

Research Article

Study on the Durability of Recast Nafion/Montmorillonite Composite Membranes in Low Humidification Conditions

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Nafion composite membranes were formed from a recasting procedure previously reported by the authors. Montmorillonite (MMT) was used as a filler in the recasting procedure, and dimethylformamide (DMF) was used as the casting solvent. Fuel cell tests performed with the recast membrane showed that at low relative humidity (R.H.) the conductivity of the MMT-containing membranes is 10% higher than that of the MMT-free samples. In order to investigate the durability of such composite perfluorosulfonate membranes, long-term fuel cell experiments have been carried out. Results evidenced a strong effect of low RH on the lifetime of commercial polymer membranes, but the addition of a small silicate amount to the polymeric membrane reduced strongly the membrane degradation.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) based on proton exchange membranes (PEMs) are considered as the leading candidates to replace the traditional power sources like the internal combustion engines. Also, these systems find application in the cogeneration power for both stationary and portable systems. In the cell, fuel is oxidized at the anode, oxygen is reduced to water at the cathode and electrical energy is delivered with very high yield in a production process having near-zero emissions. At present, one of the most common perfluorosulfonic acid-based membranes employed in fuel cells is Nafion, a registered mark of DuPont. Under high humidity conditions, this membrane has many desirable properties including good chemical stability, high mechanical strength, and high ionic conductivity. However, the proton conductivity of the perfluorosulfonate membrane is strongly dependent on the water content and decreases considerably at low relative humidity (R.H.), leading to large relative losses and a reduction of the cell voltage and efficiency. In the field of membrane research for fuel cells, the key issue is to find alternative polymer electrolytes to Nafion able to overcome its disadvantages as well as to lead to stack cost reduction. In this regard, a very interesting approach is the formation of montmorillonite (MMT)

composite membranes [1–4]. In previous paper [5], we have investigated the conductivity of a Nafion/MMT composite membrane formed by a recast process as a function of the relative humidity. Results showed that the addition of this inorganic compound allows a PEFC to operate with low humidification, though maintaining a performance superior to that of unmodified Nafion. In this paper, long-term experiments have been performed in order to verify the severity of degradation mechanisms and their relative contribution to the loss of performance at low R.H. condition [6].

According to Huang et al. [7], when membranes are exposed to dry conditions over a long time, they may become brittle and develop crazes or cracks. The authors have stated the need to understand the membrane kinetics and the MEA embrittlement process as a function of local conditions, in particular temperature and R.H. [7]. Because the membrane degradation is probably among the main factors capable of reducing the lifetime of PEM fuel cells [8], it is important to study it in extreme R.H. conditions. Besides, operation of a fuel cell at low relative humidity can result in several advantages [9]: (i) no subsystem for gas humidification is needed, (ii) removal of water in vapour form reduces the amount of heat to be removed from the cell by the latent heat of vaporization, and (iii) less condensed water (present in the fluid flow channels for the gases in the bipolar plates and gas

diffusion electrodes) enhances the fuel cell performance. Because of the advantages, there is a growing interest to develop and commercialize PEFCs that work under such conditions. Very few works were devoted to the long-term study of in-situ performance at low R.H. and constant current mode [9–12]. Since these works are different with respect to materials (membrane, catalyst, etc.) and operative conditions (current, cell temperature, etc.), it is very complicated to understand whether the differences are due only to the effect of R.H. on the membrane or to the degradation of other materials.

In the present paper, we aimed at comparing the durability of Nafion commercial membranes and Nafion recast composite membranes at low humidification conditions. Long-term tests have been performed using Nafion 112 and recast Nafion composite membranes [5] to clarify the main aspects related to perfluorosulfonate ionomer (PFSI) membrane degradation in low humidification conditions and give possible explanations to the observed phenomena.

