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Performance of a Ceramic Fiber Reinforced Polymer Membrane as Electrolyte in Direct Methanol Fuel Cell

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Abstract: Direct Methanol Fuel Cell (DMFC) is considered as a candidate technology for applications in stationary, transportation as well as electronic power generation purposes. To develop a high performance direct methanol fuel cell (DMFC), a competent electrolyte membrane is needed. The electrolyte membrane should be durable and methanol crossover must be low. One of the approaches to increase the stability of generally used polymer electrolyte membranes such as Nafion against swelling or thermal degradation is to bond it with an inorganic material physically or chemically. In Noritake Company, we have developed a novel method of reinforcing the polymer electrolyte matrix with inorganic fibers. Methanol crossover values measured were significantly lower than the original polymer electrolyte membranes. These fiber reinforced electrolyte membranes (FREM) were used for DMFC study and stable power output values as high 160 mW/cm^2 were measured. The details of the characteristics of the membranes as well as I-V data of fuel cell stacks are detailed in the paper.

Keywords: *DMFC, electrolyte membranes, hybrid membranes, swelling resistance, fuel cell*

1. Introduction

A direct methanol fuel cell uses a proton selective membrane as electrolyte to separate the cathode and anode sides of the cell. The membrane in principle should conduct only protons, but in practice it allows significant amount of methanol crossover to the cathode side. This problem arises because of the swelling of the polymer electrolyte normally used as the membrane. Swelling and associated non-selective permeation is in general a severe problem affecting most of the organic membranes. Processing of hybrids/composites with inorganic materials is considered as the best method to control swelling behavior of polymers. Several studies are reported in the literature regarding the processing of such composites of Nafion and other electrolyte polymers with inorganic materials such as silica, ZrP, etc[1-5]. Our group has also studied the processing of such membranes in the past. Improvement in fuel cell behavior was found in most cases just as reported in the literature. However, there were several processing problems of which the ability to make membranes with good repeatability was the most severe. Therefore, we have adopted two other strategies.

One strategy to improve performance is called pore-filling method. This method developed by Yamaguchi et al., of University of Tokyo, Japan involves the incorporation of new generation polymer electrolytes in the pores of an inorganic mesoporous membrane. Membranes with good proton conductivity and very low methanol crossover values could be processed by the method. The processing of the membrane and the properties are detailed elsewhere[6-8].

The second strategy developed in Noritake involves the reinforcing of polymer electrolyte matrix with inorganic fibers (hereafter mentioned as Fiber Reinforced Electrolyte Membrane, FREM)[9,10] to control swelling of the polymer electrolyte material. Swelling has two deteriorating effects on the fuel cell membrane behavior. On one hand swelling will increase crossover

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of methanol fuel to the cathode side and on the other hand swelling will damage the 3-phase interface between the electrode, electrolyte and the catalyst. We have used fibrous inorganic materials to reinforce the polymer matrix and thereby reduced swelling and shape deterioration. Consequently, these hybrid electrolyte membranes showed methanol crossover significantly lower than polymer electrolyte membranes. These, fiber reinforced electrolyte membranes (FREM) were used for DMFC study and stable power output values as high 160 mW/cm^2 were measured. The details of the characteristics of the membranes as well as I-V data of fuel cell stacks are detailed in this paper.

2. Experimental

Nafion® was used as the polymer electrolyte material. Nafion® polymer dispersion obtained from E.I. du Pont de Nemours Company was used without any pretreatment. Silica based inorganic fibers with diameter in the range 2-3 μm were used to reinforce Nafion matrix. FREM films with thickness <50 μm were cast in PTFE trays. The cast films were heat-treated in controlled atmosphere to obtain thin films of the hybrid electrolyte membranes.

FREM films were characterized in terms of shape stability. For shape stability study, FREM films and Nafion membranes of identical thickness were immersed in water and 1 mol/ℓ methanol solution for a given time and the membrane area change was measured.

