proper places. A small glass nail was passing through each hole. A long glass nail was then passing through the holes of the small nails in each row which keeps the small nails in their places. In this way, the membrane was fixed loosely between the frame and the nails, and does not roll or move to the surface of the solution.

The setup for the Fenton's reaction test is shown in Fig. 1b. For each test, a certain amount of $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ was measured and added to a completely dry dish (Table 1). The glass frame with the membrane was placed in the dish. In the last step a certain amount of H_2O_2 (30 v/v%) was added to the dish and the top of the dish was closed. This dish was placed in a paraffin bath at 80 °C. A distillation column was connected to the top of the dish. Table 1 summarizes the conditions for each test. After the test, the membrane was washed in distilled water for 1 h and dried at 110 °C overnight in a vacuum oven and prepared for the solid-state NMR and ATR-IR measurements. The remaining Fenton's solution was used for the liquid-state NMR measurements. The latter solution was kept at room temperature under a slow N_2 gas flow for about 2 days. During this time, water evaporated and the total amount of the solution decreased to about 10 ml which was then used for the solution ^{19}F NMR experiments.

Table 1
Fenton test conditions in the present work.

Sample	Test duration	FeCl ₂ concentration in H ₂ O ₂ 30 v/v% (molar)	Results
Nafion 117 (thickness: 0.007 in.)	0	0.1	Fig. 3
	3 h		
	6 h		
	12 h		
	1 day		
	2 days		
Nafion 117	3 h	0 0.0002 0.0005 0.001 0.01 0.05 0.1	Fig. 4
Nafion 117	0	0.0002	Figs. 5 and 6
	1 h		
	3 h		
	6 h		
	12 h		
	1 day 2 days		
Nafion 112 (thickness: 0.002 in.) and Hyflon Ion E87 (thickness: 0.00078 in.)	0	0.0002	Figs. 7–10
	6 h		
	12 h		
	18 h		
	1 day		

2.2. NMR spectroscopy

All NMR experiments were performed at 376.09 MHz for ¹⁹F on a Varian InfinityPlus 400 NMR spectrometer. The solid-state NMR spectra were acquired under MAS conditions using a 4 mm HFXY magic-angle spinning probe at a spinning frequency of 15 kHz. Sixteen transients were recorded for each experiment with a recycle delay of 2 s and a dwell time of 5 μs. The ¹⁹F 90° pulse length was 3 μs. The ¹⁹F NMR signal of Teflon at –121 ppm (relative to CFCl₃ with δ=0 ppm) was used as a secondary external reference. All experiments were performed at 80 °C which provided a better spectral resolution.

Solution ¹⁹F NMR spectra of the remaining Fenton's solutions were recorded at room temperature using the MAS probe with the same experimental parameters, but without sample spinning. In all solution NMR measurements, 1024 transients were recorded and averaged.

Spectral deconvolution was done with the Spinsight software (Varian). For fitting the CF₂ signal we found it necessary to use four resonances at –119.3, –120, –121 and –122.5 ppm. In fact, in the paper by Chen and Schmidt-Rohr [35], done at sample spinning speed of 30 kHz (with better spectral resolution) even five subspectra could be resolved. In the present case, four subspectra were found to be sufficient to reproduce the CF₂ signal, while for each of the OCF₂, SCF₂ and CF segments only a single signal was needed in the deconvolution analysis.

Fluoride emission was calculated from the solution NMR spectra by calibration of the signal intensity with a potassium fluoride solution of known concentration, and with a known amount of polymer which was subjected to the respective Fenton test.

2.3. Attenuated total reflection infrared (ATR-IR) spectroscopy

ATR-FTIR spectra were measured with a Bruker IFS 66 spectrometer using a single reflection diamond ATR accessory. Spectra were recorded with a DTGS detector at a resolution of 2 cm⁻¹. The membranes were squeezed between the surface of a diamond crystal by pressing a counterpart. For all measurements 250 scans were averaged covering a spectral range of 400–4000 cm⁻¹.

