

Preparation and Characterizations of Direct Methanol Fuel Cell Membrane from Sulfonated Polystyrene/Poly(vinylidene fluoride) Blend Compatibilized with Poly(styrene)-*b*-Poly(methyl methacrylate) Block Copolymer

P. Piboonsatsanasakul,¹ J. Wootthikanokkhan,¹ S. Thanawan²

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

²Institute of Science and Technology for Research and Development, Mahidol University, Nakorn Pathom 73170, Thailand

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ABSTRACT: This work concerned a development of sulfonated polystyrene (SPS)/poly(vinylidene fluoride) (PVDF) blend membrane for use as an electrolyte in a direct methanol fuel cell. The aim of this work was to investigate effects of the blend ratio on properties of the blend membranes. The partially SPS with various degrees of substitution were prepared by using propionyl sulfate as a sulfonating agent. After that, the optimum SPS was selected for further blending with PVDF, at various blend ratios. Poly(styrene)-poly(methyl methacrylate) block copolymer (PS-*b*-PMMA), used as a compatibilizer, was synthesized via a controlled radical polymerization through the use of an iniferter. Thermal behaviors, water uptake, proton conductivity, and methanol permeability of various blend membranes were determined by using TGA, gravimetry,

impedance analyzer, and gas chromatography, respectively. From the results, it was found that, water uptake and methanol permeability of the blend membranes tended to increase with the weight ratio of SPS. It was also found that the blend membranes were incompatible, especially those containing more than 40 wt % of the SPS. However, by adding 5 wt % of the block copolymer, the blend became more compatible. Mechanical strength, proton conductivity, and resistance to methanol crossover of the blend membrane remarkably increased after the compatibilization. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1325–1336, 2008

Key words: blends; membranes; polystyrene; polyelectrolytes; compatibilization

INTRODUCTION

Electrolyte polymeric membrane is considered to be one of the most important parts in a membrane electrode assembly, which is used in a proton exchange membrane fuel cell (PEMFC). The main function of the membrane is to act as a solid electrolyte, conducting protons from anode to cathode to complete the redox reaction. Normally, for the PEMFC utilizing hydrogen as a fuel, the Nafion membrane, which is basically a perfluorinated polymer containing sulfonic acid groups, is commonly used as an electrolyte polymeric membrane because of the fact that

proton conductivity, thermal stability, and chemical stability of the material are sufficiently high. However, the Nafion membrane still has some limitations and disadvantages such as a considerably high cost of the material amounting to US \$700/m²,^{1,2} a reduction of proton conductivity at an operating temperature high above water boiling point,³ and a poor methanol resistance of the membrane.

Methanol resistance of an electrolyte polymeric membrane has been an important issue in developments of direct methanol fuel cells (DMFC). The DMFC is a kind of PEMFC, which utilize methanol, directly used as a fuel without reforming the alcohol into hydrogen. When Nafion membrane is used as an electrolyte in the DMFC, it was reported⁴ that about 40% of the methanol was lost through the process called "methanol crossover." Furthermore, the presence of methanol in the cathode side would reduce cathode voltage and efficiency of the fuel cell. Therefore, some new electrolyte polymeric membranes that can be used as a replacement of the Nafion membrane in the direct methanol fuel cell

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

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have been extensively explored. Generally, those membranes being developed might be classified into three main groups¹ i.e., perfluorinated polymeric membranes such as a Nafion composite membrane,⁵ the membranes based on some partially fluorinated polymers such as poly(vinylidene fluoride)-*graft*-sulfonated polystyrene (PVDF-*g*-SPS),⁶ and the non-fluorinated polymeric membranes such as sulfonated poly(vinyl alcohol).⁷

In this study, development of electrolyte polymeric membranes from PVDF is of interest because mechanical properties, thermal stability, and chemical stabilities (in terms of resistance to oxidation and hydrolysis) of the PVDF are sufficiently high with respect to the DMFC operating conditions. In addition, since the PVDF molecules are hydrophobic, a low methanol permeability of the PVDF membrane could be expected. In fact, there have been some reports^{8,9} claiming that methanol crossover of many proton conductive polymeric membranes decreased after blending with the PVDF. However, the PVDF molecules lack sulfonic acid groups, which are responsible for promoting the proton conductivity. Therefore, some kinds of modifications of the polymer have to be carried out before use.

In our earlier study, proton conductivity of the PVDF-based membrane was induced by blending it with sulfonated poly(ether etherketone) (SPEEK).¹⁰ It was found that methanol resistance of the blend membranes increased at the expense of proton conductivity of the material. Nevertheless, the proton conductivity of the optimum blend membrane was comparable to that of Nafion 115, whereas methanol resistance of the former membrane was much lower than that of the latter. Unfortunately, cost of the poly(ether etherketone) raw material used to prepare the SPEEK is considerable. In this regard, some other inexpensive polymers capable of undergoing sulfonation by reacting with some sulfonating agents should be considered. These polymers include styrenic-based polymers such as PS and styrene-ethylene/butylenes-styrene triblock copolymer (SEBS). In these kinds of blend, compatibility between the styrene-based polymers and the PVDF is considered to be one of the most important factors affecting properties of the blend membranes and that should be controlled. For example, Mokriani et al.¹¹ developed a new electrolyte polymeric membrane by blending PVDF with the SEBS, using poly(methyl methacrylate-butylacrylate-methyl methacrylate) block copolymer as a compatibilizer. It was found that, by using the block copolymer, mechanical properties, ion exchange capacity, and proton conductivity of the blend membrane increased at the expense of their water uptake. The results were discussed in the light of change in morphology of the blend membranes that could also be translated into changes in connec-

tivity and geometry of the hydrophilic/hydrophobic domains.

