

# Proton Conductivity and Methanol Permeability of Sulfonated Poly(vinyl alcohol) Membranes Modified by Using Sulfoacetic Acid and Poly(acrylic acid)

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**ABSTRACT:** Sulfonated poly(vinyl alcohol) (PVA) for use as a proton conductive membrane in a direct methanol fuel cell (DMFC) was prepared by reacting the PVA with sulfoacetic acid and poly(acrylic acid). The effects of the amount of sulfoacetic acid and poly(acrylic acid) on proton conductivity, methanol permeability, water uptake, and ion exchange capacity (IEC) of the sulfonated PVA membranes were investigated by using impedance analysis, gas chromatography, gravimetric analysis, and titration techniques, respectively. The water uptake of the membranes decreased with the amount of the sulfoacetic acid and

the amount of poly(acrylic acid) used. The proton conductivity and the IEC values of the membranes initially increased and then decreased with the amount of the sulfoacetic acid. The methanol permeability of the sulfonated PVA membranes decreased continuously with the amount of the sulfoacetic acid. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 838–845, 2007

**Key words:** ionomers; membranes; polyelectrolytes; ion exchangers

## INTRODUCTION

There has been a considerable interest in developing new electrolyte polymeric membranes that can be used as an alternative proton exchange membrane in a direct methanol fuel cell (DMFC). This is mainly because the Nafion membrane, which is commonly used in hydrogen fuel cells, is poorly resistant to methanol crossover. Consequently, the use of Nafion in DMFCs suffers from a loss of about 40% of the methanol fuel.<sup>1</sup> In addition, the permeation of methanol through the membrane into the cathode resulted in a reduction of the fuel cell's efficiency.

Many polymer membranes have been developed for use in DMFCs, for example, sulfonated poly(etheretherketone),<sup>2</sup> Nafion composite membranes,<sup>3</sup> sulfonated polystyrene,<sup>4</sup> and sulfonated poly(vinyl alcohol) (PVA).<sup>5,6</sup> The sulfonated PVA membrane is of interest because of a relatively low cost and an inherent resistance to methanol of the material. The PVA membrane has been used in a pervaporation process to separate alcohol from water.<sup>7</sup> To induce proton conductivity and to provide water stability of

the material, the PVA has to be modified by using some sulfonating agents, such as sulfosuccinic acid, sulfophthalic acid. These chemicals are multifunctional molecules containing both sulfonic acid groups and carboxylic acid groups. Consequently, they are capable of serving as both the sulfonating agent and crosslinking agent.

Our earlier study<sup>8</sup> on the properties of sulfonated PVA membranes prepared by using sulfophthalic acid showed that the proton conductivity of the membranes increases with the amount of the sulfonating agent at the expense of methanol resistance. This is because the higher the degree of sulfonation, the greater the polarity of the sulfonated PVA. As a result, the sulfonated polymer has more water uptake, promoting more methanol solubility and methanol permeability. Similar results were observed by Rhim et al.<sup>6</sup> from studies on sulfonated PVA membranes prepared by using sulfosuccinic acid as a sulfonating agent and the results were explained in a similar fashion.

In this regard, it is of interest to control the proton conductivity and methanol permeability of the sulfonated PVA by using a sulfonating agent and a crosslinking agent separately. It was believed that proton conductivity of the membrane would be mainly controlled by the amount of the sulfonating agent whereas the methanol permeability of the membrane would be mainly controlled by the amount of the crosslinking agent. In this study, sulfoacetic acid and poly(acrylic acid) were used as the sulfonating agent

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and the crosslinking agent, respectively. The aim of this study is to investigate the effects of the amount of sulfoacetic acid and poly(acrylic acid) on water uptake, ion exchange capacity (IEC), methanol permeability, and proton conductivity of the sulfonated PVA membranes.

## EXPERIMENTAL

### Materials

Poly(vinyl alcohol) (PVA, Buchs, Switzerland, degree of hydrolysis = 86.7–88.7%,  $M_w = 72,000$  g/mol). Sulfoacetic acid disodium salt (99%, from Acros, St. Louis, MO), sulfoacetic acid (technical grade from Aldrich), poly(acrylic acid) (from Acros, NJ), and methanol (AR grade from Fisher, Chemicals, Loughborough, UK) were used as received.

