Preparation of ion exchange membranes for fuel cell based on crosslinked poly(vinyl alcohol) with poly(styrene sulfonic acid-co-maleic acid)

Kim, Dae Sik; Guiver, Michael D.; Nam, Sang Yong; Yun, Tae Il; Seo, Mu Young; Kim, Se Jin; Hwang, Ho Sang; Rhim, Ji Won

Publisher's version / Version de l'éditeur:
https://doi.org/10.1016/j.memsci.2006.03.025
Journal of Membrane Science, 281, 1-2, pp. 156-162, 2006-09-15

Available online at www.sciencedirect.com
ScienceDirect
Journal of Membrane Science 281 (2006) 156–162
journal of MEMBRANE SCIENCE
www.elsevier.com/locate/memsci

Preparation of ion exchange membranes for fuel cell based on crosslinked poly(vinyl alcohol) with poly(styrene sulfonic acid-*co*-maleic acid)

Dae Sik Kim [a], Michael D. Guiver [a], Sang Yong Nam [b], Tae Il Yun [c], Mu Young Seo [c], Se Jin Kim [c], Ho Sang Hwang [c], Ji Won Rhim [c,*]

[a] *Institute for Chemical Process and Environmental Technology, National Research Council, 1200 Montreal Road, Ottawa, Ont., Canada K1A 0R6*
[b] *Department of Polymer Science and Engineering, Gyeongsang National University, Chinju 660-701, Republic of Korea*
[c] *Department of Chemical Engineering, Hannam University, 133 Ojung-Dong, Daeduk-Gu, Daejon 306-791, Republic of Korea*

Received 19 January 2006; received in revised form 14 March 2006; accepted 16 March 2006
Available online 19 April 2006

Abstract

In the present study, crosslinked poly(vinyl alcohol) (PVA) membranes were prepared using poly(styrene sulfonic acid-*co*-maleic acid) (PSSA_MA) at different crosslinking temperatures. The crosslinked PVA membranes were prepared by varying the content of PSSA_MA (5–11 wt%). The PSSA_MA was used both as a crosslinking agent and as a donor of the hydrophilic group (–SO_3H and/or –COOH). The crosslinked PVA/PSSA_MA membranes were characterized using FT-IR spectroscopy, thermogravimetric analysis (TGA) and investigated in relation to proton conductivity and methanol permeability. The proton and methanol transport decreased with increasing the PSSA_MA content. The effect of crosslinking may be more dominant than that of the increase of the number of ionic exchange sites in this system. The proton conductivities and the methanol permeabilities of all the membranes were in the range of 10^{-3} to 10^{-2} S/cm and 10^{-7} to 10^{-6} cm^2/s, respectively, in the temperature range of 25–90 °C, depending on the crosslinking conditions.

Keywords: Proton conductivity; Methanol permeability; Crosslinked poly(vinyl alcohol) membranes; Poly(styrene sulfonic acid-*co*-maleic acid)

1. Introduction

Nafion, which is a perfluorosulfonated membrane with a hydrophobic fluorocarbon backbone and hydrophilic sulfonic pendent side chain, is the only commercially available and successfully used membrane in PEMFC applications [1]. Nafion has excellent proton conductivity, but it has been found that over 40% of methanol can be lost in direct methanol fuel cell (DMFC) across the membrane due to excessive swelling [2]. The proton transfer through the membrane is associated with the transport of water molecules through the membrane. Methanol can also be transported by an electro-osmotic drag (methanol crossover), which is due to selected physical properties of methanol such as its dipole moment, which consequently leads to a decrease in cell performance [3,4]. To improve the performance of a DMFC, it is necessary to reduce the loss of fuel across the cell [5]. It also requires highly proton conductive polymer membranes in order to obtain a high voltage per current density in the unit cell. Therefore, many researchers have focused on the development of highly proton conductive membranes with lower methanol transport to achieve the goal of commercialization of DMFC [6].

Poly(vinyl alcohol) (PVA) appears to be very attractive material for preparing proton exchange membrane (PEM) because this polymer can function as an excellent methanol barrier [7]. PVA also has both very good mechanical properties and chemical stability, which are adequate for preparing PEMs [8]. Although PVA itself does not have fixed charges, several organic groups like hydroxyl, amine, carboxylate, sulfonate, and quaternary ammonium can be incorporated to impart hydrophilicity and/or ionic group [9,10]. Several crosslinking methods have been published for different use, since as a rule, all multifunctional compounds capable of reacting with hydroxyl groups can be used to obtain three dimensional networks in PVA [11]. In our previous study [12–14], we reported the preparation of crosslinked membranes employing PVA as a base material

* Corresponding author. Tel.: +82 42 629 7531; fax: +82 42 623 9489.
E-mail address: jwrhim@mail.hannam.ac.kr (J.W. Rhim).

0376-7388/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2006.03.025

and sulfosuccinic acid (SSA) or poly(acrylic acid-*co*-maleic acid) (PAM) as both a crosslinking agent and a donor of the hydrophilic group ($–SO_3H$). As reported earlier [15,16], it was assumed that the crosslinking of the completely miscible blend system occurs via dehydration between carboxylic acid and hydroxyl group, that is, esterification and bond formation during thermal activated reaction.