Alternatively, poly(styrene sulfonic acid) (PSSA) or SPS or both might be considered for use as a proton conducting polymer for blending with PVDF. Even though the PSSA membrane might chemically degrade during the fuel cell operation in the long term, owing to an attack at the tertiary hydrogen at the α -carbon by peroxide intermediate,¹² by grafting the PSSA onto PVDF, it was reported that the degradation of PSSA membranes can be delayed.^{13,14} To overcome a tentative poor compatibility between PSSA and the PVDF, Chen and Hong¹⁵ used poly(styrene sulfonic acid-methyl methacrylate) random copolymer [P(SSA-*r*-MMA)], for blending with the PVDF prior to casting the solution blend into a membrane. In this case, the presence of poly(methyl methacrylate) (PMMA) repeating units in the P(SSA-*r*-MMA) copolymer promoted a better compatibility between the copolymer and the PVDF. It was also found that there is an optimum ratio of PSSA repeating units in the copolymer, over which the blend membrane became fragile, and no substantial increase in proton conductivity could be gained. A similar work on the development of an electrolyte membrane based on PSSA/PVDF blend was carried out by Prakash et al.¹⁶ In that case, however, the PSSA was blended with the PVDF in a form of semi-interpenetrating polymer network (sIPN). This was performed by immersing PVDF membrane into a mixture of styrene monomer and divinylbenzene crosslinker, prior to carrying out a polymerization of the monomer through the use of AIBN initiator. After that, the sIPN membrane was impregnated in chlorosulfonic acid to attach sulfonic acid groups into aromatic rings of the PS molecules. Compatibility between the PSSA and PVDF was believed to be attributed to the crosslinking structure in the sIPN, restricting a phase separation between the two polymers.

In our present study, development of an electrolyte polymeric membrane by blending PVDF with partially SPS is of interest. By blending the two polymers together, it is believed that an optimized blend membrane with a compromised proton conductivity, methanol resistance, and cost would be obtained, depending on the blend ratio. To cope with a tentative poor compatibility between the SPS and the PVDF, PS-*b*-PMMA block copolymer will be used as a compatibilizer in this system. It is believed that PS block in the copolymer would be miscible with the partially SPS, whereas the PMMA block in the copolymer is known to be miscible with PVDF.^{17,18} The aim of this study is to investigate effects of blend ratio and the use of PS-*b*-PMMA copolymer on water uptake, proton conductivity, and methanol permeability of the SPS/PVDF blend membranes.

EXPERIMENTAL

Materials

Polystyrene (PS, Styron 656D, MFI = 8.5) was purchased from the Sigm Polystyrene Co. Ltd (Rayonga, Thailand). Weight-average molecular weight (M_w) and number-average molecular weight (M_n) of the polymer determined from GPC were 230,000 and 140,000 g/mol, respectively. Poly(vinylidene fluoride) (PVDF, $M_w = 530,000$) was supplied from Fluka (Buohs, Switzerland). Sulfuric acid (analytical grade from Merck, Darmstadt, Germany), propionic anhydride (purum grade from Fluka), methanol (analytical grade obtained from Fisher Chemicals, Pittsburgh, PA), and dimethyl formamide (DMF, analytical grade from Univar, NSW, Australia) were used as received.

Preparation of partially sulfonated polystyrene

In this study, rather than carrying out a sulfonation of PS by immersing the polymeric membrane in conc. sulfuric acid solution¹⁹ or in chlorosulfonic acid²⁰ or in both as commonly used in some literatures, the PS was sulfonated by reacting it with acyl sulfate. This method was preferable because the reaction system is homogeneous, and thus a more uniform sulfonated polymeric membrane can be obtained. Generally, an acetic anhydride is commonly used as a starting chemical to react with sulfuric acid to yield an acetyl sulfate,²¹ which is considerable to be the real sulfonating agent. In our experiment, however, propionic anhydride had to be used as a replacement for the acetic anhydride, because the use of acetic anhydride is prohibited in our country. Experimentally, the sulfonation can be divided into two main steps, i.e. preparation of propionyl sulfate and the chemical reaction between PS and propionyl sulfate.

Preparation of propionyl sulfate

The first step was the preparation of propionyl sulfate. In a typical experiment, 7 mL of propionic anhydride was mixed with 17.5 mL chloroform in a test tube. The solution was cooled below 10°C, and then 1 mL of sulfuric acid (96 wt %) was slowly added under vigorous stirring. After mixing completely, the mixture was diluted with chloroform to yield 50 mL solution. Noteworthy, this propionyl sulfate is rather unstable; therefore, the freshly prepared solution had to be used immediately after the preparation.²²

Sulfonation reaction

In the second step, a solution of PS was prepared by dissolving 9 g of the polymer in 100 mL of cyclohex-

ane in a three-neck round bottom flask, at 60°C. After that, a given amount of the freshly prepared propionyl sulfate was slowly added to the polymer solution under vigorous stirring. The solution was purged with nitrogen for 15 min and kept stirring at 60°C for 3 h. Change in color of the solution from colorless to brown can be noted, indicating the progress of the sulfonation. To obtain the partially SPS with a higher degree of substitution, the amount of the propionyl sulfate should be increased.

After the sulfonation was finished, the solution was precipitated in 6500 mL of methanol. The precipitate was washed with boiling water for 5 h by refluxing. This was repeated by several times (5–7 times) until the solution is neutral. The precipitate was washed twice with ethanol, each for 2 h. Finally, the precipitate was dried under vacuum at 70°C for 3 days.

Determination of the degree of substitution

About 0.3 g of the sulfonated polymer was dissolved in 30 mL of toluene/methanol mixture (90/10% v/v). After that, the SPS solution was titrated with 0.02 mol/L of NaOH solution in methanol, using phenolphthalein as an indicator. The degree of substitution (DS) was expressed in terms of milliequivalent of sulfonation per 100 g of the sulfonated polymer.²³

Characterizations of the sulfonated polystyrene

Fourier Transform Infrared Spectroscopy (FTIR) technique was used to detect the sulfonic acid ($-\text{SO}_3\text{H}$) groups in the SPS. The FTIR spectrum was recorded by using a Bruker FTIR (Equinox 55). The polymer sample was prepared in the form of KBr pellet, and the spectrum was scanned over the wavenumber ranging between 600 and 4000 cm^{-1} . Sixteen scans were taken with a resolution of 2 cm^{-1} .

In addition, chemical structure of the SPS was characterized by using a ^{13}C NMR spectroscopy. The polymer sample was dissolved in chloroform-*d*, and then the ^{13}C NMR spectrum was recorded in a Bruker instrument (Advance DPX400). Chemical shift was referred to that of TMS reference.

