

Preparation of Ion Exchange Membranes for Fuel Cell Based on Crosslinked Poly(vinyl alcohol) with Poly(acrylic acid-co-maleic acid)

Dae Sik Kim, Ho Bum Park, Chang Hyun Lee, and Young Moo Lee

National Research Laboratory for Membranes, School of Chemical Engineering, College of Engineering, Hanyang University, Seoul 133-791, Korea

Go Young Moon

CRD, Research Park, LG Chem., 104-1, Moonji-dong, Yusung-Gu, Daejeon 305-380, Korea

Sang Yong Nam

Department of Polymer Science and Engineering, Engineering Research Institute, Gyeongsang National University, Jinju 660-701, Korea

Ho Sang Hwang, Tae Il Yun, and Ji Won Rhim*

Department of Chemical Engineering, Hannam University, Daejeon 306-791, Korea

Received March 14, 2005; Revised July 18, 2005

Abstract: Crosslinked poly(vinyl alcohol) (PVA) membranes were prepared at various crosslinking temperatures using poly(acrylic acid-co-maleic acid) (PAM) containing different PAM contents. The thermal properties of these PVA/PAM membranes prepared at various reaction temperatures were characterized using differential scanning calorimetry (DSC). The proton conductivity and methanol permeability of PVA/PAM membranes were then investigated as PAM content was varied from 3 to 13 wt%. It was found that the proton and methanol transport were dependent on PAM content in their function both as crosslinking agent and as donor of hydrophilic -COOH groups. Both these properties decreased monotonously with increasing PAM concentration. The proton conductivities of these PVA/PAM membranes were in the range from 10^{-3} to 10^{-2} S/cm and the methanol permeabilities from 10^{-7} to 10^{-6} cm²/sec. In addition, the effect of operating temperature up to 80 °C on ion conductivity was examined for three selected membranes: 7, 9 and 11 wt% PAM membranes. Ion conductivity increased with increasing operating temperature and showed a maximum at 80 °C, respectively. The effects of crosslinking and ionomer group concentration were also examined in terms of water content, ion exchange capacity (IEC), and fixed ion concentration. In addition, the number of water molecules per ionomer site was calculated using both water contents and IEC values. With overall consideration for all the properties measured in this study, 7-9 wt% PAM membrane prepared at 140 °C exhibited the best performance. These characteristics of PVA/PAM membranes are desirable in applications related to the direct methanol fuel cell (DMFC).

Keywords: ionomeric membranes, proton conductivity, methanol permeability, crosslinked poly(vinyl alcohol) membranes, poly(acrylic acid-co-maleic acid), direct methanol fuel cell.

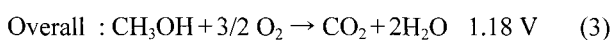
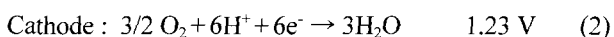
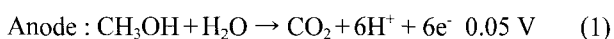
Introduction

Today, the air pollution level is mainly due to internal combustion motor vehicles. Fuel cells represent a promising alternative for portable power generation and transportation. Amongst the different types of such systems, direct methanol fuel cells (DMFC) take advantage of a higher energy density per unit volume with respect to hydrogen-fed units,

so-called solid polymer electrolyte fuel cells (SPEFC). Therefore, DMFC consisting of a polymer electrolyte membrane (PEM) has the attraction of no liquid acidic or alkaline electrolyte and uses methanol.

The DMFC is a three-phase electrochemical reactor involving simultaneous mass, charge, and energy transfer. It generates electrical energy by electrochemical oxidation of methanol at moderate temperatures. Methanol is oxidized to carbon dioxide at the anode and oxygen is reduced to water at the cathode as the following reaction scheme:¹

*Corresponding Author. E-mail: jwrhim@mail.hannam.ac.kr



It is reported that the liquid feed system of methanol/water mixtures shows better performance than the vapor system since the conductivity decreases with decreasing water content in the membrane. The water in the liquid system acts as a carrier for the reactant methanol and serves for the removal of excess heat.¹

