Dehydrofluorination of PVDF and Proton Conductivity of the Modified PVDF/Sulfonated SEBS Blend Membranes

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Abstract

Electrolyte membranes based on sulfonated styrene-(ethylene-butylene)-styrene triblock copolymer [SEBS] blended with dehydrofluorinated poly (vinylidene fluoride) [PVDF] were developed for a direct methanol fuel cell application. Prior to blending, the sulfonated SEBS was prepared by reacting the SEBS with propionyl sulfate whereas dehydrofluorination of the PVDF was carried out by reacting the polymer with sodium hydroxide solution. After that, the two polymers were then blended at various blending ratios via a solution blending process before casting onto glass substrates. The water uptake, proton conductivities, methanol permeabilities and mechanical properties of the dried blend membranes were measured using gravimetry, impedance analysis, gas chromatography, and a tensile test, respectively. It was found that the blend membranes are partially compatible, depending on the blend ratio. More importantly, by using the dehydrofluorinated PVDF, the water uptake and proton conductivity values of the blend membranes remarkably improved. The results were related to change in chemical structure of the PVDF which was confirmed by the FTIR technique. In this study, the best membrane is that obtained by blending 40 wt% of dehydrofluorinated PVDF with 60 wt% of the sulfonated SEBS.

Key words: Proton exchange membrane fuel cell, Blends, Sulfonation, SEBS, Dehydrofluorination.

Introduction

A direct methanol fuel cell (DMFC) is a kind of proton exchange membrane fuel cell (PEMFC), which utilizes methanol as a fuel to generate electricity without the use of any reforming unit. Normally, a perfluorinated polymer with some sulfonic groups, namely Nafion, has been widely used as an electrolyte polymeric membrane in the PEMFC. This is attributed to the fact that Nafion® is highly proton-conductive and thermally stable. In relation to DMFC applications, however, some alternative membranes with a better methanol resistance and a lower cost have yet to be explored and developed.

In this regard, one possible strategy for reducing the methanol crossover through the membrane is by blending the some sulfonated polymers with a hydrophobic polymer.1) (In our earlier work, we demonstrated that by blending PVDF with sulfonated SEBS (Wootthikanokkhan, 2006), methanol permeability through the membrane decreased at the expense of their proton conductivity. Noteworthy, the above membranes were incompatible and the compatibility can be improved by using PS-b-PMMA block copolymer as a compatibilizer. The similar works were studied by Mokrini, et al. (2001) using an extrusion process for preparing the blend membrane.

In this study, modification of the chemical structure of PVDF via a dehydrofluorination, prior to blending is explored to further improve proton conductivity of the sulfonated SEBS/PVDF blend membranes. It was believed that after the chemical modification, polarity of the PVDF molecules will increased and a grater water uptake of the resulting blend membrane can be expected. Consequently, we hope that proton conductivity of the blend membrane which is known to be strongly dependent with the amount of water molecules Ganguly and Bhowmick, (2008) will also be improved. The aim of the study is to investigate the
proton conductivity of the dehydrofluorinated PVDF/sulfonated SEBS blend membranes as a function of the blend ratio. In addition, water uptake and methanol permeability in the blend membranes are also of our interest.

**Materials and Experimental Procedures**

**Materials**

Styrene-(ethylene-butylene)-styrene triblock copolymer (SEBS) \([G\ 1652, \ 30\ wt.%\ styrene, \ M_w = 125,000]\) was supplied by Kraton Polymers LLC. Poly(vinylidene fluoride), \([PVDF, \ M_w = 530,000]\) was supplied from Fluka Co. Ltd. Sulfuric acid (analytical grade from Merck Co. Ltd.), propionic anhydride (purum grade from Fluka Co. Ltd.), methanol and toluene (analytical grade) were obtained from Fisher Chemicals Co. Ltd. Dimethyl formamide (analytical grade) was obtained from Univar Co. Ltd. All of these chemicals were used as received.

