Modified Polyaniline-Nafion®-Silica Nanocomposites for DMFC

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1. Introduction

Among the different fuel cell technologies, the direct methanol fuel cell (DMFC), with methanol as the energy carrier, has one of the best application prospects as an energy converter for portable electronic devices and environmentally benign vehicles [1]. Currently Nafion® (poly-perfluorosulphonic acid) membranes are used as solid electrolytes in DMFC applications due to their excellent chemical stability and ionic conductivity [2]. However, these membranes suffer from methanol crossover (diffusion of the methanol from anode to cathode through the polymer electrolyte membrane). Methanol crossover has a severe negative impact on the overall performance of the DMFC due to a reduction in fuel efficiency through wasted oxidation at the cathode, as well as catalyst poisoning [3]. Indirect approaches, such as the use of diluted methanol as a fuel and low operation temperatures, have been used in order to reduce the methanol crossover but have failed in obtaining significant fuel cell improvements [4].

Recent studies [5-7] have shown that the structural modification of Nafion® membranes can lead to considerable reduction in methanol crossover but also result in an undesirable reduction of proton conductivity, both key factors in determining overall fuel cell performance. In previous studies [8-9] the addition of polyaniline to a fuel cell electrode has shown an increase in catalytic activity of methanol electro-oxidation. This study aims at modifying Nafion® and Silica-Nafion membranes with polyaniline, an electron conductive polymer, in order to modify the membrane structure to reduce the methanol cross-over.

2. Experimental

Silica nanoparticles were embedded into the hydrophilic clusters of Nafion using a sol-gel technique as described elsewhere [10]. Polyaniline was deposited on the silica-Nafion as well as un-doped Nafion membranes using a chemical route (redox polymerization). The catalytic species were attached to the sulfonic functional groups of Nafion by immersion in a ferric chloride solution, and the in situ polymerization of polyaniline was obtained by immersion of the activated membrane into an aniline-nitric acid solution.

The methanol and water permeation through the membranes was determined using a pervaporative system (Fig.1). The polymer electrolyte membrane was hermetically clamped between two metallic bulbs, and fed on one side with a liquid stream (methanol-water solution) of which the methanol concentration is maintained constant by means of a reflux using a peristaltic pump. At the other side, the permeate vapour was carried by a helium stream and collected in a glass condenser immersed in liquid nitrogen. The weight of permeate was determined using a digital balance and the concentration by means of gas chromatography. Various temperature levels (25, 50, 75ºC) and methanol concentrations (0, 50, 100%) were studied.
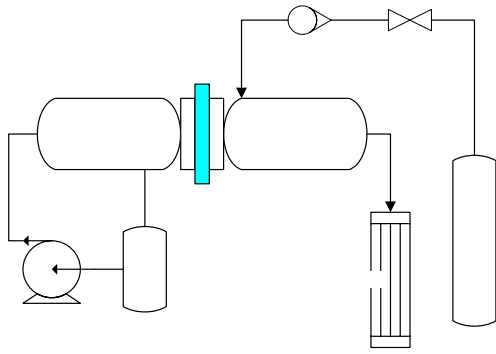
Fig. 1. Permeability measurement set up

Fig. 2. Distilled water permeability on Nafion-based membranes

The normal direction conductivity of the fully hydrated membranes at ambient temperature was measured by means of impedance spectroscopy using a Solartron 1260 impedance analyser (StandAlone mode, frequency sweep 10MHz to 1Hz). The membrane resistance was obtained from the difference between the measured resistance and the contribution of the short circuited electrodes.