The major problems of the DMFC are the poor anode kinetics, the undesired methanol crossover through the PEM, and the blockage of the anode structure by released bubbles of carbon dioxide as can be seen in eqs. (1) and (3). At concentrations higher than 2 mol/dm³, the cell voltage declines significantly due to the permeation of methanol crossover. This permeation results in a mixed potential at the cathode with a significant loss in oxygen reduction performance and also poor fuel utilization. Thus, an important field to improve the DMFC performance is in PEM.² In general, the PEM has the sulfonic acid ionic group for the protons to pass through the membranes easily, which its ion exchange capacity (IEC) is between 1.4 and 1.7 at least to get low ionic resistances.³ The uncrosslinked sulfonated membranes at aforementioned IEC ranges showed high swelling ratio which led to poor mechanical properties and low ion permselectivity, and thus disqualified them for the application in electromembrane processes. To date the vast majority of PEM fuel cell work has been performed using Nafion even though it had significant disadvantages for the applications such as methanol crossover rate of 100 mA/cm² resulted in cathode performance decay and the loss of fuel, thermal stability beyond 100 °C and relative expensive prices due to fluorine-based synthesis.⁴ There have been several attempts to explore other membranes to overcome the disadvantages of NafionTM for use in DMFCs. One of them is to use basic polymers of poly(benzimidazole) (PBI) and poly(acrylamide) (PAAm) doped with inorganic acids.⁴ PBI membranes showed a tenfold decrease in methanol crossover compared with NafionTM, satisfactory thermal stability and cheaper price.⁵ Cussler *et al.*⁶ investigated pervaporation membranes to look for good methanol barriers and proton conductivity. They concluded that pervaporation membranes offered no significant advantages over NafionTM in DMFC application.

In this paper, we focused on the proton conductivity and the methanol permeability of crosslinked PVA membrane containing carboxylic groups under different crosslinking conditions as a proton exchange membrane for future DMFC applications. To look for both effective proton conductors and methanol barriers, poly(vinyl alcohol) (PVA) was considered. In particular, PVA membranes have been used in

the pervaporation dehydration of alcohols mixture and in direct methanol fuel cell because they selectively pass water molecules over ethanol or methanol.⁷⁻⁹ Since PVA is water soluble polymer and poor proton conductor, poly(acrylic acid-co-maleic acid) (PAM) with a low molecular weight of 3,000 which had tetra-carboxylic acid in its repeating unit was used to give the ion exchange capability and to prevent the methanol crossover through crosslinking. This system of a base polymer PVA and a crosslinker PAM (M.W. 70,000) has been investigated for the pervaporation dehydration of light oil.¹⁰ Also the prepared membranes have been performed successfully in pervaporation of water-ethanol mixtures by authors.¹¹

The crosslinking temperature and the content of PAM were controlled to seek the best performance in terms of methanol crossover and ion conductivity measurements. The water contents, IEC values and the fixed ion concentration measurements of the resulting membranes were carried out.

Experimental

Materials. The fully hydrolyzed PVA with a molecular weight of 89,000 and the PAM with a molecular weight of 3,000 as a crosslinking agent and as a donor of the hydrophilic property were purchased from Aldrich Chemical Co., Milwaukee, WI, USA. Methanol was analytical grade from Merck (Darmstadt, Germany). The water used was the ultrapure produced from Younglin Pure Water System (Seoul, Korea).

Membrane Preparation. Aqueous 10 wt% PVA solutions were prepared by dissolving preweighed quantities of dry PVA in ultrapure water and heating at 90 °C for at least 6 h. Aqueous 10 wt% PAM solutions were diluted from an original 50 wt%. Then two solutions were mixed together by varying each component composition to form a homogeneous solution for at least 1 day at room temperature. Homogeneous membranes were cast onto a Plexiglass plate using a Gardner knife with predetermined drawdown thickness. The membranes were allowed to be dried in air at room temperature, and completely dried membranes were then peeled off. The dried and blended membranes were then heated in a thermosetted oven at desired temperatures for 1 h to induce crosslinking reaction. The thickness of the resulting membranes showed 100~150 μm.

Differential Scanning Calorimetry (DSC). The thermal properties of PVA/PAM membranes were measured by a DSC 2010 thermal analyzer (TA instrument, New Castle, DE, USA) with a DSC module, purged with nitrogen gas, and quenched with liquid nitrogen. The specimens were scanned from 50 to 250 °C by a heating rate of 5 °C/min. The cell was calibrated using an indium standard. The weight of the sample was 10-15 mg.

Water Content. Water contents of the PVA/PAM membranes were measured using following method. The sorp-

tion capacity of the membrane was measured by immersing the membrane samples in the pure water at 25 °C. After being wiped with the cleansing tissue, the membranes were weighed as quickly as possible. This procedure was repeated about 10 times until satisfactory reproducibility was obtained. Then the samples were dried in a vacuum oven until a constant weight was obtained. Water content (W) was calculated as follows:

$$\text{Water content}(W) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} = \frac{\text{gH}_2\text{O}}{\text{g dry membrane}} \quad (4)$$

where W_{wet} and W_{dry} are the wet and dry membrane weights, respectively.