Preparation of the block copolymer

In this study, PS-*b*-PMMA block copolymer, used as a compatibilizer for the SPS/PVDF blends, was synthesized via a controlled free radical polymerization technique using tetraethylthiuram disulfide (TD) as an iniferter. More details concerning the mechanism of the iniferter polymerization can be found elsewhere.²⁴ In this experiment, 0.0685 g of TD (7.7×10^{-3} mol/L) was added into a solution of purified styrene (7.2 mol/L in toluene). The monomer solu-

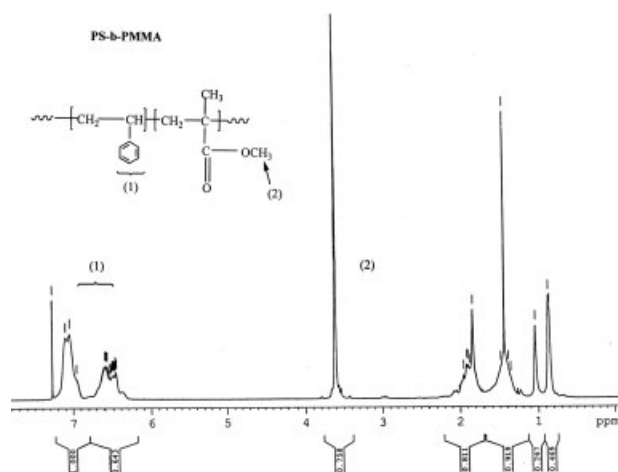


Figure 1 ^1H NMR spectrum of the polystyrene-*b*-poly(methyl methacrylate).

tion was then purged with nitrogen and sealed. After that, the reaction flask was exposed to UV radiation for 16 h. After a given time, the content in the reaction flask was precipitated in a large amount of methanol before drying. The obtained PS is considered to be a macroiniferter that can be further used to react with methyl methacrylate (MMA) to generate PS-*b*-PMMA block copolymer. In this second polymerization step, 0.3 g of the purified macroiniferter along with the MMA monomer (2.12 mL) was dissolved in 5 mL of toluene. The mixture was then purged and sealed before exposure to UV radiation for 6 h. Finally, the content in the reaction flask was precipitated in methanol and then dried in a vacuum oven at 70°C until reaching a constant weight.

Characterizations of the prepared block copolymer by using a gel permeation chromatography (GPC) technique revealed that number-average molecular weight (M_n) and polydispersity index of the synthesized block copolymer were 64,950 g/mol and 2.5, respectively. In addition, by using the integrated area under the peaks in the ^1H NMR spectrum of the copolymer (Fig. 1), the composition of PS block in the copolymer could be calculated, and the obtained value was 57%. This value was in a good agreement with the result from GPC showing that the molecular weight (M_n) of the PS macroiniferter was 37,700 g/mol, which accounted for about 58% of the average molecular weight of the block copolymer.

Preparation of the blend membranes

Two separate solutions of SPS and PVDF were prepared by using dimethyl formamide (DMF) as a solvent. To obtain the solution blend at the desired ratio, a suitable quantity of PVDF solution was added to the SPS solution and stirred at room tem-

perature for a further 30 min. The concentration of the blend solution was kept constant at 10% w/v solution. A suitable amount of the solution was then cast onto a clean glass substrate before drying in an oven at 110°C for 1 h to obtain an $\sim 50\text{-}\mu\text{m}$ -thick membrane. After that, the membrane was peeled off from the substrate and then dried in a vacuum oven at 70°C for a further 12 h to remove any residual solvent. The membrane was kept in deionized water before tests.

Characterization and testing of the blend membranes

Thermal behaviors

The thermal stability of the SPS/PVDF blend membranes was examined by using a thermogravimetric analyzer (TGA, NETZSCH STA 409 C/CD). About 20 mg of the sample was used. The TGA experiment was scanned over temperatures ranging between 28 and 800°C under oxygen (air) atmosphere, at a heating rate of 10°C/min.

Water uptake

The measurement of water uptake of the various membranes was conducted by immersing the membrane into deionized 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_{dry} and W_{wet} are the weight of dry and water-swollen membranes, respectively.

Scanning electron microscopy

Miscibility and the interfacial region between the SPS and PVDF phase in the blend membrane were examined by using a scanning electron microscopy (JEOL JSM5800). The SEM specimen was gold-coated by using a sputtering machine without any staining or etching. This was because osmium tetroxide was not a selective staining agent for this blend system. The use of a stronger staining agent such as ruthenium tetroxide was also not practical in this study, because of the unavailability and a poor stability²⁵ of the chemical. In addition, there was no suitable selective solvent available for etching the minor phase. In this regard, the contrast between the two polymeric phases in the SEM image of the blend membrane was attributed to a topographic contrast. The SEM experiment was operated at 20 kV accel-

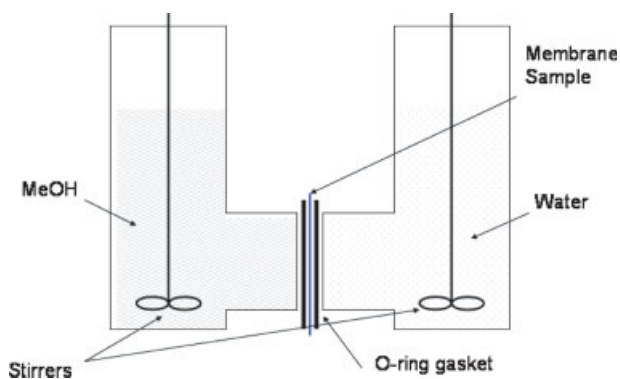


Figure 2 Diagram showing the measurement of methanol permeability by using a diffusion cell. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ating voltage. The detector used was a secondary electron detector.

Atomic force microscopy

An Atomic Force Microscope Multimode Nanoscope IIIA, from Digital Instruments, Santa Barbara, USA, was employed to investigate the surface morphology in contact mode. The specimen was scanned by silicon nitride probe with spring constant of 0.58 N/m. Topographical (height) and deflection images were recorded at tip velocity of 25 $\mu\text{m/s}$, with the image resolution of 512 lines. The presented images were flattened with the second-order plane fit that was implied to remove the tilt and distortion in the images.

Methanol permeability

The resistance to methanol crossover of the membrane was evaluated by measuring the methanol permeability of the membrane. A two-identical-compartment glass cell was used as a diffusion cell for the measurement (Fig. 2). The membrane was placed between the two compartments and then clamped. After that, 20 mL of methanol solution (2M) and 20 mL of deionized 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 compartment B was measured as a function of diffusion time by using a gas chromatography (GC) technique with a FID detector (Agilent, containing porapak QS column). The Injection temperature and the column temperature used for the GC experiment were 220 and 150°C, respectively. The area under the methanol peak from each GC chromatogram was used in combination with a calibration curve to determine the methanol concentration. Finally, the methanol permeability was calcu-

lated from the slope of the plot between the methanol concentration and diffusion time, using 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 compartments 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 DK is the membrane permeability.

