

Sulfonated Polyether Sulfone-Poly(vinylidene fluoride) Blend Membrane for DMFC Applications

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Received 16 April 2009; accepted 1 July 2009

DOI 10.1002/app.31087

Published online 26 March 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Direct methanol fuel cell (DMFC) proton exchange membranes were prepared by blending poly(vinylidene fluoride) (PVDF) with sulfonated poly(ether sulfone) (SPES). Using a diffusion cell and gas chromatographic technique, the effects of PVDF content on methanol permeability in the blended membranes were investigated. The thermal resistance and proton conductivity of the membranes were also determined by using a thermal gravimetric analysis (TGA) and an impedance analysis technique respectively. The presence of sulfonic acid groups in SPES was confirmed by Fourier transform infrared (FTIR). It was found that the methanol permeability in the blended mem-

branes decreased with PVDF content at the expense of proton conductivity. Blended membranes show methanol permeability values much lower than that of Nafion 115, whereas the proton conductivities of the membranes are comparable with that of Nafion. The thermal stability of these blended membranes is above 250°C, which is sufficiently high for use in DMFC. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 801–808, 2010

Key words: direct methanol fuel cell (DMFC); poly(ether sulfone) (PES); membranes; blends; poly(vinylidene fluoride) (PVDF)

INTRODUCTION

The interest of the research, in particular during the past 20 yr, was addressed to the improvement of the existent polymer electrolyte membranes for fuel cells and the development of new ones. So far, perfluorinated polymers such as Nafion membranes have been the most commonly studied and used for their excellent proton conduction at 80°C and unsurpassed longevity in fuel cell environment.¹ However, the nafion membranes have three major drawbacks: very high cost, loss of conductivity at high temperature (>80°C), and high methanol permeability, which hinders their further application.² Alternative aqueous membranes to the perfluorinated sulfonic acid-based systems possessing high proton conductivity at lower relative humidity and stability at elevated temperatures is currently the focus of a lot of research and development. Many approaches have been attempted to develop novel proton-conducting alternative membranes in a variety of strategies. Among these, modification of arylene main-chain polymers was motivated by their excellent chemical and mechanical stability.³

Sulfonation of these materials involves either using sulfonated monomer in the polymer synthesis or a va-

riety of methods for postsulfonation. Several families of polymers have been developed in this context. These include poly(ether ether ketone) (PEEK) (Linkous et al., 1998; Alberti et al., 2001; Kaliaguine et al., 2003), poly(ether sulfone) (PES) (Kim et al., 1999; Ma et al., 2003), and polysulfide sulfone (PSS) (Lufrano et al., 2000). One possibility to introduce the linking group such as sulfonic group into the polymer structure is through sulfonation, which depends mainly on the properties of polymer base unit and sulfonating agent. It is a simple reaction and required shorter overall reaction time as compared with other processes. Hence, the membrane production cost has been reduced.⁴ Sulfonating agent is one of the important factors to enhance the reactivity of sulfonation process. The sulfonating agents such as concentrated sulfuric acid, chlorosulfonic acid, pure or complex sulfur trioxide, and acetyl sulfide are among those that have been used in sulfonation process. Frequently, researchers used concentrated sulfuric acid as the sulfonating agent. This is because sulfuric acid can prevent cross-linking reaction and polymer degradation effect during the sulfonation process with 100% sulfuric acid or chlorosulfonic acid as sulfonating agents. However, the degree of sulfonation (DS) can be controlled by changing reaction time, temperature, and acid concentration by diluting strong acid such as fuming sulfuric acid with concentrated sulfuric acid.⁵

Among many polymer family, we focus on poly(ether sulfone) (PES). Because, in addition to its extremely high resistance to hydrolysis, high thermal

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stability, and oxidative resistance, PES also possesses very high group dipole moments and hence should result in much stronger dipole-dipole interactions with water than in the case of the other functional groups. Thus, the membrane should retain water at higher temperatures.⁶ The commercial SPES, which is highly sulfonated, shows good conductivities up to around 120°C, but the mechanical properties deteriorate above 130°C, namely, the polymer film either dissolves completely or degrades in the presence of water. Sulfonated poly(ethersulfone) (SPES), contains many polar groups (e.g., SO₂ (sulfone) and —O—) along the backbone chain, which contribute to the water uptake but contribute little to proton conductivity.

