

Effects of Crosslinking Time and Amount of Sulfophthalic Acid on Properties of the Sulfonated Poly(vinyl alcohol) Membrane

C. Chanthad,^{1,2} J. Wootthikanokkhan^{1,2}

¹Division of Materials Technology, School of Energy and Materials, King Mongkut's University of Technology Thonburi (KMUTT), Bangkok 10140, Thailand

²Fuel cells research group, King Mongkut's University of Technology Thonburi (KMUTT), Bangkok 10140, Thailand

Received 15 August 2005; accepted 2 November 2005

DOI 10.1002/app.23660

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A proton-exchange membrane for a direct methanol fuel cell was prepared by modifying the chemical structure of poly(vinyl alcohol) (PVA) via a sulfonation. The sulfonation was carried out by using sulfophthalic acid (sPTA) as a sulfonating agent. The sulfonated PVA membranes, with a variety of degrees of substitutions, were obtained by varying the crosslinking time and the amount of sulfonating agents. The chemical structure and thermal stability of the sulfonated PVA were characterized by using FTIR and thermogravimetric analysis techniques, respectively. The ion-exchange capacity (IEC) and water uptake of the sulfonated membranes was evaluated by titration and gravimetry techniques, respectively. It was found that the

IEC of the membrane increased with the amount of sPTA. Water uptakes of the membranes could either decrease or remain unchanged with the crosslinking time, depending on the amount of the sulfonating agent used. Methanol permeability values of the membranes treated with 10% sPTA were relatively low, comparing with that of the Nafion 115 membrane. Proton conductivity values of the sulfonated PVA membranes ranged between 0.024 and 0.035 S/cm and they did not remarkably change with the crosslinking time. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1931–1936, 2006

Key words: functionalization of polymers; ionomers; membranes

INTRODUCTION

A direct methanol fuel cell (DMFC) is a kind of proton-exchange membrane fuel cell, which utilizes methanol as a fuel to generate electricity directly from a redox reaction without the use of any reforming unit. In this case, methanol is electro-oxidized at the anode, generating electrons, protons, and carbon dioxide. The proton is transported through an electrolyte polymeric membrane to the cathode and then reacts with oxygen and electron, producing water as a by-product. In this regard, the proton conductivity and methanol resistance of the polymeric membrane are important factors determining the performance of the fuel cell. Conventionally, perfluorinated polymeric membranes such as Nafion have been widely used for hydrogen fuel cells because of good thermal stability, good chemical resistance, and good proton conductivity of the material. However, the use of Nafion mem-

brane in DMFC suffered from a problem of high methanol crossover. Therefore, many efforts have been made to develop a new electrolyte polymeric membrane for the DMFC. Examples of the membranes being developed include sulfonated PEEK,^{1,2} PVDF-grafted polystyrene,^{3,4} Nafion-based composite membranes,^{5,6} and poly(vinyl alcohol) (PVA) membranes.^{7–9}

This research is concerned with the development of DMFC membrane from PVA. A PVA membrane has been used in a pervaporation process to separate a water–alcohol mixture,¹⁰ suggesting that methanol resistance of the membrane is good. However, the main disadvantage restricting the use of a PVA membrane in DMFC is lack of proton conductivity of the polymer. Therefore, PVA has to be modified to induce proton conductivity of the material. Shao et al.⁹ developed a membrane for DMFC by coating Nafion with PVA. Methanol resistance of the membrane increased at the expense of its proton conductivity. In addition, interfacial adhesion between the two polymeric phases has yet to be improved.

In this study, properties of PVA membranes modified with sulfophthalic acid (sPTA) were studied. The sPTA contains carboxylic groups, capable of reacting with the hydroxyl groups of the PVA molecules. Consequently, crosslinked PVA containing sulfonic acid

Correspondence to: J. Wootthikanokkhan (Jatuphorn.woo@kmutt.ac.th)

Contract grant sponsor: National Metal and Materials Technology Center (MTEC); contract grant number: MT-B-47-POL-20–302-G.