Proton conductivity measurement

The proton conductivities of the membranes were measured by using a four-point probe technique (Fig. 3). The impedance of the membranes was measured by using an impedance analyzer (Autolab, PGSTAT 30) at a frequency of 10.0 kHz. The impedance test was carried out at 25°C and 82% relative humidity. The membranes were cut into 3 cm \times 3 cm strips and immersed in deionized 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 the AC potential difference between the two inner electrodes. The conductivity (σ) was calculated by using the following equation:

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

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 (cm^2), and l is the distance between the counter electrode and the working electrode (cm).

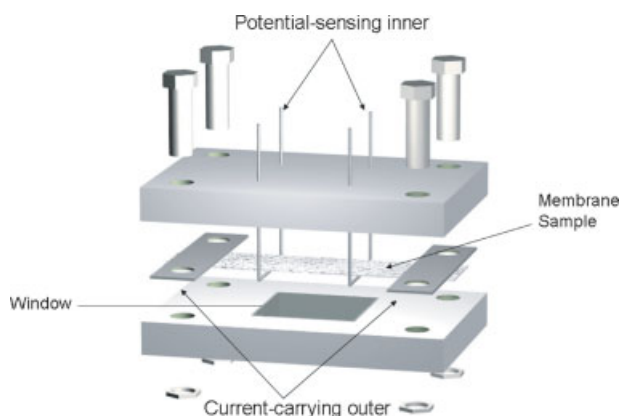


Figure 3 Diagram showing the measurement of proton conductivity by using the four-point probe technique. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

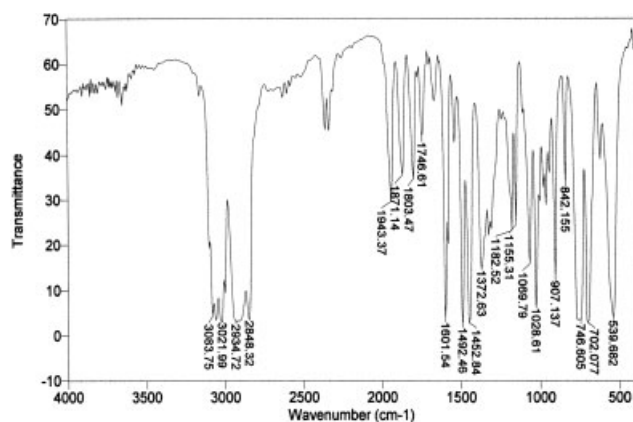


Figure 4 FTIR spectrum of polystyrene.

RESULTS AND DISCUSSION

Characterizations of the sulfonated polystyrene

Figures 4 and 5 show FTIR spectra of PS before and after the sulfonation, respectively. FTIR of the SPS shows new peaks at 1037 and 1126 cm^{-1} . These could be ascribed to the symmetric stretching vibration $\nu_{\text{sym}}(-\text{S}=\text{O})$ and asymmetric stretching vibration $\nu_{\text{asym}}(-\text{S}=\text{O})$ of the SO_3H groups attached to phenyl ring, respectively. In addition, a broad peak at $\sim 3407 \text{ cm}^{-1}$ was noted and that could be ascribed to the stretching mode of O—H bonds in SO_3H groups and in water molecules retained by the sample.

In addition, Figure 6 shows ^{13}C NMR spectrum of the SPS. The chemical shift of the methylene (CH_2) and CH aliphatic group were near 41 and 44.5 ppm,

and the chemical shifts of various types of carbons in the aromatic ring (B_1 , B_2 , and B_3) were near 146, 126.7, and 128.3 ppm, respectively. The peak at the chemical shift of 127.4 ppm could be ascribed to the sulfonated aromatic carbon (B_4). The above results from FTIR and NMR spectroscopy are sufficient to confirm that SPS was successfully prepared.

By carrying out the titration, the degree of substitution (DS) values of SPS obtained by reacting 9 g of PS with 25 mL of the propionyl sulfate was found to be 4.0 (mmole/100 g PS). Further increase in the amount of the sulfonating agent to 150 mL resulted in the SPS with the DS value of 18.3 (mmole/100 g PS). The water uptake of the SPS membrane also increased with the amount of the sulfonating agent. However, by increasing the amount of propionyl sulfate beyond these levels, it was found that the content in the reaction flask could not be precipitated in methanol and water. This was probably because the degree of sulfonation and polarity of the SPS became too high. To obtain a membrane from this solution, the content in the reaction flask might be precipitated in some nonpolar solvents before casting. However, the cast membrane might not be useful for DMFC application, since it would be soluble in water and methanol.

Properties of the sulfonated PS/PVDF blend membranes

Thermal stability

Figure 7 shows TGA thermogram of the SPS (DS value = 4.0). The small initial weight loss ($\sim 4.7\%$)

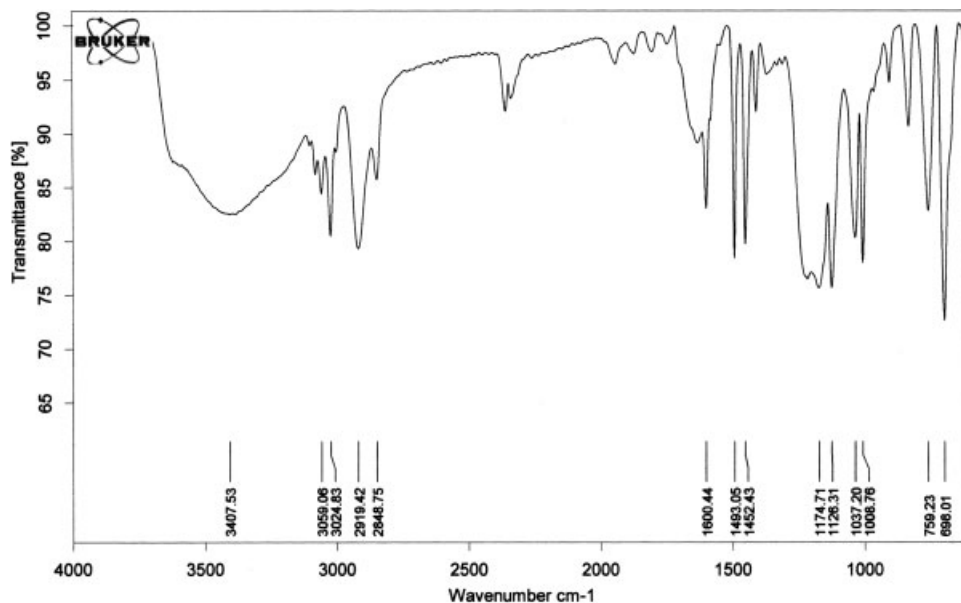


Figure 5 FTIR spectrum of the sulfonated polystyrene.

