

NANOCOMPOSITE POLYMER ELECTROLYTE MEMBRANES: METHANOL CROSSOVER AND CONDUCTIVITY

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ABSTRACT

Commercial Nafion[®] 117 membranes were successfully modified by in-situ reactions (sol-gel of TEOS and/or polymerization of aniline) within Nafion structures. Water-methanol permeability and proton conductivity were investigated in order to determine the potential performance of these membranes for DMFC systems. Silica-polyaniline modification resulted in 84% methanol crossover reduction, from $2.45 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ for conventional Nafion membranes to $3.71 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ for the modified silica-polyaniline composite membrane at 75°C. In addition, conductivity was not hindered, as the polyaniline-Nafion membrane increased from 12.2 to 15 $\text{mS} \cdot \text{cm}^{-1}$ as compared to Nafion, while a reduction of 11% was observed for silica-polyaniline-Nafion composite membrane. The results in this work strongly suggest the potential of polyaniline nanocomposites to enhance the performance of DMFCs.

INTRODUCTION

The direct methanol fuel cell (DMFC) is a promising device to replace batteries for a high energy operation of portable electronic products. When compared to gas-fed fuel cells, DMFCs have several advantages including a) higher efficiency of fuel utilisation; b) use of fuel without reforming; c) elimination of fuel vaporiser and its associated heat source and controls; d) elimination of complex humidification and thermal management systems; and e) and significant reduction in size, weight, and operation temperature (Kordesch, 1996). As a key part of a DMFC, a polymer electrolyte membrane is used between the anode and cathode to provide proton conductivity and to prevent internal electronic current between the two electrodes. Currently Nafion[®] (poly-perfluorosulphonic acid) membranes are used as solid electrolytes in DMFC applications due to their excellent chemical, mechanical and thermal stability as well as high proton conductivity (Liu et al, 2005). Despite these outstanding properties, Nafion membranes suffer from methanol crossover (i.e. diffusion of the methanol from anode to cathode through the polymer electrolyte membrane).

The crossover of methanol in DMFCs has a severe negative impact on its overall performance because of the reduction on fuel efficiency by wasteful oxidation at the cathode side while seriously depolarising the cathode (Ramya 2003). In addition, the methanol reaction in the cathode increases the demand for oxygen leading to higher stoichiometric flow rates. 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 (Dillon *et al*, 2004).

A large number of structural modifications of Nafion-based polymer electrolyte membranes for DMFC applications have been studied in order to reduce the methanol crossover (Shao *et al*, 2002; Yamaguchi *et al*, 2003; Jung *et al*, 2002). These have led to a significant reduction in methanol transport but also result in an undesirable reduction of proton conductivity, both key factors in determining overall fuel cell performance. In previous studies (Niu *et al*, 2003; Prasad *et al*, 2002), the addition of polyaniline to a fuel cell electrode has shown an increase in catalytic activity of methanol electro-oxidation due to its electron conductive properties.

This study aims at modifying Nafion[®] membranes with silica nanoparticles in order to create a physical barrier for methanol diffusion through the polymer electrolyte membrane and with polyaniline in order to reinforce the polymeric backbone of the membranes and to increase the electrochemical activity of the electrodes during electricity generation. Methanol crossover and conductivity of the fabricated membranes are investigated in order to determine the potential of this technology for DMFC application.

EXPERIMENTAL

Silica nanoparticles were embedded into the hydrophilic clusters of Nafion using a sol-gel technique as described elsewhere (Ladewig *et al*, 2003). Polyaniline was deposited on Nafion and Silica-Nafion membranes using a chemical route (redox polymerisation). The catalytic species were attached to the sulphonic functional groups of Nafion by immersion in a ferric chloride solution, and the *in-situ* polymerisation of polyaniline was obtained by immersion of the activated membrane into an aniline-nitric acid solution.

The methanol and water permeation on the membranes was determined using a pervaporative system (Figure 1). The polymer electrolyte membrane was hermetically clamped between two metallic bulbs, and fed at one side with a liquid stream (methanol-water solution) which concentration was maintained constant by recycling 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 scale and the concentration by means of gas chromatography. Various levels of temperature (25, 50, 75°C) and methanol concentration (0, 50, 100% (v/v)) were studied.