Nafion membranes were made by casting Nafion solution (similar to the one used for FREM processing) in PTFE trays. Heat-treated Nafion films were used for shape stability study as well as fuel cell testing. Membrane electrode assembly's (MEA) of Nafion and FREM for the fuel cell testing were prepared as follows.

MEA's were prepared by fixing the membranes between two porous carbon paper electrodes. The electrodes were prepared by coating the carbon paper with carbon black/catalyst slurry. Pt/Ru was used as the anode side catalyst and Pt was used as the cathode side catalyst. Platinum loading of about 0.8 mg/cm^2 was used in both electrodes. MEA area used in the study was 25 cm^2.

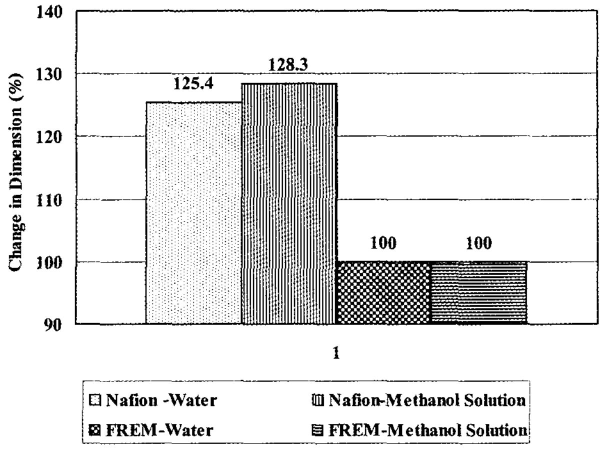


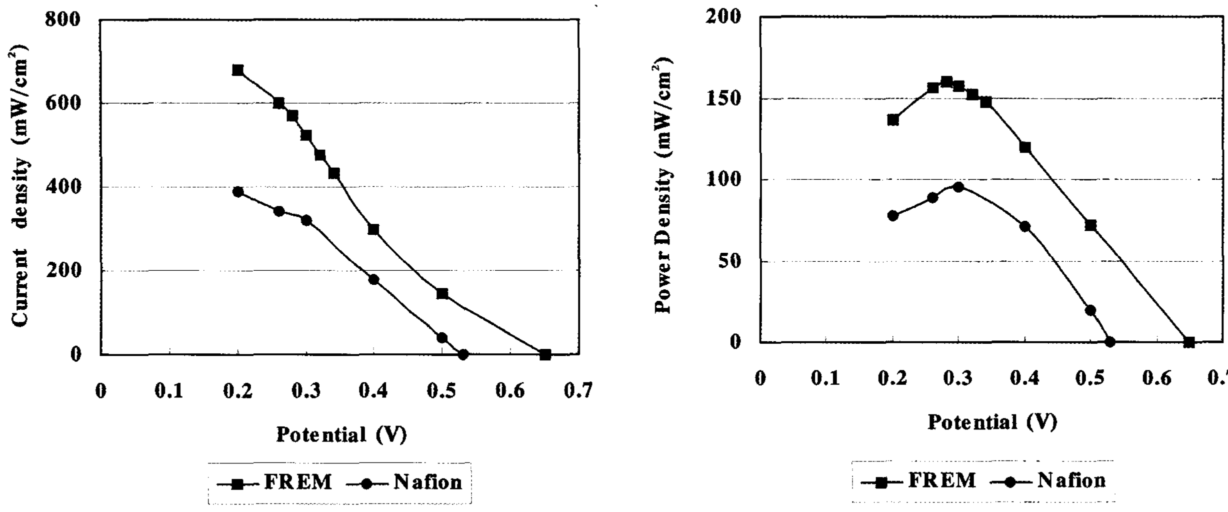
Fig. 1. Histogram showing arbitrary values of shape stability of FREM membranes in comparison with Nafion membranes of similar thickness. Area of films were measured before and after wetting with solvent mentioned in the figure legend "Methanol solution used was 1 mol/ℓ solution".