3. Results

¹⁹F MAS NMR spectra of Nafion and Hyflon Ion are shown in Fig. 2. The given ¹⁹F signal assignment is based on former solution and solid-state NMR investigations [32,35,36], and is shown in Fig. 2. The ¹⁹F NMR spectra exhibit separate signals for the side and the main chain segments of the Nafion and Hyflon Ion membranes. The CF₂ groups of the backbone give rise to a resonance at –121 ppm similar to a signal of ¹⁹F NMR in Teflon, while the ¹⁹F resonance at –138 ppm denotes the backbone CF group at which the side chain is attached. The signal of the CF group in the side chain appears at –144 ppm which is missing in the Hyflon Ion spectrum due to the shorter side chain. The ¹⁹F resonance at –117 ppm reflects the SCF₂ groups, while two peaks referring to the two OCF₂ groups and the CF₃ group of the side chain appear at about –80 ppm. For Hyflon Ion, the peak at –80 ppm represents only the signal of the OCF₂ group. The solid-state NMR spectra in this paper were recorded with a sample spinning frequency of 15 kHz. At this spinner frequency the low field signal at –80 ppm is broadened due to

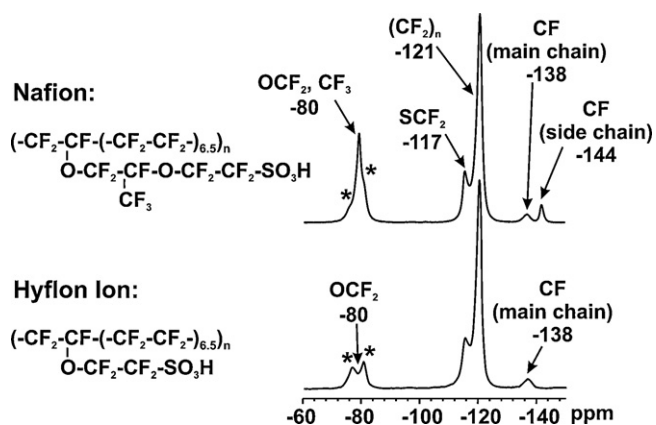


Fig. 2. Chemical structures and solid-state ¹⁹F NMR spectra of Nafion 117 and Hyflon Ion. Asterisks indicate spinning side bands. The given spectra are normalized to the dominant peak of the backbone CF₂ groups.

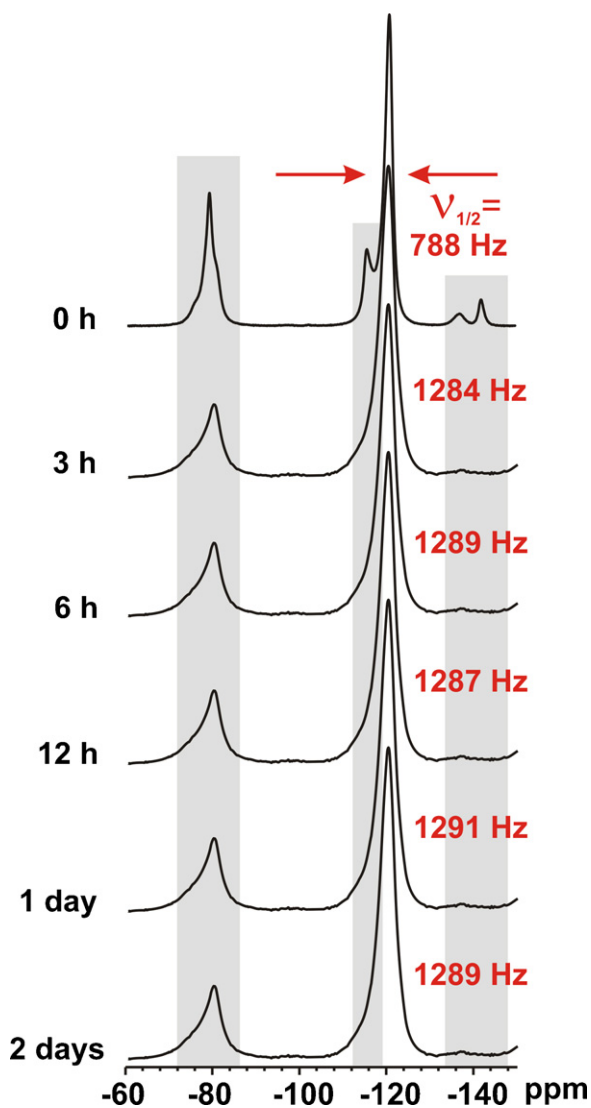


Fig. 3. Solid-state ^{19}F NMR spectra of Nafion 117 samples after treatment with 0.1 M Fe^{2+} in 30 v/v% H_2O_2 . The line widths, $\nu_{1/2}$, of the peak at -121 ppm, referring to the backbone CF_2 groups, are shown. Exposure times are given to the left of the figure.