**Preparation of Sulfonated SEBS**

Sulfonated SEBS was prepared by reacting the SEBS with propionyl sulfate, using the method described in the related literature.\(^{(5)}\) Firstly, the propionyl sulfate was prepared by slowly adding 2 ml of sulfuric acid (96 wt %) into the reaction flask containing a solution of propionic anhydride (14 ml) in toluene (17.5 ml), at 10ºC and under vigorous stirring. After that, the mixture was diluted with toluene to yield 50 ml of solution. Next, 9 g of the dried SEBS was dissolved in 100 ml of toluene. The solution was heated to 60 ºC and purged with nitrogen for 15 min. After that, a given amount of the freshly prepared propionyl sulfate was slowly added to the polymer solution and kept stirring for 3 h at 60ºC. After carrying out the chemical reaction for the given time, the solution was then precipitated in methanol. The precipitated product was refluxed in boiling water for 3 h and this step was repeated 2-3 times, until the solution was neutral. The precipitated product was then further washed twice with ethanol for 2 h. Finally, the precipitated product was dried in a vacuum oven at 70ºC for 48 h.

**Preparation of Dehydrofluorinated PVDF**

An aqueous solution of sodium hydroxide at a given concentration (ranging from 1 to 6 Mole/L) was prepared and transferred into a two necked round bottom flask equipped with a condenser. The solution was heated to a desired temperature (70, 80, 90ºC) for five minutes. Then 3.00 g of PVDF powder was added to the reaction flask and then purged with nitrogen gas. The solution was stirred for further 3 h. After that, the content in the flask was precipitated in a large amount of methanol before filtrated and washed with deionized water and ethanol, respectively. Finally, the sample was dried to a constant weight.

**Preparation of the Blend Membranes**

Two separated solutions, one of which containing sulfonated SEBS in toluene/methanol mixture (90/10% v/v) and another one contained dehydrofluorinated PVDF in dimethyl formamide (DMF) were prepared before blending. A suitable quantity of the PVDF solution was added to the sulfonated SEBS solution at the desired blending ratio and then stirred at room temperature for a further 30 min. The concentration of the total polymers in the solution was kept constant at 5.6% w/v.

The solution was then cast onto a clean glass substrate before drying in an oven at 110ºC for 1 h. After that, the membrane was peeled off from the substrate and then dried in a vacuum oven at 60ºC for a further 24 h to remove any residual solvent. The membrane was kept in de-ionized water before tests.

**Characterization**

Changes in the chemical structure of the modified SEBS and PVDF were followed by a fourier transform infrared spectroscopy technique [FTIR], using a Perkin Elmer (Spectrum One) instrument. The sample was prepared in the form of a solution before casting onto the NaCl window cell. The spectrum was recorded over wave-numbers ranging between 4,000 and 500 cm\(^{-1}\).

**Water Uptake**

The water uptake of the blend membrane was determined by immersing the membrane in de-ionized water at 25ºC 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:
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\[ W(\%) = \left( \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \right) \times 100 \]  \hspace{1cm} (1)

Where \( W_{\text{dry}} \) and \( W_{\text{wet}} \) are weights of the dried and the water-swollen membrane, respectively.

**Proton Conductivity**

Proton conductivities of the blend membranes were determined by using a four-point probe technique. The impedance of the membrane was measured using an impedance analyzer (Autolab, PGSTAT 30) at a frequency of 10 kHz. The membrane was cut into a 3 x 3 cm² 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 conductivity (\( \sigma \)) was calculated using the following equation:

\[ \sigma = \frac{l}{RS} \]  \hspace{1cm} (2)

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 (cm²), and \( l \) is the distance between the counter electrode and the working electrode (cm).

**Methanol Permeability**

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

\[ C_B(t) = A(DK) C_A(t - t_0) / VBL \]  \hspace{1cm} (3)

Where \( C_A \) and \( C_B \) are the concentrations 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.

