Hybrid Membranes Based in Nafion-metallic Oxides: Performance Evaluations

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Proton exchange membrane fuel cells (PEMFCs) are a class of low temperature fuel cells characterized by a high energy density, good compatibility with the environment and a wide variety of applications. In this work, four hybrid membranes organic-inorganic based on Nafion [Nafion-TiO₂, Nafion-ZrO₂, Nafion-(TiO₂-ZrO₂) and Nafion-YSZ] have been fabricated and evaluated in order to be used as electrolytes in intermediate temperature proton exchange membrane fuel cells (IT-PEMFCs). Doctor Blade technique has been the method used to fabricate these membranes since it simplifies the synthesis and scale-up of hybrid films. Thereby, very homogeneous nanocomposite membranes with high reproducibility, low thicknesses and large size have been easily obtained. The hybrid membranes have been evaluated in terms of water uptake and further characterized by thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). Finally, the hybrid membranes were used in the fabrication of membrane-electrode assemblies (MEAs), placed in single cells, and tested in operating conditions. In this study the method for films preparation has been improved and the presented results allowed to identify the membranes with the best performance and potential applicability as electrolytes in IT-PEMFCs.

1. Introduction

One of the most promising Fuel Cells technologies is the proton exchange membrane fuel cells (PEMFCs), which operate at low temperature, do not use fossil fuels and are environmental friendly (Kahveci et al., 2014). For this reason, PEMFCs can be considered to be used in remote sites, for transport, and also for mobile applications. The perfluorosulfonic acid membranes, such as Nafion, are the most used electrolyte in PEMFCs due to their high proton conductivity and excellent chemical stability. However, Nafion presents poor performance under low relative humidity (RH) operation. According to (Thiam et al., 2011), the proton conductivity of the Nafion membrane is mainly affected by the amount of water inside the membrane. In fact, the maximum proton conductivity is reached when the Nafion is fully hydrated.

Nowadays, the scientific community is focusing on developing new hybrid organic-inorganic composite membranes, which are able to: increase the bound water in the membrane structure, improve the membrane self-humidification, reduce the fuel crossover and electro-osmotic drag, enhance proton conductivity, and increase mechanical, thermal strengths and chemical stability of composite membranes at higher operation temperatures (Kim et al. 2015) and low relative humidity (Klaysom et al. 2011).

This work shows the fabrication parameters and the physical, chemical and electrochemical results for four different organic-inorganic hybrid membranes, that are based on a mixture of metal oxide nanoparticles (3 wt.%: ZrO₂, TiO₂, YSZ, TiO₂-ZrO₂) and Nafion polymer. Among other membrane preparation methods, Doctor Blade technique was used because it simplifies the fabrication process, reduces the cost and improves the reproducibility of the membranes thickness.
2. Materials and Methods

2.1 Materials

For hybrid membranes preparation, Nafion® solution D2021 20 wt.% (Ion Power Inc.), Zirconium (IV) oxide (ZrO₂), and Titanium (IV) oxide (TiO₂) (Aldrich), Yttria stabilized zirconia powder (YSZ) (Hwnano), all nanopowder < 100 nm, were used. Ethanol (Panreac), H₂O₂ and H₂SO₄ (Scharlau), Potassium Hydrogen Phthalate (Sigma-Aldrich), were used as received.

Electrodes were fabricated by using Pt/C 40% Pt on Vulcan XC72 catalyst (Sigma-Aldrich), Nafion perfluorinated resin 5 wt.% solution (Sigma-Aldrich), Isopropanol (Scharlau), Sigracet 29BC carbon paper, and deionized water (conductivity lower than 0.1 μS·cm⁻¹).

2.2 Membrane preparation

Nafion composite films with TiO₂, ZrO₂ and YSZ nanoparticles were prepared using the Doctor Blade (BYK Instruments) technique. By means of this technique, it was possible to use the commercial solution 20 wt.% Nafion D2021 dispersed in low weight alcohols and water. This process really simplifies the synthesis and the scale-up of the hybrid films (Río et al., 2014). Automatic film applicator (showed in Figure 1a) was used to prepare the membranes. This method includes a velocity deposition control and a vacuum subjection system. Due to the automatization of the system, very homogeneous hybrid-membranes with high reproducibility, controlled thickness and large size (close to the A4 size) were easily obtained.