### Sulfonation of PVA and preparation of the sulfonated PVA membrane

For a comparison purpose, two different types of sulfonating agents namely sulfoacetic acid and sodium salt of sulfoacetic acid were used in this study. The sulfonation was commenced by preparing 10% aqueous solution of PVA and then heated at 90°C for 6 h. Next, a given amount of a sulfonating agent (ranged between 5 and 20% by weight of the PVA) and poly(acrylic acid) (ranged between 10 and 80% by weight of the PVA) were added to the solution drop-wise. After that, the solution was stirred 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 140°C for a 4 h to complete the sulfonation and crosslinking. After that, the membrane was peeled off from the substrate and then rinsed with de-ionized water to remove some residual acid. Thickness of the casted membrane was about 125  $\mu\text{m}$ . Noteworthy, the PVA membranes sulfonated with sodium sulfoacetate were treated with hydrochloric acid (0.1M) for 12 h to replace the sodium ions in the sulfonate groups with protons. However, this was not the case for the PVA sulfonated with sulfoacetic acid because the sulfonic acid groups have already been existed in the molecules. Finally, all of the sulfonated PVA membranes were stored in de-ionized water prior to testing.

### Characterizations

The chemical structure of the modified PVA was determined by  $^{13}\text{C}$  NMR techniques using a Bruker Advance DPX 400 NMR spectrometer at 20°C, using deuterated dimethyl sulfoxide (DMSO- $d_6$ ) as a solvent.

The chemical shift of tetramethylsilane (TMS) was used as internal standard reference.

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  $W_{\text{dry}}$  and  $W_{\text{wet}}$  are the weight of dry and water swollen membrane, respectively.

### Ion exchange capacity

Ion exchange capacity (IEC) of the membrane was measured by a titration technique. About 0.3–0.5 g of the sample was immersed in 0.1M of NaCl solution for 24 h to allow exchange between protons and sodium ions. After that, the solution was titrated with 0.1M NaOH aqueous solution to evaluate the amount of HCl generated from the exchange process. From the titration, IEC value was then calculated by using the following equation;

$$\text{IEC} = M_{\text{NaOH}}/W_{\text{dry}} \quad (2)$$

where  $M_{\text{NaOH}}$ , mol equivalent (mequiv) of NaOH and  $W_{\text{dry}}$ , weight of the dry membrane.

### Methanol permeability

Resistances to methanol crossover of the membranes was 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 compartment 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 the 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 and  $V_A$  and  $V_B$  are the volumes of liquids in compartment A and B, respectively.  $A$  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.

#### 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,

PGSTAT 30) at a frequency of 10 kHz. The membrane was cut into a  $3 \times 3 \text{ cm}^2$  square 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 0.35 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 ( $\sigma$ ) was calculated by using the following equation:

