

Resistance to peroxide degradation of Hyflon[®] Ion membranes

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Abstract

Perfluorosulfonic acid (PFSA) membranes have been used for 40 years as solid electrolytes in low temperature fuel cells and are considered from the scientific community superior to other polymeric products due to their good combination between chemical resistance and proton conductivity. In recent years, development of the class of PFSA membranes known as ‘short side chain’ membranes has been restarted from Solvay Solexis (Hyflon[®] Ion).

Although PFSA are highly stable, still, decay in fuel cell performance might be detected over time due to membrane degradation, especially under certain working conditions. Different degradation mechanisms, mainly based on Nafion[®] structure, have been proposed by several Authors and both ex situ and in situ test protocols have been developed to perform accelerated testing. The generally accepted opinion is that the degradation problem is mostly related to peroxide radical attack. A short review of the degradation mechanisms is first presented in this work.

For the first time a campaign of chemical degradation tests (open circuit voltage fuel cell operation and ex situ Fenton tests) on the short-side-chain PFSA is presented and discussed, both for standard extruded and chemical stabilized membranes.

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Keywords: Fuel cell; Membrane; Degradation; Hyflon[®] Ion; Dow ionomer; Stabilization

1. Introduction

1.1. Long- and short-side-chain perfluorinated ionomer membranes

PFSA ionomers are known since the late 1960s, when the Nafion[®] ionomers were developed by the Du Pont company and employed as polymer electrolyte in a GE fuel cell designed for NASA spacecraft missions. Since then, Nafion[®] polymers have found wide application especially in the chlor-alkali industry as membrane materials, but also in other applications where very high chemical inertness (given by the perfluorinated structure) and low resistances to cation transport are required at the same time.

In more recent years these materials were considered and studied as proton-exchange membranes (PEMs) in fuel cells.

In the mid-1980s Ballard Power Systems showed significant improvements in fuel cell performance using ionomer

membranes obtained from Dow chemical [1]. This ionomer, commonly known as the Dow ionomer, is perfluorinated and similar in structure to Nafion[®], save for a shorter pendant side-chain which carries the functional ion-transporting group (see Fig. 1), wherefrom this ionomer is known as the short-side-chain (SSC) ionomer. Correspondingly, Nafion[®] is sometimes referred to as the long-side-chain (LSC) ionomer. Though demonstration of a higher power-generating capability in fuel cell was given using the Dow ionomer, after the filing of a series of patents by the Dow company [2–10], the industrial development of this interesting ionomer structure was abandoned.

Recently, due to a different and simpler route for the synthesis of the base monomer for SSC ionomers [11], Solvay Solexis has restarted the development of polymer electrolyte membranes based on this perfluorinated ionomer type. The commercial name for this ionomer (and the membranes and ionomer dispersions made there from) is Hyflon[®] Ion.

1.2. SSC ionomers: polymer and membranes properties

The works by Tant et al. [12,13] and by Moore and Martin [14] contain very significant data on SSC ionomers of different equivalent weights (EWs) and highlight important differences

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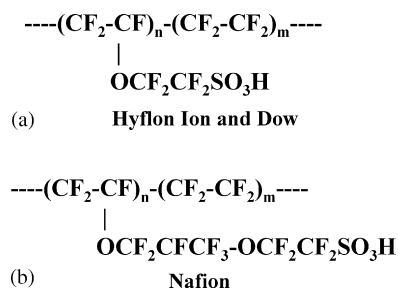


Fig. 1. (a) Hyflon[®] Ion/Dow and (b) Nafion[®] polymer structures.

induced by the shorter length of the side chain compared to a LSC ionomer. The most significant differences found are the much higher crystallinity at given equivalent weight of the SSC ionomer compared to the LSC one and the higher glass transition temperature (T_g) of the SSC ionomer. These properties allow for a wider operating window towards lower EW ionomers still retaining good mechanical properties and substantial water insolubility and possible use of these products in the range of high temperature PEM (80–120 °C).

Additional physical data on SSC ionomers are reported in [15–27].

1.2.1. Hyflon[®] Ion ionomers: polymer and membranes properties

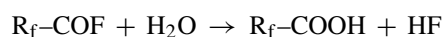
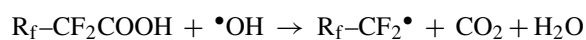
Data on Hyflon[®] Ion membranes, including fuel cell performance, mechanical characteristics and hydration properties were published in [28,29] and resulted in most cases comparable to the data published on the Dow ionomer.

