

Nanocomposite Nafion-silica membranes for direct methanol fuel cells

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Abstract

Commercially available proton exchange membranes such as Nafion do not meet the requirements for high power density direct methanol fuel cells, partly due to their high methanol permeability. The aim of this work is to develop a new class of high-proton conductivity membranes, with thermal and mechanical stability similar to Nafion and reduced methanol permeability. Nanocomposite membranes were produced by the in-situ sol-gel synthesis of silicon dioxide particles in preformed Nafion membranes. Microstructural modification of Nafion membranes with silica nanoparticles was shown in this work to reduce methanol crossover from $7.48 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for pure Nafion[®] to $2.86 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for nanocomposite nafion membranes (Methanol 50% (v/v) solution, 75°C). Best results were achieved with a silica composition of 2.6% (w/w). We propose that silica inhibits the conduction of methanol through Nafion by blocking sites necessary for methanol diffusion through the polymer electrolyte membrane. Effects of surface chemistry, nanoparticle formation and interactions with Nafion matrix are further addressed.

Keywords: proton exchange membranes, in-situ sol-gel, functionalisation, proton conduction and methanol diffusion.

1. Introduction

Fuel cells are electrochemical devices that convert chemical energy to electrical energy at an efficiency much higher than that of traditional heat engines. 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 [1]. However, polymer electrolyte membranes generally allow the methanol molecules to diffuse from the anode to the cathode side. This so called methanol crossover has a 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]. Although diluted methanol in water mixtures and low operation temperatures are strategies used to reduce the effect of methanol crossover, these approaches have yet to deliver significant fuel cell performance improvements [4].

Modification of nafion polymeric matrix by the incorporation of nanoparticles forms part of a concerted effort by the scientific community to address this issue. Silica has been embedded into Nafion membranes through both solvent casting and in-situ synthesis from silicon alkoxide precursors. Dimitrova et al. [5] reported a three-fold increase in the proton conductivity of a 4.3% SiO₂/Nafion composite membrane ($\sigma = 0.3 \text{ S.cm}^{-1}$) over as-received Nafion 117 membrane, where the Silica was incorporated from Aerosil A380 fumed silica. Nafion-silica membranes formed from in-situ synthesis techniques have also shown comparable proton conductivity to that of Nafion. Jung et al. [6] claimed an optimum SiO₂ content of approximately 12 wt%, having $\sigma = 0.08 \text{ S.cm}^{-1}$ and delivering a current density of 650 mA.cm^{-2} at 0.5 V and 125 °C in a DMFC. Similarly, the incorporation of 3–5 wt% TiO₂ in Nafion membranes has shown superior performance in high temperature DMFCs, with a power density of 350 mW.cm^{-2} at 145 °C with oxygen feed. The performance of the cell also increased with

decreasing TiO₂ particle size, thus further suggesting that the filler morphology influences the electrochemical properties of the composite membrane [7].

Various phosphates have also been employed to alter the properties of Nafion, including calcium hydroxyphosphate, which at 5 wt% loading in recast Nafion gave $\sigma = 0.18 \text{ S.cm}^{-1}$ [8] and zirconium phosphate, which at 23 wt% loading in a H₂/O₂ cell operated at 130 °C and 3 bar, gave a fourfold increase in current density over a MEA based on commercial Nafion [9]. The addition of mordenite to Nafion showed only a slight increase in proton conductivity over that of Nafion at temperatures greater than 80 °C, and a corresponding minor increase in H₂/O₂ cell performance [10]. Structural modification of Nafion polymer has also been reported in the literature. Approaches have included grafting of styrene monomer on Nafion by means of supercritical CO₂ impregnation in order to build a hydrophobic (methanol repellent) barrier (Sauk 2004), pore-filling type PEM using Teflon as substrate and acrylic acid-vinyl sulfonic acid copolymer as the proton conductive matrix (Yamaguchi 2003), and Nafion modification with polyvinyl alcohol (Shao 2002). All these studies resulted in the reduction of the methanol permeation, but at the expense of reduced proton conductivity.

This work investigates at the effect of silica modified Nafion membranes for application in DMFCs. The silica loading is studied in terms of proton conduction and methanol crossover.

