

Effect of the Molecular Weight of Poly(vinyl alcohol) Blended with Sulfonated Polysulfone Membranes for Fuel Cell Applications

Sung Hyuk Chang, Sung-Il Chung, and Ji Won Rhim[†]

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

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Abstract: In order to improve the mechanical properties of the sulfonated polysulfone (SPSf) membranes previously synthesized in our laboratory, poly(vinyl alcohol) (PVA) was blended which is well known as the excellent physical and chemical properties. The resulting membranes blended with several molecular weight of PVA varying from 13,000 to 124,000 have been characterized to investigate the effect of PVA molecular weight in terms of ion conductivities, methanol permeabilities, water contents and ion exchange capacities for both heat treated and untreated membranes at 150°C. The proton conductivity is decreased as the molecular weight of PVA increases. The plain SPSf-6.0 showed the proton conductivity of 0.078 S/cm whereas the blended membrane with M.W. 31,000 PVA indicated 0.04 S/cm. For methanol permeabilities, when PVA is added to SPAf-6.0, methanol crossover is increased because of the gain of the hydrophilicity from 3.4 to $6.5 \times 10^{-6} \text{ cm}^2/\text{s}$. For the annealed blended membranes (with M.W. 31,000 PVA), both the methanol crossover and proton conductivity showed very consistent values, about $2.3 \times 10^{-6} \text{ cm}^2/\text{s}$ and 0.036 S/cm, respectively.

Keywords: Direct methanol fuel cell, polymer electrolyte fuel cell, cation exchange membrane, sulfonation polysulfone, methanol permeability, proton conductivity

1. Introduction

Today, the air pollution is mainly due to internal combustion motor vehicles. Fuel cells represent a promising alternative for portable power generation and transportation. Since the last a few years, the development of membrane materials for polymer electrolyte fuel cell (PEFC) has been a hot issue in fuel cell applications[1-4]. PEFC is one of fuel cell types and particularly can be operated at ambient temperatures from room temperature to 100°C[5]. PEFC is fundamentally an assembly consisting of catalyzed electrodes and proton exchange membrane(PEM), and commonly hydrogen and methanol have been used as proton donors [6]. Here, although the percentage of PEM in overall cost is about 10%, the role of PEM is very important

to optimize PEFC.

Nafion[®], only commercially available PEM, has been used since early stage of development of PEFC because of its high proton conductivity ($\sim 0.1 \text{ S/cm}$), excellent thermal and chemical stability, and good mechanical properties. However, Nafion[®] has some drawbacks in PEFC application. At first, it is still high cost at present although its cost might have cut down considerably in the future. In addition, it seems to be inappropriate to be used in methanol-fueled PEFC, so-called direct methanol fuel cell (DMFC) because of high methanol permeability in an order of magnitude of $10^{-6} \text{ cm}^2/\text{sec}$ at ambient temperature. For these reasons, many engineering thermoplastic polymers such as polyimides[7,8], polybenzimidazoles[9], polyphosphazenes [10], polyetheretherketones[11], and polysulfones[12-14] have been investigated in their sulfonated forms as alternative materials of Nafion[®].

Of these polymers, polysulfone is a high performance

[†] Author for all correspondences
(e-mail : jwrhim@mail.hannam.ac.kr)

polymer and a thermoplastic resin with good thermal and chemical stability and high mechanical strength. And it is very resistant to hydrolysis and oxidation, and withstands prolonged exposure to high temperature and repeated sterilization. As such, it has been used for various membrane applications[15-17]. Sulfonated polysulfone(SPSf) ionomer membranes has been tested for PEFC application[18,19]. Proton conductivity of SPSf membranes is a reasonable value up to 10^{-2} S/cm at room temperature to 80°C but still lower than that of sulfonated perfluoropolymer(Nafion 117). However, SPSf membranes have lower permeability of gases and liquids(water and methanol) preventing the loss of fuel from anode to cathode and hence, maximize the voltage in the region of low current densities.

In previous study[20], sulfonated polysulfone synthesized in our laboratory showed poor mechanical strength for fuel cell applications as the sulfonation degree increased. In this paper, poly(vinyl alcohol) (PVA) is considered to reinforce the poor mechanical properties of SPSf. Besides, the various molecular weight of PVA is added into SPSf to elucidate its dependence on the ionic properties. In general, a simple annealing effect has been used to stabilize the glassy polymer membrane [21]. The heat treatment has caused a densification of the polymer matrix and leads to a reduction of chain mobility and at the same time hinders the membrane plasticization by sorption of gas and liquid molecules. Therefore, in this study, the heat treatment is also carried out for the resulting blended SPSf and PVA membranes.