The Hyflon[®] Ion membranes used in the experimental part of this work have an EW in the range of 850–870 g equiv.⁻¹ This EW range guarantees good mechanical properties due to the high crystallinity level and a hydration level high enough to give high proton conductivity, the measured T_g of these membranes is 127 °C (dry polymer) versus the 67 °C of Nafion[®] [28], indicating mechanical stability of the membrane in the range of high temperature PEM.

1.3. Membrane peroxide degradation: state of the art

The literature regarding PFSA membranes' degradation is almost exclusively referred to Nafion[®] degradation. Among the mechanisms reported in the literature which describe the degradation of PFSA membranes, the one generally recognized as the most relevant by the scientific community is the so-called 'unzipping reaction' originated by peroxide radical attack. This is described, for example, by Curtin et al. [30].

The 'unzipping reaction' process starts from the carboxylic end groups present in the polymer as a consequence of the polymerization process and disaggregates the main chain of the polymer according to the following reaction scheme:



During this process evolution of CO₂ and HF can be detected. In fact the preferred methods for checking the degradation level are:

- (1) The weight reduction of the polymer [35].
- (2) The measure (via selective electrodes or ionic chromatography) of the F⁻ ions released [31–34].
- (3) Measure of the pH reached by the solution [34] (in direct relation with the amount of F⁻ due to the low acid force of HF, $K_a = 6.7\text{E}-4$). This last should be considered carefully because of the possible presence in solution of R_f-SO₃H residuals that reduce further the pH level.

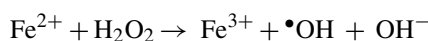
Other minor mechanisms of degradation are described but it is generally agreed that, if present, these have a reduced relevance compared with the unzipping reaction:

- (1) Scission of the CF₂-CF₂ bond of the main chain so that two new end groups are created [35]. An important reduction of the average molecular weight of the polymer was observed during a peroxide based degradation process, which was related to a scission of the main chains.
- (2) Scission in the side chain at the level of the branch, when branched pendants are present [36]. Hicks [36] observed a higher degradation rate in the case of model compounds with branched side chains compared to the degradation rate of model compounds with linear side chains. The fact that some degradation of the model compounds with linear side chains was still present suggests that some peroxide attack can occur at the level of the C-O bond between the main chain and the side chain as well.

It is generally recognized that the degradation mainly occurs due to the presence of the $\bullet\text{OH}$ species that is guaranteed by the decomposition of H₂O₂. The H₂O₂ is present preferentially on the anode side, where the potential is low enough, and is formed as a consequence of oxygen crossover [37] through the membrane. Hydrogen peroxide had been detected in both anode and cathode condenses in a concentration directly proportional to the membrane gas crossover level [38]. Other factors that can influence and increase the presence of hydrogen peroxide in a working fuel cell are the type of catalyst and the presence of chlorine ions in the catalyst [39] as well, those are residuals from noble metal precursors in some catalyst productions.

The decomposition of H₂O₂ to give the peroxide radical species is definitely increased by the presence of traces of metal ions such as iron [34], copper [40] or titanium [41], but the degradation of PFSA membranes is described even in the absence of these pollutants [35,43].

Tests based on Fenton reagents [41,30] are often used to simulate peroxide attack to PFSA membranes before carrying out long-term fuel cell tests. However, a shared Fenton test protocol is not yet defined. The main reaction occurring in the Fenton medium is



A more complete mechanism is well described by Namkung and Sharratt [42] (for the details see Appendix A).

Other ex situ tests are described for testing the resistance of membranes to peroxide degradation:

- (1) Membrane exposed to H_2O_2 in the gas phase [35]. The degradation of the polymer is quantified by measure of weight and analysis of the residuals.
- (2) Production of an ink with Pt/C catalyst and ionomer dispersion followed by drying to fabricate an electrode [43]. The electrode is then reduced to powder, mixed with water and left for several hours with a flow of hydrogen, air or hydrogen /air mixtures. The collecting of fluoride ions is used to quantify the polymer degradation which has occurred.

In these two cases no metal contaminants are added to the system.

Whatever the method for assessing the resistance to degradation, it is recognized that the peroxide degradation rate of PFSA membranes is directly related to the amount of carboxylic ($-\text{COOH}$) end groups present in the polymer. This is proven by studies on model compounds [44,36] and from the direct testing of membranes realized with a reduced content of end groups. These products are usually presented as ‘stabilized’ [30,44,45].

Regarding the fuel cell testing it is usually preferred to test the membrane in high voltage conditions (OCV above all), especially with low reactants humidification and high operating temperature; these conditions often enhance the membrane tendency to degradation [46], even if there are examples where the difference in degradation between OCV and low drained current is present but not very significant [32].