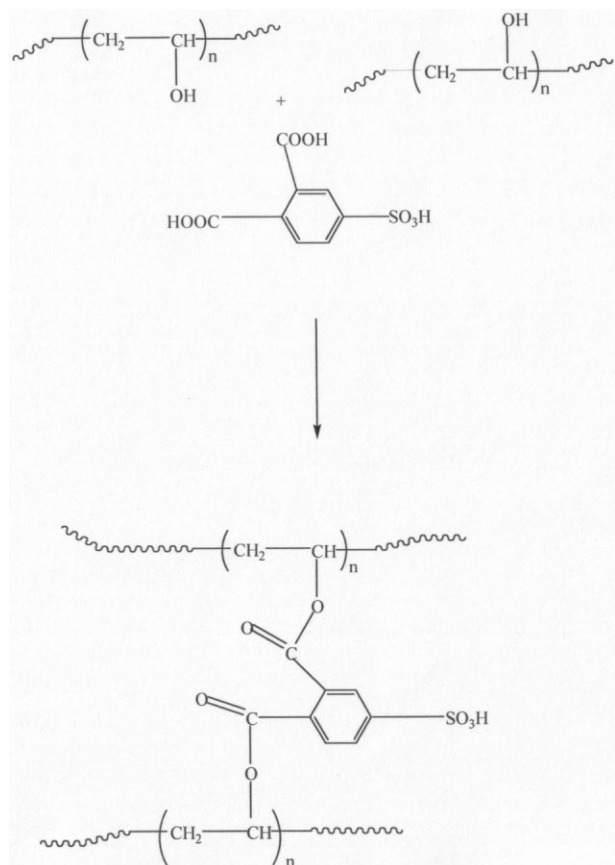


Figure 1 This illustrates a chemical reaction between PVA and sPTA, leading to the formation of a sulfonated PVA.

groups can be obtained (Fig. 1). The aim of this work is to investigate the effects of crosslinking time and amounts of the sPTA on ion-exchange capacity (IEC), proton conductivity, methanol permeability, water uptake, and thermal stability of the sulfonated PVA membranes.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA, 99.5% hydrolyzed, $M_w = 72,000$ g/mol) and sulfophthalic acid (sPTA, 50% aqueous solution) was supplied from Acros (Fairlawn, NJ). Methanol used was an AR grade obtained from Merck.

Sulfonation of PVA and membrane preparation

Aqueous solution (10%) of PVA was prepared and then heated at 90°C for 6 h. After that, a given amount of a sPTA, ranged between 10 and 40% (by mole of COOH group per OH group of the PVA), was added to the solution drop-wise, followed by stirring the solution at room temperature for 24 h.

After carrying out the chemical reaction for a given time, the PVA solution was cast onto an acrylic sheet. The cast membrane was allowed to dry at 60°C for 12 h. Finally, the dried membrane was heated at 120°C for a given time to complete the sulfonation and crosslinking. Thickness of the cast membrane ranged between 100 and 150 μm was obtained. After the crosslinking was finished, the membrane was peeled off from the substrate and then rinsed with de-ionized water to remove some residual acid. The washed membranes were stored in de-ionized water prior to testing.

Characterization

Changes in chemical structure of the modified membrane were monitored by using the Fourier transform infrared spectrophotometer (Perkin-Elmer, FTIR-GX) using an ATR mode. The sample was prepared by a film casting technique and the FTIR spectrum was recorded over the wavenumber ranging between 650 and 4000 cm^{-1} .

Thermal stabilities of PVA and the modified PVA membranes were examined by using a thermogravimetric analyzer (TGA, Perkin-Elmer, Pyris 1 TGA). About 6.7 mg of the sample was used. The TGA experiment was scanned over the temperature ranging between 40 and 700°C under oxygen atmosphere, at a heating rate of 10°C/min.

Water uptake

Measurements of water uptake values of sulfonated PVA membranes were conducted by immersing the membrane into the de-ionized water at 25°C for 24 h. After that, the water swollen membrane was taken out, wiped with tissue paper, and immediately weighed. The water uptake (W) was then calculated from the following equation:

$$W(\%) = [(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}}] \times 100 \quad (1)$$

where W_{wet} is the weight of the water swollen membrane and W_{dry} is the weight of membrane which was dried at 60°C for 24 h.