2. Experimental

2.1. Materials. Commercially available 30 wt.% Pt/C catalyst powders on carbon black (Vulcan XC72) were purchased from E-Tek Inc. Three-layer (substrate/diffusive layer/catalyst layer) gas diffusion anode and cathode were prepared using a spray technique described in detail in previous paper [13]. The substrate was carbon paper (Toray TGP090). The weight composition of the diffusion layer was 50 wt.% of carbon and 50 wt.% of PTFE, with carbon loading of about 2.5 mg cm^{-2} . The catalyst layer was prepared by mixing appropriate amounts of carbon-supported catalyst (30 wt.%) and 5 wt.% Nafion ionomer solution from Aldrich. The platinum loading in all anodes and cathodes was kept constant at 0.54 mg cm^{-2} . Membrane electrode assemblies (MEAs) were prepared using different polymeric electrolyte membranes: commercial Nafion 112 with an equivalent weight (EW) of 1020 [2], and recast Nafion containing 1 wt.% of the inorganic filler montmorillonite (MMT), both with a hydrated nominal thickness of $50 \mu\text{m}$. Briefly, to recast the composite membranes of this paper, 9 mL of dimethylformamide (DMF) and 0.150 g of ionomer powder were mixed in a vial. Appropriate amounts (1 wt.%) of montmorillonite K10 (Sigma Aldrich) were separately added to the formed DMF/PFSI mixture and were sonicated for 30 minutes to form homogeneous dispersions. The dispersions were poured into flat Petri dishes and heated in a furnace at 165°C for 90 minutes [5]. The whole preparation is described in detail in previous works [2, 5].

The hydrated membrane thicknesses were averaged over several measurements taken by an ATS FAAR digital micrometer in different regions of the samples. The membranes were equilibrated in distilled water and their surfaces were carefully dried with paper prior to measuring the thickness at room temperature.

Both membranes were used after purification treatment in 5% (w/v) H_2O_2 solution at 80°C for 1 hour, followed by a second treatment in 1 M H_2SO_4 . The MEAs were formed

by hot pressing the electrodes (2 cm^2) onto the membrane at 130°C for 1–5 minutes and $50\text{--}100 \text{ kg cm}^{-2}$.

2.2. Physicochemical Characterization. Long-term electrochemical tests have been performed on a 2-cm^2 active area single cell FC2/40 Fuelcon quickConnect (Germany) equipped with a titanium plate. The special feature of this test cell is the possibility to adjust the pressure on the active area, being the pressure infinitely variable by means of a pressure cylinder control system. In all the measurements, the adjusted pressure was settled at 1.5 N mm^{-2} and the cell was inserted in a Globe Tech Inc. mod. 850C station.

Both cells were fed with low humidified H_2/O_2 gases (R.H. 23%), under a pressure of 2-abs bar and a stoichiometric ratio of 1:2. All the MEAs have been submitted to a galvanostatic polarization by means of a programmable power supply interfaced with a computer for data acquisition. All the measurements have been carried out in the same operative conditions. The ohmic cell resistance has also been measured continuously by the periodic current pulse transient [14]. In this kind of measure, the cell current is rapidly removed and the cell voltage sampled after a time delay of $20 \mu\text{s}$.

Long-term tests have been performed on the MEA assemblies at 50°C and 250 mA cm^{-2} in H_2/O_2 flux at 50 and 100 mL min^{-1} . In order to simulate a periodic startup and to study the effect of these parameters on the membrane ageing, the cell was switched off and left in air overnight at room temperature (25°C) for about a hundred times. Cell voltage versus time plots have been recorded continuously. Periodically, polarization plots were recorded at R.H. 100% for H_2 and 46 % for O_2 in order to evaluate the changes in the whole cell performance.

Water was collected periodically at the exhausts using plastic containers and stored for analysis. Subsequently, the conductivity of the samples was measured with a Crison mod. 525 conductivity meter. The fluoride amount released into the product water was determined using a Mettler Toledo F^- ion selective electrode. Scanning electron microscopy (SEM) was used to investigate the thickness of the as-prepared specimens as well as those submitted to long-term tests. All the micrographs were acquired with a JEOL mod. JSM5510LV microscope.