the overlap with the spinning sidebands (indicated by asterisks) of the backbone CF_2 and the side chain SCF_2 group signals.

To examine the degradation of the present membranes during the Fenton test, in a first attempt Nafion 117 was treated with a 0.1 M Fe^{2+} solution, as also done in the aforementioned ex situ Fenton study [12]. Fig. 3 shows the respective solid-state ^{19}F NMR spectra of these samples after exposure to the Fenton test reagent for the periods given in the figure. A general line broadening was observed for all samples after treatment with the Fenton's solution. In agreement with the former work, the spectra of the treated samples are practically identical, and exhibit a substantial line broadening by almost a factor of two as compared to the untreated sample (see top spectrum). Hence, it is very likely that the line broadening obscures all other spectral alterations which might occur during the ex situ test.

To further clarify these findings, the test was repeated with different concentrations of the Fenton's reagent. Fig. 4 displays ^{19}F NMR spectra of Nafion 117 samples which were exposed for 3 h to the Fenton's reagent with different Fe^{2+} concentrations, as given in the figure. It is seen that the line widths strongly vary with the actual concentration. As an example, the line widths, $\nu_{1/2}$, of the main chain CF_2 group are reported in the figure. The difference in spec-

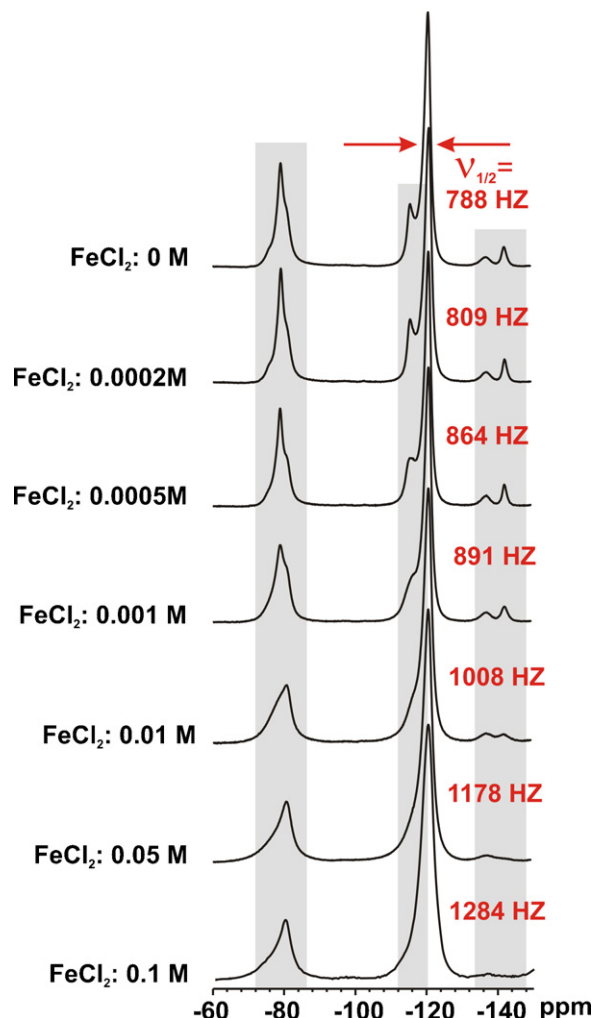


Fig. 4. Solid-state ^{19}F NMR spectra of Nafion 117 samples after 3 h of Fenton test with different Fe^{2+} concentrations, as indicated, in 30 v/v% H_2O_2 solutions. The line widths, $\nu_{1/2}$, of the peak due to the backbone CF_2 groups are shown.

tral line width for the samples treated with 0.0002 M and 0.1 M Fe^{2+} solution is almost 500 Hz. Hence, for Fe^{2+} concentrations >0.0005 M the SCF_2 group signal only appears as a shoulder next to the dominant CF_2 peak, and at the highest concentrations it is completely obscured. A similar line broadening effect is seen for all other resonances. Nevertheless, independent of the spectral broadening, a decrease of the relative intensity for the side chain SCF_2 group can be identified for the solutions with lower Fe^{2+} concentration.