The optimal amount of metal oxides nanoparticles incorporated to Nafion solution was determined by analysing the mechanical properties of the prepared membranes. After this preliminary study, the chosen solid contents were 3 wt.% TiO₂, 3 wt.% ZrO₂, 1.5 wt.% TiO₂/ZrO₂ and 3 wt.% YSZ.

The membrane fabrication procedure was the following: firstly, the optimal amount of nanoparticles into the Nafion solution was completely dispersed by magnetic and ultrasonic stirring. After that, the mixtures were tape casted by Doctor Blade and dried at ambient temperature for 24 h. Once the solvent was evaporated, the membranes were placed in a vacuum oven heated at 155 ºC for 1 h in order to improve the mechanical stability through the increase in the degree of crystallinity of the polymer and the reduction of the free volume between polymeric chains (Subianto et al., 2013). Finally, the membranes were purified and activated in a solution of 3% H₂O₂, 0.25 M H₂SO₄ and deionized water, subsequently. Each step was carried out at 80 ºC for 1 h. The thicknesses of the membranes obtained were between 65 and 90 μm. An example of a finished membrane is reported in figure 1b.

2.3 MEA preparation

The electrodes were manufactured by scattering the catalyst ink over carbon paper as gas diffusion layers, and by using the Nordson EFD Dispensing Robot. The catalyst ink was prepared by sonicating for three hours a solution composed by a mixture of Pt/C, 5% Nafion perfluorinated, isopropanol and deionized water. The catalytic loading for anode and cathode was 0.4 mgPt·cm⁻² in all fabricated electrodes. Finally, the membrane and the electrodes were carefully placed in an ElectroChem’s single cell of 5 cm² of active area and then, the set was self-assembled in the cell with 2 N·m torque. In Figure 1c some prepared MEAs are shown after testing.

Figure 1: Pictures represented MEAs fabrication’s step, (a) Doctor Blade casting method, (b) An active membrane and (c) MEAs of synthesized membranes after testing.
3. Experimental Procedures

3.1 Membrane morphology

The morphology of the membranes was characterized by scanning electron microscopy (Jeol JSM 6010) with an accelerating voltage of 5-15 kV. Energy dispersive X-ray spectroscopy (EDS) was carried out by using a Jeol EDS detector.

3.2 Thermal properties

Thermal stability of the membranes between 30 °C and 900 °C was evaluated by high resolution TGA on a thermal analyser (Q600, TA Instruments). The heating rate was 10 °C/min in air atmosphere.

3.3 Water uptake measurements

Water uptake of samples was measured by soaking the membranes, previously blotted dry (in a vacuum oven to 80 ºC and 10 mbar), in distilled water for three days. After this period, they were wiped with a filter paper and immediately weighed in a microbalance (SARTORIUS CPA225D, ± 0.0001 g). Water uptake was determined by gravimetric method using Eq(1). Where $W_{\text{wet}}$ is the weight of the hydrated sample, and $W_{\text{dry}}$ is the weight of the dry sample.

$$\text{water uptake} = \frac{W_{\text{wet}}-W_{\text{dry}}}{W_{\text{dry}}} \times 100$$ (1)

3.4 MEA Measurement

The polarization curves were recorded in a Scribner 850e test station. The measurements were carried out at atmospheric pressure, 70 °C temperature, 100% RH, anodic (H₂) and cathodic (O₂) flow rates of 200 ml·min⁻¹ and a stoichiometric of 1.5 for both gases. The constant current and scan current regimens were applied to each membrane-electrode assemblies for a period of time and then the polarization curves were obtained.