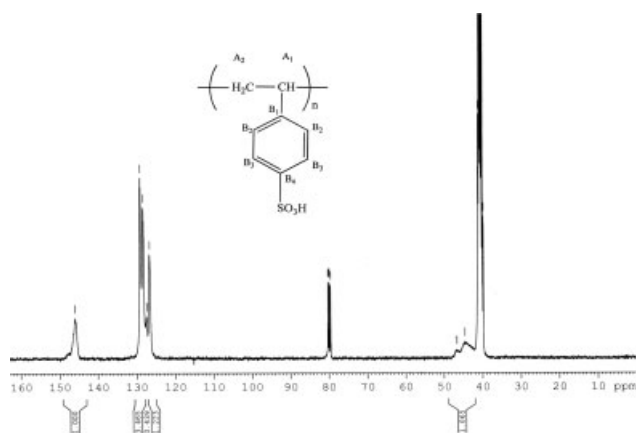


Figure 6 ¹³C NMR spectrum of the sulfonated polystyrene.

over the temperature ranging between 80 and 160°C was due to the loss of some water uptake within the membrane as well as some adsorbed water. The second weight loss (83.42%) occurred over the temperature range between 360 and 460°C and that could be ascribed to the depolymerization of the SPS.²¹ Finally, the third weight loss occurred over the temperature range from 500 to 700°C, owing to the decomposition of the residual solid.

When the SPS was blended with 40 wt % of PVDF, the TGA thermogram slightly changed (Fig. 8). The percentage weight loss of the initial transition decreased to 2.4% because of a lower weight fraction of the sulfonated polymer in the blend sample. In addition, there were two new derivative peaks that occurred at 466.8 and 567.2°C, corresponding to the decomposition of the PVDF molecules.²⁶ TGA thermogram of the blend membrane containing 60 wt % of PVDF (Fig. 9) also shows a similar profile in terms of the onset temperatures and the number of the transitions. However, as the PVDF content in the

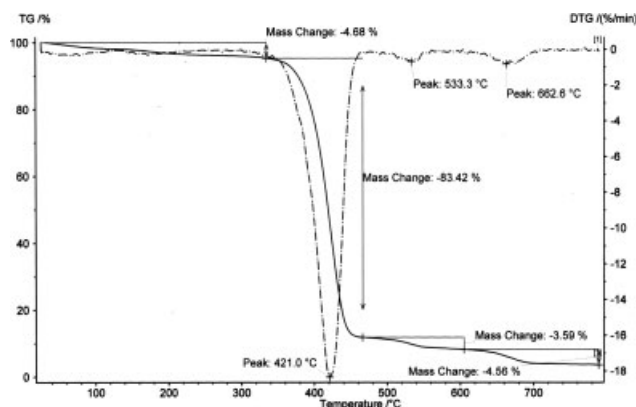


Figure 7 TGA thermogram of the sulfonated polystyrene membrane (DS = 4.0).

blend was increased, the percentage weight loss in the transitions corresponding to the PVDF phase increased, whereas those corresponding to the transitions in the SPS phase decreased. Nevertheless, the results from the above TGA thermograms suggest that the SPS/PVDF blend membranes are thermally stable up to 300°C, which is far above a normal operating temperature of the DMFC (~ 90–120°C).²⁷

Water uptake

Figure 10 shows water uptake values of two sets of SPS/PVDF blend membranes. For the blend containing SPS with a DS value of 4.0, water uptake values of the blend membrane were very low, regardless of the blend ratio. This was probably due to a relatively low degree of sulfonation. As a result, no further attempts were made to determine proton conductivity and methanol permeability of these membranes, since the proton conductivity of an electrolyte polymeric membrane, containing sulfonic acid groups, is strongly dependent on the water uptake value, in accordance with the “vehicle mechanism.”²⁸

To enhance the water uptake and proton conductivity of the blend membranes, the SPS with a higher DS value should be considered. In this study, the SPS with a higher degree of substitution (DS = 18.3) was used as a replacement for blending with PVDF and for further studies. It was found that water uptake values of the resulting blend membranes improved remarkably (Fig. 10). The water uptake value also increased with the ratio of the SPS in the blend. Again, the results can be ascribed to a greater amount of the polar SPS in the blend membrane.

Proton conductivity

Figure 11 compares the proton conductivity values of various membranes. The proton conductivity values

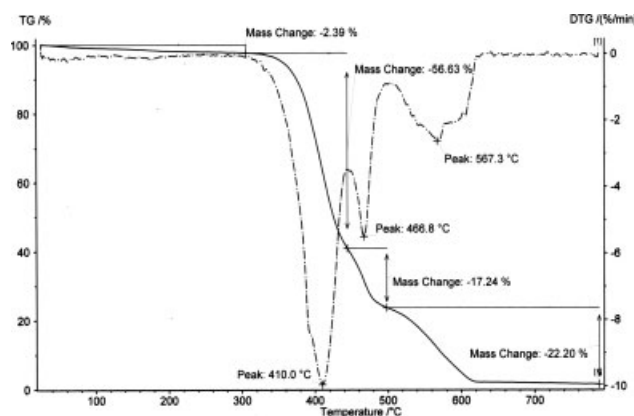


Figure 8 TGA thermogram of the sulfonated polystyrene/PVDF blend membrane (60/40% w/w).