Recently, Kang et al. reported the preparation of PVA based (i.e. PVA/poly(styrene sulfonic acid-*co*-maleic acid), PSSA_MA) PEM [17,18]. They have utilized glutaraldehyde (GA) as a crosslinking agent. The proton conductivities and methanol permeabilities of the membrane were in the range of 10^{-2} S/cm and 10^{-8} to 10^{-6} cm^2/s, respectively, depending on the blend conditions. Since a maleic acid group has two ion-exchangeable sites in its molecular structure [18] and also could be crosslinked with –OH group of PVA, the introduction of PSSA_MA into the PVA polymer matrix can control the membrane charge density and also prevent excessive swelling.

In this paper, we focused on the proton and methanol transport of crosslinked PVA membrane containing $–SO_3H$ and/or –COOH under different crosslinking conditions as a proton exchange membrane for future DMFC applications. The crosslinking temperature and the content of PSSA_MA were controlled to seek the best performance in terms of methanol permeability and proton conductivity measurements.

2. Experimental

2.1. Materials

Fully hydrolyzed PVA (99% hydrolyzed, average Mw = 89,000–98,000) and the PSSA_MA (sodium salt, styrene (Sty) sulfonic acid:maleic acid = 3:1, average Mw = 20,000 g/mol) as a crosslinking agent and as a donor of the hydrophilic $–SO_3H$ and –COOH group were purchased from Aldrich Chemical Co., Milwaukee, WI, USA. Methanol was analytical grade from Merck (Darmstadt, Germany). The water used was the ultrapure water produced from Younglin Pure Water System (Seoul, Korea).

2.2. Membrane preparation

Aqueous 10 wt% PVA solutions were prepared by dissolving dry PVA in water and then heating at 90 °C for 6 h, and aqueous 20 wt% PSSA_MA solutions were prepared. Two solutions were mixed together by varying each component composition to form a homogeneous solution for at least 1 day at room temperature. The membranes were prepared by casting the mixed solution onto a Plexiglass plate using a Gardner knife with predetermined drawdown thickness. The membranes were allowed to dry in air at room temperature for more than 5 days, and the resulting dried membranes were then peeled off. The prepared membranes were annealed at different temperatures for 1 h to induce crosslinking reaction. The selected crosslinking temperatures were 120, 130, and 140 °C. The thickness of the resulting membranes were in the range of 100–150 μm. Fig. 1 shows the proposed reaction mechanism of PVA and PSSA_MA.

2.3. Membrane characterization

The FT-IR spectra of the membranes were measured using a Nicolet IR 860 spectrometer (Thermo Nicolet, Madison, WI, USA) operating in the wavenumber range 4000–500 cm^{-1}. The degradation process and the thermal stability of the membranes were investigated using thermogravimetry (TGA) (TA Instruments TGA 2050, New Castle, DE, USA). The TGA measurements were carried out under a nitrogen atmosphere using a heating rate of 10 °C/min from 50 to 700 °C.

2.4. Measurement of the water content

The water content was measured by soaking the samples in distilled water for more than 24 h. After this period, they were

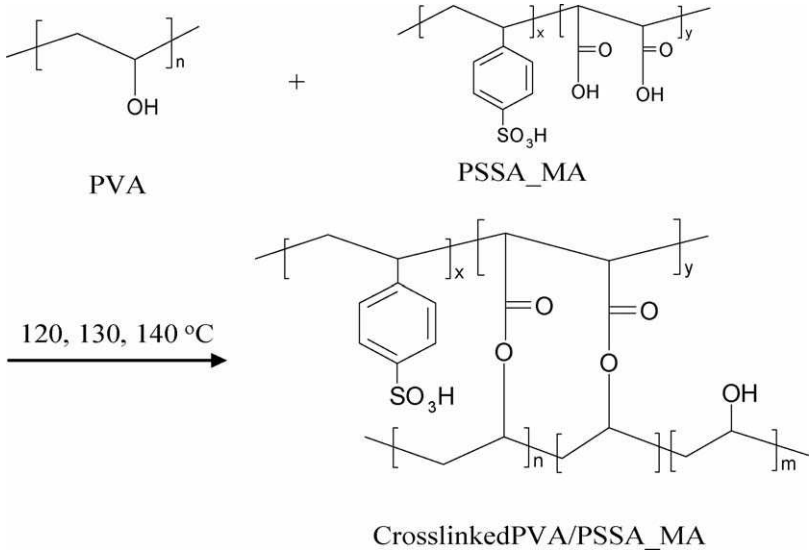

Fig. 1. Possible reaction mechanism of PVA and PSSA_MA.

wiped with a filter paper and then weighed immediately. The samples were then dried under vacuum until a constant weight was obtained. The water content (g H_2O/g membrane) was determined using the following equation:

$$\text{Water content} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \quad (1)$$

where W_{wet} and W_{dry} are the wet and dry membrane weights, respectively. The values of the water content reported are the mean of at least five measurements, and the average estimated error was ±8%.