2. Experimental

2.1. Materials

Polysulfone (PSf, Udel P-3500, Amoco, USA) was dried for more than 48 h at 60°C in a circulating hot air oven for further use. Chlorosulfonic acid (CSA, 99% Aldrich, Milwaukee, WI, USA) and chloromethylsilane (TMCS, 98% Aldrich) were used as sulfonating agents. Triethylamine (TEA, 99.5%, Aldrich) was employed to remove HCl gas evolved during sulfonation. Fully

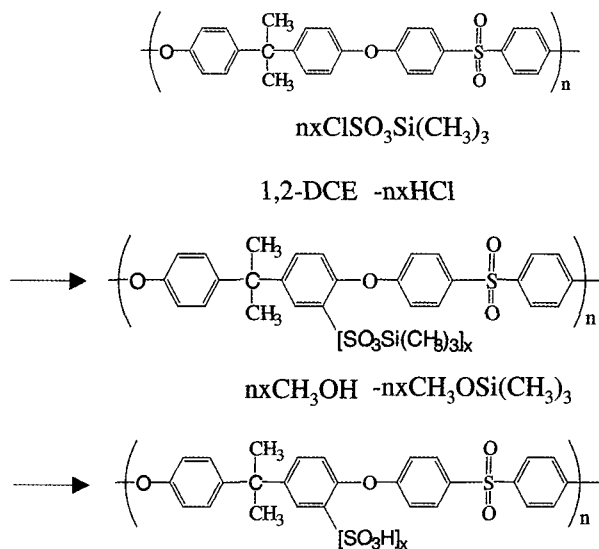


Fig. 1. Reaction mechanism of sulfonated polysulfone

hydrolyzed poly(vinyl alcohol) (PVA) with several molecular weight of 13,000, 31,000, 89,000 and 124,000 was purchased from Aldrich Co. (Milwaukee, USA). The other chemicals used in this study, methanol (MeOH), HCl, NaOH and H_2SO_4 from Hayman, Junsei, Aldrich and Merck, respectively.

2.2. Preparation of Sulfonated Polysulfone [20]

The dried PSf 10 g is dissolved in DCE 100 mL for more than 12 h with stirring. The sulfonating agents are prepared with the mole ratio 1:1 of CSA and TMCS. Since the mole ratio 6 between the repeating unit of PSf and the prepared sulfonating agent (CSA+TMCS) in the previous study showed the best results, this ratio is always used to prepare SPSf in this study (we call SPSf-6.0 afterwards). The synthesized PSf-6.0 is dried for 3 days in vacuum oven at 60°C . The postulated reaction mechanism is shown in Figure 1.

2.3 Preparation of Blended Membranes

The synthesized SPSf-6.0 is mixed together with 10% PVA solution having various molecular weight from 13,000 to 124,000. To obtain homogeneous solution, it is stirred for more than 24 h. The mixed solution was cast onto Teflon glass plate using a Gardner knife and then the cast solution was evaporated and

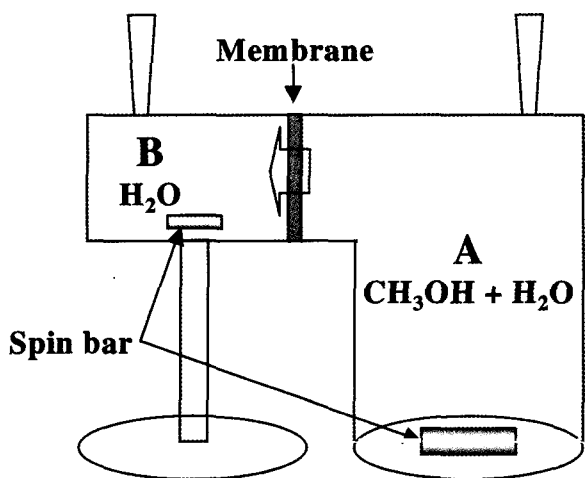


Fig. 2. Diffusion cell for methanol permeability measurement.

well-dried at 60°C in a vacuum oven for overnight, and finally SPSf-PVA membranes were carefully peeled off. One part of these SPSf membranes was annealed at 150°C for 2 h. All prepared membranes were dipped and soaked in deionized water for 24 h in order to measure proton conductivity and methanol permeability.