Fu et al.⁷ prepared sulfonated polystyrene/polyvinyl chloride (SPSt/PVC) composite proton-conductive membranes through styrene-impregnated polymerization and subsequent sulfonation. The obtained membranes had the semi-interpenetrating polymer network (sIPN) structure, where the polystyrene chains were interpenetrated with those of the reinforcing PVC film. Hence, the two components, polystyrene and PVC, were completely compatible. Recently, new locally and densely sulfonated poly(ethersulfone)s were successfully prepared for fuel cell applications by the nucleophilic substitution of 4,4'-dichlorodiphenylsulfone with 1,2,4,5-tetrakis([1,1'-biphenyl]-2-oxy)-3,6-bis(4-hydroxyphenoxy)benzene and 2,2-bis(4-hydroxyphenyl)hexafluoropropane, followed by sulfonation using chlorosulfonic acid.⁸ Novel cross-linked sulfonated poly(ethersulfone)s, prepared by azide-assisted thermal irradiation, show not only low methanol permeability but also exceptionally high proton conductivity with oxidative and hydrolytic stability.⁹

Poly(vinylidene fluoride) (PVDF) is a kind of hydrophobic material and can reduce the water absorption and methanol transport rate in PEMs.¹⁰ It is reported that by blending with a partially fluorinated polymer such as PVDF in the form of a sIPN¹¹ degradation of the sulfonated PS membrane can be prolonged. More interestingly, the methanol crossover of the sIPN membrane decreased when compared with that of Nafion 117. This result suggests that the blending of sulfonated polymers with PVDF is an interesting strategy for improving methanol resistance of the DMFC membrane. New composite membranes were prepared by solution casting from sulfonated PEEK, PVDF, and phosphotungstic acid. The composite membranes showed higher selectivity values when compared with Nafion117 membrane.¹⁰

In this article, we reported a new composite membrane that has been prepared by using sulfonated poly(ethersulfone) (SPES) and PVDF. PVDF is mechanically strong and tough. In addition, it was believed that PVDF is inherently resistant to metha-

nol crossover because of the hydrophobic nature of the material. Therefore, by blending PVDF with sulfonated PES, a membrane with optimum proton conductivity and methanol resistance can be expected. The aim of this study is to investigate the effects of blending ratios on water uptake, ion exchange capacity (IEC), proton conductivity, methanol permeability, and the thermal properties of sulfonated PES/PVDF blend membranes. Also, the membranes were then characterized through Fourier transform infrared (FTIR), scanning electron microscope (SEM), and atomic force microscope (AFM) studies.

EXPERIMENTAL

Materials

Poly(ethersulfone) (PES) was received from Gharda Chemicals Ltd. PVDF [$M_w = 530,000$] was supplied from Fluka (Bangalore, Karnataka, India). Other chemicals such as sulfuric acid, methanol and *N,N'*-dimethylformamide (DMF) (all are analytical grade) were received from Merck (Bangalore, Karnataka, India) and were used as received.

Sulfonation of poly(ether sulfone)

Poly(ethersulfone) (PES) polymer powder was sulfonated by the following procedure. One gram of PES was dried in a vacuum oven at 100°C and then dissolved in 20 mL of concentrated (95–98%) sulfuric acid (H₂SO₄) at room temperature to suppress the heterogeneous sulfonation. After completing the dissolution of PES (~ 1 h), the polymer solution was brought to the desired temperature ranging from 47 to 63°C and held for 3 h. To terminate the sulfonation reaction, the polymer solution was decanted into large excess of ice-cold water under continuous stirring and left overnight. The precipitated polymer was filtered and washed with distilled water until a neutral pH of the polymer was reached. The neutral SPES was then dried at 100°C overnight.