2.5. Ion exchange capacity and hydrolytic stability

The ion exchange capacity (also known as the IEC value) was measured using the classical titration technique. After immersing the samples in distilled water, they were soaked in a large volume of 0.1 M HCl solution to change them into the H^+ form. The samples were then washed with distilled water to remove excess HCl, and then equilibrated with 100 ml of 0.1 M NaCl solution for 24 h. The remaining liquid was titrated with 0.1 M NaOH solution using phenolphthalein as an indicator. The IEC value (mmol/g) was calculated using the following equation:

$$\text{IEC} = \frac{M_{\text{O,NaOH}} - M_{\text{E,NaOH}}}{W_{\text{dry}}} \quad (2)$$

where $M_{\text{O,NaOH}}$ is the mmol/g of NaOH in the flask at the beginning of the titration, $M_{\text{E,NaOH}}$ the mmol (meq) of NaOH after equilibrium, and W_{dry} is the weight of the dry membrane (g). The reported values were the mean of at least five measurements, and the average estimated error was ±3%.

To confirm the stability of membrane in hydrolytic condition, the membranes were immersed in boiling water for 1 week. The IEC value of the membrane was measured after boiling water test.

2.6. Proton conductivity

The proton conductivity of the membranes was measured using the normal four-point probe technique at relative humidity (RH) = 100%. The impedance of the membranes was determined using a Solartron Analytical Full Material Impedance System 12608W consisting of a Frequency Response Analyzer 1260 and Electrochemical Interface 1287 unit. Each sample was cut into sections 4 cm × 1 cm prior to being mounted on the cell. The proton conductivity (σ) was obtained using the following equation:

$$\sigma = \frac{l}{R \cdot S} \quad (3)$$

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

2.7. Methanol permeability

The methanol permeability of the membranes was determined using a diaphragm diffusion cell [12]. This cell consisted of two reservoirs, each with a capacity of approximately 60 ml, separated by a vertical membrane. The membrane was clamped between the two reservoirs, the contents of which were stirred during the experiments. Prior to the test, the membranes were equilibrated in deionized water for at least 12 h. Initially, one reservoir (V_A) contained a 2 M methanol–water solution, and the other reservoir (V_B) contained pure deionized water. The increase in concentration of methanol in the initially pure water reservoir was measured against time using gas chromatography. In the gas chromatography measurements, 1-μl samples were analyzed using a Shimadzu GC-14B gas chromatograph. The methanol permeability was calculated [12].

3. Results and discussion

3.1. FT-IR spectroscopy

The FT-IR spectra of pure PVA, PSSA_MA, and crosslinked PVA/PSSA_MA membranes are shown in Fig. 2. The broad bands occurring at around 3600–3200 cm^{-1} (characteristic of O–H stretching vibration) are observed due to hydrogen bonding and OH single vibration. In comparison with the O–H peak of pure PVA (3342 cm^{-1}), the O–H peak of PVA/PSSA_MA membrane shifts to higher wavelength region (3500 cm^{-1}), indicating that the formation of hydrogen bonds between –OH of PVA and $–SO_3H$ of PSSA occurs and the interaction between –OH groups of PVA is stronger than that between –OH and $–SO_3H$ [18,19]. The absorption bands at 1718 cm^{-1} (characteristic of C=O vibration, maleic acid) and at 1038 cm^{-1} (characteristic of $–SO_3^-$, PSSA) are observed in PVA/PSSA_MA membrane. In addition, the absorption band at 1234 cm^{-1} is observed in the crosslinked membrane, indicating the formation of ether bonds (C–O–C) between –OH of PVA and –COOH of maleic acid.

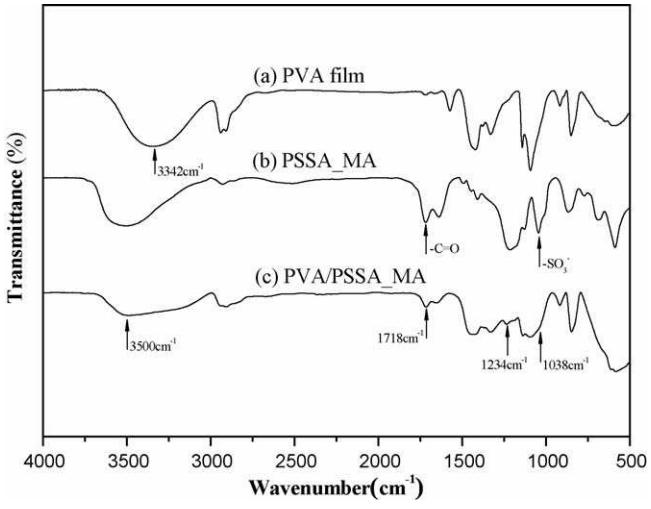

Fig. 2. FT-IR spectra of: (a) PVA, (b) PSSA_MA, and (c) PVA/PSSA_MA membranes (crosslinking temperature: 140 °C).