3. Results and Discussion

The cell voltage versus time of a MEA with a N112 and Nafion/MMT membrane curves related to the particular conditions of low humidity (R.H. 23%) are depicted in Figure 1. For N112, the MEA performance at 50°C and current density of 250 mA cm^{-2} decreases at a rate of $-154 \mu\text{V h}^{-1}$ after 600 hours with an average voltage of $0.64 \pm 0.03 \text{ V}$. An increase until a maximum of 0.7 V has been reached in about 72 hours and then the voltage was kept constant up to about 180 hours. In the same conditions, the current density of Nafion/MMT membranes decreased at a rate of $-73 \mu\text{V h}^{-1}$ after 600 hours with an average voltage of $0.69 \pm 0.05 \text{ V}$. Also in this case, an increase until a maximum of 0.75 V has been reached in about 200 hours, and then

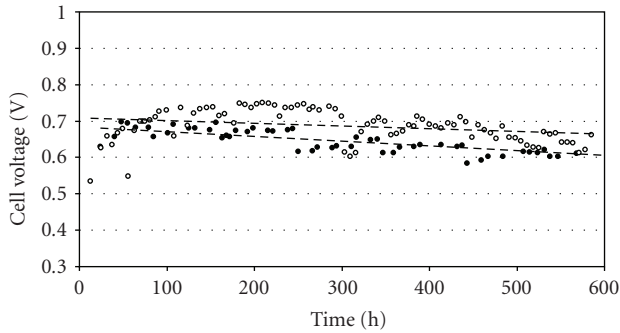


FIGURE 1: Cell voltage versus time plot for MEA with Nafion 112 (●) and Nafion/MMT E87-05 (○) at 250 mA cm^{-2} .

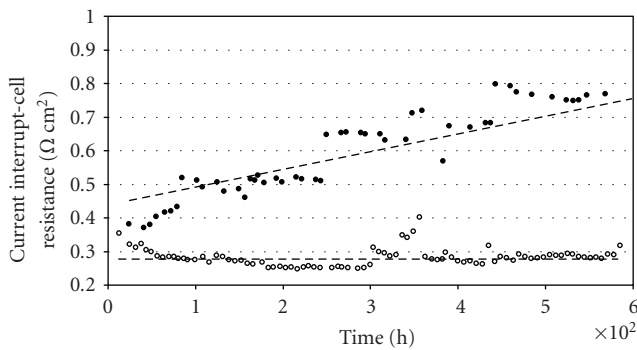
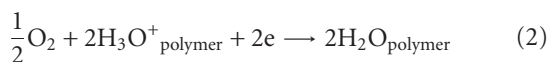
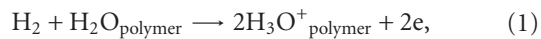


FIGURE 2: Current interrupt resistance versus time plot for MEA with N112 (●) and Nafion/MMT (○) at 250 mA cm^{-2} .

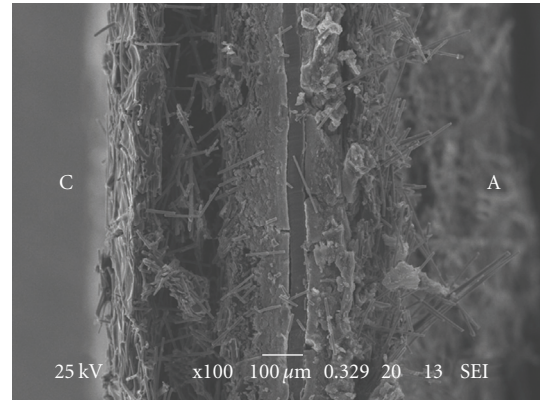
the voltage was kept constant up to about 300 hours. In the subsequent hours, the decrease was slow though constant.

The increase of potential in the first hours, known in the initial working stage of a fuel cell as the “activation process”, can be explained considering the water production in the cathode catalytic layer and its effect on the conductive polymer phase. Equations (1) and (2) evidence the importance of water diffusion into the polymeric phase and its role in both the electrodes reactions as follows:

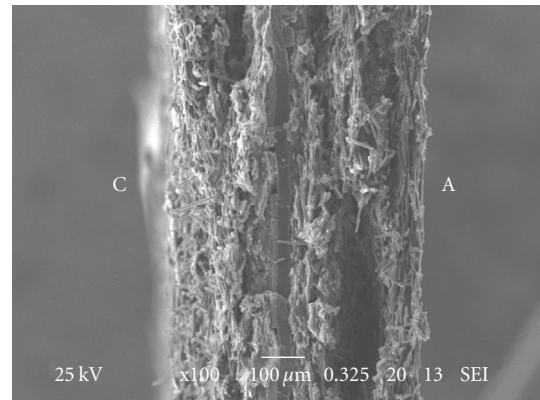


In the first hours, we have observed an increase of performance due mainly to hydration of Nafion directly in contact with the catalyst (Pt-Nafion). Figure 2 shows the resistance measured by means of a transient technique (R_{TT}) for both samples. The starting value was similar ($0.35 \Omega \text{ cm}^2$), although the behaviour was very different. The N112-containing cell showed a linear and irreversible resistance increase of about $0.52 \pm 0.03 \text{ m}\Omega \text{ cm}^2 \text{ h}^{-1}$. On the opposite, the resistance of the Nafion/MMT-containing cell remained constant except for a temporary increase at 350 hours.

Chen and Fuller [15] have reported that the membrane resistance values measured with the current interruption



(a)



(b)

FIGURE 3: SEM images of MEA with Nafion 112 (a) and Nafion/MMT (b) after long-term test.

method are close to the real values. In our case, this technique demonstrated to be very useful in order to evaluate the fuel cell long-term behaviour. The change in the membrane resistance is clearly related to a conductivity decrease, as shown in previous paper [5]. The decrease of Nafion 112 conductivity due to the membrane degradation in low humidity condition has been explained by several authors. Chen and Fuller [15] have observed a strong decrease of the Nafion 112 thermal stability after a 120-h fuel cell durability OCV testing at low humidity (R.H. 36%). In particular, they verified pinholes and delamination near the anode side and close to the center. Moreover, a significant decrease of membrane thickness from the nominal $50 \mu\text{m}$ to $35 \mu\text{m}$ was seen together with an 8.3% reduction in the ion exchange capacity that they attributed to side chain degradation due to the S–O–S cross linking [15]. By means of SEM analysis (Figure 3), we have found a final average thickness of $35 \pm 3 \mu\text{m}$ for Nafion 112, that is, a 10% reduction with respect to the thickness measured on the starting MEA after the hot pressing process ($39 \mu\text{m}$). The final thickness was the result of an average of 50 different points along the membrane profile.

As regards the Nafion/MMT membrane, a final average thickness of $30 \pm 1 \mu\text{m}$ was found, which represents a 10% thickness reduction compared to that measured on the MEA after the hot pressing process ($33 \mu\text{m}$).

TABLE 1: Average fluoride concentration, conductivity, and final degradation rate during time tests.

Type	[F ⁻]/ppm Cathode	[χ]/ $\mu\text{S cm}^{-1}$ Cathode	[F ⁻]/ppm Anode	[χ]/ $\mu\text{S cm}^{-1}$ Anode	Degradation rate/ $\mu\text{V h}^{-1}$ (600 hours)
Nafion 112	0.40	6.7	0.47	18.7	-154
Nafion-MMT	0.33	7.0	0.36	15.2	-72

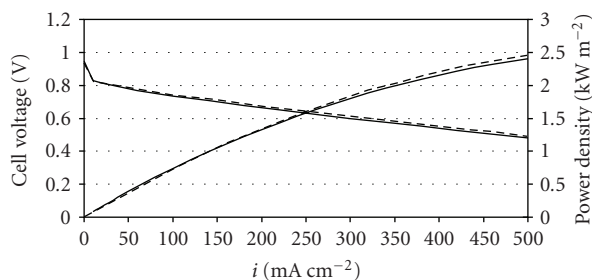


FIGURE 4: Cell voltage and power density versus current density plot for MEA with Nafion 112 (---) and Nafion/MMT (bold continuous lines) at 50°C in the early hours at low R.H.

The difference in membrane thickness after the hot processing process (39 μm against 33 μm) could be explained by different mechanical properties (e.g., water uptake [5]) due to the presence of the filler, although a further analysis on this subject is needed. Anyway, the final thickness reduction cannot be attributed simply to dehydration and/or hot processing process, but should also be ascribed to a real material degradation as already proposed by the above-cited authors [15]. By means of ex situ hygrothermal aging on Nafion112 for 400 days, Collette et al. [16] have reported membrane degradation through a modification of sulfonic acid end groups consisting in the formation of sulfonic anhydride from condensation. Substitution of an ionic end group by less hydrophilic anhydrides leads to a significant decrease of water uptake and conductivity. Other works have interpreted the anhydride formation in terms of the oxidation mechanism caused by hydrogen peroxide formed by oxygen reduction at the cathode [17, 18]. With regard to our experimental conditions, both the hypotheses can be considered.