Ion-exchange capacity

IEC of the membrane was measured by a titration technique. The membrane was immersed in 10 mL of 0.1M NaOH solution for 24 h. After that, the IEC value was determined by carrying out a back titration of the solution with 0.1M HCl to evaluate the amount of remaining NaOH. The IEC value was calculated by using the following equation:

$$\text{IEC} = [M_{o, \text{NaOH}} - M_{E, \text{NaOH}}] / W_{\text{dry}} \quad (2)$$

where $M_{o, \text{NaOH}}$ is mol equivalent (mequiv) of NaOH; $M_{E, \text{NaOH}}$ is mequiv of NaOH after equilibrium; and W_{dry} is weight of the dry membrane

Methanol permeability

Resistances to methanol crossover of the membranes were evaluated by measuring methanol permeability of the membranes. A two identical compartment glass cell was used as a diffusion cell for the measurement. The membrane was placed between the two compartments and then clamped. After that, 20 mL of methanol solution (2M) and 20 mL of de-ionized water were filled in compartments A and B of the cell, respectively. Both compartments were magnetically stirred at room temperature during the permeation experiments. The concentration of methanol in the compartment B was measured as a function of diffusion time by using gas chromatography (GC) technique (Shimadzu GC-9A, containing BX-10 column). The injection temperature, column temperature, and detection temperature used for the GC experiment were 120, 85, and 150°C, respectively. Area under the methanol peak from each GC chromatogram was used in combination with a calibration curve to determine the methanol concentration. Finally, methanol permeability was calculated from the slope of a plot between the methanol concentration and diffusion time through the use of the following equation:

$$C_B(t) = A(DK)C_A(t-t_0)/V_B L \quad (3)$$

where C_A and C_B are the concentration of methanol in compartments A and B, respectively. V_B is the volumes of liquid in compartment B. A and L are the area and thickness of the membrane, and D and K are the methanol diffusivity and partition coefficient, respectively. The product of DK is the membrane permeability.



Figure 2 FTIR spectrum of PVA.

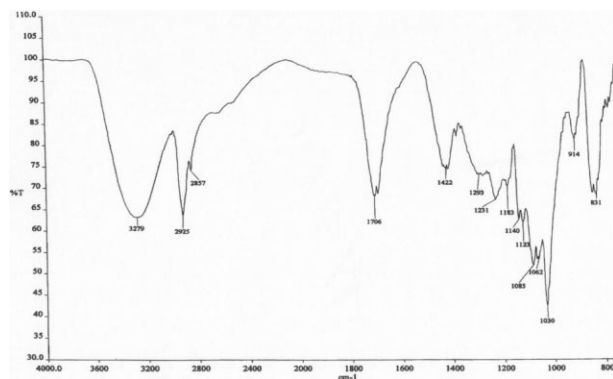


Figure 3 FTIR spectrum of sulfonated PVA modified with 10% (by mole) of sPTA.

Proton conductivity measurement

Proton conductivities of the modified PVA membranes were measured by using a four-point probe technique. The impedance of the membrane was measured by using an impedance analyzer (Autolab, PG-STAT 30) at a frequency of 1 mHz. The membrane was cut into a 1 cm × 3 cm strip and immersed in the de-ionized water for 12 h prior to the measurement. The hydrated membrane was mounted onto the cell and an AC current of 0.01 mA was applied to the cell. The conductance of the sample was obtained from an AC potential difference between the two inner electrodes. The conductivity (σ) was calculated by using the following equation:

$$\sigma = l/RS$$

where σ is the proton conductivity (S/cm), R is the bulk resistance of the membrane, S is the cross-sectional area of the membrane (cm²), and l is the distance between the counter electrode and the working electrode (cm).