4. Results

4.1 Membrane morphology

The morphological properties of the composite membranes depend on the degree of compatibility and dispersibility between the polymer and inorganic components. The morphological properties of the Nafion-TiO₂, Nafion-ZrO₂, Nafion-(TiO₂/ZrO₂) and Nafion-YSZ hybrid membranes, were characterized by SEM. Figure 2 a-d shows the SEM cross-section images (top), surface images (middle) and EDS images (bottom) of the nanocomposite membranes. The morphology of the Nafion-TiO₂, Nafion-ZrO₂ and Nafion-YSZ membranes are uniform and smooth, the defects observed in the cross-section images of this membranes could be caused by the cutting damage on polymer. The Nafion-(TiO₂/ZrO₂) sample is not homogeneous and significant agglomerations of TiO₂/ZrO₂ nanoparticles are clearly visible. The EDS image indicated that the distribution of Ti and Zr elements on the surface of the composite membranes was uniform in the Nafion-TiO₂, Nafion-ZrO₂ and Nafion-YSZ membranes as result of the interaction of hydrogen bonding between the sulfonic acid groups in the Nafion and metallic oxides. In contrast, Zr and Ti aggregations are clearly visible in the Nafion-(TiO₂/ZrO₂) composite membrane. Direct mixing of inorganic component into the polymer matrix is the simplest method to prepare organic–inorganic hybrid PEMs, but dispersion of inorganic nanoparticles in a polymer matrix sometimes lead to undesirable agglomeration as is the case of Nafion-(TiO₂/ZrO₂).
4.2 Thermal properties

Thermal stability of the Nafion-TiO₂, Nafion-ZrO₂, Nafion-(TiO₂/ZrO₂) and Nafion-YSZ hybrid membranes was studied by TGA analysis through thermal dehydration, decomposition and degradation losses. TGA curves were compared in Figure 3. The thermal decomposition events typically observed in hybrid inorganic-organic Nafion based membranes are evident. The first noticeable mass loss, for all examined membranes, is observed between 50 and 200 ºC and is attributed to the evaporation of adsorbed water. Above 300 ºC, a second noticeable mass loss is observed, assigned to decomposition of the sulfonic acid groups present in the membranes. The third and final mass loss, which onsets at 400 ºC, is due to decomposition of ether linkages and the polymer main-chain. The weight remained in the samples at 530 ºC is ordered as follows: Nafion-ZrO₂ > Nafion-YSZ > Nafion-(TiO₂/ZrO₂) > Nafion-TiO₂. TGA results suggest that the Nafion-ZrO₂ hybrid membrane has greater thermal stability.

![Figure 3: TGA analysis of Nafion hybrid membrane](image-url)
Table 1 shows the water values of the membranes fabricated. Nafion® 112 commercial membrane was used as reference materials to compare the influence of the solid incorporation into the membrane water adsorption capacity. The values remained of water uptake are ordered as follows: Nafion-ZrO₂ > Nafion-YSZ > Nafion-TiO₂ > Nafion-(TiO₂/ZrO₂) > Nafion® 112. Those results suggest that the Nafion-ZrO₂ hybrid membrane has greater water uptake capacity.

The enhanced water uptake can be attributed to the solvation phenomena of Nafion-nanoparticles cross-links. The solvation phenomena are expected to become more significant as the strength of the Nafion-nanoparticles cross-links increases, i.e. as the ionic character of the Nafion-nanoparticles becomes higher. The difference in the interactions between the –SO₃H groups of the Nafion host polymer and the nanoparticles in the hybrid membranes is ascribed to the acid-base properties of the surface of the latter component. It is well known that the basic character of the oxides studied in this work increases as follows: TiO₂ < TiO₂/ZrO₂ < YSZ < ZrO₂. Thus, the surface of the ZrO₂ nanoparticles is expected to be much more basic than the surface of the TiO₂ nanoparticles, so that the ZrO₂ nanoparticles are capable of triggering the formation bridges owing to non-directional ionic interaction, while the TiO₂ nanoparticles can only give rise to localized and highly directional dipolar interactions (Di Noto et alt. 2012). From the obtained results, these positive effects of basic character of the oxides on Nafion properties can be confirmed, which also is a key design objective for high temperature membranes.