Thus prepared MEA's were used for fuel cell testing. Single cells were prepared by holding the MEA between two unique separators made of graphite. The cells were held between metallic end plates connected with standard fuel cell testing apparatus and I-V curves were plotted. Methanol feed concentration was 2 mol/liter and measurement temperature was 95°C. Oxygen was used as the cathode side gas and was fed at atmospheric pressure.

Methanol crossover was measured by analyzing methanol concentration in the cathode exit of the membrane. Samples were collected and gas chromatographic testing was carried out to measure the concentration of methanol in the cathode exit.

4. Results and Discussion

FREM membranes were prepared and microscopic evaluations were performed to identify pinholes and gas bubbles in the membrane. It was found that membrane films with rather large areas (~300 cm^2) could be produced without any visible defects. The results of shape stability analysis are shown in Fig. 1.



(a) (b)

Fig. 2. (a) Current-Voltage curves and (b) Power-Voltage curves corresponding to FREM and Nafion membranes. Testing temperature was 95°C. 2 mol/ℓ methanol solution was used in the anode side and Oxygen was used in the cathode side.

It is shown that FREM membranes showed no change in surface area after immersing in water and methanol. Compared to this, Nafion membranes of similar thickness showed an increase in surface area of about 25~30%. It is clear from the data in Fig. 1 that FREM membranes have good shape stability as well as good resistance against swelling compared to Nafion membranes.

Fuel-cell tests were carried out using MEA's made of FREM films as well as Nafion films. The testing conditions were detailed in the experimental section. The results are shown in Fig. 2 (a &b). Typical values of power output were much higher than that of Nafion membranes of similar thickness. The values shown for Nafion membranes might be lower than some other published reports. One reason might be the inferior quality of the Nafion membrane made in our group. Another reason could be attributed to the difference in catalyst concentration and separator design adopted in our research work. Yet, the power output values measured using FREM incorporated MEA's such as the 160 mW/cm^2 measured at 300 mV is considerably higher than most of the published results on DMFC made with Nafion based MEA.

A comparison of methanol crossover values is shown in Fig. 3. The methanol concentration values were

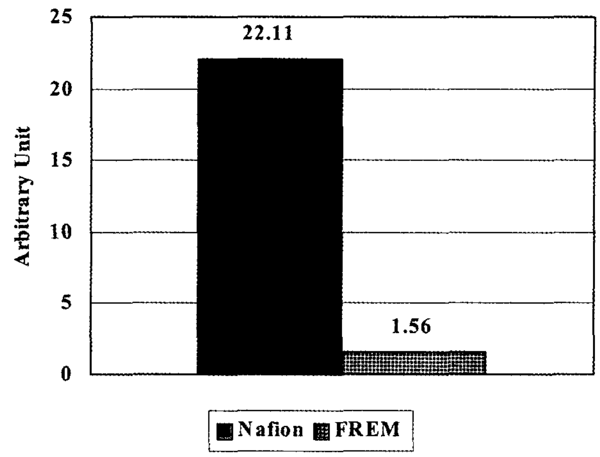


Fig. 3. Histogram showing arbitrary values of methanol-crossover of FREM membranes in comparison with Nafion membranes of similar thickness.

measured under the fuel cell testing condition. So, the ratio of the absolute values of crossover due to membrane swelling might be lower than the value shown in Fig. 3. However, the data in Fig. 3 clearly indicate the better performance of FREM compared to Nafion membranes. It should be noted that FREM also contains Nafion as the organic phase of the electrolyte membrane material. So, it can be concluded that fiber reinforcement of the polymer electrolyte should have provided it with swelling control ability.

5. Conclusions

A novel approach to fabricate proton conducting electrolyte membranes for Direct Methanol Fuel Cell (DMFC) application is detailed. In the example Nafion electrolyte was reinforced with inorganic fibers. Such Fiber Reinforced Electrolyte Membranes (FREM) showed good shape stability and good resistance against swelling. Fuel cell testing was carried out using these membranes. Peak power output values as high as 160 mW/cm^2 were measured.

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