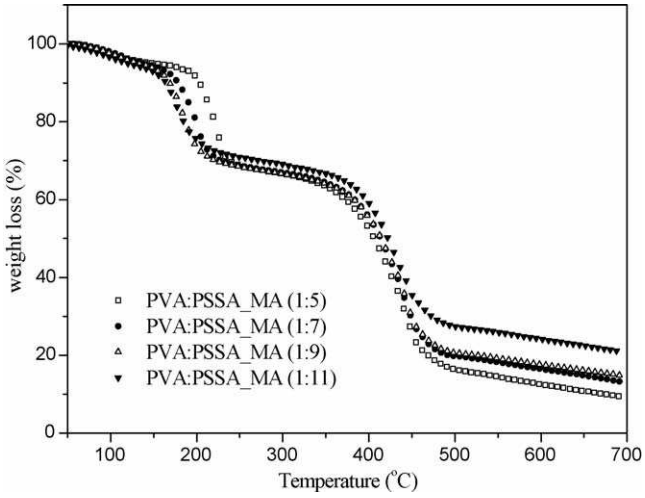

Fig. 3. TGA curve (crosslinking temperature: 140 °C).

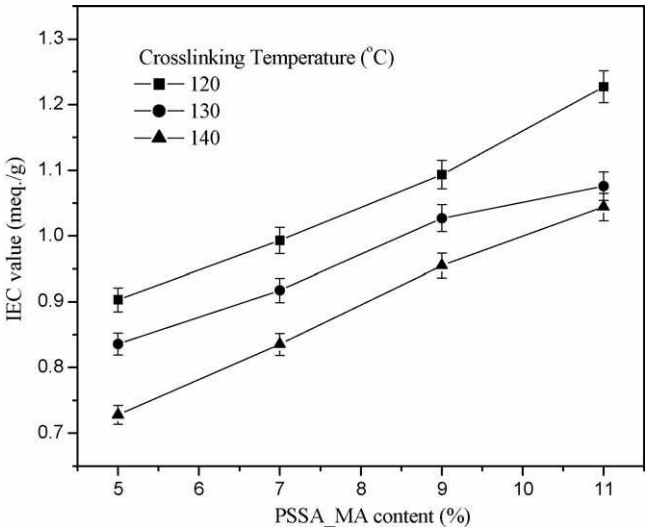

Fig. 4. Ionic exchange capacities of crosslinked membranes.

3.2. Thermal analysis

Thermal properties of membrane were investigated by thermogravimetry programmed from 50 to 700 °C at a heating rate of 10 °C/min under N_2 gas. As shown in Fig. 3, the TGA curve of the membranes was fitted using three main degradation stages arising from the processes of thermal solvation, thermal desulfonation, and thermooxidation of the polymer matrix. The first weight loss up to 150 °C is closely associated with the loss of absorbed water molecules. Most of these absorbed water molecules are supposed to exist in a bound state, rather than in the free molecular state [20], and seem to be bound directly to the polymer chains and/or the $–SO_3H$ groups via hydrogen bonds. As can be seen in Table 1, the $T_{d5\%}$ of polymer decrease with increasing the PSSA_MA content. The absorbed water content increases with increasing the PSSA_MA content.

The second weight loss region (occurring between temperatures of 150 and 300 °C) corresponds to the loss of sulfonic acid group by desulfonation. In the third weight loss region (at temperatures >400 °C), the polymer residues were further degraded at $T = 450$ °C, which corresponds to the decomposition of the main chains of the PVA.

The weight remaining after the polymer decomposition depended on the content of the PSSA_MA. As shown in Table 1, the weight residue of membrane increases with increasing the PSSA_MA content due to the higher degree of crosslinking. An increase in PSSA_MA content induces more crosslinking in the PVA matrix, which leads to an increase in the residual char formed at $T = 700$ °C.

Table 1
Ion exchange capacities before and after boiling water test and thermal property

PSSA_MA content (wt%)	IEC (mmol/g (meq/g))		$T_{d5\%}$ (°C)[a]	Ash[b]
	Before boiling water test	After boiling water test		
PVA/PSSA_MA (1:5)	0.73	0.70	153.6	9.4
PVA/PSSA_MA (1:7)	0.84	0.81	138.4	13.1
PVA/PSSA_MA (1:9)	0.96	0.91	132.8	15.0
PVA/PSSA_MA (1:11)	1.08	0.97	120.8	20.9

[a] 5% weight loss temperature.
[b] Residual ash is the char yield (wt%) at 700 °C.

3.3. Ion exchange capacity and hydrolytic stability

Fig. 4 shows IEC of PVA/PSSA_MA membranes as a function of PSSA_MA content (wt%). The prepared membranes indicated IEC values of 0.73–1.22 mmol/g dry membrane. The IEC of PVA/PSSA_MA membranes crosslinked at 120, 130, and 140 °C increased with increasing the PSSA_MA content due to the increasing portion of ionic group ($–SO_3H$ and –COOH) in membrane. The ionic site would be decreased at higher crosslinking temperature due to the greater reaction of $–SO_3H$ and/or –COOH group in repeating units of PSSA_MA with –OH of PVA. Note that typical temperatures for inducing the esterification between PVA and acidic monomer or polymer are known to be 120–130 °C [12,14]. Therefore, the IEC value decreased with higher crosslinking temperature. The numbers of molecules per sulfonic acid (λ) are listed in Table 2. For the Nafion membrane series, λ values showed 21–22 for Nafion 112, Nafion 115, and Nafion 117 and 27–28 for Nafion 105 membranes, respectively [21]. The membrane having 11 wt% PSSA_MA and crosslinked at 130 °C shows a similar value ($\lambda = 25$).