2.4 Methanol Permeability

The diffusion cell shown in Figure 2 was used to determine methanol permeability of the SPSf/PVA blended membranes. This glass cell consisted of two chambers separated by a membrane. One compartment of the cell (V_A , 250 mL) was filled with a 2 M solution of methanol in deionized water. The other side (V_B , 35 mL) was filled with pure ionized water. The membrane (effective area 7.02 cm²) was clamped between the two compartments and these were kept under stirring during 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 $C_B \gg C_A$, the methanol concentration in the receiving compartment as a function of time is given by:

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

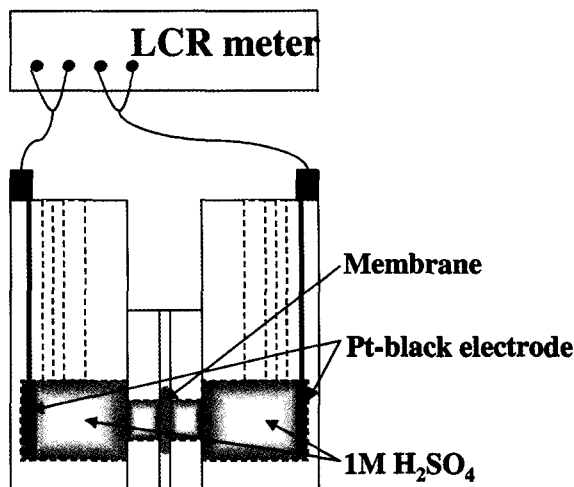


Fig. 3. Schematic diagram of ion conductivity measurement.

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).

$$P = \frac{1}{A} \cdot \frac{c_B(t)}{c_A(t - t_0)} \cdot V_{BL} \quad (2)$$

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 a gas chromatography equipped with Porapak Q column (Younglin Model 690D, Korea). During permeability tests the diffusion cell was immersed in a thermostatic water bath to maintain a constant temperature.

2.5. Ion Conductivity Measurement

The ion conductivity of membranes was determined using LCR hitester (Reactance Capacitor Resistor, Hioki Model 3522) connected with the measurement cell (See Figure 3). Prior to the measurement, the membrane samples were immersed in 1mol/L H₂SO₄ solution at 25°C over 1day and then inserted into the

cell and current (1 V) was supplied by LCR hitester with a frequency 1000Hz. The ion conductivity (σ) was obtained by a following equation;

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

where σ is proton conductivity (S/cm), l is membrane thickness (cm), R is resistance (Ω) and S is surface area for ion to penetrate through (cm²).

2.6. Ion Exchange Capacity (IEC) and Fixed Ion concentration

The ion exchange capacity (IEC value) was measured by the classical titration (ASTM 2187) of the released amount of H^+ of the pre-weighed polymer in an acid form in 1M 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:

$$A_w = IEC / W \quad (4)$$

where W is water content.

2.7. Water Content

Water contents of SPSf-6.0/PVA blended membranes were measured using following method. The sorption capacity of the membrane was measured by immersing the membrane samples in the pure component 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 at room temperature to a constant weight. Water content (W) was calculated as follows:

$$\begin{aligned} \text{Water content } (W) &= \frac{W_{wet} - W_{dry}}{W_{dry}} \\ &= \frac{g \text{ H}_2\text{O}}{g \text{ dry membrane}} \end{aligned} \quad (5)$$

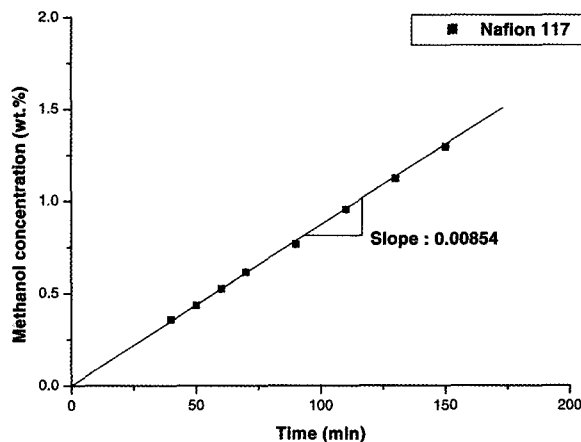


Fig. 4. Typical diffusion data of Nafion 117.

3. Results and Discussion

3.1. Methanol Permeability

Figure 4 shows the linear relationship between the methanol concentration in the receiver (chamber V_B) and the time for the commercial Nafion 117 membrane at 25°C. The calculated methanol permeability from the slope is $2.11 \times 10^{-6} \text{ cm}^2/\text{s}$. Since this value is close to the published permeability $2.3 \times 10^{-6} \text{ cm}^2/\text{s}$, it is considered that the measured values from the diffusion cell designed by our laboratory would be reasonable.