Ion Exchange Capacity (IEC) and Fixed Ion Concentration. The ion exchange capacity (IEC) was measured by the classical titration (ASTM 2187) of the released amount of H^+ of the pre-weighed polymer in an acid form in 1 M NaCl with 0.01 M NaOH by using a phenolphthalein indicator. The IEC value was recorded as an average value for each sample in units of milliequivalents NaOH per gram of the polymer (meq/g).

A fixed ion concentration (A_w) can be calculated from the following equation:

$$A_w = \text{IEC}/W \quad (5)$$

where W is water content.

Proton Conductivity. Proton conductivity in hydrated PVA/PAM membranes is normally measured with a four-point probe technique. The impedance of membrane was determined by Full Material Impedance System 12608W consisted of a Frequency Response Analyzer 1260 and Electrochemical Interface 1287 (Solatron analytical). Each sample for the measurement was prepared with the surface area of $4 \times 1 \text{ cm}^2$ and the membrane thickness of 100 to 150 μm . The proton conductivity was obtained by a following equation.

$$\sigma = l/(R \times S) \quad (6)$$

where σ is the proton conductivity (S/cm), l is the distance between the electrodes used to measure the potential (1 cm), R is the impedance of membrane (Ω), and S is the surface area for a proton to penetrate through the membrane (cm^2). The impedance of each sample was measured five times to ensure good data reproducibility.

Methanol Permeability. The diffusion cell shown in Figure 1 was used to determine methanol permeability of the PVA/PAM membranes. This glass cell consisted of two chambers each approximately 35 mL, separated by a vertical membrane. One compartment of the cell (V_A) was filled with a 2 M solution of methanol in deionized water. The

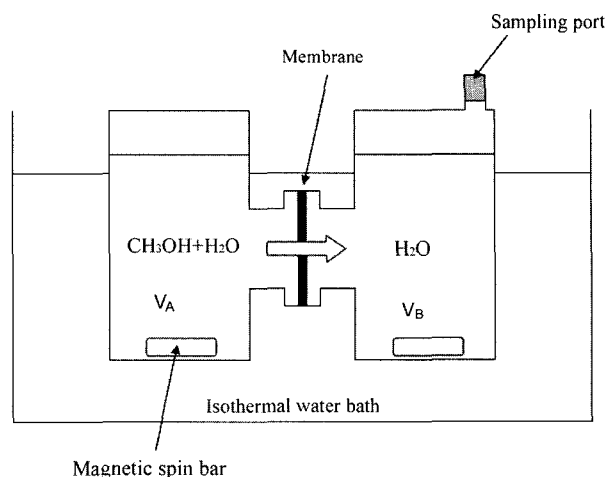


Figure 1. Two chamber diffusion cells used to measure methanol permeability through PVA/PAM membranes in this study.

other (V_B) was filled with pure ionized water. The membrane (effective area 7.02 cm^2) was clamped between the two compartments and these were kept under stirring during an experiment. A flux of methanol penetrates across the membrane as a result of the concentration difference between the two compartments. Under pseudosteady-state conditions, which prevailed during our experiments and for $c_A \gg c_B$, the methanol concentration in the receiving compartment as a function of time is given by:

$$c_B(t) = \frac{A DK}{V_B L} c_A(t-t_0) \quad (7)$$

where c is concentration, A and L the membrane area and thickness; D and K are the methanol diffusivity and partition coefficient between the membrane and the adjacent solution, respectively. The assumptions are made in this study that D inside the membrane is constant and K does not depend on concentration. The product DK is the membrane permeability (P).

$$P = \frac{1}{A} \cdot \frac{c_B(t)}{c_A(t-t_0)} \cdot V_B L \quad (8)$$

C_B is measured several times during the experiment and the permeability is calculated from the slope of the straight line. The methanol concentrations were measured by gas chromatography with a thermal conductivity detector (Shimadzu, model 14B, Tokyo, Japan). During permeability tests the temperature was controlled by means of a thermostatic water bath.