In order to follow the time evolution of the spectra during the ex situ Fenton test, a Fe^{2+} concentration of 0.0002 M has been chosen. The respective ^{19}F NMR spectra are given in Fig. 5. It is seen that line width of the main chain CF_2 peak, as denoted in the figure, slightly increases by about 50 Hz, if the non-treated membrane is compared to the membrane being in the Fenton's solution for 2 days. At the same time, in contrast to situation shown in Fig. 3, a continuous decrease (with exposure time) of the SCF_2 group intensity can be clearly identified. These changes in the relative signal intensities will be quantified by spectral deconvolution, as will be further outlined below.

The structural evolution of the Nafion 117 sample during the Fenton test was also studied by ATR-FTIR spectroscopy. The respective IR spectra of the same Nafion samples are shown in Fig. 6. The major peaks in these ATR-FTIR spectra and their assignment [37] are also listed. The comparison of the spectra before and after the Fenton degradation test displays a general decrease in

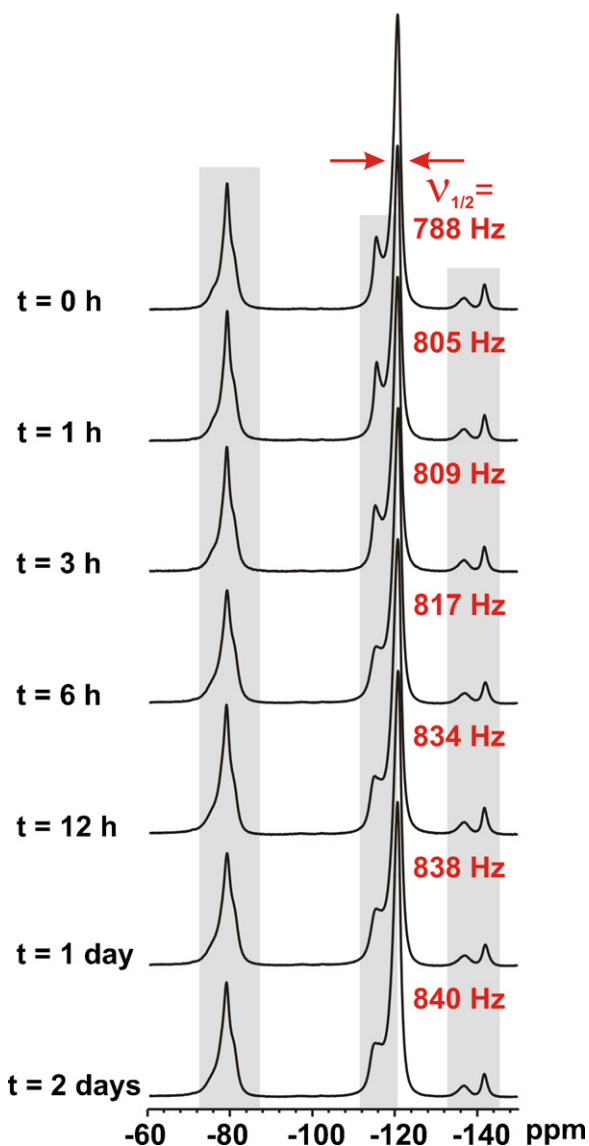


Fig. 5. Solid-state ^{19}F NMR spectra of Nafion 117 samples after Fenton tests with 0.0002 M Fe^{2+} in $30\text{ v/v\% H}_2\text{O}_2$. Exposure times are given to the left of the figure.