RESULTS AND DISCUSSION

Chemical structure of the modified PVA

Figures 2 and 3 show FTIR spectra of PVA and the PVA modified with sPTA, respectively. From Figure 2, a broad peak at a wavenumber ranging between 3000 and 3400 cm⁻¹, representing the hydroxyl group of PVA, can be observed. In addition, a small sharp peak at 1713 cm⁻¹ was noted. This is attributed to the presence of some residual vinyl acetate repeating units in the 99.5% hydrolyzed PVA molecules. After performing the sulfonation, new FTIR peaks at wavenumbers of about 1030–1034 and 1226–1231 cm⁻¹ emerged (Fig. 3). These peaks represent the S=O (asym) and S=O (sym) bonds of the modified PVA, respectively. In addition, the intensity of the carbonyl

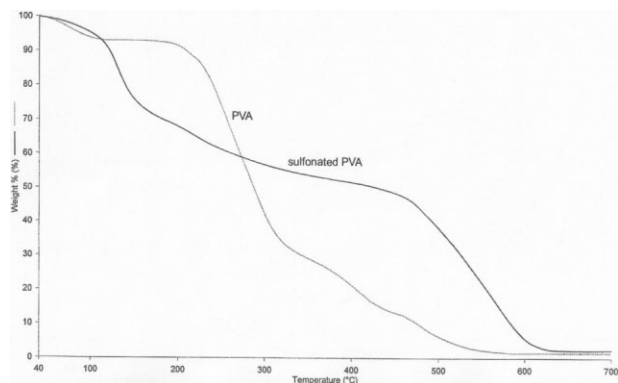


Figure 4 Overlaid TGA thermograms of PVA, sulfonated PVA modified with sPTA.

peak at about 1710 cm^{-1} became stronger with respect to that of the hydroxyl peak after the PVA was chemically modified. The aforementioned results suggested that the PVA molecules have been sulfonated in accordance with the reaction mechanism illustrated in Figure 1.

Thermal stability of the modified PVA

Figure 4 shows overlaid TGA thermograms of the normal PVA and the sulfonated PVA reacted with 30% sPTA for 30 min. For the normal PVA, 5% weight loss occurred over temperatures ranging between 60 and 100°C and that was attributed to a loss of some absorbed water. After that, about 65% weight loss occurred over temperatures ranging between 250 and 320°C and that could be related to the elimination of hydroxyl groups and hydrogen atoms from the PVA molecules. For the sulfonated PVA sample, the first transition involving about 20% weight loss occurred over temperatures ranging from 120 to 140°C . This transition was attributed to a weight loss of absorbed water or waters generated as by-products from further esterifications of the sulfonated PVA membranes. Beyond this temperature zone, the second broad transition occurred over temperatures ranging between 200 and 460°C and that was related to the desulfonation and dissociation of the ester bond ($\text{RCOO}-\text{R}'$) of the modified PVA. Finally, the third transition occurred over temperatures ranging between 460 and 600°C and that could be attributed to thermal oxidation of the desulfonated PVA.

IEC of the modified membranes

Figure 5 shows the changes in IEC value of the sulfonated PVA membrane as a function of crosslinking time and sPTA content. The IEC value increased with the sPTA content, regardless of the crosslinking time. The change in IEC value with the crosslinking time

was not remarkable. The results suggested that IEC of the membrane is strongly dependent on the amount of the sulfonic acid group, which was controlled by the amount of sPTA added and not by the crosslinking time.

Notably, the IEC values of many membranes measured by this method are higher than the theoretical value (3.4 mequiv/g) assuming that all the hydroxyl groups are reacted with the sPTA. This could be due to the fact that strong base such as sodium hydroxide is also capable of reacting with free hydroxyl and carboxylic groups in the membrane. This means that the IEC values measured by this method cannot be directly related to the degree of sulfonation. To accurately determine the amount of sulfonic acid in the membrane, it is suggested that the membrane should be first treated with a dilute solution of a salt such as sodium chloride to exchange proton between sulfonic acid and the salt. Then the exchanged proton can be titrated with a base such as sodium hydroxide.

Water uptake of the modified membranes

Figure 6 shows that water uptake values of the membranes modified with 10% sPTA are relatively low and rarely change with the crosslinking time. This is probably because when the low amount of sPTA was used, degree of sulfonation and polarity of the modified polymer were low. In addition, the sulfonation and crosslinking of the polymer might have already been completed within a short period of reaction time. Therefore, water uptake value of the membrane did not further increase with the time.