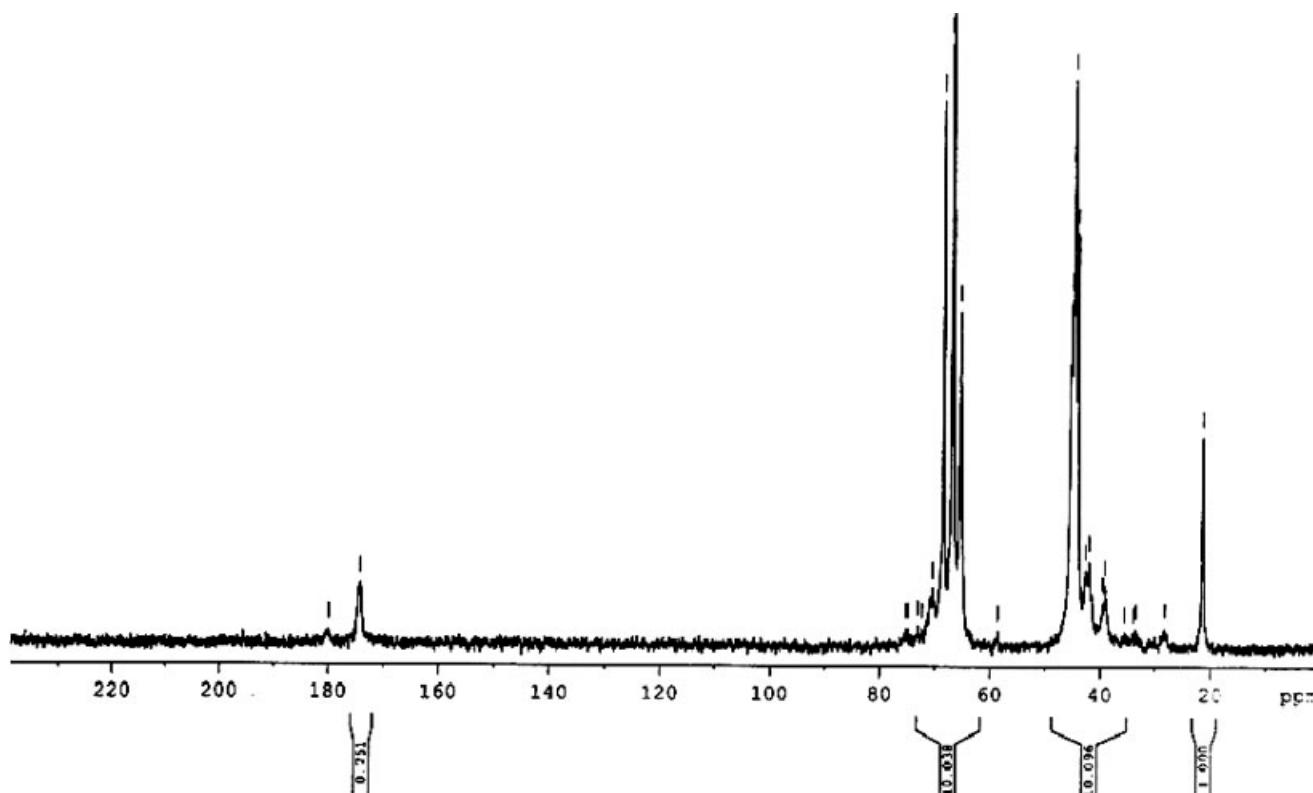
$$\sigma = l/RS \quad (4)$$

where  $\sigma$  is the proton conductivity (S/cm),  $R$  is the bulk resistance of the membrane,  $S$  is the cross-sectional area of the membrane ( $\text{cm}^2$ ), and  $l$  is the distance between the counter electrode and the working electrode (cm).

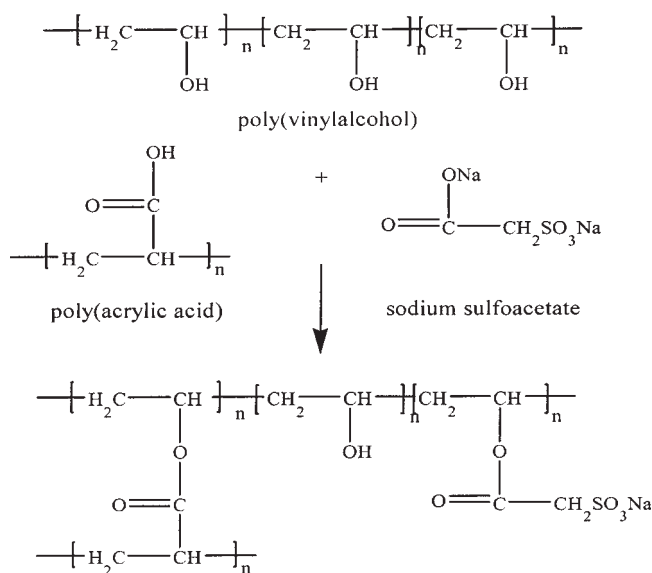
## RESULTS AND DISCUSSION

#### Characterizations of the modified membranes

Figure 1 shows the  $^{13}\text{C}$  NMR spectrum of the modified PVA membrane obtained by reacting PVA with 10% poly(acrylic acid) and 5% sodium sulfoacetate. The peaks in the chemical shift range between 65.38 and 75.21 ppm are attributed to the carbon from CH groups of the polymer backbone. The NMR peaks



**Figure 1**  $^{13}\text{C}$  NMR spectrum of sulfonated PVA membrane obtained by reacting PVA with 10% poly(acrylic acid) and 5% sodium sulfoacetate.