2. Experimental

2.1. Membrane preparation

Ionomer precursor polymers were obtained by semi-batch emulsion copolymerization of the perfluorinated short-side-chain sulfonyl-fluoride-vinyl-ether (SSC-SFVE) of formula $\text{CF}_2=\text{CF}_2-\text{O}-\text{CF}_2-\text{CF}_2-\text{SO}_2\text{F}$ (perfluoro-5-sulfonylfluoride-3-oxa-1-pentene) with tetrafluoroethylene (TFE) in an autoclave by using fixed TFE pressures and SSC-SFVE feed rates in order to obtain the desired EW.

The polymer was recovered by freeze-thawing the latex, washed with demineralized water, and oven dried above 100°C . The polymer was then pelletized and melt-extruded into a film of the desired thickness in a screw extruder at a temperature at least 30°C above the complete melting of the polymer as determined by DSC.

The film thus obtained was converted into the salt form by immersion in a KOH/water 10/90 (w/w) solution at 80°C for a time long enough to detect complete disappearance of the SO_2F groups by IR analysis (transmission). The film was then washed and acidified twice in an excess amount of HNO_3 . The resulting membrane was finally washed in demineralized water.

2.2. Ionomer dispersion preparation

Ionomer precursor polymers similar to what described above for membranes were synthesized, recovered from the latex, washed and dried. The obtained polymer powder was then hydrolysed converting it to the salt form by immersion in a KOH/water 10/90 (w/w) solution at 80°C for a time long enough to detect complete disappearance of the SO_2F groups and then acidified in an excess amount of HNO_3 . The polymer powder was then washed and dried.

The polymer dispersion was then obtained by dissolving the polymer powder in an autoclave by a high temperature process similar to what described by Grot [47].

2.3. Membrane electrode assembly preparation and cell assembly

The testing apparatus consists in 25 cm^2 single cells (Fuel Cell Technologies[®]) with triple serpentine pattern flow fields, mounted on Arbin[®] 50 W test stations.

The Hyflon[®] Ion membranes thickness was $50\ \mu\text{m}$ and the equivalent weight $870\ \text{g equiv.}^{-1}$. The electrodes were fabricated on a PTFE support by casting hydro-alcoholic inks produced from ionomer dispersion 830EW and a commercial Pt/C 50% by weight on Vulcan XC-72. The casting blade height was adjusted in order to have a Pt load of $0.25\ \text{mg cm}^{-2}$ of platinum on both anode and cathode electrodes. The two electrodes were transferred by high temperature “decal” onto the membrane; the cells were assembled using two commercial carbon felt gas diffusion layers $0.4\ \text{mm}$ thick, with a thin “micro-diffusion layer” on one side. The gas diffusion layers were assembled with the micro-diffusion layers facing the electrodes. The cells were closed with a torque of $5\ \text{Nm}$ on each of the eight tie rods. Rigid gaskets $0.26\ \text{mm}$ thick were present on both anode and cathode side. The MEAs were protected with a thin, rigid subgasket on both sides before assembly; the active area was reduced to $20\ \text{cm}^2$ by the presence of the subgasket.

Before starting the test, the MEAs were conditioned for 8 h in the following operating conditions:

- Fixed current: $1000\ \text{mA cm}^{-2}$.
- Cell temperature: 75°C .
- Air flow: $1300\ \text{sccm}$ (2.5 bara, dew point 80°C).
- Hydrogen flow: $650\ \text{sccm}$ (2.5 bara, dew point 80°C).

2.4. Fenton test procedure

The following Fenton test conditions were adopted:

- Iron salt: $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$.
- Iron concentration: 36 ppm of Fe^{2+} in solution.
- Hydrogen peroxide concentration: 15 or 30% (v/v).
- Bath temperature: 55°C .
- Reaction time (without inserting fresh H_2O_2): 6 h.
- Membrane sample weight: 1 g.

The reagents are mixed at ambient temperature by correcting the pH of the Fe^{2+} solution with H_2SO_4 in order to reach a pH level below 3 before the addition of H_2O_2 . The membrane sample is then added and the solution is heated to 55°C . The 6 h of reaction are considered to start when the set temperature of 55°C is reached.

The fluoride ion is measured with an Ion Selective Electrode Ionplus 9009BN after the removal of the non-reacted H_2O_2 and the addition of a buffer solution (TISAB III).