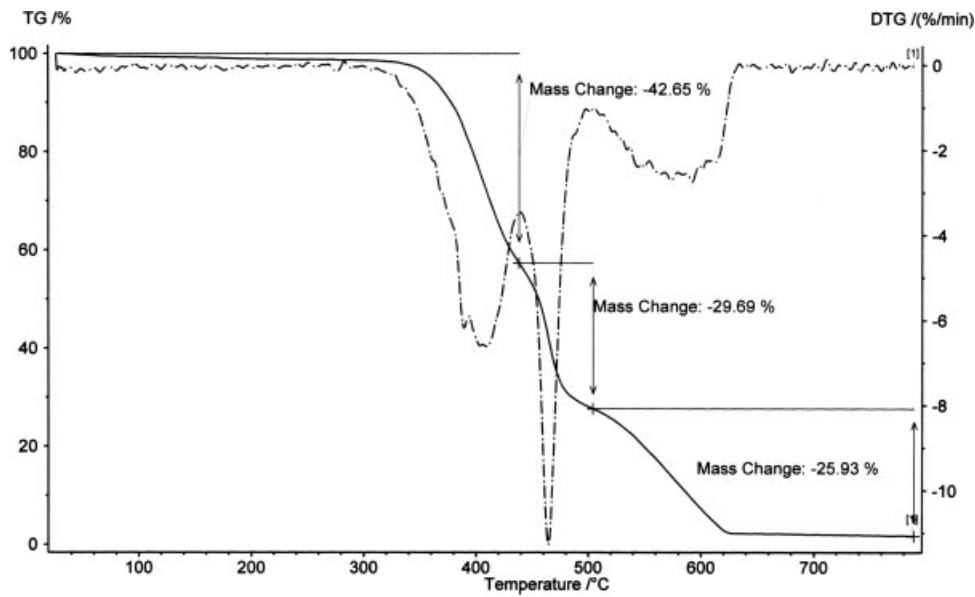


Figure 9 TGA thermogram of the sulfonated polystyrene/PVDF blend membrane (40/60% w/w).

of the SPS membranes increased from 3.69×10^{-3} to 6.91×10^{-3} S/cm, as the DS values of the polymer increased from 4.0 to 18.3. The proton conductivity value of the latter membrane was only slightly lower than that of the Nafion 115 membrane (8.18×10^{-3} S/cm), measured by using the same apparatus. Noteworthy, proton conductivity value of the SPS membrane gradually increased with the DS value of the polymer. This is because proton conductivity of the sulfonated polymer membrane is not only dependent on the DS value, other factors such as per-

centage water uptake and microstructure of the material also influence the proton conductivity of the membrane. In relation to this study, it should be remembered that the water uptake of the membrane increased rapidly from 3 to 20%, as the DS value was increased from 4.0 to 18.3. Generally, an increase in proton conductivity with the percentage water uptake is usually expected, since the water molecules dissociate the acid functional groups and facilitate proton transport. However, a study on SPEEK membranes²⁹ revealed that the relationship

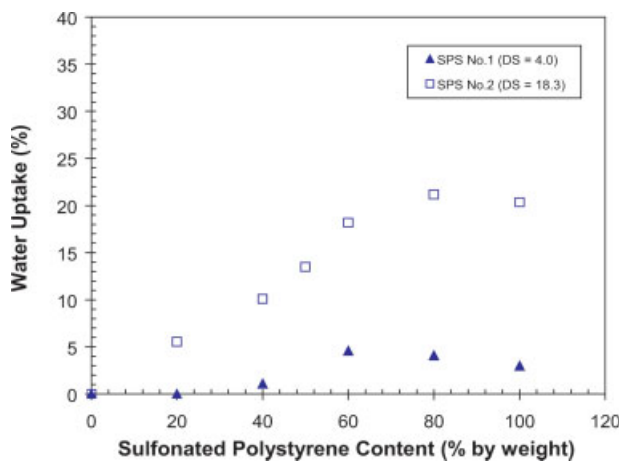


Figure 10 Changes in water uptake value of the blend membranes as a function of sulfonated polystyrene content. Two types of the sulfonated polystyrene (SPS) were used for blending, i.e., the SPS No. 1 (DS = 4.0) and the SPS No.2 (DS = 18.3). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

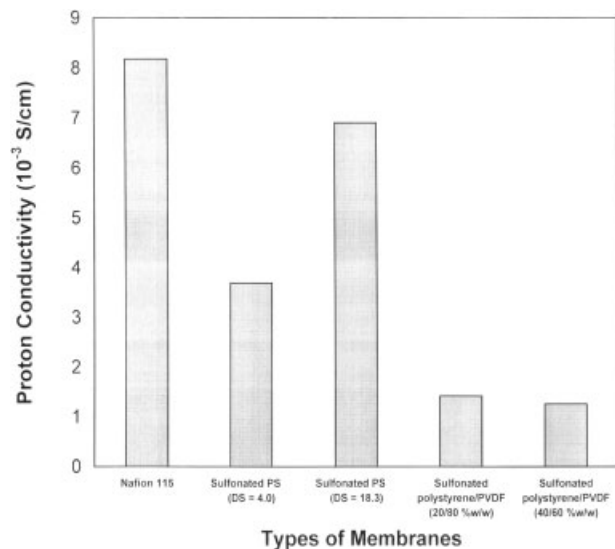


Figure 11 Proton conductivity values of various membranes.

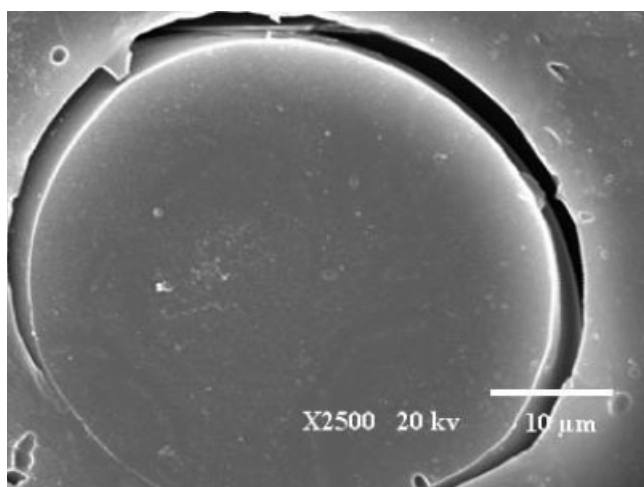


Figure 12 Scanning electron micrograph showing an interfacial area in the sulfonated polystyrene/PVDF blend membrane (40/60% w/w).

between the proton conductivity and the water uptake can be nonlinear. The conductivity increased rapidly from 1×10^{-2} to 9×10^{-2} S/cm, as the water uptake was increased from 33 to 42%. After that, the conductivity only increased slightly from 9×10^{-2} to 10×10^{-2} S/cm, as the water uptake was rapidly increased from 42 to 115%. In our opinion, the above effect might be related to some changes in proton conducting mechanisms with the percentage water uptake. However, some further extensive work has yet to be carried out to clarify this complicated issue. Besides the mechanisms, role of membrane microstructure also deserves a consideration. For example, it was believed that both types of the SPS membranes have a heterogeneous microstructure with polar ion-rich domains separated from a nonpolar matrix. The ion-rich domains in both membranes might be disconnected from one another, and thus the long range proton conductions were limited, regardless of the increase in DS value.