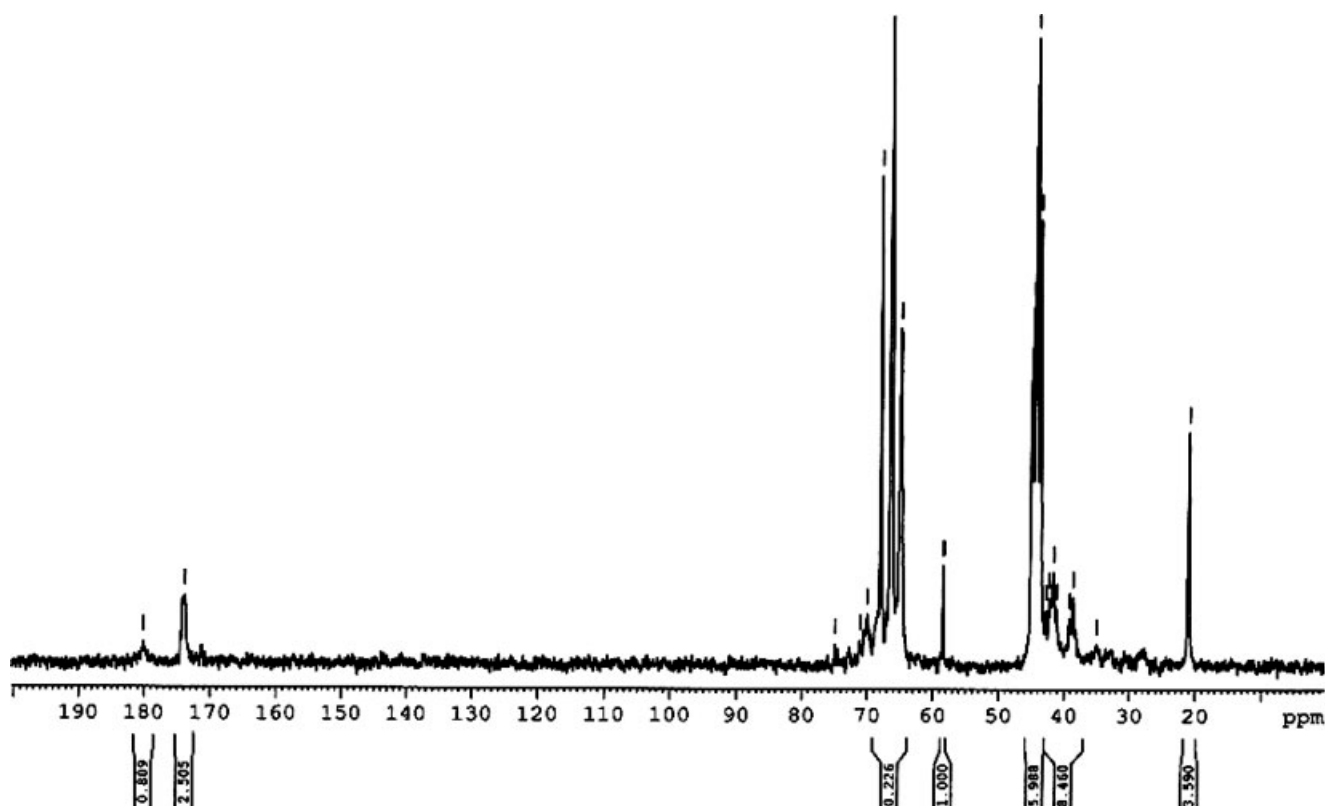


**Figure 2** Basic reaction mechanism for the sulfonation of poly(vinyl alcohol) by using with sulfoacetic acid sodium salt and poly(acrylic acid).

