



Durability study and lifetime prediction of baseline proton exchange membrane fuel cell under severe operating conditions

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ABSTRACT

Comparative studies of mechanical and electrochemical properties of Nafion[®]- and sulfonated polyetheretherketone polymer-type membranes are carried out under severe fuel cell conditions required by industrials, within stationary and cycling electric load profiles. These membranes are proposed to be used in PEM between 70 and 90 °C as fluorinated or non-fluorinated baseline membranes, respectively. Thus, though the performance of both membranes remains suitable, Nafion[®] backbone brought better mechanical properties and higher electrochemical stabilities than sulfonated polyetheretherketone backbone. The performance stability and the mechanical strength of the membrane–electrode assembly were shown to be influenced by several intrinsic properties of the membrane (e.g., thermal pre-treatment, thickness) and external conditions (fuel cell operating temperature, relative humidity). Finally, a lifetime prediction for membranes under stationary conditions is proposed depending on the operation temperature. At equivalent thicknesses (i.e. 50 μm), Nafion[®] membranes were estimated able to operate into the 80–90 °C range while sulfonated polyetheretherketone would be limited into the 70–80 °C range. This approach brings baseline information about the capability of these types of polymer electrolyte membrane under fuel cell critical operations. Finally, it is revealed as a potential tool for the selection of the most promising advanced polymers for the ensuing research phase.

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1. Introduction

During the last decade, more progress was achieved in proton exchange membrane fuel cells (PEMFCs) technology with respect to the operation at high temperature (80–130 °C) and low relative humidity. The use of polymer membranes at high temperature requires good chemical and mechanical stabilities as well as sufficient proton conductivities independently of the relative humidity level. Still, one of the main technological issues of the PEMFC is the limitation of lifetime under typical operating conditions, both for automotive and micro-CHP (combined heat and power) applications, even under operation with pure hydrogen. Lifetime is further reduced with reformed gas. Requirements for micro-CHP are about 40 000 h and transportation applications (cars) around 6000 h. Now, additional industrial demands like the absence of external water provision, an increase of the operating temperature ranging between –30 and 120 °C are raised in order to simplify the architecture of the fuel cell system. Thus, approaches were made to optimize the intrinsic properties of the membrane. The modification of the microstructure within hybrid cross-linking methods

between polymers and inorganic particles/network [1–4], or the hierarchical organization of multilayer/porous arrangements [5,6], allows improvements in terms of mechanical strength, water management, and electrochemical properties.

Still, the membrane–electrodes assembly (MEA) can be affected by several failure modes which are either irreversible or which reversibly reduce performance.

Typical membrane degradation in fuel cell results from mechanical, chemical, and electrochemical mechanisms occurring with time and which may cause pin-hole formation as well as fuel cross-over. The majority of the chemical degradation studies of the membrane have been performed via an *ex situ* aging procedure using Fenton's reagent test, based on hydrogen peroxide immersion, on Nafion[®]-type membrane [7–9]. These tests allow the evaluation of the chemical strength of the polymer, particularly its resistance against the attacks of free radicals. Comparisons between *in situ* (fuel cell operation) and *ex situ* (Fenton's test) results were recently reported [10]. However, H₂O₂ sensitivity may not be the main issue during the long-term operation of a fuel cell. Alternatively, degradation experiment can be done with *in situ* cell operation. In that case, it turned out that the effect of the catalyst properties of the electrodes on the durability of membrane performances was relevant [11,12]. Even more, load cycling [13–15] or thermal cycling [16] with the presence of hydrogen and oxygen

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as the reactant gases accelerate the membrane degradation rate. Thereby, these results seem to reflect adequately both electrochemical performance and mechanical stability of the membrane. However, even if many works in the literature relate the study of the performance and the degradation mechanisms of polymer, up to now no correlation between the stability and the lifetime of the membrane electrolyte is clearly described in the literature.

In this paper, an assessment of the mechanical and electrochemical properties of baseline membranes is carried out, based on an *in situ* accelerated aging procedure which is validated in our laboratory. The purpose of this study is, firstly, to reveal the modification of the physico-chemical and electrochemical properties of the membrane that are likely to be encountered during a classical long-term operation for, secondly, estimating the lifetime of membranes under the specific operating conditions.

2. Experimental procedure

2.1. Materials

Nafion[®]- and sulfonated polyetheretherketone-type polymers are described in this paper and are referred as respectively fluorinated and non-fluorinated electrolyte membrane, likely to be used in PEM technology. Nafion[®]-type polymer (Nafion[®] 212 named N-212 and Nafion[®] 115 named N-115) was a commercial membrane supplied by Hydro2Power Srl Company and sulfonated polyetheretherketone (noted S-PEEK)-type polymer was supplied by the Fumatech GmbH Company. Table 1 describes the intrinsic sample properties studied.