Results and Discussion

DSC Results. The thermal properties of PVA/PAM mem-

branes were simply investigated due to the practical importance in the performance of membranes in processes operating at elevated temperatures and also to provide fundamental information on polymer properties. Figure 2 illustrates the melting temperature (T_m) of prepared membranes (9% PAM in membranes) varied with the reaction temperature. As expected, T_m value increases with increasing the reaction temperature. It was reported that T_m of PVA homopolymer is known as about 180-190 °C.^{12,13} Starkweather¹⁴ carried out a study of the thermal studies of Nafion™ ionomers having different equivalent weights (EW, $g\ eq^{-1}$) ranging from 1,100 to 1,500. The T_m of Nafion™ membranes showed from 207 to 249 °C. Therefore, it may be desirable that the T_m 's of crosslinked 9% PAM membrane are over 200 °C as shown in Figure 2.

Water Content. The water contents for the PVA/PAM membranes as defined in eq. (4) are illustrated in Figure 3. As the reaction temperature increases, i.e. the crosslinking reaction precedes more to make the membranes more rigid and compact, the water content decreases. For the 3 wt% PAM in membranes, the water content decreases from 200 to 63% with increasing crosslinking temperature. In addition, the water content decreases as the PAM content increases. In this case, two factors of the crosslinking degree and the quantities of ionomer, -COOH, could be considered.⁹ If the effect of crosslinking degree is smaller than that of ionomer contents, the water content would increase. Therefore, it could be considered that the effect of crosslinking degree is larger than that of ionomer content. Nafion™ membranes have the water contents ranging from 24-33% depending on the content of sulfonic groups; typically Nafion 117 indicates 24-26%.¹⁵ For the membranes crosslinked 140 °C, it is ranged from 22-63% for different PAM content membranes. Both 7 and 9 wt% PAM membranes show the similar water contents of 36-24% with Nafion™ membranes.

IEC Values and Fixed Ion Concentrations. Figure 4

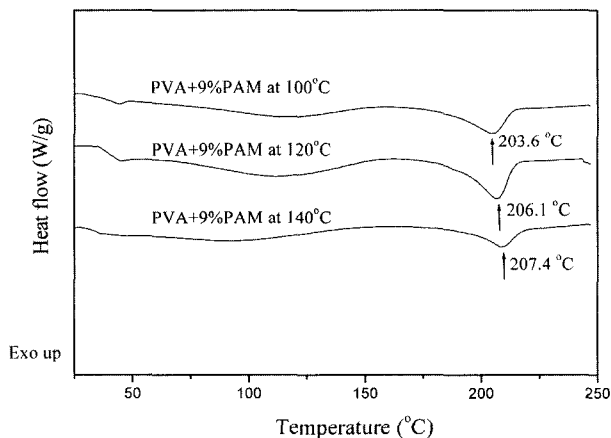


Figure 2. DSC melting curve of the PVA+9 wt% PAM membrane.

shows IEC values of PVA/PAM membranes as a function of PAM content (wt%). The prepared membranes indicated the ion exchange capacity of 0.59-1.66 meq/g dry membrane. Since PAM contains negative charged fix ion-carboxylation which led to increase proton exchange capacity, IEC values of PVA/PAM membranes crosslinked at 100, 120, and 140 °C increased with PAM contents. The more crosslinking between PVA and PAM by esterification occurred at elevated reaction temperature. Therefore, the lower IEC value can be found at higher reaction temperature due to the more reaction of carboxylic acid groups in repeating units of PAM polymer with hydroxyl groups in PVA. As a result, we expect that the proton conductivities of PVA/PAM membranes would increase with the IEC values, that is, PAM contents. However, this expectation is totally different when compared to the results of proton conductivity measurement. This behavior will be discussed in the following sections.

Figure 5 illustrates fixed ion concentration of PVA/PAM membranes as a function of PAM content. These values

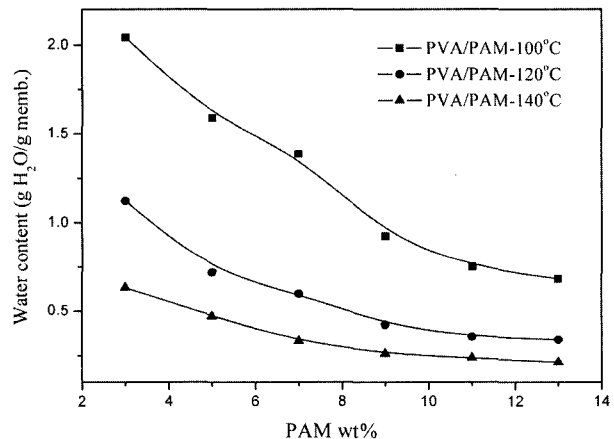


Figure 3. Water content vs. PAM wt%.