2.5. Fuel cell OCV test procedure

With the same apparatus described for the conditioning phase the OCV test is carried on in the following operating conditions:

Cell temperature	70 or 90°C
Cell current density	0 mA cm^{-2}
Gas inlet relative humidity	50 or 100%
Air flow	500 sccm (outlet pressure 1.5 bara) Compressed air ($1\ \mu\text{m}$ filter applied)
Hydrogen flow	500 sccm (inlet pressure 1.5 bara) Pure hydrogen (5.5 grade)

2.5.1. Fuel cell test diagnostic

At beginning of life and at fixed time intervals during the OCV test the status of the MEA was analysed after a short period (1 h) of cell re-conditioning in the operating conditions described above for the initial conditioning.

The characterization consists in the measure of the polarization curve, measure of cell impedance (20,000–0.1 Hz), measure of hydrogen crossover current and measure of voltammetry (100 mV s^{-1} scans) on the cathode electrode. The hydrogen crossover current was always measured in the following operating conditions:

- Cell temperature: 75°C .
- Working electrode flow: nitrogen, 800 sccm, 100% humidification, 1 bara.
- Reference electrode: hydrogen, 250 sccm, 100% humidification, 1.2 bara.

The electrochemical characterization was implemented with a PGSTAT30 equipped with FRA2 and with a 20 A current elevator from ECO-CHEMIE.

3. Results and discussion

3.1. Fenton test results

As shown from the error bars in Fig. 2 the Fenton tests gave quite spread results (the Hyflon[®] Ion values are the average of 30 tests). The fluoride release value of Hyflon[®] Ion extruded membrane (E87-05) is aligned to the value obtained on the Nafion[®] N112 membrane, the cast Nafion[®] membrane (NR112) showing a slightly lower value. It might be questioned whether the lower value of the cast membrane reflects an actual lower tendency to degradation or could be affected by the apparently different

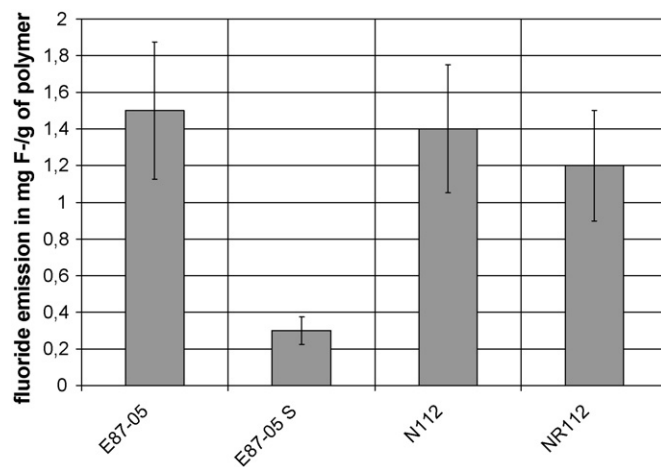


Fig. 2. Fluoride emission in $\text{mg F}^{-}/\text{g}$ of polymer for standard extruded Hyflon[®] Ion, stabilized extruded Hyflon[®] Ion, Nafion[®] N112 (extruded) and Nafion[®] NR112 (cast) membranes.

surface behaviour of the cast membrane (lower hydrophilicity) that could slow down the Fenton reaction.

A substantially lower fluoride release is observed by testing a stabilized Hyflon[®] Ion membrane, named E87-05 S.

In order to check the evolution in time of the degradation of the polymer when subject to peroxide radical attack, a second kind of test was carried out by extracting the membrane from the Fenton solution every 6 h, purifying it by acid treatment and washing, and reinserting the membrane in fresh Fenton reagents. The fluoride amount in the different solutions obtained in this way was measured. The result of this test, shown in Fig. 3, is a linear increase of the cumulative fluoride emissions with time for both standard and stabilized grades. The difference in degradation rate between the standard and the stabilized Hyflon[®] Ion is maintained in this prolonged test and there is no evidence of the reduction or increase of the degradation rate during time. This suggests that the number of chain sites which are attacked by the peroxide radicals remains constant in time. This is consistent with the ‘unzipping reaction’ mechanism, where from a carboxylic end group another identical group is generated (no change in number, see scheme in Section 1.3), in a situa-