2.2. Membrane pre-conditioning

According to the nature of the polymer, the membranes are beforehand treated by the following procedures:

- **Nafion[®] polymer type:** the membrane (size 5 cm × 5 cm) is immersed into a 250 ml H₂O₂ 3 vol.% solution at 80 °C during 1 h in order to remove any organic impurity. After rinsing with deionized water the membrane is introduced into 250 ml of H₂SO₄ (0.5 M) solution during 1 h in 60 °C in order to remove any metallic impurities and perform the H⁺ form. The membrane is then immersed into 250 ml of deionized water during 1 h in 100 °C.
- **Sulfonated polyetheretherketone polymer type:** the membrane (size 5 cm × 5 cm) is treated into 250 ml of H₂SO₄ (1 M) solution during 1 h at 60 °C. After rinsing with deionized water, the membrane is swollen into 250 ml of deionized water at 80 °C during 1 h.

2.3. Fuel cell tests

The *in situ* dynamic tests were conducted on a home-made Fuel Cell Test Station by using a 5 cm² active surface area single cell. A mechanical pressure of 5 N/m is fixed at ambient temperature for the cell assembly to allow the reasonable electrode–membrane contacts. Some commercial E-TEK LT250EW electrodes (0.5 mg Pt cm⁻² and 0.7 mg Nafion[®] cm⁻²) were used for the membrane–electrodes assembly. The gases pressure is

maintained at 1.5 bar (abs) with stoichiometric coefficients of respectively 1.5 for H₂ and 2 for O₂. We assume the fuel cell performances are far from being optimized, however the data can be compared since the electrode–membrane interfaces were similar for all experiments and the study is mainly focused on the membrane quality.

Firstly, an “activation” phase of the cell is led under 100% of relative humidity of external inlet gases. An adjustment of constant current is led during a short period to stabilize the potential of the cell around 0.7 V at 70 °C. Then, an intermediate heating-up phase is made by increasing the operating temperature [5 °C h⁻¹] to reach the desired operating temperature. A by-pass system valve allows the validation of the dry-gases mode. The current density is adjusted to fix the potential of the cell into 0.65 V range. Cycling electrical loading steps are then acted to simulate a dynamic swelling–deswelling behaviour of the membrane likely to be encountered during a long-term testing. The experimental procedure describes an open circuit voltage (noted OCV) step of a short period (30 s) to avoid potential catalyst diffusion phenomena through the membrane. After that, the initial current density value is made during 1 h. The evolution of the potential of the cell and the mechanical strength of the membrane are then assessed. Series of tests under cycling dynamic conditions and stationary conditions were run over 70–90 °C of operating temperature range. In order to verify the accuracy of experimental results, at least two experiments have been led on each sample and only the best results are reported here. The end of lifetime corresponds to either the membrane mechanical rupture inducing a gas mixing with a sudden potential drop or over 150 of loading cycles achieved by the cell.

2.4. Post-test membrane characterization

After each test, the electrodes have been carefully removed out and the membrane chemical structure has been analysed. A comparison of mechanical strength of polymer membrane microstructure mechanical before and after the aged test was led by traction measurement under a NFT 51-304 norm process within a transverse direction. Three test tubes of H3 type for each probe of membrane are studied under a speed rate of 10 mm min⁻¹ and a tensile value of 0.1 kN. The standard experimental conditions are fixed at 50%RH ± 5%, at 25 °C. The chamber's temperature can be controlled between 25 and 95 °C and the humidity rate between 0 and 98%.

The hydration number calculation was done in order to rationalize the impact of hydration/dehydration cycles on the intrinsic physical backbone properties. So, membrane water content, defined as the number of mole of water per mole of ion exchange site, $\lambda = \text{H}_2\text{O}/\text{SO}_3^-$, have been calculated before and after the test with the following formula:

$$\lambda = \frac{M(W_1 - W_2)}{18.0W_2}$$

where M is the equivalent weight of the membrane, and W_1 (g) is the weight of a membrane piece after immersion into deionized water at 20 °C for 6 h and W_2 (g) is the weight of a membrane piece after drying at 60 °C during 24 h.