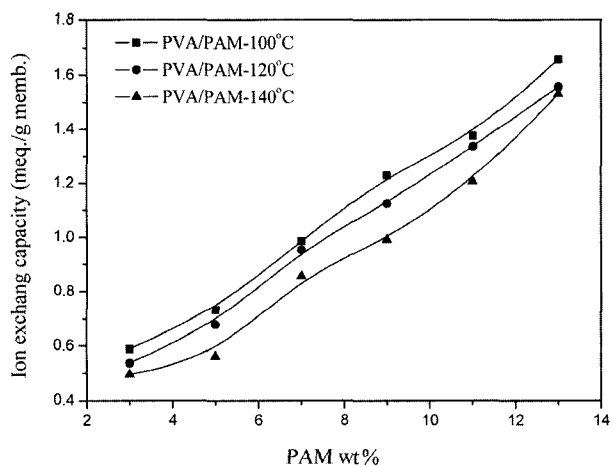


Figure 4. IEC values of PVA/PAM membranes as a function of PAM content (wt%).

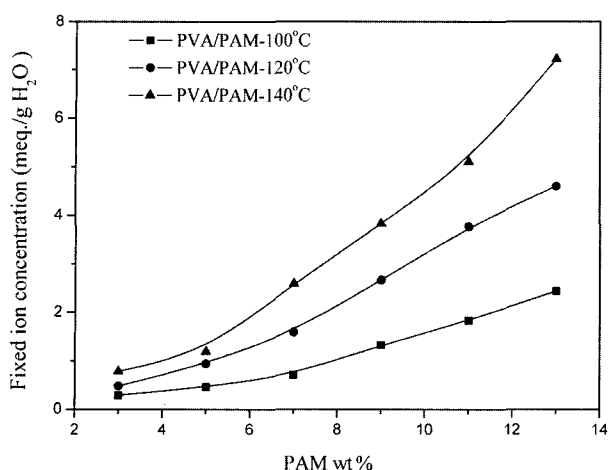


Figure 5. Fixed ion concentration of PVA/PAM membranes as a function of PAM content (wt%).

were taken from IEC values divided by total water contents. With an increase of the ion exchange capacity of the membranes, the fixed ion concentration increased. And also the fixed ion concentration showed the monotonous increase as PAM was added.

Buchi and Scherer¹⁵ investigated the relationship between water content in term of the number of water molecules per sulfonic site (λ) using the following equation;

$$\lambda = \frac{WC \times EW}{M_o} \quad (9)$$

where WC is the water content defined in previous section and EW is the equivalent weight (g eq^{-1}) and M_o is the molecular weight of water (18 g mol^{-1}).

For NafionTM membrane series, λ values showed 21-22 for N112, N115 and N117 and 27-28 for N105 membranes, respectively. When it is applied to our membranes, the calculated results are illustrated in Table I. In the viewpoint of the number of water molecules per ionomer site, it could be concluded that the membrane having higher PAM content is better when lower crosslinking temperature is applied and the membrane having lower PAM content is better when higher temperature is applied as the shaded boxes are indi-

cated in Table I. However, if the water content as another factor is considered to choose the best performance membrane, the membrane having 7-9 wt% PAM and crosslinked at 140°C could be a candidate.

Proton Conductivity. Figures 6 and 8 are plots of the proton conductivities as a function of PAM contents (wt%) and as a function of operating temperatures from 25 to 80°C for selected PVA/PAM membranes, respectively. The proton conductivities of PVA/PAM membranes lie in the range between 10^{-3} and 10^{-2} S/cm. As can be seen in Figure 6, although more introduction of PAM indicates more number of carboxylic acid groups PVA/PAM membranes, the proton conductivities decrease with increase of PAM contents in PVA. Simply, the proton conductivity depends on both content of crosslinking agent (PAM) and crosslinking temperature. Before a trial for the conductivity measurement, we could expect that increase of PAM content in PVA matrix might lead to the improvement of the proton conductivity because the amount of carboxylic acid groups ($-\text{COOH}$) in PVA matrix were increased. In addition, these expectations were based on IEC values of PVA/PAM membranes measured before the conductivity measurement. However, the contents of crosslinking agents turned out quite insensitive to the proton conductivity. It may be considered that the