2. Experimental

Silica nanoparticles were embedded into the hydrophilic clusters of Nafion using an in-situ sol-gel technique. Nafion 117 membranes cut in squares with an approximate area of 4 cm² were modified with silica following the technique developed by Ladewig (2004). In this technique, silica nanoparticles were embedded into the hydrophilic clusters of the perfluorinated membrane using a sol-gel process. After pre-treated, the membranes were dried at 100°C and atmospheric pressure. Then, the membranes were stabilised in a media with a controlled relative humidity of 40% for 30min and then immersed on a solution of TEOS-Ethanol 1:8 (M/M) for 1min. After this step, the membranes were rinsed in pure ethanol in order to eliminate any build-up of silica on the surface of the membranes. The process was repeated several times to increased the silica loading in the Nafion matrix.

Nafion-functionalised silica composite membranes were produced using the same technique, using 3-mercaptopropyl trimethoxysilane (MPTMS) in addition to tetraethyl orthosilicate (TEOS) as a silicon alkoxide precursor, in a molar ratio of 1:1:8 (MPTMS:TEOS:EtOH). As shown in Fig. 1, treatment of the Nafion-functionalised silica composite membranes in 30% H₂O₂ at 60 °C for 1h was employed to oxidise the thiol groups to sulfonic acid groups [15].

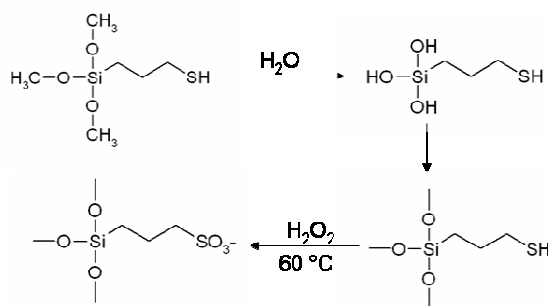


Figure 1. Hydrolysis, condensation and oxidation of MPTMS

The methanol and water permeation on the membranes was determined using a pervaporation system (Fig. 2). 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 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 scale and the concentration by means of gas chromatography. All measurements were made at 50 °C, with a feed concentration of 50 vol% or 69 vol% for Nafion-silica and Nafion-sulfonated silica samples respectively.

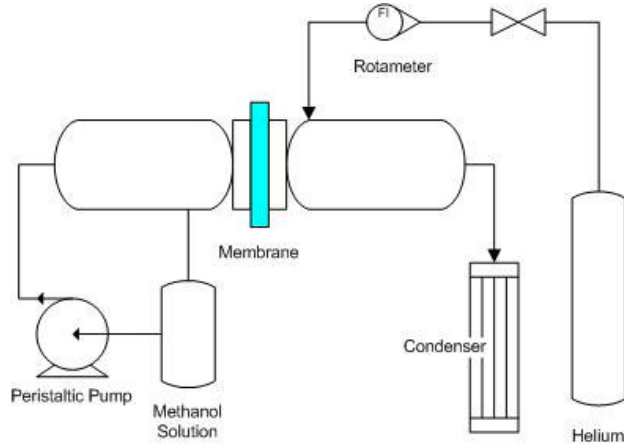


Figure 2. Permeability measurement set up

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 was obtained by the difference between the measured resistance and the contribution of the short circuited cells.

3. Results and Discussion

Generally speaking, the measured values of proton conductivity for both the Nafion-silica and the Nafion-sulfonated silica membranes were equivalent to or lower than that of Nafion 117 alone (0% Si loading), as shown in Figure 3.