By blending with 80 wt % PVDF, the proton conductivity values of the SPS membranes (DS = 18.3) decreased to 1.42×10^{-3} S/cm. This could be ascribed to the fact that the PVDF is hydrophobic, and thus the water uptake of the blend membrane decreased with the PVDF content (see also Fig. 10). Consequently, the amount of water molecules acting as “vehicles”²⁸ for a transportation of protons decreased. By further increasing the percentage weight of the SPS from 20 to 40 wt %, proton conductivity of the blend membrane hardly changed (1.26×10^{-3} S/cm), taking into account the standard deviation value, which is about 0.11×10^{-3} . This might be attributed to the fact that both blend membranes contain high amount of PVDF, which form a continuous matrix phase. Consequently, transportation and conductivity of protons through the hydrophobic

PVDF matrix phase in the blend membrane were inhibited, regardless of the amount of SPS.

For the blend membranes containing more of the SPS content (above 40 wt %), their proton conductivity values could not be reported. This was because the state of compatibility between the PVDF and the SPS in those membranes were very poor. For instance, it was found that the blend membrane contained 50 wt % of PVDF separated into two layers. The top layer was the PVDF phase, whereas the bottom layer (which was attached to the glass substrate during casting) was the polar SPS. With this poor state of compatibility and homogeneity, data obtained from the proton conductivity measurement could be misleading.

Methanol permeability

Result from the measurement of methanol permeability in the blend membrane containing 20 wt % of the SPS (DS = 18.3) suggested that there was no methanol crossover through the membrane, since no peak corresponding to retention time of the methanol was observed in the GC chromatogram. However, by increasing ratio of the SPS in the blend to 40 wt %, the GC peak corresponding to methanol could be observed. By using the area under the GC peaks in conjunction with the calibration curve, the methanol permeability of the membrane was calculated and the obtained value was 9.8×10^{-9} cm²/s. This permeability value was remarkably lower than that of the Nafion 115 membrane, which was about 3.39×10^{-7} cm²/s.

In our opinion, the increase in methanol permeability of the blend membrane with the SPS content

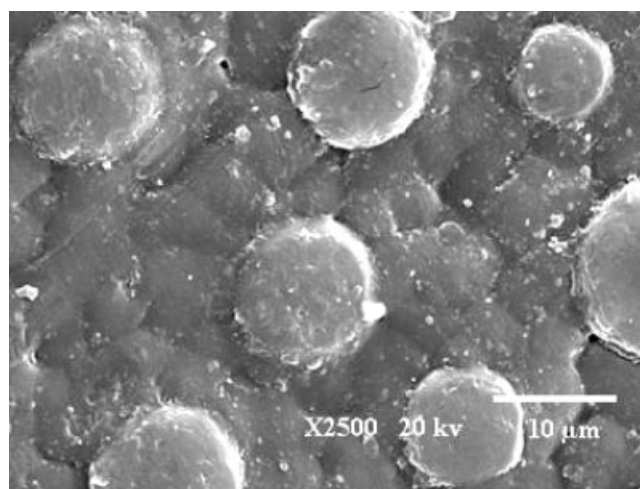


Figure 13 Scanning electron micrograph of the sulfonated polystyrene/PVDF blend membrane compatibilized with PS-*b*-PMMA block copolymer.

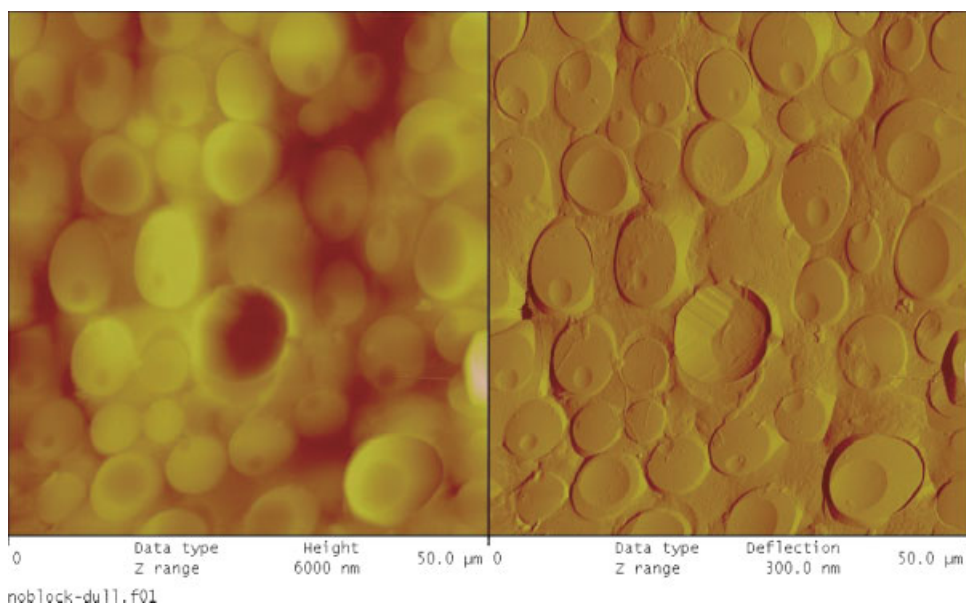


Figure 14 Atomic force micrograph of the sulfonated polystyrene/PVDF blend membrane (40/60% w/w) showing a topographical image (left) and a deflection image (right). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

might be attributed to many factors. These include a higher water uptake value of the blend membrane, which promoted more solubility and diffusibility of methanol through the membrane. In addition, compatibility between the two polymers should be taken into account. It seems that the higher the SPS content, the poorer the compatibility between the two polymers in the blend. Consequently, as the SPS content increased, adhesion between phases in the blend

membrane could become weaker, with the presence of some voids and cracks at the interface (Fig. 12), allowing more methanol to penetrate through the membrane.