Membrane preparation

Two separate solutions of SPES 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 SPES solution and stirred at room temperature for further 30 min. The concentration of the blend solution was kept constant at 10% wt/vol 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 a ~ 50- μ m-thick membrane. After that, the membrane was peeled off from the substrate and then dried in a vacuum oven at 70°C

for further 12 h to remove any residual solvent. The membrane was kept in deionized water before tests.

Characterization methods

Thermogravimetric analysis

The thermal stability of the SPES/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 25 and 1000°C under oxygen (air) atmosphere, at a heating rate of 20°C/min.

Fourier transform infrared

The FTIR spectra of sulfonated and unsulfonated membranes were obtained by using a Perkin-Elmer Spectrum One FTIR spectrometer with membrane samples.

Scanning electron microscopy

The morphology of the membranes was investigated by using SEM. Specimens for the SEM were prepared by freezing the dry membrane samples in liquid nitrogen up to 10 min and breaking them to produce a cross-section. Fresh cross-sectional cryogenic fractures of the membranes were vacuum sputtered with a thin layer of gold by using an ion sputtering (Biorad Polaron Division) before viewing on the SEM (Phillips SEMEDAX; XL 40; PW6822/10) with a potential of 10 kV under magnifications ranging from 500× to 2000×.

Atomic force microscope

The morphology of SPES/PVDF composite membranes was further determined by AFM. AFM is performed with SHIMADZU SPM-9500 JZ Scanning Probe Microscope, Japan, in tapping mode. A silicon microcantilever (spring constant 2 Nm⁻¹ and resonance frequency ~ 70 kHz; Olympus Co., Japan) with an etched conical tip (radius of curvature ~ 40 nm as characterized by scanning over very sharp needle array; NT-MDT, Russia) is used for scan. The scan rate ranged from 1.0 to 2.0 Hz has been used to optimize the image quality. Each scan line contains 256 pixels and a whole image is composed of 256 scan lines.

Titration analysis

The IEC of the sulfonated PES membrane, which is defined as the amount of ion exchanged (referring to hydrogen ion of sulfonic acid groups) in SPES, was determined by using the titration method as described by Shao.¹² About 0.5 g of SPES-H was

immersed into 3M sodium chloride (NaCl) solution (50 mL) for 24 h, which was found to be sufficient to convert SPES-H into SPES-Na. A 0.01N sodium hydroxide (NaOH) solution was used for titration. Phenolphthalein as the universal indicator was adopted to determine the neutral point. By measuring the amount of NaOH consumed in the titration, the molar quantity of the sulfonic acid groups (SO₃H) contained in the SPES-H sample can be determined. By using this value, the IEC can be estimated by the following equation:

$$\text{Ion - exchange capacity(IEC)} = \frac{\left(\text{Volume of NaOH consumed} \times \text{Normality of NaOH} \right)}{\text{Dry weight of SPES}} \text{ meq/g}$$

Proton conductivity

The proton conductivity is temperature dependence at certain relative humidity¹³ for most of the polymer electrolyte materials. The conductivity of the membranes in acid form was measured by AC impedance technique using a Autolab potentiostat/Galvanostat Electrochemical analyzer. The impedance spectra were recorded over the frequency range of 10 MHz–10 Hz with 50–500 mV oscillating voltage. Membrane sample was equilibrated in deionized water for 24 h at room temperature before testing. Then, the surface water was removed, and the swollen membrane was rapidly placed between two stainless-steel electrodes in a conductivity cell (this cell is used to host the sample). The water content of the membrane was assumed to remain constant during the short period of time required for the measurement. All the impedance measurements were performed at room temperature. The membrane resistance (*R*) was obtained from the intercept of the impedance curve with the real-axis at the high-frequency end. Then, the proton conductivity of membrane, σ [Siemens per centimeter (S/cm)], was calculated according to the following equation, where σ is defined as the reciprocal of *R*.

$$\sigma = \frac{L}{RS}$$

Where *L* and *S* are the thickness and area of the membrane, respectively.