For the PVA membranes modified with 40% sPTA, the water uptake values are higher than that of the membrane modified with 10% sPTA. In addition, the

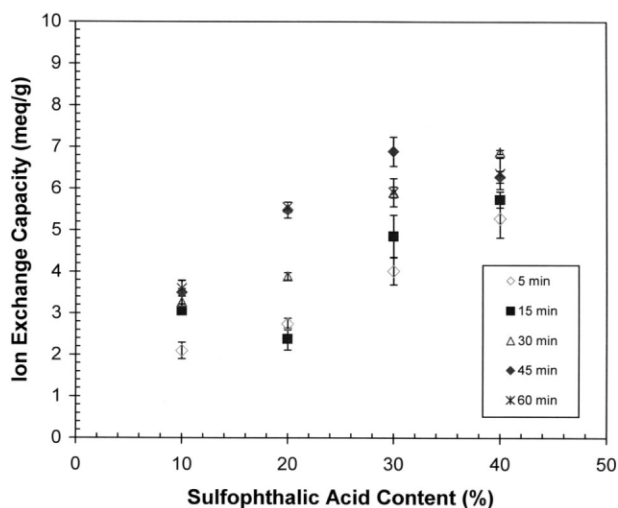


Figure 5 Changes in IEC values of the sulfonated PVA membranes as a function of curing time and sPTA content.

water uptake value of the former tended to decrease linearly with the crosslinking time. This is due to the fact that water uptake is inversely proportional to the crosslink density of the membrane, which, in this case, increases with the crosslinking time.

Notably, data from water uptake measurement of the sulfonated PVA membrane were not completed. It was found that the PVA membranes modified with high sPTA content (20–40%) and experiencing a short crosslinking time (5 and 15 min) were unstable in water solution. Therefore, water uptake of the membrane cannot be accurately measured. This effect might be attributed to a relatively high polarity of the sulfonated PVA molecules and an incomplete crosslinking of these PVA membranes. To promote a higher crosslinking level of the membrane, it is suggested that the crosslinking process might be carried out under vacuum. This is due to the fact that the crosslinking is basically a condensation reaction. Therefore, by using the vacuum, condensate will be removed and the reaction will be driven forward.

It is worth mentioning that some of the sulfonated PVA membranes experienced long crosslinking time and high amount of the sulfonating agents became darker and more brittle. This could be attributed to the introduction of chromophore groups and strong attractive forces that taken place among the $-\text{SO}_3\text{H}$ ionic associations.¹¹ Consequently, only some of the membranes were tested for methanol permeability and proton conductivity. In this study, proton conductivity and methanol permeability of the membranes treated with 10% sPTA for various curing times were measured and reported.

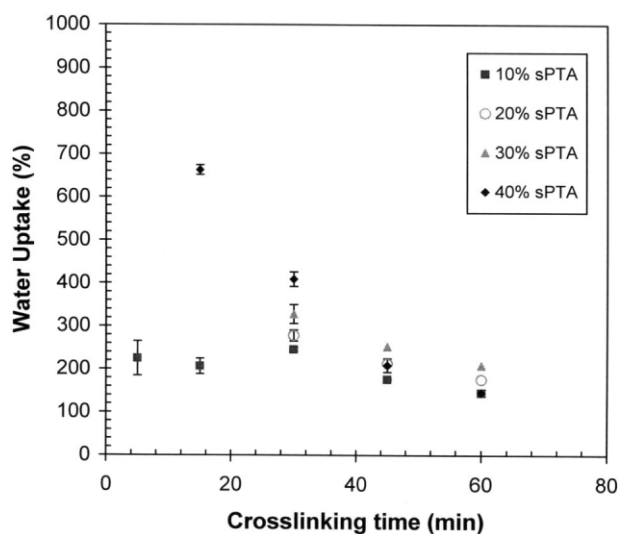


Figure 6 Changes in water uptake of the sulfonated PVA membranes as a function of curing time and sPTA content.