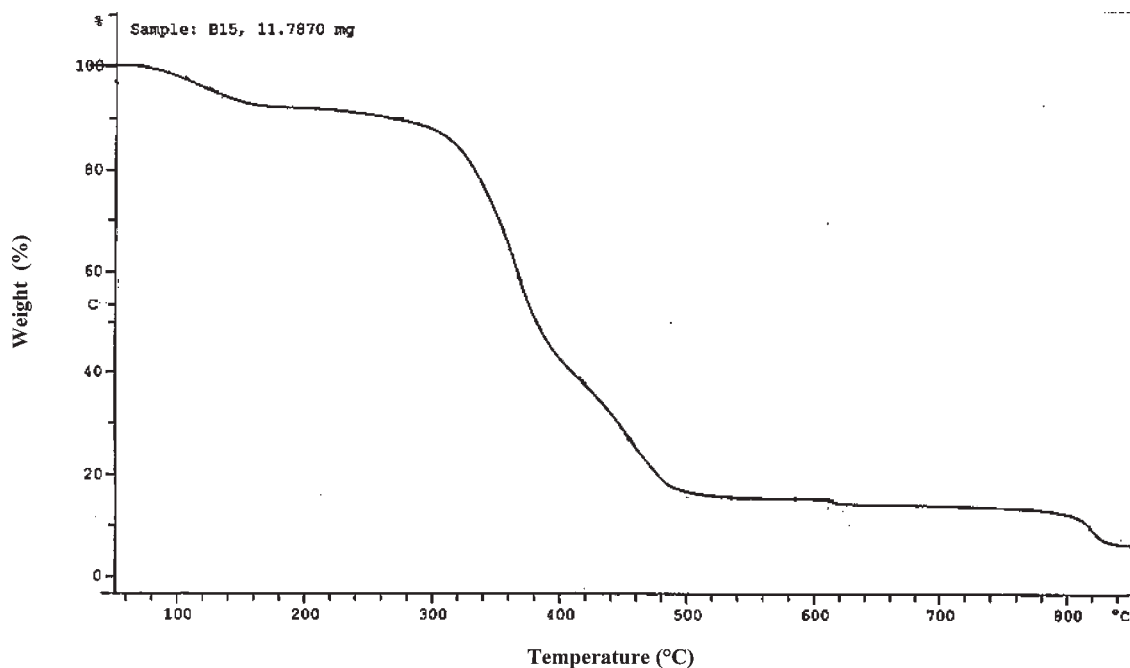
located between 39.06 and 45.22 ppm could be ascribed to the signals of carbon from methylene groups ( $-\text{CH}_2-$ ) of the polymer backbone. The two small peaks at 174.21 and 179.94 ppm represent car-

bonyl carbons ( $>\text{C}=\text{O}$ ) in the ester bonds of the sulfonated PVA (Fig. 2). The peak at 174.21 ppm results from the condensation between PVA and poly(acrylic acid), whereas the peak at 179.94 ppm is attributed to the condensation between PVA and sodium sulfoacetate. However, the NMR peak at 58.59 ppm corresponding to a signal from the carbon atom of a methylene group connected to the sulfonate group ( $-\text{CH}_2-\text{SO}_3\text{Na}$ ) was not found in the spectrum. The above results suggest that this modified PVA contains a very small amount of the sulfonate groups. However, by increasing the amount of sodium sulfoacetate from 5 to 20%, the NMR peak at 58.48 ppm can be seen more clearly (Fig. 3). This suggests that the degree of sulfonation in the modified polymer increased with the amount of the sulfonating agent. Notably, there is a sharp peak located at 21.37 ppm in the NMR spectra. It was believed that this peak might be attributed to the signal from a methyl group in a residual by-product resulting from an oxidation of the sodium sulfoacetate during the crosslinking process.

Figure 4 shows a TGA thermogram of the sulfonated PVA membrane modified by reacting PVA with 10% poly(acrylic acid) and 15% sodium sulfoacetate. It can be seen that there are four transitions in the thermogram. The initial weight loss occurred



**Figure 3**  $^{13}\text{C}$  NMR spectrum of sulfonated PVA membrane obtained by reacting PVA with 10% poly(acrylic acid) and 20% sodium sulfoacetate.



**Figure 4** TGA thermogram of the sulfonated PVA membrane obtained by reacting PVA with 10% poly(acrylic acid) and 15% sodium sulfoacetate.

over temperatures ranging between 80 and 180°C due to an evaporation of some absorbed water. The second loss, which occurred over temperatures ranged between 250 and 400°C, could be ascribed to the desulfonation and dissociation of ester bonds in the modified PVA molecules. The third transition occurred over the temperature range between 420 and 480°C, and is attributed to the thermal degradation of the desulfonated PVA. Finally, the fourth weight loss at a temperature above 800°C is attributed to a decomposition of the carbon residue. TGA thermograms of other sulfonated PVA also show a similar profile. The sulfonated PVA membranes are thermally stable up to 250°C which is far above the operating temperature of DMFCs which lies between 80 and 100°C.<sup>9</sup>