We have also performed a hydrolytic stability test (i.e. boiling water test for 1 week) for PVA/PSSA_MA membranes crosslinked at 140 °C. The boiling water test is a simple initial accelerated test to evaluate the possibility as membrane materials for fuel cell [12]. Before and after boiling water test, the IEC values are listed in Table 1. Although the IEC values only decrease slightly, perhaps due to partial decomposition during the boiling water test, the membranes maintain adequate IEC values after boiling water test. Therefore, it is believed that the crosslinked PVA/PSSA_MA membranes have moderate hydrolytic stability.

Table 2
Number of water molecules per ionic site (–SO_3H and –COOH)

Sample	120 °C			130 °C			140 °C		
	WC	EW	λ[a]	WC	EW	λ	WC	EW	λ
PVA/PSSA_MA (1:5)	1.87	1107	115	1.39	1196	92	0.85	1373	65
PVA/PSSA_MA (1:7)	1.82	1006	101	1.00	1090	60	0.56	1196	37
PVA/PSSA_MA (1:9)	1.76	914	89	0.9	973	48	0.28	1046	16
PVA/PSSA_MA (1:11)	1.59	814	71	0.5	929	25	0.22	957	11

[a] Calculated by $\lambda = (WC \times EW)/M_o$, where WC is the water content, EW the equivalent weight (g/mol), and M_o is the molecular weight of water (18 g/mol).

3.4. Water content

The water contents of membranes are plotted as functions of the PSSA_MA content and crosslinking temperature in Fig. 5. Before attempting the water content measurements, we expected that an increase in PSSA_MA content in the PVA matrix would lead to an improvement in the water content because the sulfonic acid groups (–SO_3H) have a strong solvation property compared to PVA. In addition, our expectations were based solely on the IEC values of the membranes that had been measured before the water content measurements. If the effect of crosslinking degree is smaller than that of ionic group (–SO_3H and –COOH), the water content would increase. However, the water content decreases with the PSSA_MA content as shown in Fig. 5. Therefore, it could be considered that the effect of crosslinking degree is larger than that of ionic group. This behavior was shown in our previous study [12,13]. Further, hydrogen bond between the –OH group of PVA and the sulfonic acid group and/or unreacted carboxylic groups of PSSA_MA acted as physical crosslinking in the membrane matrix [17]. Therefore, increasing the PSSA_MA content caused an increase in the physical crosslinking by hydrogen bond formation as well as esterification reaction. As the crosslinking temperature increases, i.e. the esterification reaction between –OH of PVA and –COOH of PSSA_MA as well as –OH of PVA and –SO_3H of PSSA_MA proceeds more, making the membranes more rigid and compact, and reducing free volume, thereby resulting in a decrease in the water content. The water contents of the membranes crosslinked at 130 and 140 °C are lower than that of the membrane crosslinked at 120 °C. In this case, two esterification reactions, between –OH of PVA and –COOH or –SO_3H of PSSA_MA, could be considered. However, we do not know which esterification reaction is the dominant one controlling in this case, but as shown in Fig. 5, it could be considered that the effect of two esterification reactions at 130 and 140 °C is larger than that at 120 °C.

For the membranes crosslinked at 140 °C, the water content is in the range of 22–85% for different PSSA_MA content membranes. Nafion membranes have the water contents ranging from 24 to 33% depending on the content of sulfonic group; typically Nafion 117 has values of 24–26% [22]. Both 9 and 11 wt% PSSA_MA membrane crosslinked at 140 °C show a similar water content with Nafion membranes.

3.5. Proton conductivity and methanol permeability

The proton conductivity measurements of PVA/PSSA_MA membrane were run at RH 100% as a function of PSSA_MA content and crosslinking temperature in the longitudinal direction by ac impedance spectroscopy and the results are shown in Fig. 6. This trend in behavior was the same as that observed for the water content behavior (Fig. 5). The proton conductivities of the crosslinked membranes measured at $T = 25$ °C were in the range 10^{-3} to 10^{-2} S/cm. Although the PVA/PSSA_MA

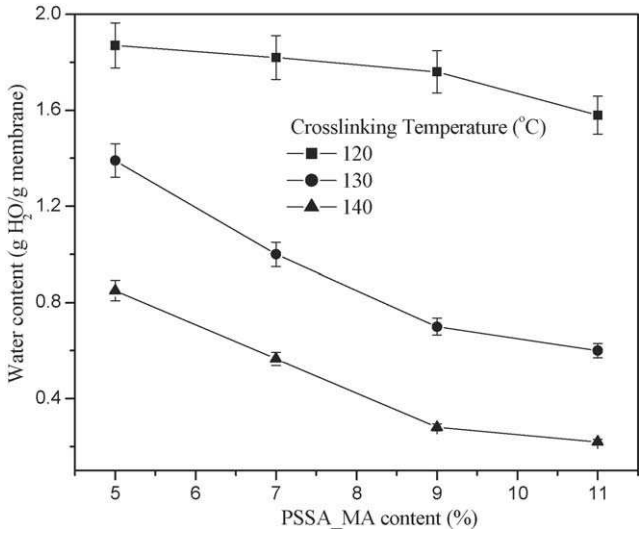

Fig. 5. Water content of crosslinked membranes.