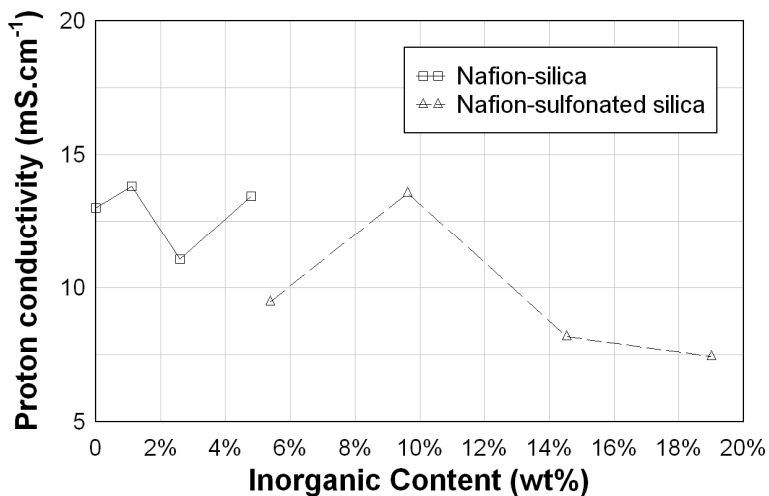


Figure 3. Proton conductivity as a function of inorganic content for Nafion-silica and Nafion-sulfonated silica membranes at 20°C.

Slight improvements were seen for the Nafion-silica 1.1 wt% and Nafion-sulfonated silica 10 wt% membranes, at 13.8 and 13.6 mS.cm⁻¹ respectively. It may be expected that, particularly at higher loadings of the sulfonated silica particles, the increased concentration of mobile protons in the composite matrix would lead to higher proton conductivity values. This is made possible by the fact that, ideally, the proton conductivity is proportional to the proton concentration. However this was not seen in this work, which may be due to a number of factors. Interestingly, the Nafion-sulfonated silica composite membranes showed a peak in conductivity at around 10 wt%, which may provide some insight into the morphological structure of the composite membrane. Proton transfer in Nafion is mediated by water molecules; the dry material has negligible proton conducting capacity as the separation distance of adjacent sulfonic acid groups is too great for unassisted transfer.

However, as the material becomes hydrated, water molecules are able to act as intermediaries and facilitate proton hopping through the material. In this light, it may be hypothesised that at lower loadings, the functionalised silica particles, with their reasonably large pendant sulfonic acid terminating propyl side chains, simply take up low energy positions within the polymer matrix, predominantly within the hydrophilic water-rich domains, and do little to impede or hinder proton transport. However at approximately 10 wt% loading a significant peak in conductivity suggests that the concentration of additional sulfonic acid groups may be reaching the critical point at which they form a proton-conducting route, or begin to interact strongly with the sulfonic acid groups of the Nafion.

The methanol permeability of the composite membranes is shown in Fig. 4. Of immediate interest are the contradictory trends in permeability with increasing filler loading; for Nafion-silica an increase in permeability is noted with increasing filler loading, whilst for Nafion-sulfonated silica the opposite is true. This suggests that, for the low silica loadings, the particles in fact cause the membrane structure to open up and allow a higher rate of methanol diffusion as compared to Nafion (0% silica loading). The downward trend in permeability for Nafion-sulfonated silica composite membranes

indicates that the inorganic particles, which are expected to occupy primarily the hydrophilic domains of the polymer matrix, are genuinely impeding the progress of diffusing methanol molecules.

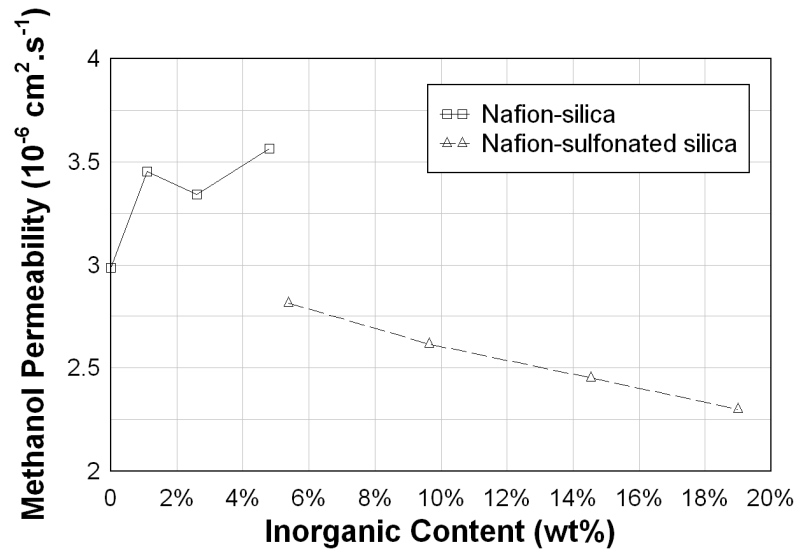


Figure 4. Methanol permeability of Nafion-silica and Nafion-sulfonated silica membranes as a function of inorganic content at 20°C.