#### Water uptake and ion exchange capacity of the membranes

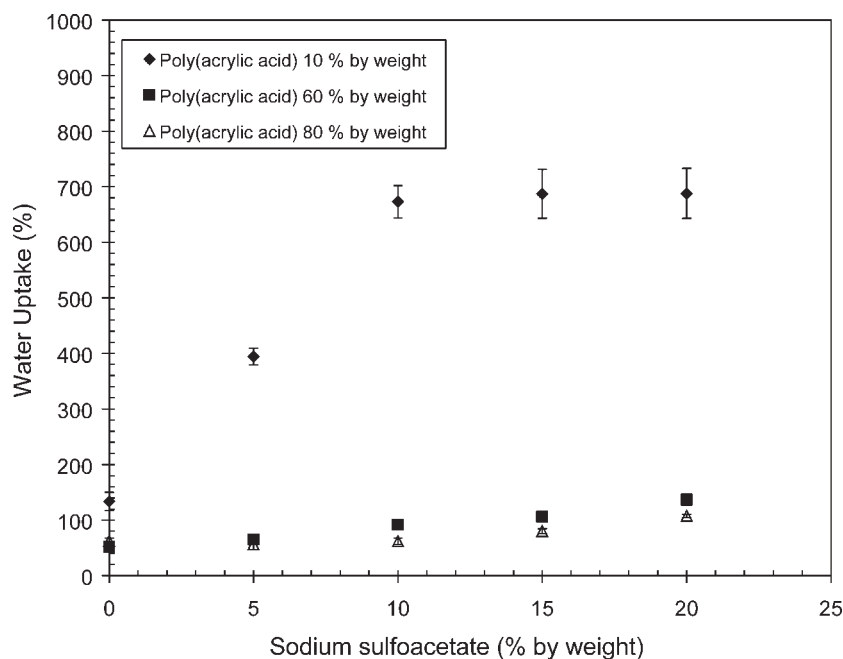
Figure 5 shows the effect of the amount of sodium sulfoacetate on the water uptake of the various membranes. It can be seen that the water uptake values of the sulfonated PVA membranes treated with 10% poly(acrylic acid) increased rapidly with the amount of sodium sulfoacetate to about 670%. This is because the polarity of the sulfonated PVA increased with the amount of sulfonating agent used. However, when the amount of sodium acetate used was further increased above 10%, the water uptake values of the sulfonated membrane did not change. In our opinion, this effect could be

attributed to the stronger ionic interaction between the sulfonated PVA molecules,<sup>10</sup> inhibiting the water uptake.

For the sulfonated PVA membranes prepared by reacting the PVA with 60 and/or 80% by weight of poly(acrylic acid), the water uptake values are remarkably lower than those of the membranes treated with 10% poly(acrylic acid), regardless of the amount of the sodium sulfoacetate used. This is because the greater the amount of poly(acrylic acid) used, the higher the crosslink density of the sulfonated membrane. Consequently, the high crosslink density membranes allow only some limited water uptake. Additionally, Figure 5 shows that the water uptake values of the membranes treated with 60 and 80% poly(acrylic acid) only increased slightly with the amount of sodium sulfoacetate used. Again, this can be related to the relatively high crosslink density of the membranes, overriding the contributory effect of the high polarity to the water uptake values.

Figure 6 shows the effect of the amount of sodium sulfoacetate on the IEC values of various membranes. The IEC values are considerably low as compared to those reported in literature for sulfonated PVA membranes modified with sulfophthalic acid<sup>8</sup> or sulfosuccinic acid.<sup>6</sup> In this case, it is worth remembering that the PVA membranes sulfonated by using sodium sulfoacetate were treated with HCl prior to the IEC test. In this regard, it might be possible that most of the sulfonate groups were dissociated from the PVA main chains, due to acid catalyzed hydrolysis. Consequently, the modified PVA