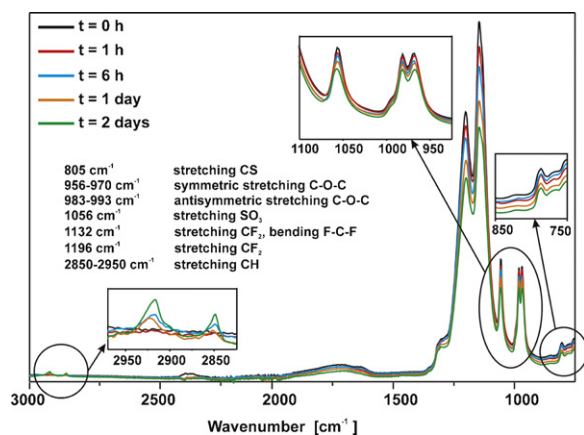


Fig. 6. ATR-IR spectra of Nafion 117 samples after Fenton tests with 0.0002 M Fe^{2+} in $30\text{ v/v\% H}_2\text{O}_2$.

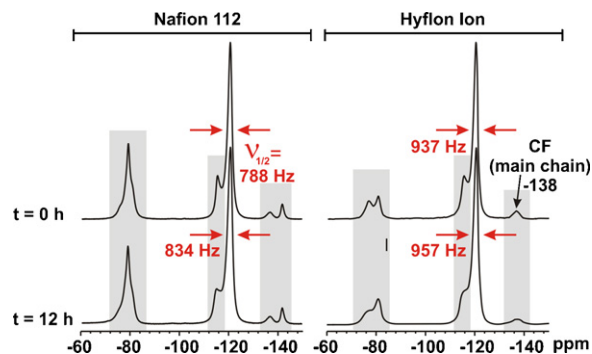


Fig. 7. Solid-state ^{19}F NMR spectra of Nafion 112 and Hyflon Ion after 12 h ex situ Fenton tests with 0.0002 M Fe^{2+} in $30\text{ v/v\% H}_2\text{O}_2$.

intensity of the C–O–C (at 960 and 980 cm^{-1}), S–C (805 cm^{-1}) and S–O (1056 cm^{-1}) stretching modes. At the same time, an intensity decrease is detected for the peaks at 1132 and 1196 cm^{-1} which are related to the stretching modes of the CF_2 groups.

A further, very interesting result is the appearance of two new peaks at around 2850 and 2920 cm^{-1} which are attributed to symmetric and asymmetric CH stretching modes, and whose intensities gradually increase with longer exposure times. It is worthwhile to note that solid-state ^1H NMR measurements were done as well. However, no ^1H NMR signals of aliphatic protons could be detected, and a unequivocal and independent proof for the presence of such CH groups could not be given, most probably due to their low concentration.

To compare the stability of Nafion and Hyflon Ion membranes, samples of these ionomers were subjected to the same Fenton test solution, with a Fe^{2+} concentration of 0.0002 M . Since the thickness of the Hyflon Ion membrane is much less than that of Nafion 117, this test was done with the thinner Nafion 112 membrane. As an example, the respective solid-state ^{19}F NMR spectra of these membranes before and after a 12 h test are shown in Fig. 7. It is seen that the side chain in Hyflon Ion is also affected by radical attack during the Fenton test.

Spectral deconvolution (see Section 2) was used to quantify the different degradation behaviour of the present membrane systems. Fig. 8 shows two representative experimental spectra for Nafion 117 together with the subspectra from the deconvolution analysis. After deconvolution of the ^{19}F NMR spectra, the individual signals of the OCF_2 , SCF_2 , and CF groups were first normalized to the main chain CF_2 signal, which itself consists of four components. The intensity for the signal prior to the test was then set to 100 as a reference for the samples after the test. These relative peak integrals of the resolvable signals prior and after the Fenton test are plotted in Fig. 9. Further details can be found in Section 2.

Inspection of Fig. 9 clearly reveals that chemical degradation in Hyflon Ion is much less pronounced than in Nafion 112. Moreover, for both membranes the main chain CF group signal is only little affected, and the biggest signal loss is detected for the SCF_2 signal.