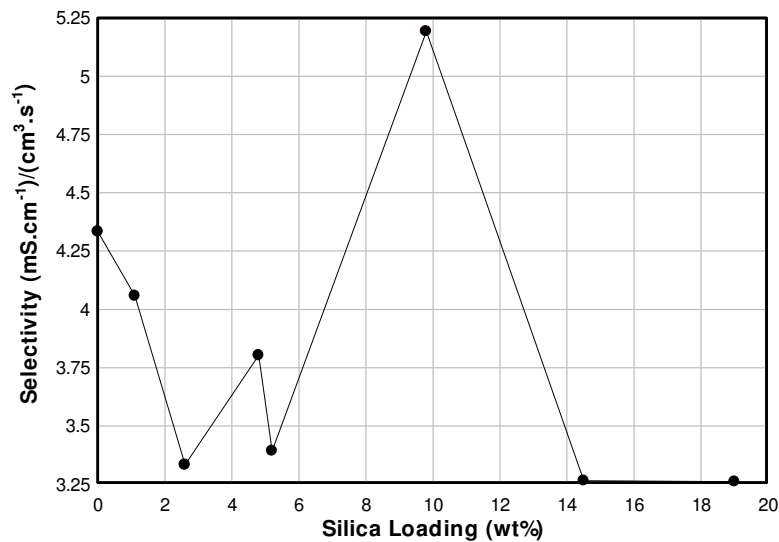


Figure 5. Selectivity results at 20°C.

Recent studies [5, 16] proposed the selectivity factor which corresponds to the ratio between the proton conductivity (σ) and the methanol permeability (P). Although this factor shows a relative performance of the DMFC without electricity generation, it is useful to compare simultaneously the proton and methanol-water transport properties of the membranes at different temperatures. In terms of DMFC, the reduction of methanol crossover (a positive effect) must be balanced against any loss (a negative effect) in proton conductivity. It is observed in Figure 5 that the 10 wt% sulfonated silica loading sample outperformed Nafion. The other membranes resulted with lower selectivities than Nafion, thus no improvements in performance may be expected.

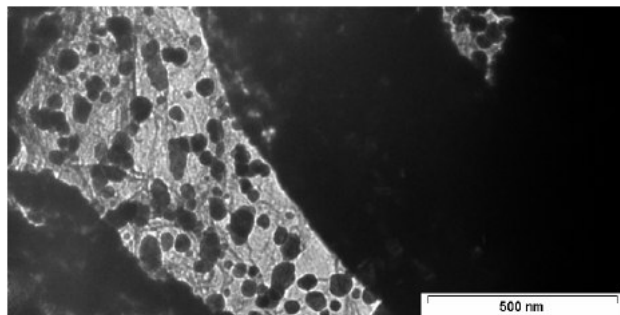


Fig. 6. TEM Micrograph of Nafion-silica composite membrane

Figure 6 shows the TEM micrograph of a 6 wt% Nafion-silica composite membrane. The silica particles are embedded in the Nafion matrix and range from small sizes (10nm) to large particle aggregates (~100 nm). These results suggest that the in-situ sol-gel process used generates varying chemical potentials in the Nafion matrix, thus leading to varying particles sizes. This point is further evidenced by the proton conduction results (Figure 3) as a function of the silica loading. The proton conductivity changes to values above and below those obtained for pure Nafion (0% silica loading). In principle, silica particles are neither particularly enhancing nor significantly impeding conductivity.

Conclusions

In situ sol-gel syntheses in the Nafion membrane showed no major improvements in terms of proton conduction and methanol crossover. However, functionalisation of particles by sulfonated silica particles at 10 wt% in Nafion allowed superior performance, in particular by a significant reduction in methanol crossover. Variation of results may be related to particle size and aggregation which may change the regimes of proton conductivity and methanol diffusion.

Acknowledgements

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