Proton Exchange Membranes using Polymer Blends of PVA(Polyvinyl alcohol)/PSSA-MA(Polystyrene sulfonic acid-co-maleic acid)

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1. Introduction

Reduction of methanol crossover in proton exchange membranes (PEMs) can be achieved by 1) the selection of materials, 2) the morphology control, and 3) the adequate crosslinking [1,2]. The selection of polymer matrix of PEM for direct methanol fuel cells (DMFCs) is very important because the proton conductivity and methanol permeability are largely dependent upon the properties of polymers. For an example of good selection of polymer matrix, poly(vinyl alcohol) (PVA) seems to be a very attracting polymer for PEM because this polymer can function as a methanol barrier [3]. As well known, PVA also has both excellent mechanical property and chemical stability which are adequate for preparing PEMs. Moreover, high hydrophilicity of this polymer can improve the transport of protons through the membrane.

Recently, Kang et al. reported the preparation of a highly water-swollen type of PVA/poly(styrene sulfonic acid-co-maleic acid) (PVA/PSSA-MA) cation-exchange membranes for separation of large molecular cations [4,5]. It was reported that the PVA/PSSA-MA membranes exhibit excellent electrochemical properties for large molecular cations due to the relatively loose structure and high fixed charge density. Since a maleic acid has two ion-exchangeable sites and exhibits the lower water uptake probability than that of the sulfonic acid group, the introduction of maleic acid group into PSSA can significantly increase the membrane charge density and also prevent excessive swelling [5] Moreover, crosslinking of PVA via successive thermal and chemical treatments was shown very easy to be controlled, dominating the transport

phenomena in the membrane [4,5]. The aim of this study is to prepare proton exchange membranes with both high proton conductivity and low methanol permeability for DMFC applications. The proton exchange membranes having optimized properties were prepared via polymer blending of PVA and acid polymer (AP, i.e., PSSA and PSSA-MA). The effects of PVA contents, maleic acid groups, and structural feature, particularly of the water cluster size, on proton conductivity and methanol permeability are investigated in this study by assessing the membrane performances and characterizing their structures.

2. Experimental

PVA (99% hydrolyzed; Avg. M_w = 89,000-98,000 g mol^{-1}; Aldrich), PSSA (H^+-form, 30 wt.% in water; Avg. M_w = 20,000 g mol^{-1}; Polysciences Inc.), and PSSA-MA (sodium salt, mole ratio (styrene sulfonic acid : maleic acid) = 3:1 and 1:1, Avg. M_w = 20,000 g mol^{-1}, Aldrich) were used to prepare cation-exchange membranes without further purification. PVA and PSSA(-MA) aqueous solutions were mixed with various ratios of solid polymer weight. The selected blend ratios of PVA and PSSA(-MA) were 12/1, 6/1, 3/1 and 1/1. The membranes were prepared by pouring the blended solutions onto Petri dishes (diameter = 9 cm) and evaporating the water at room temperature for more than 5 days. The prepared membranes were annealed at 100 °C in an oven for about 3 hours to induce physical crosslinking. After the physical crosslinking, some of them were soaked in glutaraldehyde (GA)/HCl/acetone solution at 40 °C for 3 hours in order to reduce the water uptake by chemical crosslinking. The selected GA concentration was 1.0 wt.%. Then the membranes were immersed overnight in distilled water to remove impurities and then stored in 1.0 mol dm^{-3} HCl solution for further characterizations. FT-IR analysis, ion-exchange capacity (IEC), solvent uptake, proton conductivity, methanol permeability, and synchrotron small-angle X-ray scattering (SAXS) measurements were performed for the characterizations of the prepared membranes.

3. Results and Discussion

Using PVA and PSSA(-MA), homogeneous cation exchange membranes (thickness ≈ 100-150 μm) were prepared, and they exhibited reasonable mechanical strength to form a solid film. **Figure 1** shows the solvent swelling ratio (SSR) of Nafion 117 and PVA/PSSA-MA membranes as a function of methanol concentration. Intrinsic SSR (swelled in pure water) of PVA/PSSA-MA membrane is somewhat higher than that of

Nafion 117 due to its high fixed charge concentration. However, PVA/PSSA-MA membrane shows relatively low increase in methanol uptake with an increase in the methanol concentration. Interestingly enough, SSRs of PVA/PSSA-MA membrane slightly decrease above 20 % methanol content, and thus they are two times lower than that of Nafion 117 at 100 % methanol content. This result clearly demonstrates that PVA matrix can function as an effective methanol barrier.