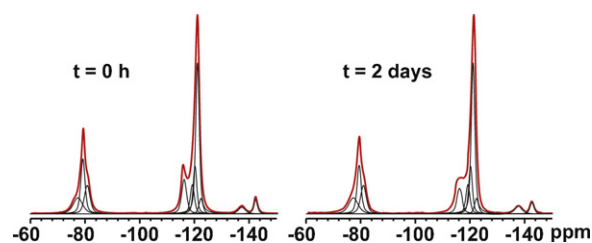


Fig. 8. Solid-state ^{19}F NMR spectra of Nafion 117 prior and after 2 days ex situ Fenton tests with 0.0002 M Fe^{2+} in $30\text{ v/v\% H}_2\text{O}_2$ together with the subspectra used for deconvolution (further details are given in Section 2).

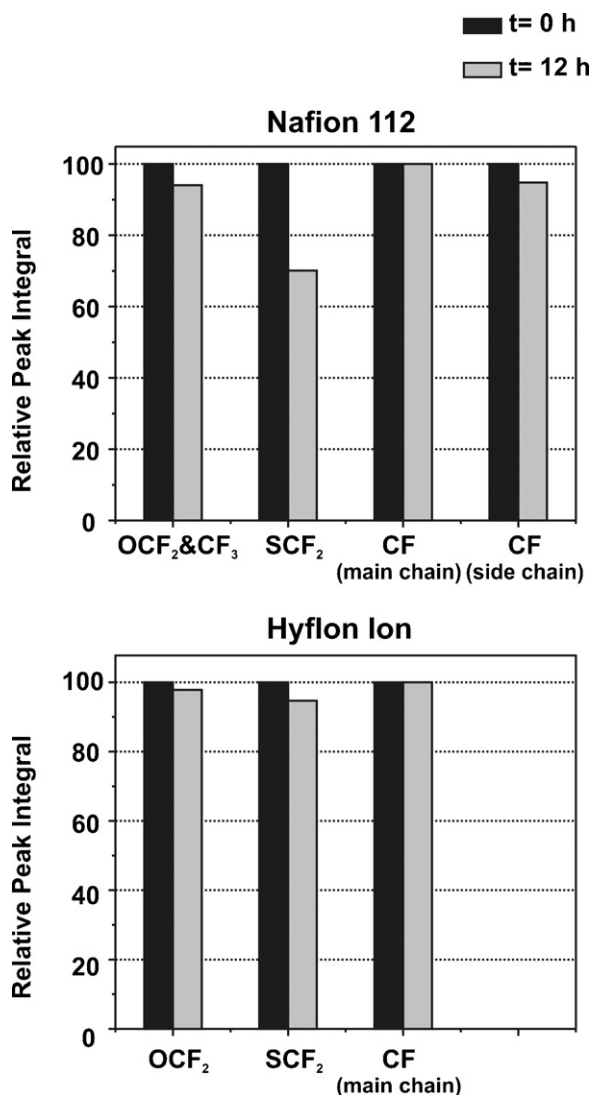


Fig. 9. Relative peak area after 12 h Fenton tests with 0.0002 M Fe²⁺ in 30 v/v% H₂O₂ of Nafion 112 and Hyflon Ion membranes. The given numbers are the ratios of the peak integrals after the in situ tests relative to the original integrals prior to the tests in percentage, as taken from the ¹⁹F NMR spectra. The experimental error is ±3%.

In general, the data imply a degradation gradient, i.e., increase in degradation towards the CF₂SO₃H group of the side chain.

As a crosscheck, solution ¹⁹F NMR measurements were done on the Fenton's test solutions resulting from the latter tests. As an example, Fig. 10 shows the ¹⁹F NMR spectrum of the Fenton solution after 12 h treatment of Nafion 112 which is compared with the ¹⁹F NMR spectrum of the fresh Fenton solution, before any membrane treatment. The signal-to-noise ratio is very poor since the ¹⁹F NMR spectra were recorded with the MAS probe and without any special precautions for high-resolution conditions. The peak in the spectrum at −127.6 ppm is attributed to the F[−] signal, in agreement with the literature data [38].

The peak intensities from these solution ¹⁹F NMR measurements were further used to calculate the fluoride emission during these Fenton tests (see Section 2), and the results for the Nafion 112 and Hyflon Ion membranes are plotted in Fig. 11. The derived data are found to be in good agreement with the reported fluoride emission from analysis of the Fenton's test solutions in other works [9,25]. In the present case, the fluoride emission for Hyflon Ion is slightly less than for Nafion 112, which is in qualitative agreement with the aforementioned solid-state ¹⁹F NMR data (see Fig. 7).