Water uptake measurements

Water uptake, which is used to determine the water content of the membrane, is one of the fundamental measurements for DMFC polymer electrolyte

membrane. First, membrane was dried in an oven at 60°C for 48 h, weighed, soaked in water overnight at room temperature, blotted dry with absorbent paper to remove any surface moisture, and reweighed. Then, water uptake was calculated from the equation given below, where, G_w is the weight of the wet membrane and G_d is the weight of the dry membrane.

$$\text{Solvent absorption} = \frac{(G_w - G_d)}{G_d} \times 100\%$$

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. 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 chromatographic (GC) technique with a FID

detector (Agilent, containing porapack 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 calculated from the slope of a plot between the methanol concentration and diffusion time, using the following equation:

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

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 of DK is the membrane permeability.

RESULTS AND DISCUSSION

Thermal properties

Figure 1(a–c) shows typical TGA thermograms of various ratios of SPES/PVDF blend membranes and nafion 115 membrane (Fig. 1, inset). The initial weight loss at about 50–100°C is because of water

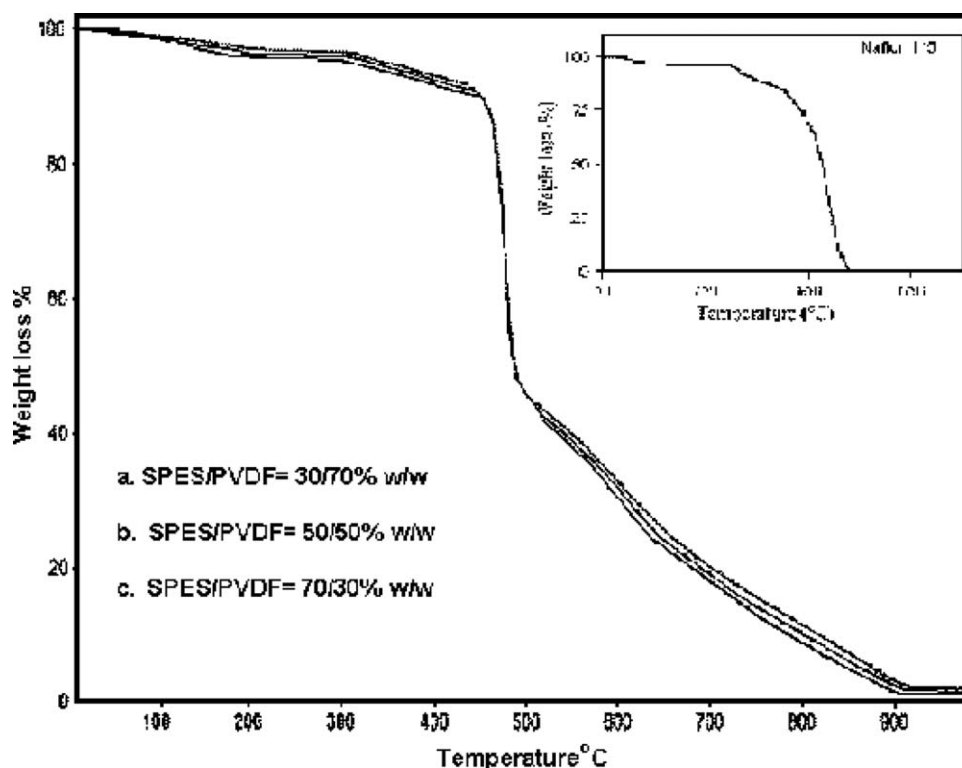


Figure 1 TGA thermogram of SPES/PVDF blend membrane with a ratio (a) 30/70% wt/wt, (b) 50/50% wt/wt, (c) 70/30% wt/wt (inset: TGA of Nafion 115).