Proton conductivities are largely dependent upon the contents of strongly acidic – $SO_3^-H^+$ groups. Although PVA/PSSA membrane presents high proton conductivity ($\sim$0.10 S cm^{-1}) at high AP content (i.e. $W_{PVA}/W_{Acid\,polym}$=1.0), the membrane also reveals very poor mechanical property. Meanwhile, PVA/PSSA-MA membrane (3:1 mole ratio (sty:maleic)) shows both strong mechanical property and excellent proton conductivity ($\sim$0.095 S cm^{-1}, at $W_{PVA}/W_{Acid\,polym}$=1.0) whish is comparable to that of Nafion117. The methanol permeabilites of PVA/PSSA-MA membrane are at least 10-fold lower than those of Nafion 117 in all MeOH concentration ranges. The increase of MeOH concentration from 15 to 40 % intriguingly leads to the slight decrease of MeOH permeability through PVA/PSSA-MA membrane, which is consistent with the results of SSRs.

From the results of proton conductivity and methanol permeability, we could calculate the selectivity parameter (Φ) to directly compare the applicability for DMFCs between the membranes. **Figure 2** shows the selectivity parameters of Nafion 117 and PVA/PSSA-MA membranes as a function of methanol feed concentration. The results show that the selectivity parameter of PVA/PSSA-MA membrane (Φ (b)) is at least 7-fold higher than that of Nafion 117 (Φ (a)) in the range of MeOH concentration considered.
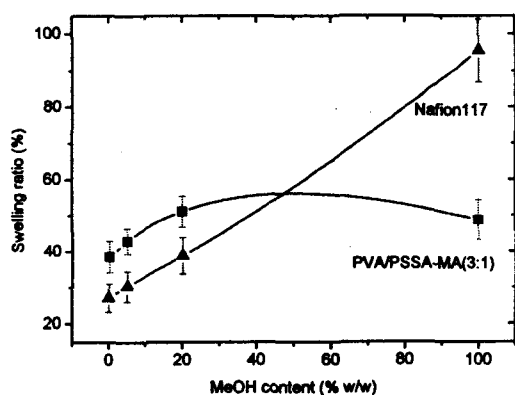
Figure 1. Solvent swelling ratio of Nafion 117 and PVA/PSSA-MA membranes as a function of methanol concentration.
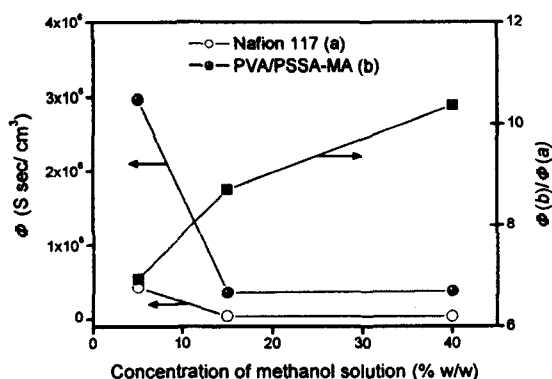
Figure 2. Selectivity parameter ($\Phi = \sigma/(P_{MeOH})$) of Nafion 117 and PVA/PSSA-MA membranes as a function of methanol concentration.

4. Conclusions

Novel PEMs using polymer blending of poly(vinyl alcohol)/AP (i.e. poly(styrene sulfonic acid-co-maleic acid)) have been prepared and characterized for DMFC applications. Crosslinked PVA/AP membranes were characterized in terms of water/methanol swelling ratio, methanol crossover, proton conductivity, and small-angle X-ray scattering (SAXS) behaviors. From the results, the degrees of swelling of PVA/AP membranes were effectively controlled by varying the membrane compositions (i.e. PVA/AP ratio, mole ratios of maleic acid groups to sulfonic acid groups in AP). Regular-sized water clusters (~42.8 Å) were observed in the SAXS profile of crosslinked PVA/PSSA-MA membrane. The PVA based membranes showed low increase in methanol uptake with an increase in methanol concentration. Crosslinked PVA/PSSA-MA membranes show both very excellent proton conductivity (~0.1 S cm^{-1}) and low methanol permeability (2.53×10^{-7} cm^2 sec^{-1} in 40 % w/w methanol solution). The results showed that the crosslinked PVA/PSSA-MA membranes are very applicable for DMFCs.

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