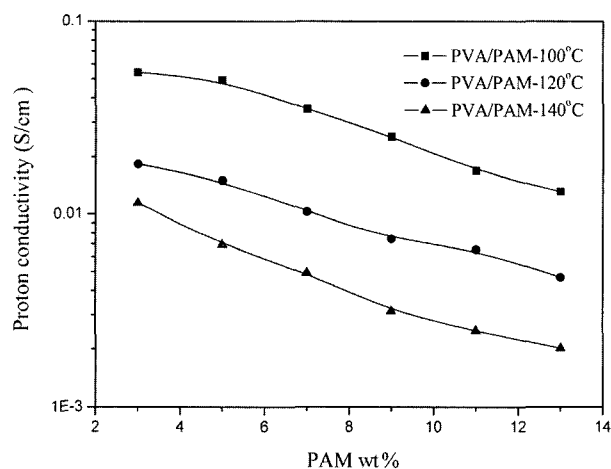


Figure 6. Proton conductivities of PVA/PAM membranes measured at 25°C as a function of PAM content (wt%).

Table I. Number of Water Molecules Per Ionomer Site ($-\text{COOH}$) Calculated by Using eq. (9)

PAM Contents (wt%)	100°C			120°C			140°C		
	WC	EW	λ	WC	EW	λ	WC	EW	λ
3	2.04	1700	193	1.22	1860	127	0.63	2020	71
5	1.59	1370	121	0.72	1470	59	0.47	1780	47
7	1.38	1010	78	0.60	1050	35	0.33	1170	21
9	0.93	810	42	0.42	890	21	0.26	1010	15
11	0.75	730	30	0.36	750	15	0.24	830	11
13	0.68	600	23	0.34	640	12	0.21	650	8

proton conductivity is controlled by the contents of PAM, different crosslinking temperature, and the intrinsic property of carboxylic acid as well. As the content of PAM in PVA matrix is increased, the polymer matrix would become more compact. The structural changes induced by the PAM were characterized using X-ray diffraction⁹ and shown in Figure 7. In general, when a polymer contains a crystalline region, then the X-ray diffraction peaks are sharp, and their intensities are high, whereas for an amorphous polymer they are broad.¹⁶ As shown in Figure 7, the crystallinity increased and d-value decreased with increase of PAM content due to the hydrogen bonding by carboxylic acid group. As a result, due to the less free volume in matrix, the proton transport would be restricted. We also confirmed this behavior in our previous study.^{9,17,18} Even if carboxylic acid is weak acid, in other words, the degree of dissociation is limited in water; the number of dissociated protons would increase with increasing the contents of crosslinking agents, PAM. Here we can say that only increase of IEC values by introduction of proton donating group in this proton exchange membranes are not main factor to increase the proton conductivities.^{9,18} That is, free volume being capable of containing water molecules in the polymeric structure should be seriously considered in the polymer design. When induced from the results of water content and proton conductivity, increase of crosslinking density in PVA/PAM membranes leads to reduction of free volume being able to associate water molecules and thus is followed by decrease of proton conductivity. Therefore, the crosslinking effect may be more dominant than those of the dissociation degree and the increase of the number of carboxylic acid group in this system. In order to obtain the desirable proton conductivity, the optimization between crosslinking density and appropriate IEC values should be achieved.

Figure 8 illustrates the effect of operating temperatures raised from 25 to 80°C on the proton conductivities of the membranes containing PAM contents, 7, 9, and 11% in PVA

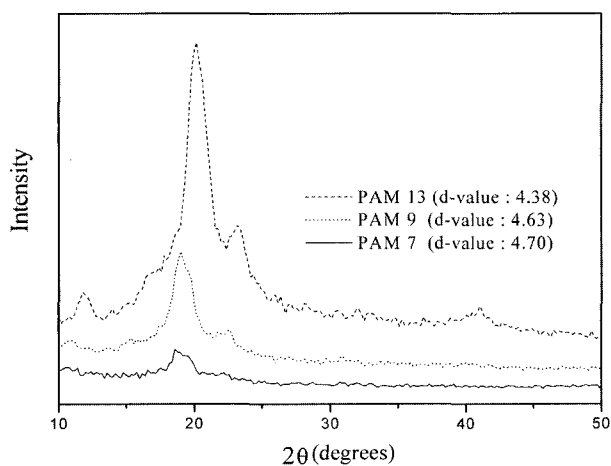


Figure 7. X-ray diffractograms of membranes.

crosslinked at 140°C. The proton conductivities increase with increasing temperature as expected. If the operating temperature is elevated, the polymer matrix structure would be loosen so that the protons can pass freely. In addition, at elevated temperature, the degree of dissociation of carboxylic acid groups would increase. Typically, at 80°C, the membrane containing PAM 7% shows the highest proton conductivity of 0.043 S/cm.