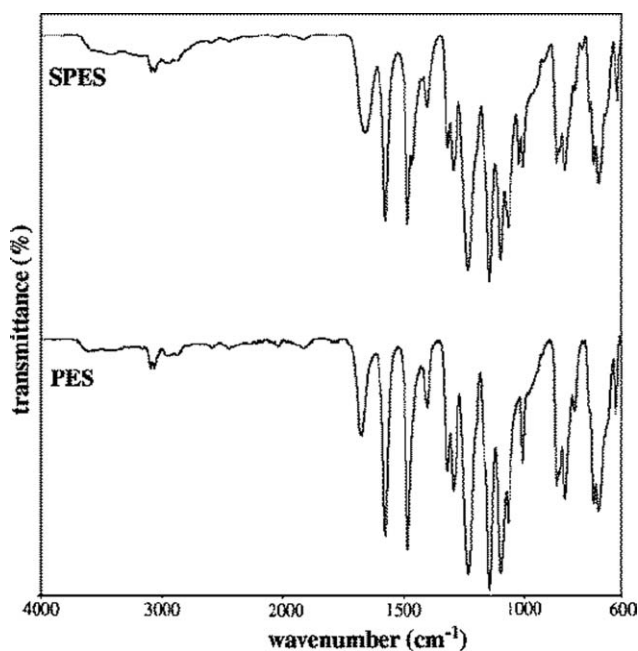


Figure 2 FTIR spectra of PES and SPES.

loss. The second transition occurring over the temperature range from 270 to 500°C is attributed to a loss of sulfonic acid groups (desulfonation) in SPES¹⁴ and in nafion 115.¹⁵ The third weight loss occurred over the temperature range between 400 and 500°C and could be ascribed to the decomposition of PVDF molecules.¹⁶ This was in a good agreement with our observation noting that the percentage mass change of this transition decreased with decreasing PVDF content. At this temperature range, nafion 115 membrane shows very high weight loss when compared with blend membranes. Finally, the fourth transition, occurring over the temperature range between 500 and 900°C, could be related with decomposition of the SPES main chain. Again, the percentage mass change of this transition increased with the SPES content. For the SPES/PVDF membranes with different blending ratios, their TGA thermograms also show a similar profile in terms of transition temperatures. These SPES/PVDF membranes are stable up to 250°C, which is far above a normal operating temperature of DMFC (about 90–120°C).¹⁷ All SPES/PVDF blend membranes showed better thermal stability than nafion 115 membrane. The results indicated that the thermal stabilities of these SPES/PVDF membranes are sufficiently high to meet the requirements of DMFC.

Fourier transform infrared

FTIR spectra were used to confirm the pendant SO₃H group on the polymer chain. Figure 2 shows the spectra of the parent PES and SPES. In comparing these spectra, one can see that in addition to the predictable

absorption peak at $\sim 3420\text{ cm}^{-1}$ due to the stretching of the hydroxyls of sulfonic acid groups, the SPES absorption peak at $\sim 1025\text{ cm}^{-1}$ is characteristic of the aromatic SO₃H symmetric stretching vibrations. It has been known that the asymmetrical stretching vibrations of sulfonic acid groups appear at $\sim 1180\text{ cm}^{-1}$, but we could not readily observe it because of near overlapping absorbances.¹⁸ However, it still can get conclusion that the sulfonic acid groups has been introduced into the polymer chains.

SEM results

SEM images of SPES, SPES/PVDF composite membrane, and Nafion 115 were shown in Figure 3. The SEM microphotograph demonstrates that the neat Nafion membrane has a homogenous structure.¹⁹ The PVDF particles treated with SPES can embedded in PES matrix, which indicated that the interfacial bonding between PVDF particles, and the PES seems to be more intense. In SEM picture of fracture surface of composite, most of monodispersed particles were observed and also the aggregation of the particles can be avoided with the increase of particle size. For most particles, the pull-out phenomenon was observed, indicating the extent of the interaction between PVDF and PES, which had a great influence on the fracture and deformation of the composites. The microstructure of Nafion 115 in this study was found similar as other microstructure being studied by other researchers in this area. In addition, the surface texture is characterized by the presence of imperfections and defects on the surface, probably due to the presence of aggregates of sulfonic acid groups at the film surface.