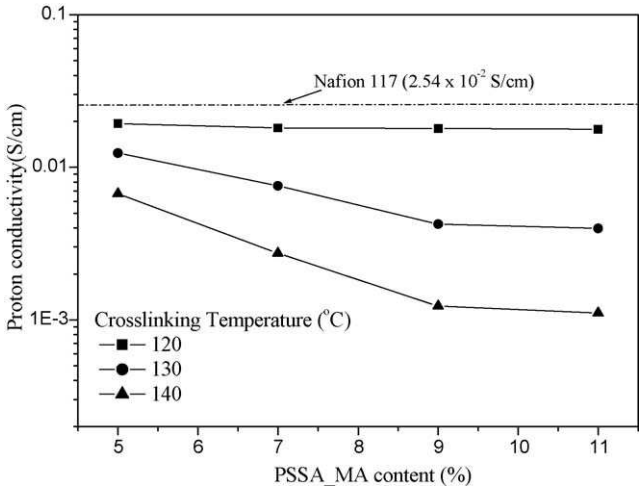

Fig. 6. Proton conductivity of Nafion 117 and crosslinked PVA/PSSA_MA membranes measured at 25 °C.

(1:5) crosslinked at 120 °C presents high proton conductivity (~0.02 S/cm), and almost closes to that of Nafion (0.025 S/cm), this membrane also reveals poor mechanical property. Although the presence of ionic donor groups such as $–SO_3H$ and –COOH increases with increasing PSSA_MA content (see IEC values), the proton conductivities decrease with increasing the PSSA_MA content. Unexpectedly, the contents of crosslinking agents (PSSA_MA) were relatively insensitive to the proton conductivity. Therefore, the effect of crosslinking may be more dominant than that of the increase of the number of ionic exchange sites ($–SO_3H$ and/or –COOH) in this system. As the content of PSSA_MA is increased, the polymer matrix would become more compact. This behavior was confirmed using XRD in our previous study [21]. In addition, the proton conductivities decrease with increasing the crosslinking temperature. This phenomenon can be explained by channel formation upon hydration. Increasing the PSSA_MA content and reaction temperature leads to reduction of free volume being able to associate with water molecules, thereby resulting in a decrease in the size of interconnecting channels for protons. Therefore, the proton conductivity decreases with increasing PSSA_MA content and reaction temperature.

Fig. 7 shows the effect of operating temperatures raised from 25 to 90 °C on the proton conductivities of the Nafion 117 and PSSA_MA membranes crosslinked at 140 °C. The degree of hydration of sulfonic and carboxylic group would increase with increasing temperature. In addition, as the proton conductivity of an electrolyte is generally thermally stimulated, it is natural to expect a rise in proton conductivity with temperature [23]. Typically, the membrane containing PSSA_MA 9% shows the highest proton conductivity of 0.0444 S/cm.

Fig. 8 shows the methanol permeability of Nafion 117 and PVA/PSSA_MA membrane crosslinked at 120, 130, and 140 °C. Compared with Nafion 117, most PSSA_MA membranes show lower methanol permeability. As can be seen, the methanol permeability decreases with increasing PSSA_MA contents and crosslinking temperature. We expected that the methanol permeability would increase with PSS_MA contents because the hydrophilic regions would be increased by the presence of $–SO_3H$ and –COOH groups of PSSA_MA. As described previously, if the effect of the introduction of hydrophilic groups ($–SO_3H$ and –COOH) were more dominant than that of the crosslinking degree, the methanol permeability would increase with PSSA_MA contents due to the affinity between hydrophilic groups in membranes and permeates in feed solution. In addition, methanol permeability is known to occur through the hydrophilic regions. However, the results of water content and methanol permeability show the opposite trend. In particular, the PVA/PSSA_MA (1:11) membrane crosslinked at 140 °C shows the lowest methanol permeability. At higher crosslinking temperatures, it could be considered that the membrane becomes hydrophobic due to the esterification reactions between –OH groups and $–SO_3H$ and/or –COOH groups. In addition, these esterification reactions affect the degree of crosslinking. Therefore, the water content and the permeability of methanol would be reduced. Kang et al. reported that crosslinked PVA/PSSA_MA membrane possesses narrower ionic channel

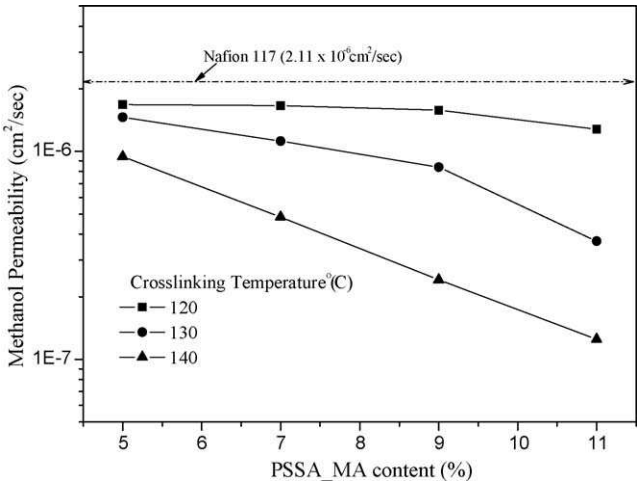

Fig. 8. Methanol permeability of crosslinked PVA/PSSA_MA membranes measured at room temperature.