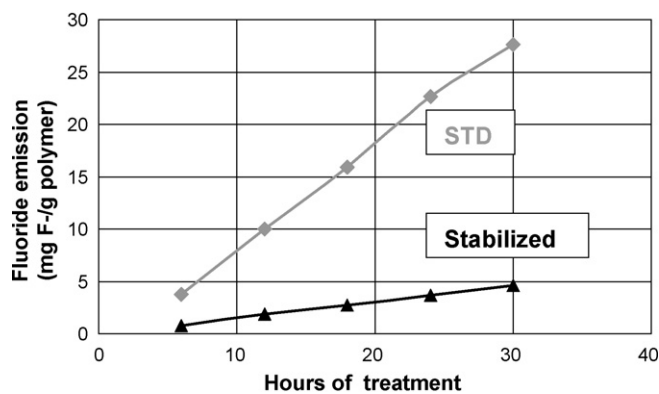


Fig. 3. Cumulative fluoride emission ($\text{mg F}^{-}/\text{g}$ of polymer) in prolonged Fenton tests for standard extruded Hyflon[®] Ion (squares) and stabilized extruded Hyflon[®] Ion (triangles) membranes.

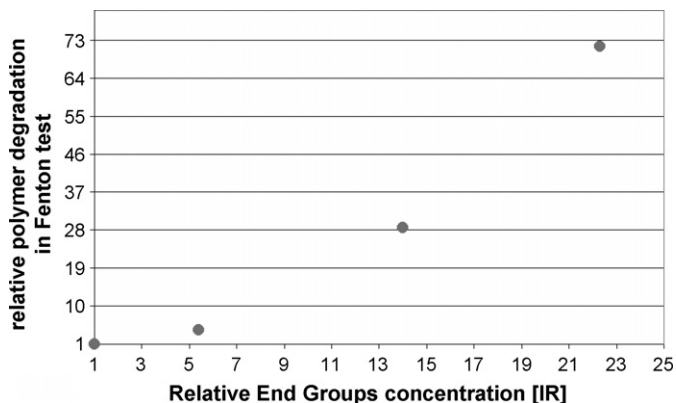


Fig. 4. Correlation in relative values between end groups in the polymer (detected by IR analysis) and fluoride emission in the Fenton test.

tion where the other mechanisms, if existing, have a negligible rate.

In Fig. 4 the correlation between the concentrations of end groups (detected by IR analysis) in the polymer and the fluoride emission of the membrane during Fenton tests is shown in relative terms. The correlation is evident, even if a linear relation (always reported for Nafion® PFSA polymer) is not observed.

3.2. Fuel cell OCV test results

A first campaign of fuel cell tests has been dedicated to verify if the contemporary presence of hydrogen and oxygen is necessary to generate PFSA membrane degradation in cell in an OCV condition.

Three cells with the same electrochemical package (i.e., MEA) were tested, with different gas reactants:

- (1) air fed on cathode side and hydrogen on anode side;
- (2) nitrogen fed on cathode side and hydrogen on anode side;
- (3) air fed on cathode side and nitrogen fed on anode side.

In all the three cases the cell temperature was set to 70 °C and the reactant humidification to 50% and the cell left in OCV condition. As it can be observed in Fig. 5, which shows the degradation of the membrane monitored by measuring the hydrogen

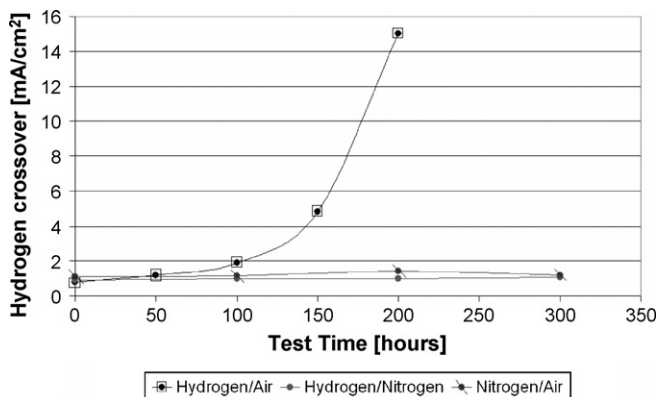


Fig. 5. Hydrogen crossover current density (mA cm^{-2}) for a Hyflon® Ion extruded membrane in OCV tests with different reactants.