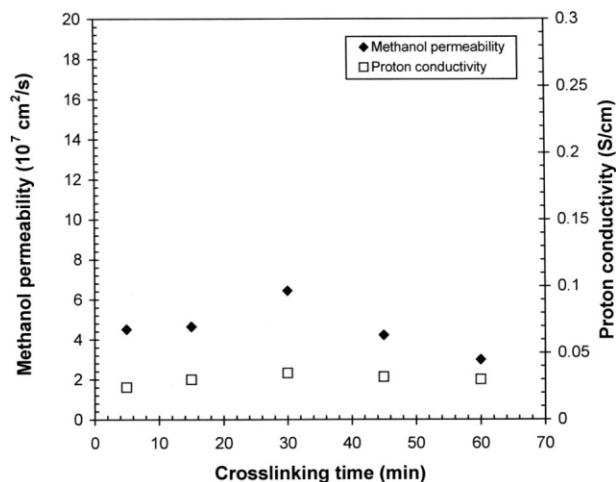


Figure 7 Changes in methanol permeability and proton conductivity of the membranes modified with 10% sPTA as a function of crosslinking time.

Methanol permeability and proton conductivity of the modified membranes

Figure 7 shows that methanol permeability and proton conductivity values of the sulfonated PVA membranes did not remarkably change with the crosslinking time. These effects could be related to fact that water uptake of the membranes rarely change with crosslinking time. For comparison purposes, methanol permeability and proton conductivity of Nafion 115 membranes were also measured using the same apparatus and testing conditions. The values of methanol permeability and proton conductivity obtained were $18.0 \times 10^{-7} \text{ cm}^2/\text{s}$ and 0.112 S/cm, respectively. The values are comparable to those reported in the literature.^{5,6} In relation to this study, most of the sulfonated PVA membranes prepared herein have lower methanol permeability than the Nafion membrane. Proton conductivities of the sulfonated PVA membranes range between 0.024 and 0.035 S/cm. These values are, however, lower than that of the Nafion115. Further attempts have yet to be made to improve the proton conductivity of the sulfonated PVA membrane. This might be achieved by optimizing the degree of sulfonation and the degree of crosslinking of the membrane.

CONCLUSIONS

PVA has been chemically modified with sPTA. IEC of the sulfonated PVA membranes increase with the amount of sPTA, whereas water uptake of the membranes tended to decreased with the crosslinking time. Methanol permeability values of the sulfonated PVA membrane modified with 10% sPTA were lower than that of the Nafion®115 membrane. Proton conductivity of the sulfonated membrane ranged between 0.024

and 0.035 S/cm and that was not remarkably changed with the crosslinking time.

The authors thank their colleagues from the Fuel Cell research group at KMUTT for a useful discussion and technical supports.

References

1. Nunes, S. P.; Ruffmann, B.; Rikowski, E.; Vetter, S.; Richau, K. *J Membr Sci* 2002, 203, 215.
2. Zaidi, S. M. J.; Mikailenko, S. D.; Robertson, G. P.; Guiver, M. D.; Kaliaguine, S. *J Membr Sci* 2000, 173, 17.
3. Ihm, C. D.; Ihm, S. K. *J Membr Sci* 1995, 98, 89.
4. Vie, P.; Peronen, M.; Stromgard, M.; Rauhala, E.; Sundholm, F. *J Membr Sci* 2002, 204, 295.
5. Dimitrova, P.; Friedrich, K. A.; Stimming, U.; Vogt, V. *Solid State Ionics* 2002, 150, 115.
6. Yamaguchi, T.; Miyata, F.; Nakao, S. L. *J Membr Sci* 2003, 539, 1.
7. Rhim, J. W.; Park, H. B.; Lee, C. S.; Jun, J. H.; Kim, D. S.; Lee, Y. M. *J Membr Sci* 2004, 238, 143.
8. Kim, D. S.; Park, H. B.; Rhim, J. W.; Lee, Y. M. *J Membr Sci* 2004, 240, 37.
9. Shao, Z. G.; Wang, X.; Hsing, I. M. *J Membr Sci* 2002, 210, 147.
10. Pivovar, B. S.; Wang, Y.; Cussler, E. L. *J Membr Sci* 1999, 154, 155.
11. Eisenberg, A.; Kim, J. S. *Introduction to Ionomers*; Wiley: New York, 1998.