A main problem arises for DMFC, as methanol is easily transported through the most PEM materials by means of (a) active transport together with the protons and their solvate water called as electroosmotic drag as well as (b) diffusion through the water-filled domains within the PEM structure and finally (c) diffusion through the PEM itself. Hence, the prevention of methanol crossover through PEM materials has become a main issue to solve in PEM design for DMFC.

The methanol permeability of the blended membranes of SPSf and PVA with untreated and annealed SPSf and PVA blended membranes as a function of the molecular weight of PVA from 13,000 to 124,000 is illustrated in Figure 5. For untreated blended membranes, the methanol permeability increased from $3.41 \times 10^{-6} \text{ cm}^2/\text{s}$ to $5.0 \times 10^{-6} \text{ cm}^2/\text{s}$ once PVA was added and

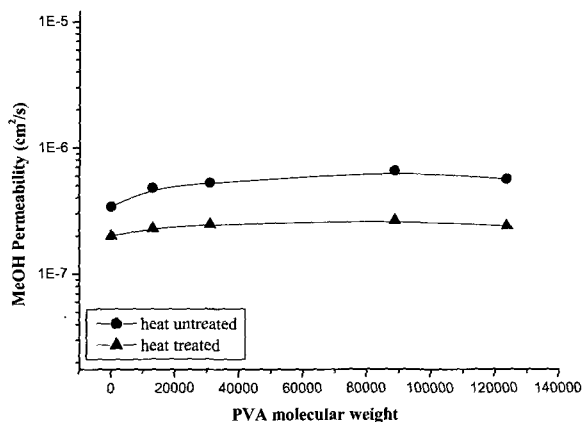


Fig. 5. Effect of the molecular weight of PVA on the methanol permeability.

then apparently reached to constant values. It is considered to be reasonable since the same amount of PVA is blended with SPSf. Generally, the introduction of hydrophilic moiety such as hydroxyl groups into a different polymer would enhance the water solubility assuming that totally miscibility each other. And it is usually accompanied by the increase of degree of swelling due to hydration of water so that methanol molecules could pass through enlarged hydrophilic channels of the membrane matrix.

In case of annealed membranes, the same trend was shown, i.e. the increase from $2.0 \times 10^{-6} \text{ cm}^2/\text{s}$ to $2.3 \times 10^{-6} \text{ cm}^2/\text{s}$. In general, the annealing leads to the reduction of the void volume in membranes through a densification of the polymer matrix resulted from the arrangement and repacking of polymer chains. However, when compared to the permeability of untreated membranes, the increase ratio is remarkably reduced.

3.2. Proton Conductivity

The main factors to determine proton conductivity in ionomer membranes are generally dependent on the amounts of proton exchange sites (sulfonic acid, carboxylic acid groups, etc.) per unit volume and the water content in the ionomer polymers. From this point on, it is meaningful to consider the relationship between the factors and the proton conductivity. Figures. 6 and 7 show the ion exchange capacities (IECs) and proton.

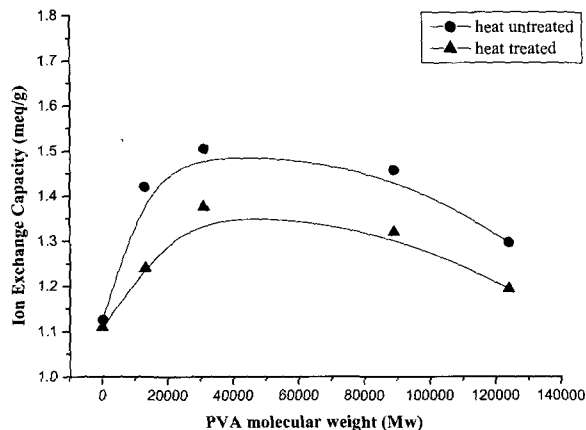


Fig. 6. Ion exchange capacity of SPSf-6.0 membranes blended with various molecular weight of PVA.