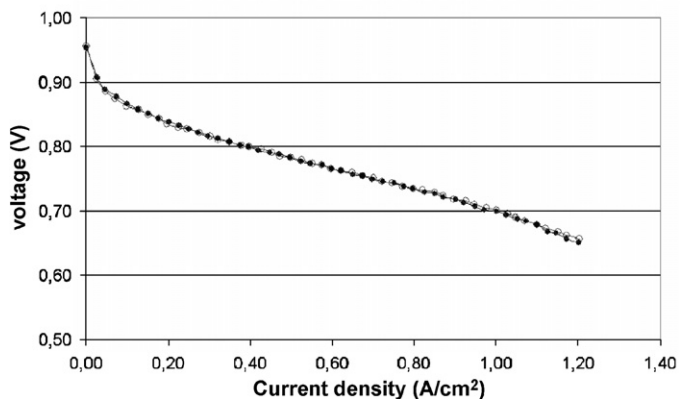
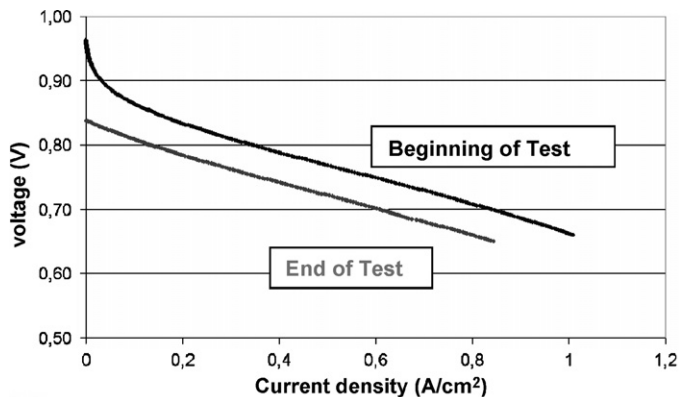


Fig. 6. Polarization curves at the beginning and end of the OCV tests with different reactants. Graph above: test with hydrogen/air. Graph below: nitrogen/air and nitrogen/hydrogen tests.

crossover, degradation occurs only in the case of OCV test with hydrogen/air configuration. This demonstrates that the hypothesis of H_2O_2 formation on the anode side due to the oxygen crossover is feasible, while the absolute potential that the cell electrodes reach in case of hydrogen/nitrogen and air/nitrogen feed is not enough to promote the formation of H_2O_2 . The analysis of the polarization curves at beginning of life and at the end of the test, reported in Fig. 6, clearly shows that in the first case (hydrogen/air) the degradation of the membrane changed a lot the polarization curve, especially at OCV (and as a consequence in the activation region). Instead, in tests 2 and 3 the polarization curves at beginning of life are exactly the same as those at the end of the test. The resistance (impedance at the frequency with iZ contribution = 0) of the three samples resulted in the range of 55–60 $\text{m}\Omega \text{cm}^2$ without any trend of change during the test.

A second test campaign was performed in order to verify the influence of the different operating conditions, particularly temperature and reactants humidification, on the PFSA membrane degradation during OCV tests. Four cells with the same electrochemical package were tested, with different temperature and reactant humidification; all the other operating conditions were exactly the same:

- (1) Cell temperature: 70 °C, reactant humidification 100%.
- (2) Cell temperature: 70 °C, reactant humidification 50%.
- (3) Cell temperature: 90 °C, reactant humidification 100%.
- (4) Cell temperature: 90 °C, reactant humidification 50%.

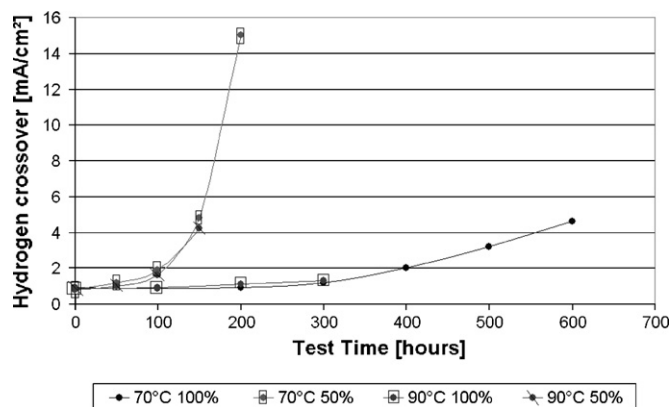


Fig. 7. Comparison of hydrogen crossover current density (mA cm^{-2}) for Hyflon[®] Ion extruded membranes in OCV tests with different operating temperature and reactants humidification.

The membrane degradation, again monitored through the hydrogen crossover, is detailed in Fig. 7. It can be observed that there is a clear increase in the degradation rate when there is a reduction of reactants humidification, while the different operating temperature does not influence the degradation rate. This indicates that, in the absence of a different degradation origin, high temperature operation itself does not represent a condition of reduced lifetime for Hyflon[®] Ion membranes. The high glass transition temperature of the Hyflon[®] Ion polymer guarantees that mechanical degradation phenomena (creep) do not occur at a temperature level around 90 °C and above.