Methanol Permeability. Figure 9 shows the concentration of permeated methanol through Nafion 117 in the diffusion cell as a function of time. As can be seen in Figure 9, the methanol concentration through Nafion 117 increased linearly as a function of time, and the slope of concentration vs. time was 0.00854. Using the slope and eq. (8), the calculated methanol permeability of Nafion 117 at 25°C was 2.11×10^6 cm²/s. Following the same procedure, the methanol permeabilities for PVA/PAM membranes were calculated.

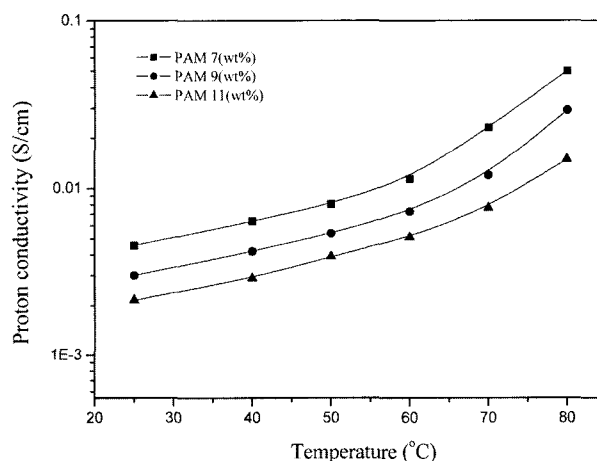


Figure 8. Proton conductivities of PVA/PAM membranes as a function of temperature (°C).

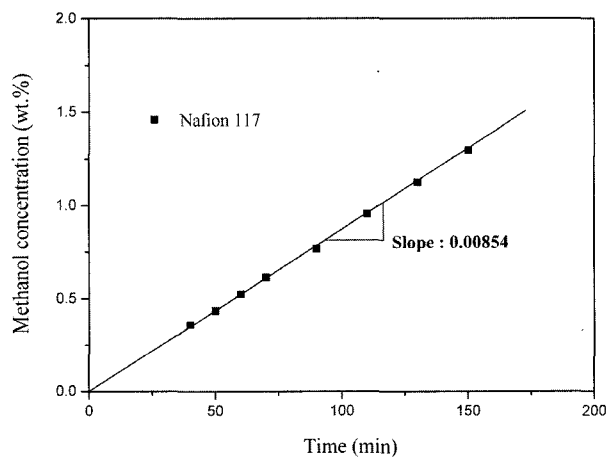


Figure 9. Typical diffusion data: the methanol-water solution was 2 M. The slope of this line is proportional to the methanol permeability.¹⁸

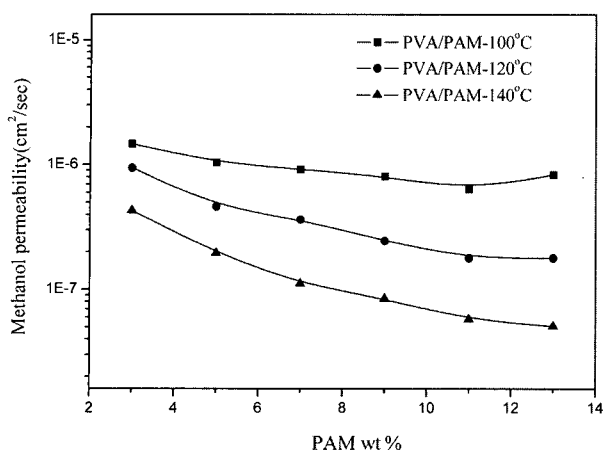


Figure 10. Methanol permeabilities of PVA/PAM membranes measured at 25 °C as a function of PAM content (wt%).

Figure 10 illustrates the methanol permeabilities as a function of PAM contents from 3 to 13 wt% treated at 100, 120, and 140 °C. As can be seen, the methanol permeability decreases with increasing PAM contents. There are two factors for this and they are crosslinking density and hydrophilic groups (-COOH) present in PAM. If the effect of the introduction of hydrophilic -COOH groups was more dominant than that of the crosslinking, the methanol permeability would increase with PAM contents due to the affinity between hydrophilic groups in membranes and permeates in feed solution. However, the results show the opposite trend, more seriously for the membranes crosslinked at 120 and 140 °C rather than at 100 °C. At higher crosslinking temperatures, it could be considered that the polymer matrix becomes more compact so that the permeability of methanol would be reduced. Thus, in this case, we can say that the effect of crosslinking degree is more controlled than that of the hydrophilic group.