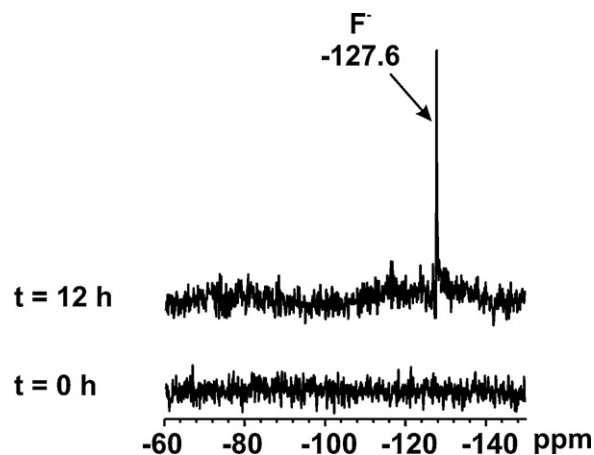


Fig. 10. Solution ¹⁹F NMR spectrum of the Fenton solution obtained for 12 hrs treatment of Nafion 112. The ¹⁹F NMR spectrum of the fresh Fenton solution is given for comparison (0 h).

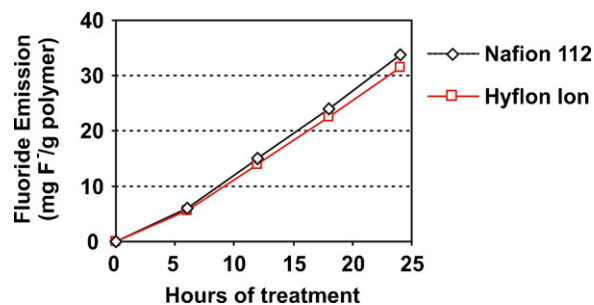


Fig. 11. Fluoride emissions for Nafion 112 and Hyflon membranes after Fenton tests with 0.0002 M Fe²⁺ in 30 v/v% H₂O₂.

4. Discussion

Recently, solid state NMR spectroscopy was successfully applied for the characterization of polymer membranes that have been subjected to in situ tests [32]. Despite the major of degradation studies which emphasised the presence of main chain degradation, these solid-state NMR studies clearly proved substantial degradation in the polymer side chains [32]. The results from the present ex situ Fenton test studies confirm these former results. They demonstrate that structural changes and bond cleavages also take place in the polymer side chains, which therefore represent an important contribution for chemical degradation of such ionomer membranes.

In the present work it is found that the membranes, after treatment with Fenton's solution at Fe²⁺ concentrations larger than 0.0005 M, exhibit substantial line broadening in the solid-state ¹⁹F NMR spectra. The spectral broadening is visible for all ¹⁹F NMR signals, but is somewhat more pronounced for the signals of the side chain region. In fact, a similar line broadening effect was also observed after soaking the membrane in a FeCl₂/water solution which implies that the spectral changes are not related to membrane degradation, but to the presence of the paramagnetic iron ions.

Iron ions not only affect the solid-state NMR data, but are also visible during other experimental studies. Hence, they can easily exchange with the acidic proton in the membrane, and—without any chemical degradation—decrease the ion exchange capacity and electric conductivity of the polymer. Normally these changes are reversible after treating the membrane with an acidic solution.

Performing the Fenton test with the lowest manageable concentration of FeCl₂ (0.0002 M = 10 ppm) yields experimental ¹⁹F NMR spectra with acceptable resolution. Their analysis shows continu-

ous degradation in the side chain region upon increasing reaction time. This is independently confirmed by the ATR-FTIR spectra which—along with the detection of the strong F^- peak in the liquid NMR spectra—also point to main chain degradation, not directly visible in the solid-state ^{19}F NMR spectra. Based on these results and in agreement with other works, the sites for radical attack in PFSA membranes are clearly both the main and the side chain regions.

