PVA/PSSA-MA와 실리카 나노파티클을 이용한 수소이온교환막

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Proton Exchange Membranes using PVA(poly(vinyl alcohol))/PSSA-MA(poly(styrene sulfonic acid-co-maleic acid)) and Silica nano-particles

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Introduction

The direct methanol fuel cells (DMFCs) have attracted considerable interest because DMFCs are a promising power source for clean energy and are expected to be a portable power source. However, DMFC performance is limited by several problems. Particularly, the methanol crossover from the anode to the cathode side across the polymer electrolyte membrane is one of the most serious problems in DMFCs, inducing the decrease in performance of the DMFCs. Therefore, in order to improve the DMFCs performance, it will be necessary to eliminate or, at least, to reduce the methanol crossover [1-5].

In this study, proton exchange membranes (PEMs) were successfully made via a polymer blend of water soluble PVA(poly(vinyl alcohol))/PSSA-MA(poly (styrene sulfonic acid-co-maleic acid)) for DMFC application. In addition, we also incorporated inorganic nano-particles, which can form the network with each other, and also with polar polymeric groups in the membrane, to achieve the reduction of methanol permeability as well as the enhancement of thermal and mechanical properties. The degree of swelling of the PVA/PSSA-MA/SiO_2 membranes was effectively controlled via successive thermal and chemical treatments.

Experimental

Aqueous polymer solutions(i.e. 5 wt.% PVA and 30 wt.% PSSA-MA) were prepared by dissolving dry polymer in water at 90 °C and at room temperature, respectively. To facilitate interaction between PVA and PSSA-MA, PSSA-MA was transformed from Na^+ form to H^+ form by using cation exchange resin and then purified with a filter paper. Aqueous PVA and PSSA-MA solutions were blended with 1/1.5 ($W_{PVA}/W_{PSSA-MA}$) ratio of solid polymer weight and various amounts of silica nano-particles by weight or volume were added into the polymer blend solutions. And then, the mixtures were vigorously stirred at room temperature for 24h. After that, the PVA/PSSA-MA/SiO_2 blend membranes were prepared by pouring the blended solutions to Petri dishes and evaporating the water at room temperature for more than 2 days. The cast membranes were heated at 100 °C in an oven for about 2h to induce thermal crosslinking between the alcohol groups of PVA. Moreover, in order to induce chemical crosslinking, the PVA blend membranes were soaked in glutaraldehyde (GA)/HCl/acetone solution (1.0 wt.% GA) at 50 °C for 3h. Then the blend membranes were immersed overnight in acetone to remove impurities and then stored in distilled water before use. The thickness of the PVA blend membranes was in the range of 90-130 μm.

Results and Discussion

Fig. 1 shows the solvent swelling ratios of Nafion 117 and the PVA blend membranes as a function of methanol concentration. When the membranes were swelled in pure water, the swelling ratios of the PVA blend membranes were somewhat higher than that of Nafion 117 due to their high fixed charge concentration. However, the PVA blend membranes show relatively low increase of solvent uptake with an increase in the methanol content. Moreover, the swelling ratios of PVA blend membrane slightly decrease above 20 wt.% methanol content, and thus they are approximately two times lower than that of Nafion 117 at 100 % methanol content. This result strongly supports that the PVA matrix can function as an effective methanol barrier. Additionally, the swelling ratios of the membranes were slightly more reduced with increasing silica nanoparticles content. This is due to the decreased free volume capable of containing water and methanol molecules by increasing silica content.

The proton conductivity data for the chemically crosslinked membranes with different silica contents obtained at elevated temperatures are plotted in Fig. 2(a). Even though the membranes were chemically crosslinked, the proton conductivities were high enough for fuel cell applications. Both membranes show very similar temperature dependency of proton conductivity. However, the activation energy value of the PVA blend membranes is somewhat lower than that of Nafion 117. Fig. 2(b) presents the results of the methanol permeability measurement. The methanol permeability of the PVA blend membranes was much lower than that of Nafion 117, and also gradually reduced with an increase in the silica content.

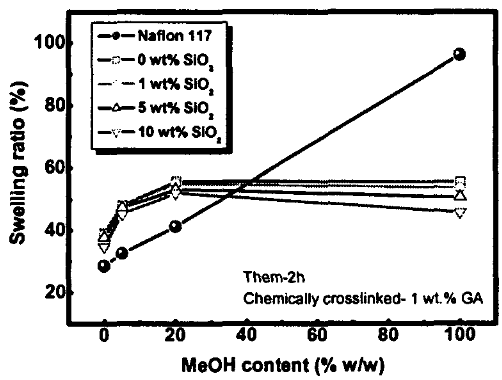

Fig. 1. Solvent swelling ratio of Nafion 117 and PVA/PSSA-MA/SiO2 membranes as a function of methanol concentration.

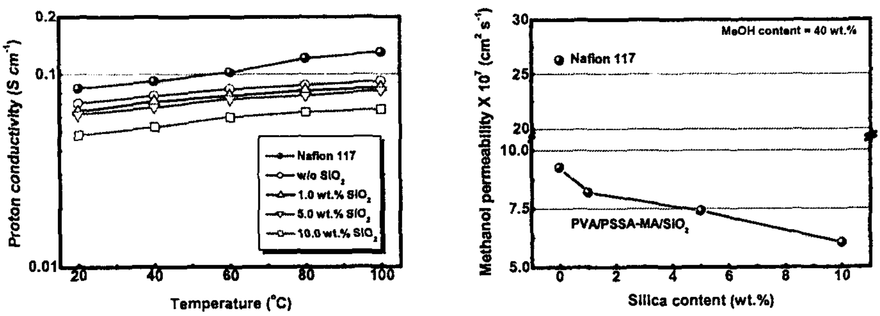

Fig. 2. (a) Proton conductivity and (b) methanol permeability of Nafion 117 and PVA/PSSA-MA/SiO_2 membranes.

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