conductivities of the SPSf-6.0 and PVA blended membranes at 25°C, respectively. As the molecular weight of PVA increases, the proton conductivities decrease monotonously decrease, whereas the IECs increase to M.W.=31,000 and then decrease. It was confirmed in the previous study [20] that the annealing at 150°C did not cause any thermal degradation of sulfonic acid groups in SPSf membranes which showed T_g 's 185°C for pure PSf and 225°C for SPSf, respectively. The addition of low molecular weight of PVA would act as the reinforcement material and hence leads to significantly lowering the proton conductivity. And the membrane densification through annealing at sub- T_g for any glass polymers like PSf increases the packing density of the membranes and, as a results, forms the hydrophilic pathway where protons pass might be narrower in the annealed SPSf-6.0 and PVA blended membranes. This trends become more severe for both the untreated and annealed blended membranes as the molecular weight of PVA increases, i.e. more membrane compaction occurs. Therefore, it is considered that the mechanical strength of the blended membranes would be increased although the proton conductivity decreases.

However, for ion exchange capacity as illustrated in Figure 7, the measured values show erratic results even if the same amount of PVA is added into SPSf-6.0. All IEC values show larger than that of plain SPSf-6.0 membranes. As mentioned in the above,

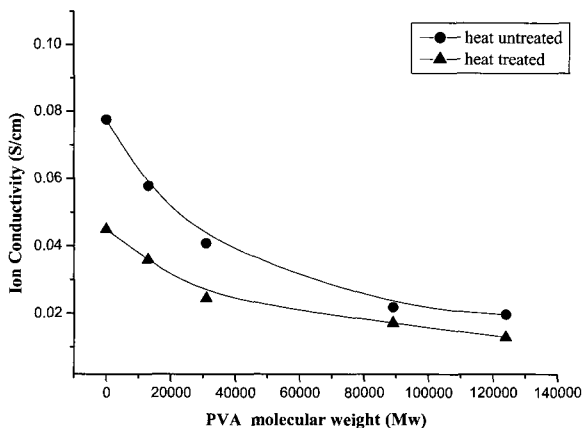


Fig. 7. Proton conductivity of SPSf-6.0 membranes blended with various molecular weight of PVA.

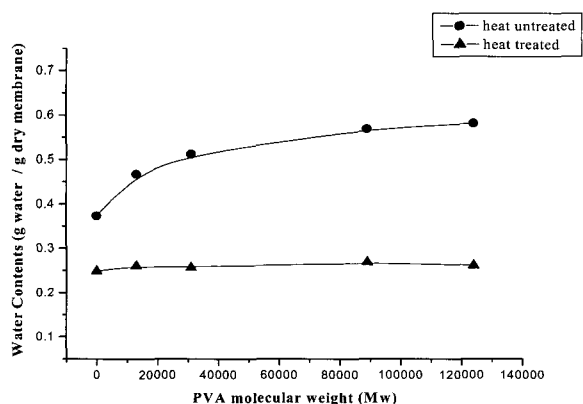


Fig. 8. Water content of SPSf-6.0 membranes blended with various molecular weight of PVA.

the proton conductivity can arise from the proton exchange sites. According to Cussler[22], the crosslinked PVA has the proton conductivity from 0.014 to 0.053 *S/cm* depending on the crosslinking density. Therefore, when the low molecular weight of PVA is used, the IECs increase whereas the IECs decrease with the use of high molecular weight of PVA due to the reduction of chain mobility.

3.3 Water Contents

Water contents and fixed ion concentration are illustrated in Figure 8. As the molecular weight of PVA increases, the water content increases. It seems that the blended membranes are very unstable since PVA is water-soluble polymer. However, the water contents of

the heat treated membranes shows very consistency.

4. Conclusions

Since the sulfonated polysulfone synthesized in our laboratory showed poor mechanical strength for fuel cell applications, in this paper, poly(vinyl alcohol) (PVA) is considered to reinforce the poor mechanical properties of SPSf. Besides, the various molecular weight of PVA is added into SPSf to elucidate its dependence on the ionic properties. The followings are concluded :

(1) The proton conductivity is decreased as the molecular weight of PVA increases. The plain SPSf-6.0 showed the proton conductivity of 0.078 *S/cm* whereas the blended membrane with M.W. 31,000 PVA indicated 0.04 *S/cm*.

(2) For methanol permeabilities, when PVA is added to SPAf-6.0, methanol crossover is increased because of the gain of the hydrophilicity from 3.4 to $6.5 \times 10^{-6} \text{cm}^2/\text{s}$.

(3) For the annealed blended membranes (with M.W. 31,000 PVA), both the methanol crossover and proton conductivity showed very consistent values, about $2.3 \times 10^{-6} \text{cm}^2/\text{s}$ and 0.036 *S/cm*, respectively.

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