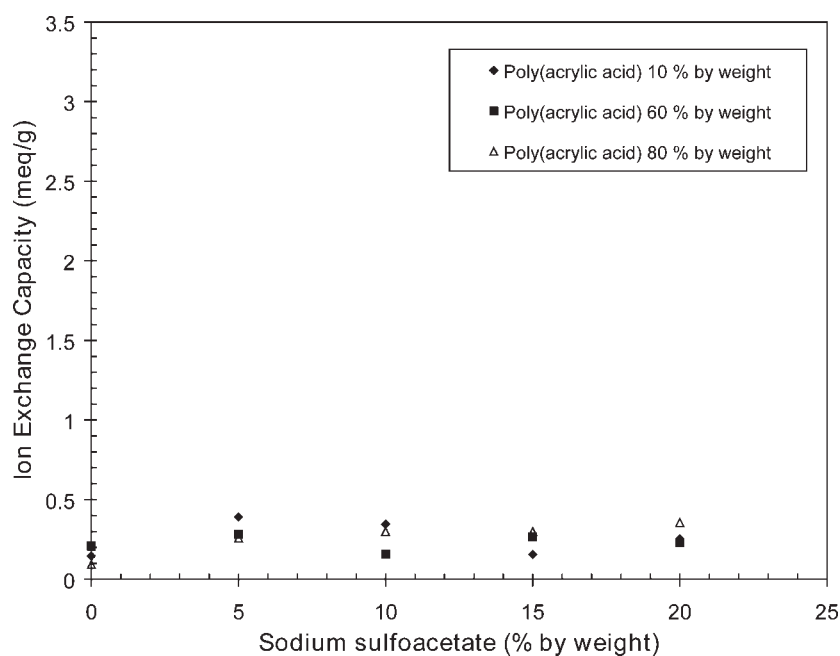
**Figure 5** Changes in the water uptake values of various PVA membranes with the amount of sodium sulfoacetate.

membranes rarely contain available sulfonic acid groups for the ion exchange process.

To verify the above hypothesis and to improve IEC values of the membranes, the sulfonation was altered by changing the type of the sulfonating agent from sodium sulfoacetate to sulfoacetic acid. In this case, only the PVA modified with 80% poly(acrylic acid) was selected for further study because of the relatively low water uptake values of the membranes

(Fig. 5) which should be good for use as a methanol resistant membrane.

Table I shows the IEC values of the sulfonated PVA membrane modified with various amounts of sulfoacetic acid. By treating the PVA with 5% sulfoacetic acid, the IEC of the membrane initially increased to the maximum value. After that, the IEC values decreased again. This was accompanied by some changes in color of the membrane from colorless



**Figure 6** Changes in the ion exchange capacity (IEC) values of various PVA membranes with the amount of sodium sulfoacetate.

**TABLE I**  
**Ion Exchange Capacity and Water Uptakes Values**  
**of Various Sulfonated PVA Membranes Modified**  
**by Using 80% Poly(acrylic acid)**

Sulfoacetic acid content (% by weight)	Ion exchange capacity (mequiv/g)	Water uptake (%)
0	0.092 ( $\pm 0.019$ )	62.48 ( $\pm 4.65$ )
5	1.015 ( $\pm 0.029$ )	39.45 ( $\pm 3.65$ )
10	0.462 ( $\pm 0.057$ )	7.20 ( $\pm 2.24$ )
15	0.484 ( $\pm 0.066$ )	3.88 ( $\pm 1.42$ )
20	0.654 ( $\pm 0.075$ )	1.84 ( $\pm 0.28$ )

to brown and dark, finally. In addition to the color changes, it was found that the sulfonated PVA membranes became more brittle as the amount of sulfoacetic acid used was increased. These changes could be attributed to the relatively high content of the sulfonic acid groups in the sulfonated PVA molecules. This would promote a stronger ionic interaction between the PVA molecules, limiting the flexibility of the PVA molecules and inhibiting the ion exchange process. Furthermore, the sulfonic acid groups might also act as chromophores, resulting in the dark color membranes. Nevertheless, the IEC values of the membranes are higher than those of the sulfonated PVA membranes modified with sodium sulfoacetate (Fig. 6), regardless of the amount of the sulfonating agent used. This indicates that the sulfonation of PVA with sulfoacetic acid is more preferable to the use of sodium acetate, taking into account the degree of sulfonation of the modified PVA obtained.

In addition to the changes in the IEC values, Table I shows that the water uptake of the sulfonated PVA membranes modified with sulfoacetic acid decreased with the amount of the sulfonating agent content. The water uptake values are also lower than those of the membranes modified with sodium sulfoacetate (Fig. 5), regardless of the amount of the sulfonating agent used. Again, this is due to the fact that the former type of membrane contains a higher amount of sulfonic acid groups. This results in the stronger ionic interaction between the sulfonated PVA molecules, limiting the water uptake values.

#### Proton conductivity and methanol permeability

Table II shows proton conductivity values of the PVA membranes modified with 80% poly(acrylic acid) and with various amounts of sulfoacetic acid. Proton conductivities of the membranes are not linearly related to the amounts of the sulfonating agent used. The conductivities initially increased with the amount of sulfoacetic acid, up to the maximum value of  $6.35 \times 10^{-3}$  S/cm. After that, the proton

conductivity of the PVA membranes decreased again as the amount of sulfoacetic acid used was above 15%. The maximum proton conductivity value herein is comparable to that of the Nafion115 membrane measured in this study ( $10.0 \times 10^{-3}$  S/cm).