The comparative studies on Nafion and Hyflon Ion membranes demonstrate that the side chains of the latter one are also sensitive to radical attack, but considerably less than those in Nafion. In general, the polymer side chains can be attacked via the C–S bond or via the tertiary carbons in the side and main chains [6,11,16,34,39].

The comparison of the CF peak integral for the side chain and main chain in Nafion after the degradation shows that the changes for the main chain CF group is very little, while for the side chain CF group signal a much stronger reduction can be found. Therefore, for Nafion the intensity decrease of the peak at -80 ppm (referring to the OCF_2 and CF_3 groups) is primarily caused by the OCF_2 peak closer to the end of the side chain and to the CF_3 group, and not by the OCF_2 group next to the polymer main chain.

The present NMR results confirm the generally accepted positions for radical attacks in these ionomers in the side chain at the S–C bond, and at the C–F bonds of the tertiary carbons. Obviously, for Nafion the C–F bond of the tertiary carbon in the main chain is more stable than that in the side chain. The absence of the $-O-CF_2-CF(CF_3)-$ segment in the Hyflon Ion membrane may directly explain its improved side chain stability. Accordingly, for Nafion the more pronounced signal decrease of the SCF_2 unit can be traced back to a radical attack at both the tertiary carbon in the side chain and the C–S bond.

The solution NMR spectra of the Fenton solution exhibit a poor signal-to-noise ratio, most likely due to the presence of iron ions. The only visible signal at -127.6 ppm reflects the release of a substantial amount of F^- ions. Additional small peaks due to various side chain fragments, as also reported in other works [16], could not be detected. Surprisingly, the present solution NMR data show very similar fluoride emissions, and thus degradation for the Nafion and Hyflon Ion membranes, and the derived values are comparable with the fluoride emission data reported from ion selective electrode measurements [9,25]. At first sight, this seems to contradict the solid-state NMR results which imply minor side chain degradation for the Hyflon Ion membrane. However, the solution NMR data represent the total amount of fluoride release during the Fenton test due to both main and side chain degradation. The results from the solid-state and solution NMR experiments can be understood by the higher main chain degradation rate in Hyflon Ion E87 as compared to Nafion 112 which proceeds from the carboxyl groups terminating the PTFE backbone [24]. In the commercial Nafion 112, the number of carboxyl groups is minimized by endcapping of the polymer main chain with CF_3 groups. In Hyflon Ion E87, such a protective endcapping was not done. Merlo et al. showed that the fluoride emission of Hyflon Ion E87 after endcapping decreases by a factor of about 5 [9,25].

It is therefore concluded that for stabilized perfluorosulfonic acid polymers the total degradation is determined primarily by the decomposition of the side chain. As shown in the present work, the ionomer with shorter side chains, Hyflon Ion, exhibits a better stability with less degradation as compared to Nafion, having longer side chains and an additional tertiary carbon. This may also explain the better performance of short side chain ionomer membranes in the fuel cell devices.

5. Conclusions

Solid-state NMR spectroscopy was successfully employed for the study of the structural changes in PFSA membranes after ex

situ Fenton tests. It was shown that great care should be taken during such Fenton tests, since the presence of paramagnetic iron ions can strongly affect the NMR results. After optimization of the test procedure, i.e., working with a minimum Fe^{2+} concentration, it was possible to follow the structural changes due to membrane degradation caused by the Fenton's reagent. The results from solid-state and solution ^{19}F NMR as well as ATR-FTIR measurements demonstrate that degradation takes place in both the polymer side and the polymer main chain.

The comparative study reveals that the Nafion and Hyflon Ion membranes exhibit similar overall degradation rates. This result is explainable by the more pronounced main chain degradation of the Hyflon Ion E87 membrane which was not further protected by endcapping of the main chain. At the same time, the shorter side chains in Hyflon Ion are more stable than the longer side chains in Nafion which is attributed to the presence of an additional tertiary carbon in the side chains of the latter polymer, and which represents a potential site for radical attack and thus degradation.

On the basis of the present results, the membrane stability should be greatly improved using polymers with short side chains (i.e., without tertiary CF groups in the side chain) and by endcapping of the main chains, both of which substantially reduce the possibility of radical attack, and thus chemical membrane degradation.

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