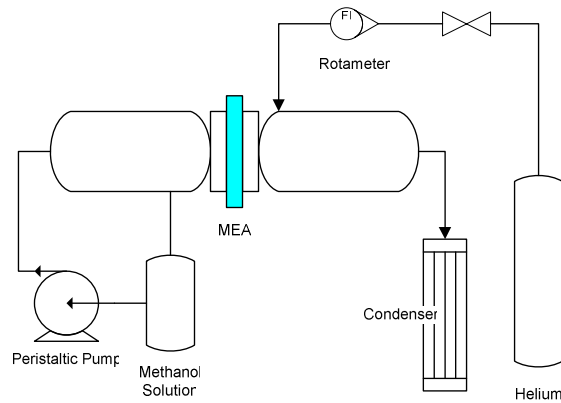


Figure 1: Permeability measurement set up

The permeabilities of water and/or methanol through the membranes tested on the pervaporation experiments were calculated using of the following formula:

$$P = \frac{JL}{A\Delta C} [cm^2 / s] \quad (1)$$

where L is the membrane thickness, J is the flux of permeate through the membrane, A the active area of mass transfer, and ΔC is the gradient of concentration between the feeding side and the permeate side.

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

$$\sigma = \frac{L}{R_m A} [S / cm] \quad (2)$$

where L is the thickness of the membrane, A the contact area between the gold electrodes and the membrane, and R_m is the real value of the electric resistance in the Nyquist plot generated by the Solartron 1260. The membrane resistance is obtained by the difference between the measured resistance and the contribution of the short circuited cells (Figure 3).

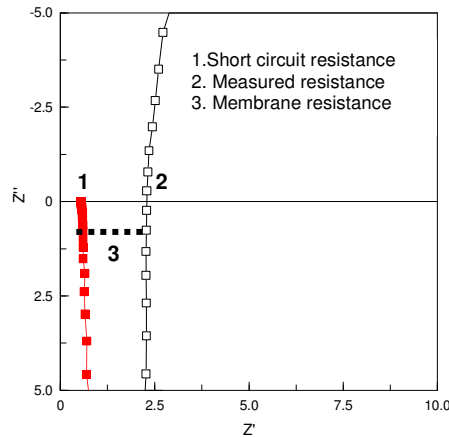


Figure 3: Representative impedance spectroscopy graph (Nyquist diagram)

RESULTS AND DISCUSSION

The hydration of the polymer electrolyte membrane is a key factor for the proton conduction on DMFCs. Hence, distilled water permeation was tested on the membranes obtaining similar permeability profiles at ambient and 50°C (Figure 3). At high temperatures (75°C) the silica-modified membranes (Silica-Nafion and Silica-Nafion-Polyaniline) showed increased permeability when compared with Nafion due to the hydrophilic nature of the silica structures, while the Nafion-Polyaniline membrane showed reduced permeability due to the hydrophobicity of the polyaniline (pani) surface. The permeability values obtained for Nafion® 117 on this study agree with previous studies (Dimitrova *et al*, 2002; Elabd *et al*, 2003) $1.98 \times 10^{-6} \text{ cm}^2/\text{s}$ for methanol 6.4%(w/w) (25°C) and $2.3 \times 10^{-6} \text{ cm}^2/\text{s}$ for methanol 3.2%(w/w) at ambient temperature respectively, while the pervaporative system in this work led to a permeation of methanol 44.2%(w/w) (equivalent to 50%(v/v)) of $1.36 \times 10^{-6} \text{ cm}^2/\text{s}$ at ambient temperature. This fact demonstrates the reliability of the experimental setting used and the adequacy of the model proposed.

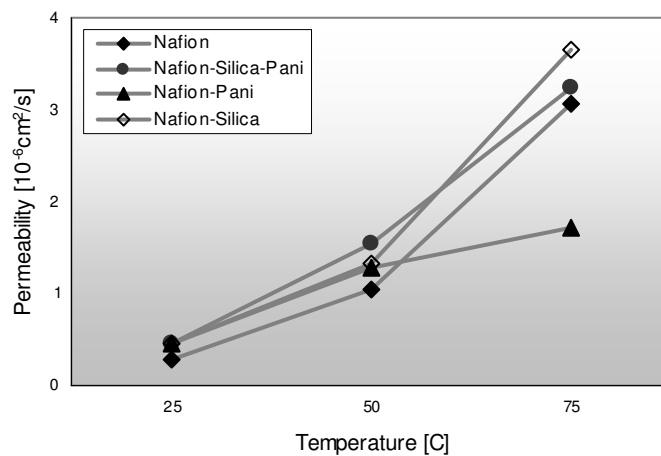


Figure 3: Distilled water permeability on Nafion-based membranes

To produce electricity, DMFCs require water and methanol at the cathode side. Therefore the permeation of water-methanol solutions is important for comparison of the permselective performance of the membranes. The results obtained indicated that polyaniline-modified membranes showed a remarkable reduction of methanol crossover for methanol 50%(v/v) solutions, specially at high temperatures (Figure 4). Silica-Nafion-Polyaniline and Nafion-Polyaniline showed a reduction of methanol crossover of 84% and 77% respectively at 75°C when compared with Nafion. The silica-modified membrane showed an almost identical behavior as Nafion, indicating that the embedding of silica nanoparticles in Nafion is not enough for achieving the goal of methanol crossover reduction.