3. Results and discussion

3.1. Fuel cell ageing tests

3.1.1. Nafion[®]-based systems

The baseline perfluorosulfonic acid membranes have been tested under various *in situ* operating conditions with temperature

Table 1
List of baseline membranes selected

| Sample | Polymer type | Thickness (μm) | IEC (mequiv. g ⁻¹) |
|--------|------------------------------------|----------------|--------------------------------|
| N-212 | Perfluorinated Nafion [®] | 50 | 0.9 |
| N-115 | Perfluorinated Nafion [®] | 130 | 0.9 |
| E-725 | Hydrocarbon S-PEEK | 25 | 1.36 |
| E-750 | Hydrocarbon S-PEEK | 50 | 1.36 |

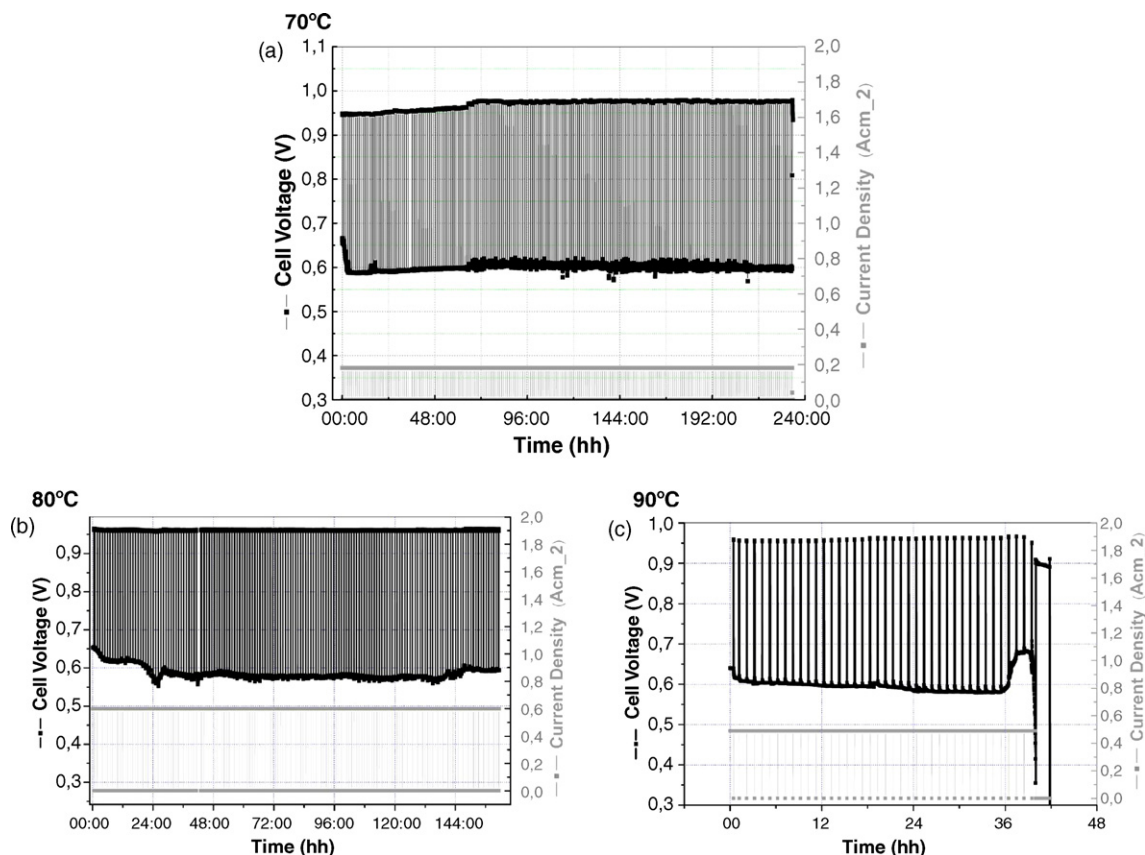


Fig. 1. Evolution of cell voltage during the ageing test of N-212 at (a) 70 °C, (b) 80 °C and (c) 90 °C.

and humidity rate as parameter keys. The voltage trend of N-212 during the drastic test is reported in Fig. 1.

Fig. 1 reveals the influence of operating temperature on the level of electrochemical performances and mechanical stabilities of N-212. First, the increase of operation temperature from 70 to 80 °C does not change the mechanical properties of the sample. Indeed, the load cycling test lasted 150 h without any failure of the membrane. Nevertheless, by elevating the operating temperature, the performance of the cell decays from 0.52 to 0.36 W cm⁻² (Fig. 1a and b). In addition, the degradation rate of the potential exhibits a similar evolution for both dynamic tests with a rapid drop of the potential value on the beginning then a rel-

ative stability of performance during the rest of the test (see Table 2). This fact can reveal the impact of the relative humidity level on the intrinsic physical properties of the backbone polymer.