Conclusions

Crosslinked poly(vinyl alcohol) (PVA) membranes were prepared at various crosslinking temperatures using poly(acrylic acid-*co*-maleic acid) (PAM) containing different PAM content. The PVA/PAM membranes were then investigated in relation to proton conductivity and methanol permeability in the PAM content from 3 to 13 wt% and in the temperature range from 25 to 80 °C. It was found that both these properties were very dependent on the effect of PAM content as a crosslinking agent and as a donor of hydrophilic COOH group. Both these properties decrease monotonously with increasing PAM concentration. The proton conductivities of these PVA/PAM membranes are in the range from 10⁻³ to 10⁻² S/cm and the methanol permeabilities are in the range from 10⁻⁷ to 10⁻⁶ cm²/sec. And also the

effect of operating temperature on ion conductivity up to 80 °C was carried out for selected membranes, 7, 9 and 11 wt% PAM membranes. Ion conductivity increases with increasing operating temperature and at 80 °C showed 5 × 10⁻², 2.9 × 10⁻², and 1.5 × 10⁻², respectively. Effects of crosslinking and a concentration of ionomer group were also discussed in terms of water content, ion exchange capacity (IEC), and a fixed ion concentration. In addition, number of water molecules per ionomer site was calculated using both water content and IEC values. In the viewpoint of all measured properties in this study, 7 wt% PAM membrane prepared at 140 °C exhibited the best performance. The methanol permeabilities through PVA/PAM membranes were linearly proportional to the proton conductivities.

Acknowledgements. This work was supported by Korea Research Foundation (KRF) (No: D00224).

References

- (1) K. Sundmacher and K. Scott, *Chem. Eng. Sci.*, **54**, 2927 (1999).
- (2) K. Scott, W. N. Taama, P. Argyropoulos, and K. Sundmacher, *J. Power Sources*, **83**, 204 (1999).
- (3) W. Cui, J. Kerres, and G. Eigenberger, *Sep. Purif. Tech.*, **14**, 145 (1998).
- (4) S. Wasmas and A. Kuver, *J. Electroanal. Chem.*, **461**, 14 (1999).
- (5) J.-T. Wang, J. S. Wainright, R. F. Savinell, and M. Litt, *J. Appl. Electrochem.*, **26**, 751 (1996).
- (6) B. S. Pivovar, Y. Wang, and E. L. Cussler, *J. Membr. Sci.*, **154**, 155 (1999).
- (7) J. W. Rhim and Y. K. Kim, *J. Appl. Polym. Sci.*, **75**, 1699 (2000).
- (8) J. W. Rhim, S. W. Lee, and Y. K. Kim, *J. Appl. Polym. Sci.*, **85**, 1867 (2002).
- (9) D. S. Kim, H. B. Park, J. W. Rhim, and Y. M. Lee, *J. Membr. Sci.*, **240**, 37 (2004).
- (10) S. Y. Nam, K. S. Sung, S. W. Chon, and J. W. Rhim, *Membrane J. (Korea)*, **12**, 255 (2002).
- (11) C. Vauclair, P. Achaetzel, R. Nobrega, and C. Habert, *J. Appl. Polym. Sci.*, **86**, 1709 (2002).
- (12) J. W. Rhim, M. Y. Dohn, H. J. Jo, and K. H. Lee, *J. Appl. Polym. Sci.*, **50**, 679 (1993).
- (13) J. W. Rhim, C. K. Yeom, and S. W. Kim, *J. Appl. Polym. Sci.*, **68**, 1717 (1998).
- (14) H. W. Starkweather, *Macromolecules*, **15**, 320 (1982).
- (15) F. N. Buchi and G. G. Sherer, *J. Electroanalytical Chemistry*, **404**, 37 (1996).
- (16) J. H. Kim and Y. M. Lee, *J. Membr. Sci.*, **193**, 209 (2001).
- (17) D. S. Kim, H. B. Park, J. W. Rhim, and Y. M. Lee, *Solid State Ionics*, **176**, 117 (2005).
- (18) J. W. Rhim, H. B. Park, C. S. Lee, J. H. Jun, D. S. Kim, and Y. M. Lee, *J. Membr. Sci.*, **238**, 143 (2004).