The morphology of the composite membranes

AFM technique has been used to study the surface morphology of the composite membranes. As shown in Figure 4, it can be seen that the surface of the SPES/PVDF composite membranes had become coarse and the number of "particle" on the surface increased with the increment of PVDF and the size of it is about 20–50 nm. When the weight ratio of the PVDF is kept at 30%, the particles were well distributed in the SPES matrix. This indicates that PVDF is homogeneously and well dispersed in the SPES membrane matrix.

Water uptake, IEC, and proton conductivity

Figure 5 represents water uptake values of various SPES/PVDF membranes. It can be seen that the membranes containing <50% SPES scarcely have any water uptake. This could be ascribed to the fact that these membranes contain high amounts of

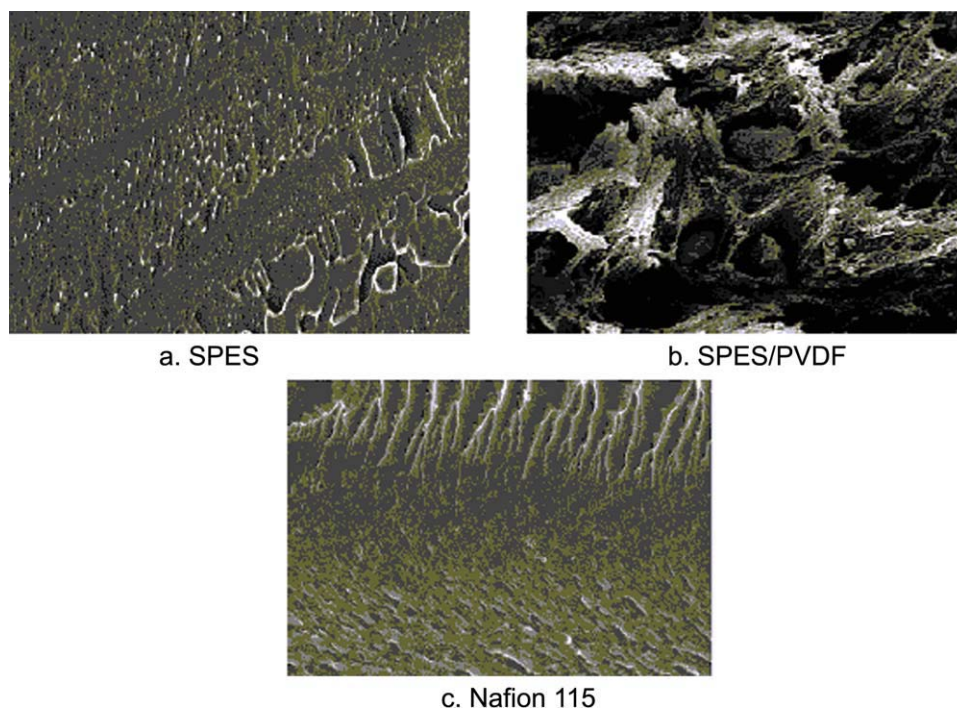


Figure 3 Scanning electron microscopy pictures of cross section of (a) SPES, (b)SPES-PVDF blend, and (c) Nafion 115 membrane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

PVDF material, which is inherently hydrophobic. However, as the SPES content was increased from 50 to 90%, the water uptake values increased. This was accompanied by our observation noting that the physical appearance of the membranes changed from a PVDF rich matrix to a SPES rich matrix. The water uptake of the pure SPES membrane was $\sim 30\%$. This is very close to that of a literature value¹ of SPES with a comparable DS (DS determined by $^1\text{H NMR}$ $1/4$ 0.75). Notably, in this study, it was found that the water uptake of the pure SPES is lower than that of the SPES/PVDF blend membranes containing 70 and 90% by weight of SPES. In our opinion, this effect could be attributed to the fact that PVDF is totally hydrophobic, whereas SPES is highly hydrophilic. Consequently, the two poly-

mers tend to be immiscible.¹⁶ Phase separation within a microstructure of the blend might create a larger “water channel,” allowing more water uptake.