According to Knights et al. works [17], drying repeated events during a test would induce a supplementary porosity into microstructure of the membrane driving to some local gas cross-over formation. This evolution on the microstructure of the membrane can be revealed by the OCV value with time. By considering the experiments made at 70 and 80 °C, it should be pointed out that the OCV values of N-212 membrane are nearly stable into 0.95–0.97 V range during the entire drastic test, revealing excellent

Table 2

Electrical degradation rate of Nafion® and sulfonated polyetheretherketone type membranes into cell according to operating conditions

| Sample | Operating temperature (°C) | Time (h) | Voltage degradation rate (mV h ⁻¹) | OCV degradation rate (mV h ⁻¹) |
|--------|----------------------------|----------|--|--|
| N-212 | 70 | 0–5 | –10 | <–0.05 |
| | | 5–150 | <–0.05 | <–0.05 |
| | 80 | 0–30 | –2.5 | <–0.05 |
| | | 30–150 | +0.08 | <–0.05 |
| | 90 | 0–36 | –1.4 | <–0.05 |
| | | 36–39 | +45 | <–0.05 |
| 39–41 | –300 | –50 | | |
| N-115 | 90 | 0–150 | <–0.05 | <–0.05 |
| E-750 | 70 | 0–150 | –0.13 | +0.08 |
| | | 0–50 | –0.2 | –0.7 |
| | 80 | 51–87 | –0.6 | –0.9 |
| | | 87–88 | –83 | –40 |
| | 90 | 0–1 | –4 | <–0.05 |
| | | 1–2 | –42 | –1.2 |
| 2–3 | –200 | –2.8 | | |

structural and mechanical strengths. The increase of the operating temperature of the cell at 90 °C implies a reduction of mechanical and electrochemical properties of the membrane. Forty-one loading cycles have been achieved before the failure of the membrane caused by a pin-hole formation at the hydrogen gas inlet channel. The initial operating conditions of the cell have been made at 0.65 V for 0.49 A cm⁻². The performance of the cell linearly reduced down to 1.4 mV h⁻¹ over 36 cycles then a rapid loss of performance is observed up to the end of the test. In parallel, the open circuit voltage value remains stable around 0.95–0.96 V during 39 loading cycles then a rapid drop occurred below 0.9 V illustrating a gas cross-over phenomena through the membrane. A rapid investigation of the membrane shows a pin-hole formation located to the hydrogen gas inlet. This reveals gas cross-over phenomena through the membrane resulting of the apparition of local hot points.

Furthermore, it is well known that the thickness of the membrane may influence not only its electrical resistance level but also the gas cross-over phenomena. Here, Nafion[®] 115 membrane type is studied at 90 °C in order to simulate an increase of thickness of Nafion[®] polymer type. Considering the same experimental procedure than for N-212, more than 150 loading cycles with a high stability level of potential was obtained with N-115, showing a better mechanical strength of the sample against the gas cross-over phenomena (Fig. 2). However, it is also noticed the performance of Nafion[®]-type membranes decreases from 0.36 to 0.13 W cm⁻². That can be mainly explained by the increase of the intrinsic electrical resistance of the membrane with the increase of its thickness.

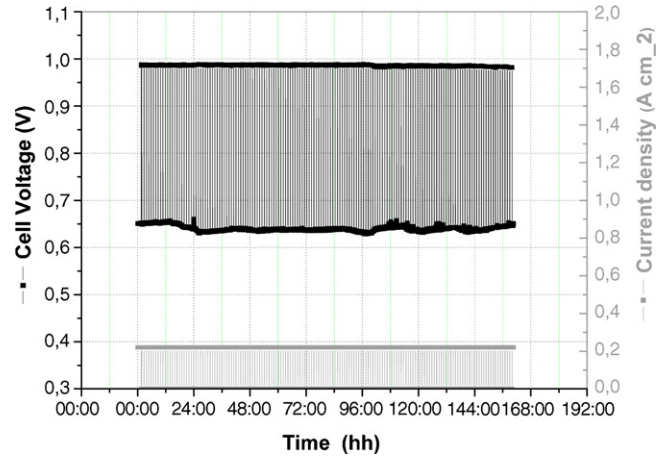


Fig. 2. Evolution of the cell voltage during the ageing test of N-115 membrane at 90 °C.

3.1.2. Sulfonated polyetheretherketone-based systems

An identical *in situ* dynamic test was conducted with sulfonated polyetheretherketone-type samples (E-750 and E-725) used as some typical non-fluorinated baseline membranes.

Fig. 3 describes the effect of the accelerated ageing procedure at, respectively, 70, 80 and 90 °C as operating temperature on mechanical and electrochemical properties of E-750 sample.