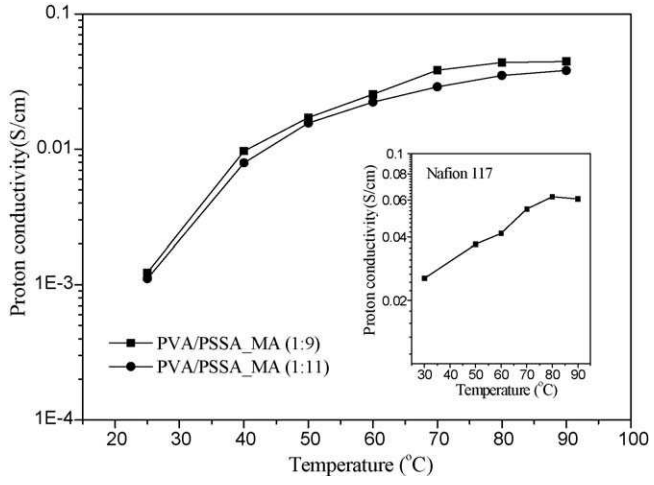

Fig. 7. Proton conductivity of Nafion 117 and PVA/PSSA_MA membranes crosslinked at 140 °C as a function of temperature.

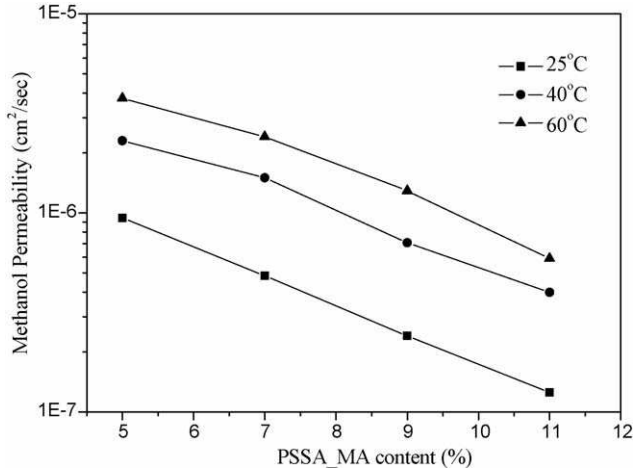

Fig. 9. Methanol permeability of crosslinked PVA/PSSA_MA membranes measured at 25, 40, and 60 °C.

size than commercial Nafion 117 as inferred from the results of SAXS study [17].

Fig. 9 shows the methanol permeability of PVA/PSSA_MA membranes crosslinked at 140 °C. The methanol permeability increases with operating temperature. If the operating temperature is elevated, the polymer matrix structure would be loosening so that the methanol can pass freely.

4. Conclusion

In our previous study [12–14], we reported the preparation of the crosslinked membranes employing PVA as the polymer matrix and sulfosuccinic acid or poly(acrylic acid-*co*-maleic acid) as both a crosslinking agent and a donor of the hydrophilic group. This work is a continuation of our study on crosslinking methodology for PVA membranes. In the present work, crosslinked poly(vinyl alcohol) membranes were prepared at various crosslinking temperatures using poly(styrene sulfonic acid-*co*-maleic acid) containing different PSSA_MA contents. The PSSA_MA was used both as a crosslinking agent and as a donor of the hydrophilic $–SO_3H$ and/or –COOH group.

PVA/PSSA_MA membranes were characterized in terms of water content, boiling water test, proton conductivity, and methanol permeability behaviors. The water content, proton conductivity, and methanol permeability decreased with increasing the PSSA_MA content. Two factors of the crosslinking degree and the quantities of ionomer, $–SO_3H$ and –COOH, could be considered, because the PSSA_MA was used both as a crosslinking agent and as a donor of hydrophilic group. The effect of crosslinking may be more dominant than that of the increase of the number of ionic exchange sites ($–SO_3H$ and/or –COOH) in this system. From the results, these behaviors of PVA/PSSA_MA membranes were effectively controlled by varying the PSSA_MA contents and appropriate crosslinking temperature. From the viewpoint of all measured properties in this study, the PVA/PSSA_MA (1:9) membranes prepared at 140 °C exhibited the best performance. The PVA/PSSA_MA (1:9) shows both high proton conductivity (0.0444 S/cm at 90 °C) and low methanol permeability (2.41×10^{-7} cm^2/s). Although the PVA/PSSA_MA (1:9) membrane maintained an adequate IEC value after boiling water test, more detailed analyses such as long-term and thermal stabilities of these types of membranes may be needed for DMFC applications. These detailed analyses are in progress.

Acknowledgement

This work was supported by Korea Research Foundation (KRF) (No. 202-D00224).