In general, high water uptake is a prerequisite for a good proton-conducting membrane because water would induce a dissociation of the protons from SO_3H groups and would also act as “vehicles” for the transportation of the protons from the anode to the cathode.²⁰ In relation to this study, only the blend membranes containing high SPES content (50, 70, and 90% by weight SPES) were used for further study on proton conductivity because water uptakes of the blend membranes containing 10 and 30% of SPES range between 0 and 3%, which is very low.

The IEC values of various membranes are shown in Figure 6. The IEC values of the blend membranes

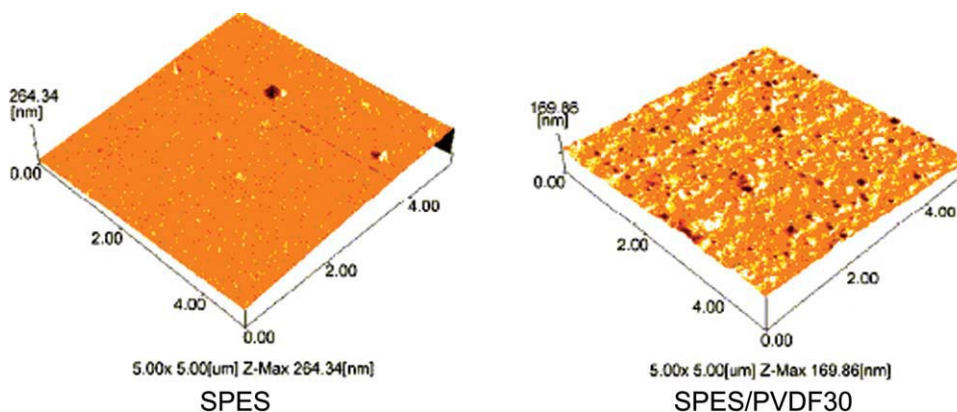


Figure 4 The topographic image of SPES and SPES/PVDF composite membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

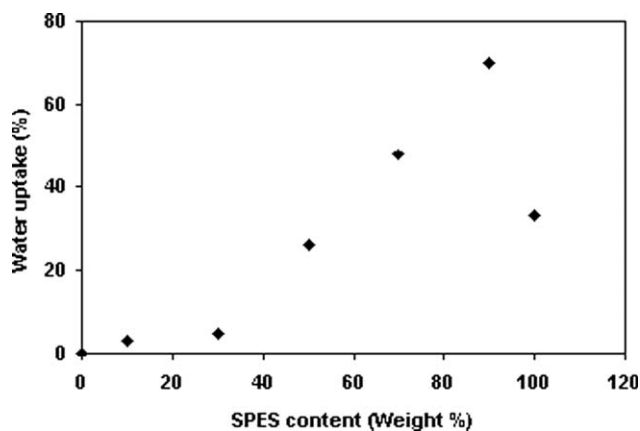


Figure 5 Water uptake values of various SPES/PVDF blend membranes.

continuously decrease with decrease in SPES content, owing to the fact that the PVDF has lack of sulfonate groups contributing to the ion exchange process. Again, the IEC of these blend membranes containing 10 and 30% SPES (Fig. 6) were relatively low, implying that proton conductivity of the blend membranes could be very low.

Table I compares the proton conductivities of various membranes. The proton conductivity of a pure SPES membrane is about 10.2×10^{-3} S/cm, which is comparable to that of a Nafion115 membrane (10.5×10^{-3} S/cm) measured by using the same apparatus and testing conditions. When the SPES was blended with PVDF, the proton conductivity of the membranes gradually decreased with PVDF content. This is due to the fact that PVDF has lack of sulfonic groups. As a result, higher the PVDF content, lower is the proton conductivity of the membrane.