At low operating temperature, the membrane keeps a good mechanical integrity with more than 150 electrical loading cycling

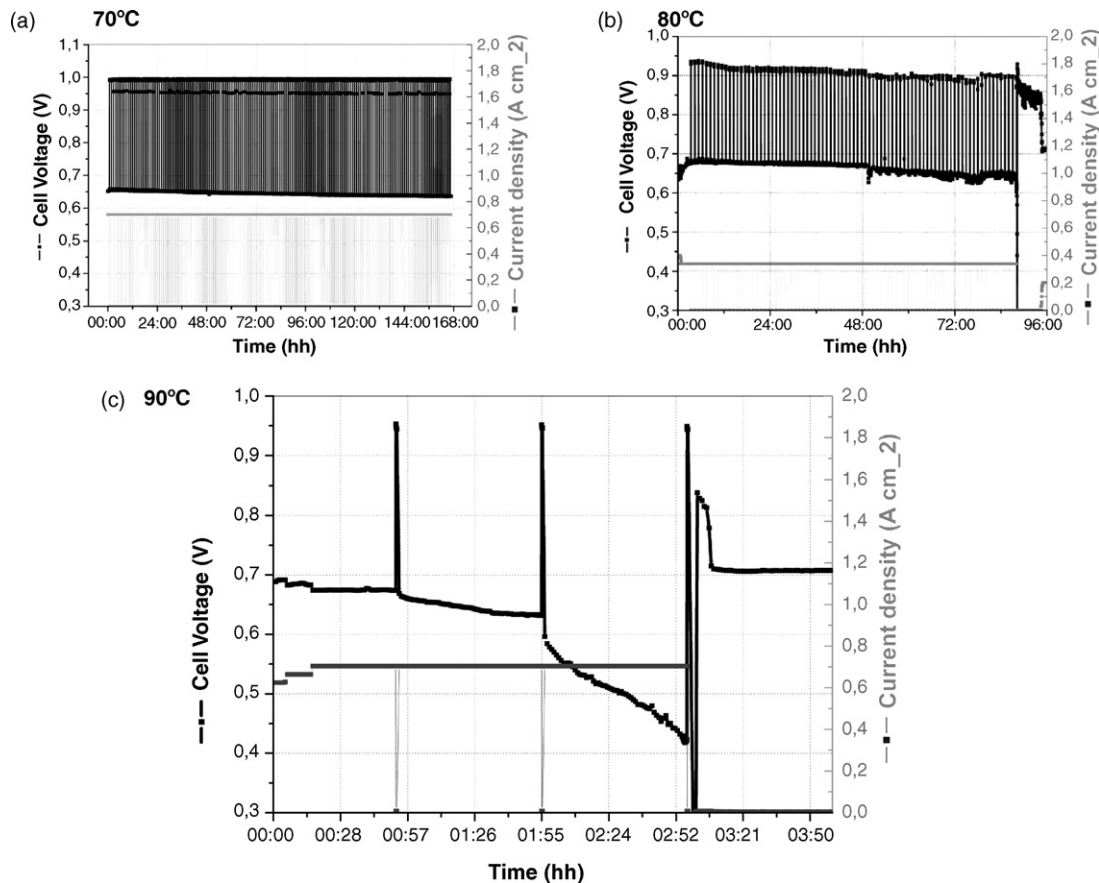


Fig. 3. Evolution of cell voltage during the ageing test at (a) 70 °C, (b) 80 °C and (c) 90 °C of E-750.

achieved. A high stability of OCV value around 0.98–0.99 V is kept during the entire test, showing the absence of effect of operating conditions on the microstructure. However, we can notice a linear decay of performance around 0.13 mV per cycle along the time of the test. A rapid investigation of the cell did not show any failure of the membrane. The same experiment has been evaluated on E-750 sample by elevating the operating temperature up to 80 °C. After a reasonable stabilization of the performance during the activation phase, a regular degradation of both potential and OCV values of the cell is then observed under drastic conditions, revealing the strong effect of the humidity level inside the MEA. Less than 88 cycles have been reached before the failure of the sample. Another test has been made at 90 °C. After the activation phase, the MEA is then stabilized at 0.7 V for 0.7 A cm⁻² at 90 °C. In these operating conditions, the degradation rate of E-750 OCV and potential values are strictly reduced after each step of electrical load cycle. Finally, a pin-hole located in the H₂ inlet gas line occurred after three load cycles. The sulfonated polyetheretherketone backbone polymer seems to be more sensitive to the hydration level than Nafion® backbone type by increasing the operating temperature of the test. The effect of thickness is investigated by using E-725 membrane (*e* = 25 μm). Fig. 4 shows the evolution of performance of E-725 sample stabilized at 80 °C under the same operating conditions described above. E-725 MEA is stabilized at 80 °C with a potential of 0.7 V for a current density of 0.2 A cm⁻². Nevertheless, a rapid and irreversible loss of potential has been observed with a shift of operating conditions. Therefore, a half reduction of thickness value affects strictly the mechanical strength of the hydrocarbon polymer membrane.