The initial increase in proton conductivity of the membrane can be ascribed to the greater content of sulfonic acid groups in the modified PVA molecules, which is responsible for conducting protons. However, the proton conductivity of a membrane is not only dependent on the degree of sulfonation of the polymer, it also changes with water uptake of the membrane. For example, it was reported<sup>11</sup> that the proton conductivity of the Nafion membrane decreased remarkably when the membrane was operated at a temperature above the boiling point of the water. This is because water molecules serve as the "vehicles" for the transportation of the protons from anode to cathode.<sup>12</sup> In this study, the water uptake values of the sulfonated PVA membranes decreased with the amount of sulfonic acid added (Table I) and so a decrease in proton conductivity with the amount of sulfoacetic acid could be expected. Therefore, there should be an optimum value of the amount of sulfoacetic acid used, in which the effect of the degree of sulfonation and the effect of water uptake on proton conductivities of the sulfonated PVA membranes are compromised. In this study, the optimum value of the amount of the sulfoacetic acid is 15% by weight. Beyond this value, the water uptake became the predominating factor affecting the proton conductivities of the membrane.

The methanol permeability values of the sulfonated PVA are also illustrated in Table II. The methanol permeability values decrease with the amount of sulfoacetic acid. This is in a good agreement with a decrease in water uptake values of the membrane with the amount of sulfoacetic acid (Table I). The methanol permeability and the water uptake of the membranes are related, i.e., the higher the water uptake is, the more the methanol solubility in the membrane and vice versa. Consequently, the methanol permeability, which is attributed from methanol

**TABLE II**  
**Proton Conductivity and Methanol Permeability Values**  
**of Various Sulfonated PVA Membranes Modified**  
**by Using 80% Poly(acrylic acid)**

Sulfoacetic acid content (%)	Proton conductivity (S/cm)	Methanol permeability (cm <sup>2</sup> /sec)	C/P ratio
0	$0.57 \times 10^{-3}$	$3.46 \times 10^{-7}$	$0.16 \times 10^4$
5	$2.52 \times 10^{-3}$	$3.94 \times 10^{-8}$	$6.39 \times 10^4$
10	$3.06 \times 10^{-3}$	$5.21 \times 10^{-9}$	$58.68 \times 10^4$
15	$6.35 \times 10^{-3}$	$2.66 \times 10^{-9}$	$238.78 \times 10^4$
20	$1.92 \times 10^{-3}$	No methanol crossover	$\infty$

solubility and diffusion coefficient of methanol through the membrane, also decreased with a decrease in the water uptake value of the membrane. Interestingly, the methanol permeability values of the sulfonated PVA membranes are much lower than those of the Nafion115 membrane measured in this study ( $3.5 \times 10^{-7} \text{ cm}^2/\text{s}$ ).

Finally, to obtain some idea about the comparative performances of the various sulfonated PVA membranes in a direct methanol fuel cell (DMFC), ratios between proton conductivity and methanol permeability (C/P) of various membranes might be considered (Table II). On the basis of the C/P ratio, it seems that the best membrane to be used in DMFCs is the one that was prepared by using 20% sulfoacetic acid. This type of membrane has zero methanol permeability and thus an infinite value of the C/P ratio. In practice, however, other factors such as mechanical behaviors of the membranes, especially when they are fully hydrated, should also be taken into account. In this study, it was observed that the sulfonated PVA membranes became more fragile as the amount of sulfoacetic acid used was increased. It seems that only the sulfonated PVA membranes modified by using 5 and 10% sulfoacetic acid are sufficiently strong and ductile for handling. Therefore, these membranes are recommended for use in DMFCs.

### CONCLUSION

Crosslinked sulfonated PVA membranes were prepared by reacting PVA with sulfonating agents and poly(acrylic acid). The use of sulfoacetic acid as a sulfonating agent is preferable to the use of sodium

sulfoacetate. The proton conductivity values of the sulfonated PVA membranes are comparable to those of the Nafion115 membrane whereas the methanol permeability values of the membranes are much lower than that of the Nafion membrane. These membranes are considered to be a good candidate for use as an electrolyte polymeric membrane in direct methanol fuel cells.

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