**Results and Discussion**

**Characterization of the Sulfonated SEBS.**

Figure 1. Shows the overlaid FTIR spectra of SEBS and the various sulfonated SEBS, obtained by reacting the polymer with different amounts of propionyl sulfate. The FTIR spectra of the sulfonated polymers show some new peaks at 1029 and 1177 cm⁻¹. These were ascribed to the symmetric stretching vibration (S=O) and the asymmetric stretching vibration (S=O) of the SO₃H groups, respectively. The above results suggest that SEBS has been sulfonated. In addition, by carrying out titration with 0.1 mol/L of NaOH solution in methanol, the degree of substitution (DS) of the sulfonated SEBS was found to be 6.19 wt%.
polyene which is resulted from the dehydrofluorination of PVDF as shown in Figure 3. Besides, the above figure also suggests that the polyene might further react with the hydroxyl anion from the base solution, leading to the formation of hydroxyl and ketone groups in the product molecules. This could be a reason why a broad peak over the wave number of about 3440 cm\(^{-1}\) was also observed in the Figure 3.

Figure 2. FT-IR spectra of PVDF and the modified PVDF

Figure 3. Proposed reaction mechanism during the dehydrofluorination of PVDF

Figure 4. Compare water uptake values of sulfonated SEBS/dehydrofluorinated PVDF blend membranes with those of the analogue blend membranes containing the normal PVDF. Obviously, it can be seen that water uptake of the former group of blend membranes are higher than those of the latter group of blend membranes, regardless of the blending ratio. The above results could be ascribed to the formation of some polar hydroxyl groups in the PVDF molecules after the chemical modification.

Figure 4. Water Uptake values of various blend membranes.

Noteworthy, the relationship between the sulfonated SEBS content and the water uptake of the blend membranes containing dehydrofluorinated PVDF is not in a linear fashion. For the blend membranes contained 20 and 40 % by weight of the sulfonated SEBS, the water uptake values are comparable and very close, taking into account the standard deviation values. However, as the sulfonated SEBS content increased above 40% by weight, a lower water uptake values in the blend membranes was observed. This could be due to the poorer compatibility of the blend membranes and the fact that water uptake value of the sulfonated SEBS is lower than that of the dehydrofluorinated PVDF (4.22 and 20.837 %, respectively). Consequently, measured water uptake of the membranes could be inaccurate and misled due to the presence of some waters trapped inside the phase separated membrane. Additionally, as the amount of sulfonated SEBS content in the blend was further increased above 40 % by weight, it was found that.

Figure 5. Compares proton conductivity values of some selected blend membrane. Noteworthy, only the blend membranes contained 20 and 40 % by weight of sulfonated SEBS were selected and tested. This is because these membranes are
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homogeneous and compatible. From Figure 5, it can be seen that proton conductivity of the pure sulfonated SEBS membrane is about $2.16 \times 10^{-3}$ S/cm which is lower than that of the Nafion 115 membrane ($11.5 \times 10^{-3}$ s/cm) measured by using the same apparatus and testing conditions. However, by blending with the modified PVDF, it was found that proton conductivity the membrane increased (Sulfonated SEBS/Dehydrofluorinated PVDF (40/60%wt) $7.9 \times 10^{-3}$ S/cm). It was also found that the higher the dehydrofluorinated PVDF content, the greater the proton conductivity of the blend membrane. The above effects were not the case for those blend membranes containing a normal PVDF material. In this regard, it is clear that the above change could be ascribed to the greater water uptake values of the membranes which is attributed to the dehydrofluorination of the PVDF.

Finally, it is worth mentioning that methanol permeability through the blend membranes containing 20 and 40 wt% of the sulfonated SEBS only slightly increased when the dehydrofluorinated PVDF was used for blending. For those blend membranes contained more than 40 wt% of the sulfonated SEBS, the methanol permeability cannot be determined and reported due to the fact that the two polymers are incompatible and the resulting blend membranes are very brittle and contains some defects.

**Conclusion**

This work has shown that by carrying out a chemical modification of PVDF via a dehydrofluorination, water uptake and proton conductivity of the dehydrofluorinated PVDF/ sulfonated SEBS blend membranes were improved. The best membrane is this study is that obtained by blending 40 wt% of dehydrofluorinated PVDF with 60% wt% of the sulfonated SEBS, without the use of any compatibilizer.

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**References**