3.2. Post-test membrane analysis

The mechanical traction measurements have been leading on non-fluorinated and fluorinated membranes before and after aged process in order to distinguish the effect of the operation conditions. Typical responses of membranes differing by polymer

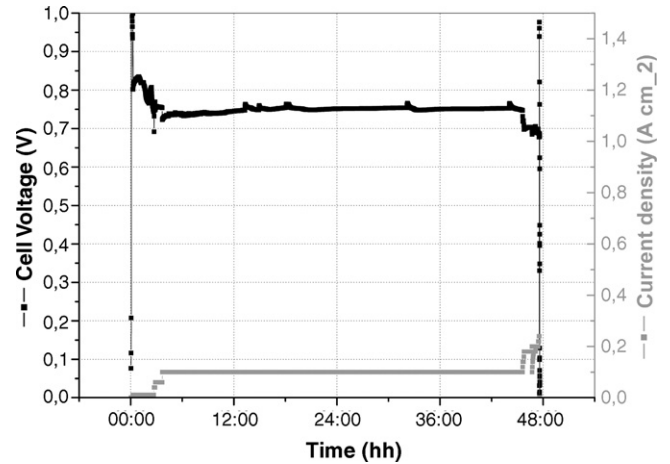


Fig. 4. Evolution of the cell voltage during the ageing test of E-725 membrane at 80 °C.

composition and conditions of test can be characterized by an elastic fraction (brittle behaviour) and a plasticity plateau (corresponding to the softness properties).

Fig. 5a reports the response of tensile strength of the active surface area of Nafion® 212 and S-PEEK E-750 membranes before and after the *in situ* accelerated aging test. Under standard conditions (i.e. ambient temperature and 55% of humidity rate), S-PEEK type exhibits a larger plasticity plateau (i.e. higher strain at break) and a lower elastomeric properties than Nafion® type (i.e. smaller elongation at break). As a result, the structure of Nafion® backbone brings a higher softness between polymer chains than sulfonated polyetheretherketone backbone. An *in situ* accelerated aging of membrane under some hydrothermal constraints induces modifications of physico-chemical and mechanical properties of both membranes. We can notice a significant increase of strain

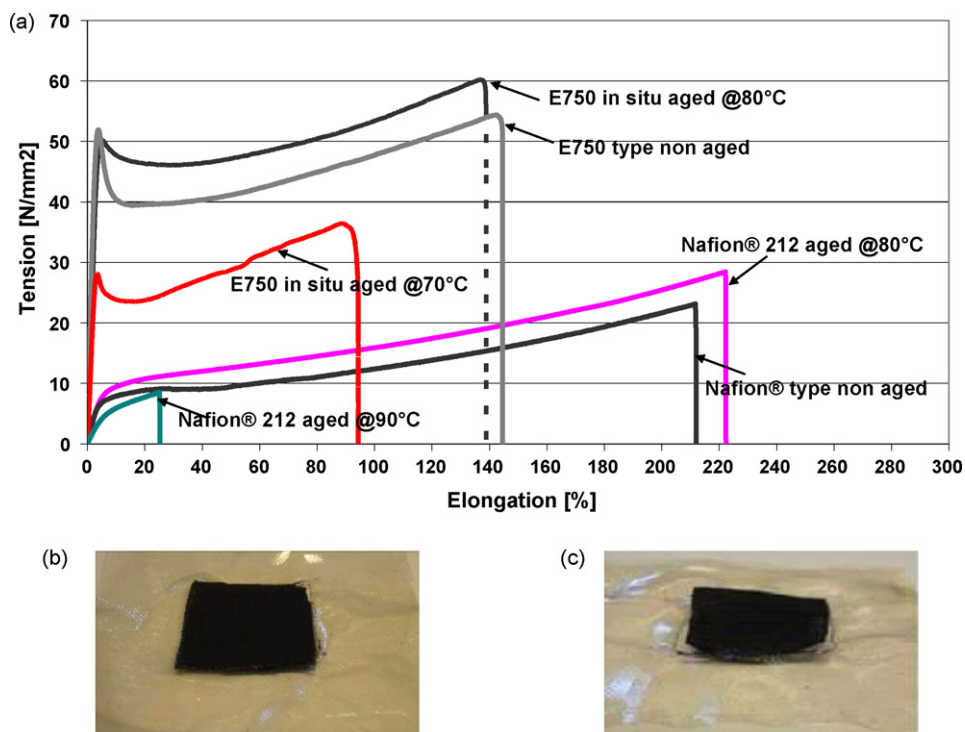


Fig. 5. (a) Evolution of mechanical traction properties of Nafion® type and S-PEEK type before and after the aged *in situ* test and E-750 MEA pictures after an *in situ* aging test at (b) 80 °C and (c) 90 °C.