The fluoride emission and the water-related conductivity [19] measured in the exhaust collected water at the anode and cathode (Table 1) were similar for Nafion 112 and Nafion/MMT, which is in agreement with the same observed thickness reduction, although the degradation rate was lower for Nafion/MMT. As previously reported by Kinumoto et al. [20], F⁻ ions can be derived from the CF bonds of the side chain and/or the main-chain of Nafion membranes and both the chains are decomposed at similar rates by peroxide radical attack. We can conclude that both degradation mechanisms (oxidation and condensation) acted under low R.H. and that the effect of MMT on the polymer was mainly to reduce the sulfonic acid condensation onto the polymer side chain, though it did not reduce the peroxide radical effect onto the Nafion main chain. This could explain the similar thickness reduction due to the main chain

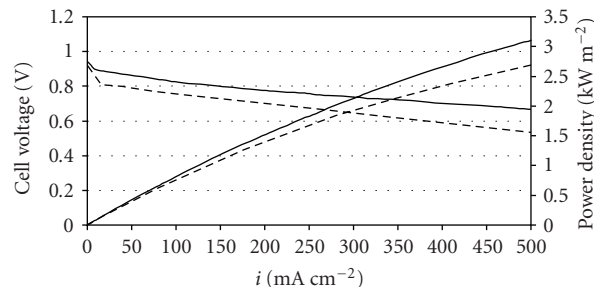


FIGURE 5: Cell voltage and power density versus current density plot for MEA with Nafion 112 (---) and Nafion/MMT (bold continuous lines) at 50°C after the early 150 hours at low R.H.

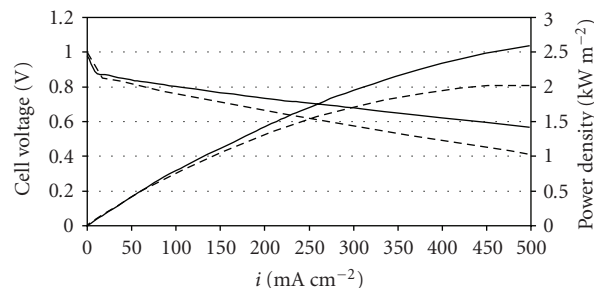


FIGURE 6: Cell voltage and power density versus current density plot for MEA with Nafion 112 (---) and Nafion/MMT (bold continuous lines) at 50°C after 600 hours at low R.H.

degradation, and the different voltage degradation rate due mainly to degradation of sulfonic acid end group.

The polarization plot, obtained after a long-term test at low R.H. and 50°C, updated the results previously obtained [5] for a short period of time showing a different decay for the two systems starting from similar performances (Figure 4).

During the activation stage, both systems had their maximum power density increased: 23% for Nafion/MMT, and 10% for Nafion 112 (Figure 5). It is difficult to explain the fact that Nafion/MMT reaches a higher power density than Nafion 112. We can hypothesize that the water produced at the cathode (2) was strongly attracted and held in the membrane by the presence of hygroscopic MMT, thus increasing the hydration of Nafion in direct contact with the catalyst (Pt-Nafion).

Subsequently, membrane degradation produced a continuous decay with a reduction of maximum power density -17% for Nafion/MMT and -24% for Nafion 112 (Figure 6). After a 600-h long-term test, the Nafion/MMT

membrane showed a power density 21% higher than that of Nafion.

4. Conclusion

Membrane conductivity is very much influenced by the relative humidity incident over its water content. Eventual dehydration treatments irreversibly change the capacity to trap water and, consequently, the results also change. Experimental data evidenced a strong effect of low R.H. on the lifetime of Nafion-based polymer membranes. Prolonged dehydration produced a continuous loss of material in the membrane confirmed by a thickness decrease. Recast Nafion composite membranes with hygroscopic properties due to a low MMT amount were submitted to long-term testing. Performance enhancement at low gas humidification demonstrated to reduce the degradation rate by 50%, especially the sulfonic acid end group degradation. A further study is needed to evaluate the degradation rate at higher temperatures and prolonged OCV conditions.

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