Table 1: Thickness, Water Uptake of Membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Thickness (μm)</th>
<th>Water Uptake (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion-TiO₂ 3%</td>
<td>66</td>
<td>17.8</td>
</tr>
<tr>
<td>Nafion-ZrO₂ 3%</td>
<td>72</td>
<td>20</td>
</tr>
<tr>
<td>Nafion-TiO₂/ZrO₂ 1.5%/1.5%</td>
<td>73</td>
<td>17</td>
</tr>
<tr>
<td>Nafion-YSZ</td>
<td>93</td>
<td>18.7</td>
</tr>
<tr>
<td>Nafion® 112</td>
<td>50</td>
<td>16</td>
</tr>
</tbody>
</table>

4.3 MEA Measurement

As it can be seen in Figure 4, the membrane electrode assemblies manufactured from hybrid membranes showed similar behaviour. In all cases the open circuit voltage values, OCV, were higher than 0.965 V, suggesting that the fuel crossover from anode to cathode and internal currents was low. The best performances of the polarization curves of hybrid systems were obtained for MEAs composed of ZrO₂ nanoparticles (Nafion-ZrO₂ and Nafion-ZrO₂-TiO₂) and slightly lower performances were obtained for the MEAs composed of TiO₂ and YSZ.

Table 2 shows the power densities and the calculated total resistances obtained from the slopes of the curves, between 0.5 A and the current corresponding to maximum power of each curve. Nafion-ZrO₂ and Nafion-ZrO₂-TiO₂ reported resistances of 0.85 and 0.88 Ω·cm², respectively, and power densities close to 210 mW·cm⁻². On the other hand, Nafion-TiO₂ and Nafion-YSZ presented resistance values of 0.90 Ω·cm² and 1.00 Ω·cm², respectively, and power densities close to 190 mW·cm⁻².

Table 2: Power density and total resistance of the MEAs

<table>
<thead>
<tr>
<th>MEA</th>
<th>Power density (mW·cm⁻²)</th>
<th>Total Resistance (Ω·cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion-TiO₂ 3%</td>
<td>189</td>
<td>0.90</td>
</tr>
<tr>
<td>Nafion-ZrO₂ 3%</td>
<td>213</td>
<td>0.85</td>
</tr>
<tr>
<td>Nafion-TiO₂/ZrO₂ 1.5%/1.5%</td>
<td>208</td>
<td>0.88</td>
</tr>
<tr>
<td>Nafion-YSZ</td>
<td>186</td>
<td>1.00</td>
</tr>
</tbody>
</table>

It is important to point out that the Nafion-YSZ membrane thickness is slightly higher than the other ones, and so an extra resistance associated to the membrane was included in the total resistance. Taking this effect into account, we can conclude that the polarization curves results suggested that the effect of Zirconium Oxide, probably due to its basic character, shows the best cell performance comparing to Nafion-ZrO₂ and Nafion-TiO₂/ZrO₂ based membranes, at least at this operation conditions (70 ºC and 100% RH). Further studies will be done at higher temperatures and low RH values where Nafion performance drastically decreases (Li et alt., 2010) in order to confirm this behaviour.
5. Conclusions

The preliminary results demonstrated that Doctor Blade (or tape casting) process can be scaled up for the fabrication of large size composite membranes used in intermediate-temperature PEMFCs. Nanocomposite membranes were prepared by Doctor Blade with different metal oxides: ZrO$_2$, YSZ, TiO$_2$ and a mixture of TiO$_2$-ZrO$_2$. This method reported suitable levels of uniformity for ZrO$_2$, YSZ and TiO$_2$ membranes. However, the presence of Zr and Ti aggregations was evidenced for the Nafion-TiO$_2$/ZrO$_2$ membrane. In terms of thermal properties, greater thermal stability was observed for Nafion/ZrO$_2$, while Nafion-TiO$_2$ showed the worst one. Water Uptake measurements suggested an increment of membranes conductivity with water content capacity, nevertheless additional research is required in order to clear up on this relation. It is important to point out that the physical-chemical characterization results were in agreement with the presented polarization curves acquired at 70 ºC and 100% RH. This preliminary work is the starting point to study the performance of different hybrid Nafion-based membranes at temperatures above 80 °C and low humidity.

References