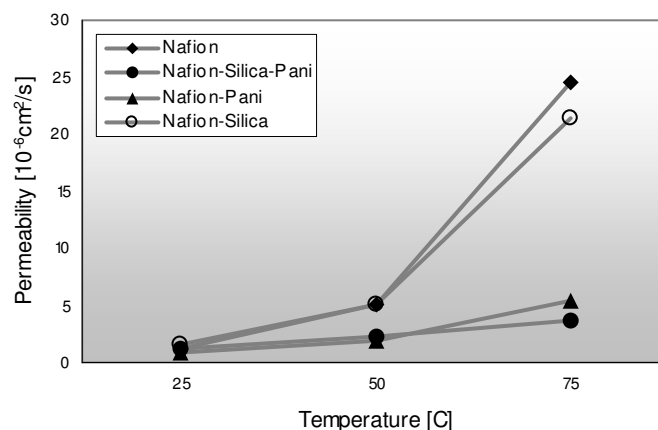


Figure 4: Methanol 50% (v/v) permeability on Nafion-based membranes

Previous studies (Barragan *et al*, 2004) 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 reached for the polyaniline modified membranes can be due a reinforcement of the microstructure of Nafion by a crosslinking effect of the polymeric chains produced during the *in-situ* aniline polymerisation. Pure methanol permeation tests (Figure 5) produced similar results, supporting this theory. However, more specific microstructure (SAXS) and functional group (FTIR) analysis are necessary to validate this issue.

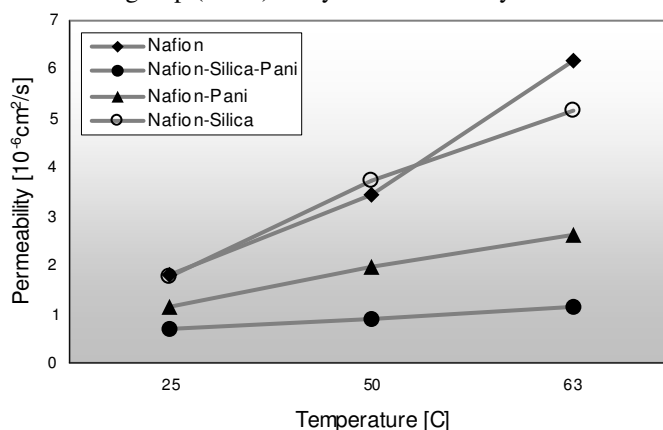


Figure 5: Methanol 100% permeability on Nafion-based membranes

Impedance spectroscopy experiments showed that the modification of the Nafion membranes with silica and/or polyaniline did not significantly affect the proton transport (Figure 6), indicating one more benefit related to our approach because the methanol crossover was successfully reduced without affecting the proton conductivity, contrary to similar previous studies.

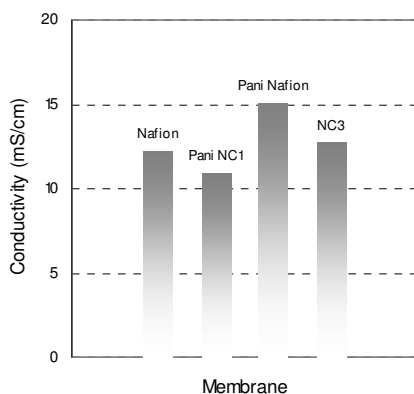


Figure 6. Conductivity of the fully hydrated membranes (22°C)

CONCLUSIONS

The introduction of polyaniline in the DMFC proton conduction nanocomposite membrane brought benefits in terms of reducing methanol crossover while maintaining conductivity. The silica-polyaniline modification resulted in 84% (at high temperature and methanol 50% solution) reduction of methanol crossover as compared to conventional Nafion membranes. In addition proton conduction increased by 23% for polyaniline-Nafion and slightly decreased by 11% for silica-polyaniline-Nafion membranes. These results strongly suggest that the polyaniline modification enhances the structural stability of the nanocomposite membranes allowing for improved performance for DMFC systems.

ACKNOWLEDGEMENTS

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