Table 3
Evolution of hydration number λ , of membranes before and after the ageing test

| Type of membrane | Operating temperature (°C) | λ value before the test | λ value after the test |
|------------------|----------------------------|---------------------------------|--------------------------------|
| N-212 | 80 | 14 | 12.5 |
| N-212 | 90 | 14 | 15 |
| E-750 | 70 | 16 | 18 |
| E-750 | 80 | 16 | 13 |
| E-750 | 90 | 16 | 4 |

at break value of E-750 membrane corresponding to increasing tensile stiffness and strength, whereas the curves shift of Nafion[®]-type monotonically “downward” with increasing the operating temperature. Over this temperature, the elongation at break of Nafion[®]- and sulfonated polyetheretherketone-type membranes significantly reduces. That could be partially explained by the instability of hydration level around the active/non-active surface area boundary of MEAs emphasized by the increase of temperature of the cell. As a result, the mechanical strength of both membranes is affected. Fig. 5b and c illustrates the status of the active surface after the ageing test done at 80 and 90 °C. Although at 80 °C the membrane keeps a relative physical integrity, S-PEEK backbone seems to be more affected at higher operating temperature such as any traction measurements was possible after 80 °C. These results are in accordance with the instability of both membranes observed during the dynamic electrical load test at 90 °C.

The results of Table 3 illustrate the influence of the water uptake value on the mechanical strength of membrane.

The hydration number of S-PEEK membrane was assessed around 16 while those of Nafion[®] type varied within the level of thickness between 12.5 and 15. Kreuer referred in the past that water is present as a second phase beyond 14 water molecules for Nafion[®] type and 10 for S-PEEK type while the primary hydration sphere is made up of 3 water molecules in Nafion[®]-type and 5 in S-PEEK-type polymers [18]. Also, Jones and Rozière related the higher influence of amount of water as a second phase for S-PEEK polymers than for Nafion[®] polymers in order to get some reasonable performance and prevent mechanical stability of membrane [19]. The comparison of results obtained before and after the *in situ* test shows a relative stability of water molecules content for Nafion[®] type up to 80 °C. S-PEEK polymer-type membrane owning a higher hydrophilic character than Nafion[®] backbone, the membrane is then more sensitive to the shift of hydration level than Nafion[®] type. By increasing the operation temperature, a significant loss of hydration number of S-PEEK below the primary

hydration sphere is noticed. This typical characteristic of hydrocarbon backbone can explain the relative higher decay rate of performance and mechanical strength observed on S-PEEK MEA by elevating the operation temperature. Moreover, as Alberti et al. have recently described [20], it is noticed that the narrow relations between the tensile modulus of the polymer with the water uptake into the backbone. The increase of the rigidity level of polymer chain is linked to the decrease of the lambda value. For any polymer-type membrane, the conformation of the polymer evolves with the operating conditions and can bring deep modifications in terms of performance stability and durability of the MEA.

3.3. Fuel cell stationary tests and lifetime prediction assessment

In this paragraph, a correlation between the accelerated ageing test taken under a dynamic mode and the “real” lifetime of sample under a continuous mode is studied. The method consists to run into a long-term testing within similar harsh operating conditions. An initial potential of cell at 0.65 V was made with a relevant current load. The potential of the cell was followed up to an irreversible degradation event. The comparison of results allows identifying the lifetime of the membrane according to the operating temperature and humidity level.

Fig. 6a illustrates the evolution of potential of E-750 MEA at 90 °C. We will notice a good correlation of results between dynamic and stationary mode (power density: 0.32 W cm⁻² against 0.36 W cm⁻²; electrical degradation rate: 4 mV h⁻¹ against 5 mV h⁻¹). Finally, 53 h of lifetime was performed. By extrapolation, one load cycle corresponds to around 17.5 h of lifetime of membrane kept into the same operating conditions.

In a same approach, Nafion[®] 212 was characterized under a stationary mode @90 °C. Again, the correspondence of evolution of performance between dynamic and stationary modes is quite similar. Up to 769 h of lifetime have been reached under drastic conditions, leading to around 19 h of lifetime per load cycle.

Table 4 summarizes the membrane lifetime estimated by this method for sulfonated polyetheretherketone- and Nafion[®]-type membranes according to the operating temperature.

We can notice S-PEEK type polymer is a promising candidate likely to be applicable below 70 °C. Indeed more than 2600 h have been estimated under our experimental conditions. On the contrary, over this temperature a large effort has to be made especially in term of mechanical stability. In parallel of that, Nafion[®] 212 type is more relevant for moderate operation temperature below 90 °C.