Methanol permeability

The methanol permeability of various membranes was determined and the results are illustrated in Table II. It can be seen that, although the methanol

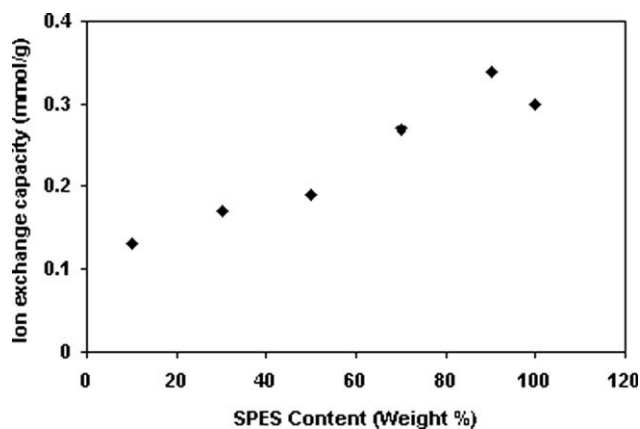


Figure 6 Ion exchange capacities (IEC) of various membranes.

TABLE I
Proton Conductivity Values of Various Membranes

Membranes	Proton conductivity (10^{-3} S/cm)
SPES/PVDF (50/50)	6.70
SPES/PVDF (70/30)	8.18
SPES/PVDF (90/10)	8.05
SPES	10.20
Nafion 115	10.50

permeability of the pure SPES membrane is considerably lower than that of the Nafion115 membrane,²¹ further improvement can be made by blending with PVDF.

This was probably due to the difference in microstructure between Nafion and SPES membrane. It was found true by Chang et al.²² and Kreuer²³ as they reported that the Nafion membrane has high hydrophobicity of the perfluorinated backbone and also high hydrophilicity of the sulfonic acid groups. In the presence of water, this character was more pronounced and consequently increased the hydrophobic/hydrophilic domains of Nafion membrane. The hydrophilic domains in the Nafion membrane, which were formed by the presence of sulfonic acid group allowed not only proton and water but also a smaller polar molecule such as methanol to migrate through this domain. However, the less pronounced hydrophilic-hydrophobic separation of the SPES membranes produced narrow channels and a highly branched structure. Hence, the amount of methanol permeated through them was minimized.²³

The methanol permeability of the SPES membrane rapidly decreased by two orders of magnitude after SPES was blended with 10 and 30% by weight of PVDF. For the blend membranes that contain >30% by weight of PVDF, a methanol peak in a GC chromatogram was absent, indicating that there was no methanol crossover through the membranes. It was believed that this is attributed to the hydrophobic nature of PVDF, which restricts methanol solubility in the PVDF rich membranes.

The methanol permeability of SPES/PVDF membranes decreased with increasing amounts of PVDF. In summary, the addition of PVDF to the SPES matrix decreased the water uptake, proton conductivity,

TABLE II
Methanol Permeability of Various Membranes

Membranes	Methanol permeability (cm^2/s)
PVDF	No methanol crossover
SPES/PVDF (10/90)	No methanol crossover
SPES/PVDF (30/70)	No methanol crossover
SPES/PVDF (50/50)	No methanol crossover
SPES/PVDF (70/30)	4.22×10^{-9}
SPES/PVDF (90/10)	4.66×10^{-9}
SPES	2.43×10^{-7}
Nafion 115	3.39×10^{-7}

and methanol permeability, which is reasonable, since PVDF is not soluble in water and it has no ionic sites to improve proton transport.²⁴

CONCLUSIONS

The methanol crossover of SPES could be effectively reduced by blending with PVDF. The extent of the interaction between PVDF and SPES indicated by the pull-out phenomenon for most particles, which had a great influence on the fracture and deformation of the composites. The sulfonation of SPES was confirmed by FTIR. The surface texture is characterized by the presence of imperfections and defects on the surface, may be due to the presence of aggregates of sulfonic acid groups at the film surface. The topographic image of SPES/PVDF composite membranes with different contents of PVDF shows that PVDF is homogeneously and well dispersed in the SPES membranes matrix. The methanol resistance of the SPES/PVDF membranes increased with the PVDF content at the expense of their ion exchange capacities and proton conductivities. The optimum blending ratios for SPES/PVDF membranes, which provide compromised proton conductivity and methanol permeability, ranged between 50/50 and 90/10% wt/wt. These membranes are potentially suitable to serve as proton exchange membranes in DMFC.

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