References

[1] J.A. Kerres, Development of ionomer membrane for fuel cells, J. Membr. Sci. 185 (2001) 3–27.
[2] V. Tricoli, N. Carretta, M. Bartolozzi, A comparative investigation of proton and methanol transport in fluorinated ionomeric membranes, J. Electrochem. Soc. 147 (2000) 1286.
[3] C. Pu, W. Huang, K.L. Ley, E.S. Smotkin, A methanol impermeable proton conducting composite electrolyte system, J. Electrochem. Soc. 142 (1995) 119.
[4] G.T. Burstein, C.J. Barnett, A.R. Kucernak, K.R. Williams, Aspects of the anodic oxidation of methanol, Catal. Today 38 (1998) 425.
[5] A. Heinzel, V.M. Barragan, A review of the state-of-the-art of the methanol crossover in direct methanol fuel cell, J. Power Sources 84 (1999) 70.
[6] C.H. Lee, H.B. Park, Y.M. Lee, R.D. Lee, Importance of proton conductivity measurement in polymer electrolyte membrane for fuel cell application, Ind. Eng. Chem. Res. 44 (2005) 7617–7626.
[7] S. Bryan, B.S. Pivovar, Y. Wang, E.L. Cussler, Pervaporation membranes in direct methanol fuel cells, J. Membr. Sci. 154 (1999) 155.
[8] S.Y. Kim, H.S. Shin, Y.M. Lee, C.N. Jeong, Properties of electroresponsive poly(vinyl alcohol)/poly(acrylic acid) IPN hydrogels under an electric stimulus, J. Appl. Polym. Sci. 73 (1999) 1675–1683.
[9] J.F. Blanco, Q.T. Nguyen, P. Schaetzel, Novel hydrophilic membrane materials: sulfonated polyethersulfone Cardo, J. Membr. Sci. 186 (2001) 267.
[10] H.B. Park, S.Y. Nam, J.W. Rhim, J.M. Lee, S.E. Kim, J.R. Kim, Y.M. Lee, Gas-transport properties through cation-exchanged sulfonated polysulfone membranes, J. Appl. Polym. Sci. 86 (2002) 2611–2617.
[11] M. Krumova, D. Lopez, R. Benavente, C. Mijangos, J.M. Perena, Effect of crosslinking on the mechanical and thermal properties of poly(vinyl alcohol), Polymer 41 (2000) 9265–9272.
[12] D.S. Kim, H.B. Park, J.W. Rhim, Y.M. Lee, Preparation and characterization of crosslinked PVA/SiO_2 hybrid membranes containing sulfonic acid groups for direct methanol fuel cell applications, J. Membr. Sci. 240 (2004) 37–48.
[13] D.S. Kim, H.B. Park, J.W. Rhim, Y.M. Lee, Proton conductivity and methanol transport behavior of cross-linked PVA/PAA/silica hybrid membranes, Solid State Ionics 176 (2005) 117–126.
[14] J.W. Rhim, H.S. Hwang, D.S. Kim, H.B. Park, C.H. Lee, Y.M. Lee, G.Y. Moon, S.Y. Nam, Aging effect of poly(vinyl alcohol) membranes crosslinked with poly(acrylic acid-*co*-maleic acid), Macromol. Res. 13 (2005) 135–140.
[15] F. Jianqi, G. Lizia, PVA/PAA thermo-crosslinking hydrogel fiber: preparation and pH-sensitive properties in electrolyte solution, Eur. Polym. J. 38 (2002) 1653–1658.
[16] H.V. Torres, J.V.C. Rodrguez, C.A.C. Rarnos, Poly(vinyl alcohol)/poly(acrylic acid) blends: miscibility studies by DSC and characterization of their thermally induced hydrogels, J. Appl. Polym. Sci. 50 (1993) 777–792.
[17] M.S. Kang, J.H. Kim, J.G. Won, S.H. Moon, Y.S. Kang, Highly charged proton exchange membranes prepared by using water soluble polymer blends for fuel cells, J. Membr. Sci. 247 (2005) 127–135.
[18] M.S. Kang, Y.J. Choi, S.H. Moon, Water-swollen cation-exchange membranes prepared using poly(vinyl alcohol) (PVA)/poly(styrene sulfonic acid-*co*-maleic acid) (PSSA–MA), J. Membr. Sci. 207 (2002) 157–170.
[19] N. Carretta, V. Tricoli, F. Picchioni, Ionomeric membranes based on partially sulfonated poly(styrene): synthesis, proton conduction and methanol permeation, J. Membr. Sci. 166 (2000) 189–197.
[20] I. Honma, O. Nishikawa, T. Sugimoto, S. Nomura, H. Nakajima, A sol–gel derived organic/inorganic hybrid membrane for intermediate temperature PEFC, Fuel Cells 2 (2002) 52–58.
[21] D.S. Kim, H.B. Park, C.H. Lee, Y.M. Lee, G.Y. Moon, S.Y. Nam, H.S. Hwang, T.I. Yun, J.W. Rhim, Preparation of ion exchange membranes for fuel cell based on crosslinked poly(vinyl alcohol) with poly(acrylic acid-*co*-maleic acid), Macromol. Res. 13 (4) (2005) 314–320.
[22] F.N. Buchi, G.G. Sherer, In-situ resistance measurements of Nafion® 117 membranes in polymer electrolyte fuel cells, J. Electroanal. Chem. 404 (1996) 37–43.
[23] S.M.J. Zaidi, S.D. Mikhailenko, G.P. Robertson, M.D. Guiver, S. Kaliaguine, Proton conducting composite membranes from polyether ether ketone and heteropolyacids for fuel cell applications, J. Membr. Sci. 173 (2000) 17–34.