3. Results and Discussion

The permeability values obtained for Nafion on this study agree with previous studies [11,12]: 1.98×10^{-6} cm^2/s for methanol 2M (25ºC) and 2.3×10^{-6} cm^2/s for methanol 1M at ambient temperature respectively, while the pervaporative system in this work led to a permeation of methanol 25M of 1.36×10^{-6}cm^2/s at ambient temperature. Because the hydration of the polymer electrolyte membrane is a key factor for the proton conduction on DMFCs, distilled water permeation was measuerd on the membranes obtaining similar permeability profiles at ambient and 50ºC (Fig.2). At high temperatures (75ºC) the silica nanoparticles on the polyaniline modified composite membrane (Pani NC1) produced an increase on water permeation when compared with Pani-Nafion due to the hydrophilic nature of silica structures.
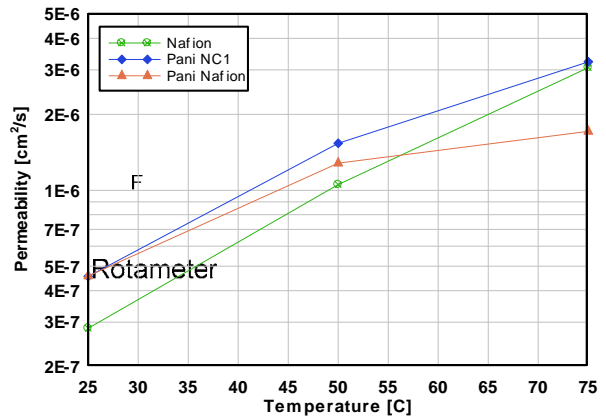
To produce electricity, DMFCs require water and methanol at the cathode side. Thus the permeation of water-methanol solutions is the most relevant factor for the comparison of the permselective performance of the membranes. As can be seen on Fig. 3, a remarkable reduction of the methanol solution (50%(v/v)) permeability at 75ºC was obtained (Pani NC1: 84%, Pani-Nafion: 77%) when compared with Nafion, indicating the benefits of this approach.
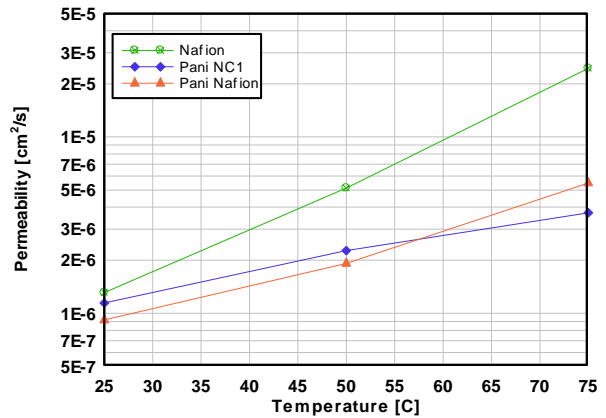

Fig. 3. Methanol 50% permeability on Nafion-based membranes

Previous studies [13] suggest that methanol produces a relaxation via solubility on the non cross-linked polymeric structure of Nafion leading to the methanol crossover. The reduction of methanol permeation measured for

the polyaniline modified membranes can be due a reinforcement of the microstructure of Nafion by a cross linking effect of the polymeric chains produced during the in situ aniline polymerization. Pure methanol permeation tests (Figure 4) produced similar results, supporting this theory. However, more specific microstructure (SAXS) and functional group (FTIR) analysis, will be conducted to validate this theory.

Impedance spectroscopy experiments showed that the modification of the Nafion and Silica-Nafion membranes with polyaniline did not significantly affect proton transport, resulting (Table 1) in a slight reduction and improvement of the Pani NC1 and Pani Nafion as compared to Nafion, respectively. These results suggest functionalisation of the silica nanocomposite (PaniNC1) is required to improve conductivity subject that very low methanol permeation levels remain the same.
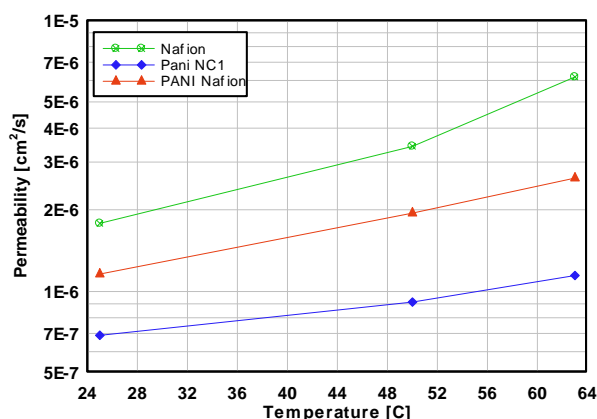

Fig. 4. Methanol 100% permeability on Nafion-based membranes

Table 1. Conductivity (σ) of the fully hydrated membranes (22ºC)

Membrane	Nafion	Pani Nafion	Pani NC1
σ (mS.cm^{-1})	12.5	15	11

4. Conclusions

Polyaniline modification on Nafion-based polymer electrolyte membranes for DMFC applications led to a significant reduction of the methanol crossover without reducing the proton conductivity of the membrane. However, silica Nafion Polyaniline nanocomposite exhibited a slight reduction of proton conductivity suggesting that silica functionalisation is warranted in further research work.

5. Acknowledgements

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