For the blend containing more than 40 wt % of SPS, the cast membranes were poorly compatible and insufficiently ductile to withstand the clamping force between diffusion cells during the measurement of methanol permeability. Consequently, the

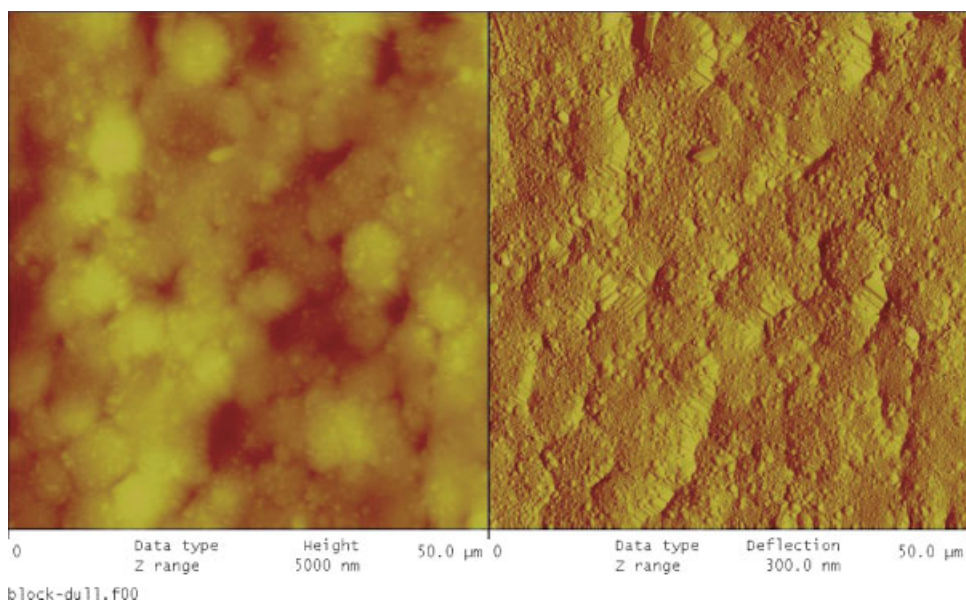


Figure 15 Atomic force micrograph of the blend membrane compatibilized with PS-*b*-PMMA block copolymer showing a topographical image (left) and a deflection image (right). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Properties of Sulfonated Polystyrene/PVDF Blend Membranes (40/60% w/w)

Membranes	Tensile strength (MPa)	Methanol permeability (cm ² /s)	Proton conductivity ($\times 10^{-3}$ S/cm)	Water uptake (%)
Sulfonated polystyrene/PVDF (40/60% w/w)	6.85	9.8×10^{-9}	1.26	10.09
Sulfonated polystyrene/PVDF (40/60% w/w) with 5% block copolymer	12.00	0 (No methanol crossover)	3.86	10.00

methanol permeability values of these membranes could not be accurately reported, unless the material was compatibilized prior to the test.

Effects of block copolymer

To enhance the compatibility between the two polymers, 5 wt % of the PMMA-*b*-PS block copolymer was added to the SPS/PVDF (40/60% w/w) blend. After adding the copolymer, it was found that the blend membranes became more homogeneous. Scanning electron micrographs of the blend membrane showed that some crack and/or gap at the interfacial area between the dispersed SPS particles and the PVDF matrix disappeared after the blend membrane was mixed with 5 wt % of the block copolymer (Fig. 13). This result suggested that the interfacial adhesion between SPS and PVDF in the blend membrane was improved after blending with the copolymer.

In addition to the above SEM images, further attempts were made to examine the interface and morphology of the blend membranes by using an atomic force microscopy (AFM) technique. From the AFM photographs (Figs. 14 and 15), it can be seen that the membrane became more homogeneous and that there is a lack of poor interfacial adhesion after the block copolymer was added to the blend. This result is in good agreement with that obtained from the above SEM experiment.

As a consequence of the above interfacial adhesion improvement, tensile properties of the blend membrane changed (Table I). For the normal blend membrane prepared without the use of block copolymer, tensile strength value of the material was 6.85 MPa. The elongation value of the material, however, cannot be detected by the tensile testing machine, since the specimen was very brittle and fractured rapidly after the tensile test was commenced. After adding the block copolymer to the blend, the obtained membrane was elongated slightly, and the detected elongation value was 5%. The tensile strength of the blend membrane also increased from 6.85 to 12.0 MPa. The above changes suggest that it is possible to use the block copolymer to improve the compatibility between SPS and PVDF. However, the above improvements have not been sufficiently great for an

application in the PEMFC. It seems that further work has yet to be carried out to improve mechanical properties of the material. For example, some other styrenic polymers such as styrene-ethylene/butylene-styrene block copolymer (SEBS), which is also known as a thermoplastic elastomer, might be sulfonated and subsequently blended with the PVDF to develop a more ductile proton-conductive membrane. This is, in fact, an aspect of our ongoing work.

Besides the change in tensile strength, the presence of the block copolymer also affected methanol permeability and proton conductivity of the SPS/PVDF (40/60% w/w) blend membrane. Results from Table I show that, after adding the block copolymer, methanol hardly permeated through the blend membrane. This result was in good agreement with the above comment describing that methanol permeability through this kind of blend membrane was related to the compatibility between PVDF and SPS, i.e., the poorer the compatibility, the more the methanol crossover, or vice versa.

Finally, it was found that water uptake of the blend membrane did not change significantly after being compatibilized with the block copolymer (Table I). Proton conductivity of the blend membrane, however, increased after the copolymer was added. The exact explanation for this effect cannot be provided at this time, but we believed that this might be related to some changes in connectivity and geometry of the hydrophilic/hydrophobic microdomains within the blend membrane. This is an aspect deserving some further extensive work to clarify.

CONCLUSIONS

This work showed that it might be possible to develop an electrolyte polymeric membrane for DMFC by blending SPS with PVDF. Properties of the SPS/PVDF blend membranes were strongly dependent on the state of compatibility between the two polymers, which in turn, are affected by the blend ratio and the use of the block copolymer as a compatibilizer. Water uptake and proton conductivity of the membranes increased, as the SPS content was

increased from 20 to 40 wt %. For the blends containing more than 40 wt % of the SPS, the cast membranes were very brittle, and the state of compatibility between the two polymeric phases became very poor. Compatibility between the two polymers can be enhanced by using PS-*b*-PMMA block copolymer as a compatibilizer. By adding 5 wt % of the copolymer, a compatibilized blend membrane with a slightly better mechanical strength, higher proton conductivity, and lower methanol permeability was obtained.

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