A third test campaign was implemented in order to test the stabilized product and verify if the lower degradation rate observed in the Fenton tests corresponds to a lower cell degradation in OCV tests.

As shown in Fig. 8 both at 70 °C/100% humidification and at 90 °C/50% humidification there is a higher resistance to degradation of the stabilized extruded membrane compared with the standard one. The OCV durability of the stabilized membrane is increased by a factor of approximately 5× and it is comparable to the ratio between the fluoride emissions in the Fenton tests on the stabilized product versus the standard extruded one. The

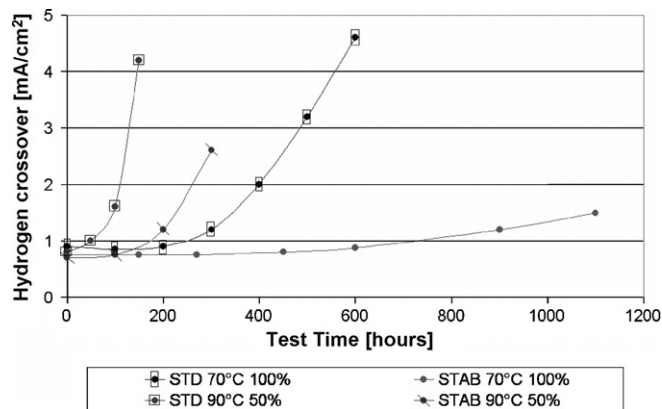


Fig. 8. Comparison of hydrogen crossover current density (mA cm^{-2}) for Hyflon[®] Ion standard extruded membranes and stabilized extruded membranes in OCV tests with different operating conditions.

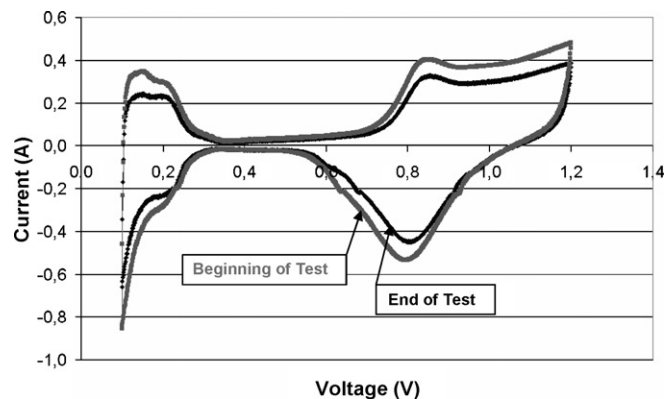


Fig. 9. Comparison of the cyclic voltammetry scan (100 mV s^{-1}) on the cathode electrode at beginning of life and after 1000 h of the OCV test with a stabilized extruded Hyflon[®] Ion membrane at 70 °C and 100% reactants humidification.

resistance of the cell was monitored during all the tests and no increase was noticed. As shown in Fig. 9, after 1000 h of test with the stabilized membrane (70 °C/100% humidification) the voltammetry analysis showed a reduction of the platinum area in the cathode catalyst (a loss of 22% of the catalytic area versus beginning of life is computed). Supposing a linear behaviour for this kind of degradation, a further increase in stability of the membrane ('next generation' stabilized membrane) would make the catalyst degradation the determining decay factor in these kinds of tests.

4. Conclusions

A review of the main mechanisms reported in the literature regarding PFSA membranes degradation has been presented focusing on degradation via peroxide radical attack.

For the first time the chemical degradation of the short-side-chain polymer has been investigated and compared to the Nafion[®] ones, already known in the literature.

The degradation of Hyflon[®] Ion ionomer has been investigated by using ex situ tests (Fenton tests) as well as fuel cell tests. The peroxide degradation mechanism has been well highlighted in open circuit voltage tests at different operating temperatures and humidification levels of the reactants.

It has been demonstrated that the peroxide formation is related to the contemporary presence of hydrogen and air, no degradation occurs in absence of one of the two reactants. In case of hydrogen/air reactants the degradation rate is largely influenced from reactant humidification level, increasing when the humidification level is low.

The influence of the operating temperature on Hyflon[®] Ion degradation is not detectable in the range analysed (70–90 °C) proving that the high T_g of Hyflon[®] Ion enables the use of this product in a range of temperatures interesting for automotive applications (80–120 °C).

Long term Fenton tests delivered a linear behaviour of membrane degradation which is consistent with the 'unzipping reaction' from chain-end groups being the dominant degradation mechanism in the range of concentrations analysed.