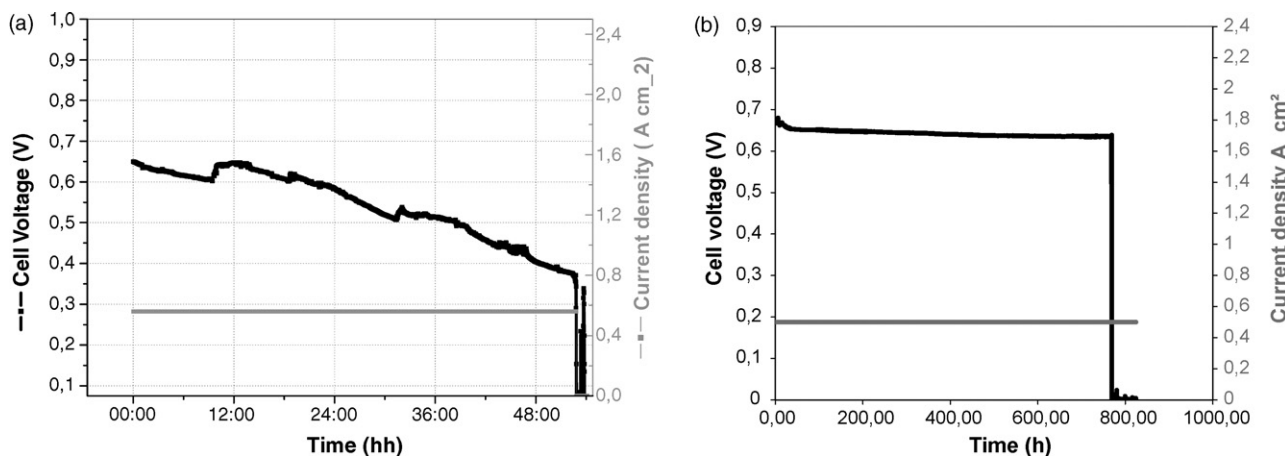


Fig. 6. Long-term testing of E-750 (a) and N-212M2 (b) under stationary conditions.

Table 4

Lifetime prediction of membranes under ElFER harsh conditions and according to operating temperature

| Type of membrane | Operating temperature (°C) | Loading cycling steps | Lifetime (h) |
|------------------|----------------------------|-----------------------|--------------|
| N-212 | ≤80 | >150 | >2820 |
| N-212 | 90 | <41 | <769 |
| N-115 | ≤90 | >150 | >2820 |
| E-750 | 70 | >150 | >2625 |
| E-725 | 80 | <1 | <17.5 |
| E-750 | 80 | <88 | <1540 |
| E-750 | 90 | <3 | <53 |

Nevertheless, its lifetime can change by a factor 3 according to the thickness level of the membrane. In any case, for both membranes their application at higher operation temperature ranking is intrinsically limited by physical properties.

4. Conclusions

Polymeric Nafion®- and S-PEEK-type membranes have been investigated under an accelerated *in situ* ageing process within some electrical load cycles. This original technique tends to assess both electrochemical and mechanical stabilities of polymeric membranes and to estimate their lifetime under some severe fuel cell stationary operating conditions required by fuel cell makers.

Excellent mechanical and electrochemical stabilities have been exhibited for any Nafion® type up to 80 °C as operating temperature after more than 150 loading cycles achieved during our drastic test. A comparison with a stationary mode test analysis allowed us to estimate the membrane's durability level over 2800 h under specific operating conditions.

Under some equivalent operating conditions, a baseline non-fluorinated type membrane as polyetheretherketone gave also good electrochemical and mechanical properties below 70 °C as the operating temperature range. At this level, the correlation between dynamic and stationary modes can estimate a reasonable durability over 2600 h. Beyond this temperature, its physico-chemical properties more hydrophilic and their intrinsic physical properties less elastomeric than Nafion® type can explain in part the higher level of mechanical fatigue under some dynamic swelling–deswelling cycle occurred during a classical test into cell. A loss of half lifetime is then estimated under our experimental conditions around 80 °C.

Over this temperature, the influence of operating conditions, the thickness of the membrane and the humidity rate become more and more critical for both fluorinated and non-fluorinated polymers.

The intrinsic properties of the backbone of S-PEEK and Nafion® membranes limit the fuel cell operation below 90 °C. In order to reach some higher operating temperature range, further studies in the optimization of the synthesis, the manufacturing and the pre-conditioning phases of the membrane are therefore required to get a reasonable improvement in term of robustness and electrical resistance of the membrane. Finally, this study brings baseline results on physical and electrochemical properties with the aim to assess the lifetime of optimized membrane based on modified sulfonated polyetheretherketone and Nafion® polymers.

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