The fluoride ions release in Fenton test grows when the presence of end groups (IR detected) in the polymer grows, but the relation is not linear as was previously shown in the literature regarding Nafion®.

For the first time results of tests on stabilized Hyflon® Ion membranes has been shown; both in single cell open circuit voltage tests and in Fenton tests (normal and prolonged) the enhanced resistance of the stabilized grade is evidenced.

Non-negligible degradation of the catalyst has been observed in open circuit tests when the test lasts up to 1000 h, which can make it the dominant decay factor if a membrane with higher stability is used.

Acknowledgements

Many thanks to all the Solvay Solexis personnel involved in ionomer synthesis, membrane preparation, ex situ characterization and fuel cell testing, whose contribution has been determining in the generation of the products and data which are the subject of the present work.

Appendix A. Fenton process reactions [42]

Number	Reaction	Rate constant (L mol ⁻¹ s ⁻¹)
1	Fe ²⁺ + H ₂ O ₂ → Fe ³⁺ + •OH + OH ⁻	63
2	Fe ²⁺ + •OH → Fe ³⁺ + OH ⁻	3 × 10 ⁸
3	H ₂ O ₂ + •OH → HO ₂ • + H ₂ O	3.3 × 10 ⁷
4	Fe ²⁺ + HO ₂ • → Fe ^{III} (HO ₂) ₂ ²⁺	1.2 × 10 ⁶
5	HO ₂ • → O ₂ ^{•-} + H ⁺	1.58 × 10 ⁵ s ⁻¹
6	O ₂ ^{•-} + H ⁺ → HO ₂ •	1 × 10 ¹⁰
7	Fe ²⁺ + O ₂ ^{•-} + H ⁺ → Fe(HO ₂) ₂ ²⁺	1 × 10 ⁷
8	Fe ³⁺ + H ₂ O ⇌ FeOH ²⁺ + H ⁺	K = 2.9 × 10 ⁻³ M
9	Fe ³⁺ + H ₂ O ⇌ Fe(OH) ₂ ⁺ + 2H ⁺	K = 7.62 × 10 ⁻⁶ M ²
10	2Fe ³⁺ + 2HO ₂ ⇌ Fe ₂ (OH) ₂ ⁴⁺ + 2H ⁺	K = 8 × 10 ⁻⁴ M
11	Fe ³⁺ + H ₂ O ₂ ⇌ Fe(HO ₂) ₂ ²⁺ + H ⁺	K = 3.1 × 10 ⁻³ (*)
12	FeOH ²⁺ + H ₂ O ₂ ⇌ Fe(OH)(HO ₂) ⁺ + H ⁺	K = 2.0 × 10 ⁻⁴
13	Fe(HO ₂) ₂ ²⁺ → Fe ²⁺ + HO ₂ •	2.7 × 10 ⁻³ s ⁻¹
14	Fe(OH)(HO ₂) ⁺ → Fe ²⁺ + HO ₂ • + OH ⁻	2.7 × 10 ⁻³ s ⁻¹
15	Fe(III)(*) + HO ₂ • → Fe ²⁺ + O ₂ + H ⁺	< 2 × 10 ³
16	Fe(III) + O ₂ ^{•-} → Fe ²⁺ + O ₂	5 × 10 ⁷
17	HO ₂ • + HO ₂ • → H ₂ O ₂ + O ₂	8.3 × 10 ⁵
18	HO ₂ • + O ₂ ^{•-} + H ⁺ → H ₂ O ₂ + O ₂	9.7 × 10 ⁷
19	•OH + HO ₂ • → H ₂ O + O ₂	7.1 × 10 ⁹
20	•OH + O ₂ ^{•-} → OH ⁻ + O ₂	1 × 10 ¹⁰
21	•OH + •OH → H ₂ O ₂	5.2 × 10 ⁹
22	H ⁺ + SO ₄ ²⁻ ⇌ HSO ₄ ⁻	1 × 10 ² M ⁻¹
23	HSO ₄ ⁻ + •OH → H ₂ O + SO ₄ ^{•-}	1.7 × 10 ⁶
24	SO ₄ ^{•-} + H ₂ O ₂ → HSO ₄ ⁻ + HO ₂ •	1.2 × 10 ⁷
25	SO ₄ ^{•-} + HO ₂ • → HSO ₄ ⁻ + O ₂	3.5 × 10 ⁹
26	SO ₄ ^{•-} + Fe ²⁺ → SO ₄ ²⁻ + Fe ³⁺	9.9 × 10 ⁸

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