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Proton exchange membranes based on poly(vinylidene fluoride) and sulfonated poly(ether ether ketone)

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Abstract

Blend membranes were obtained by solution casting from poly(vinylidene fluoride) (PVDF) and sulfonated poly(ether ether ketone) (SPEEK) in *N*,*N*-dimethylacetamide (DMAc). DSC and XRD were used to characterize the structure of the blend membranes. The effect of PVDF content on the membrane properties was investigated. The methanol permeability, water uptake and the swelling ratio of blend membranes decreased with the increase of PVDF content. Though the proton conductivity decreased upon the addition of PVDF, they were still comparable to that of Nafion® 117 membrane. Higher selectivities were also found for most blend membranes in comparison with Nafion® 117 membrane. The effect of methanol concentration on solution uptake, swelling ratio and methanol permeability of the blend membranes was also studied.

Keywords: Poly(vinylidene fluoride); Sulfonated poly(ether ether ketone); Proton exchange membrane

1. Introduction

Direct methanol fuel cells (DMFCs) are promising power sources for portable and transport applications due to their advantages of high efficiency, simple design and low emissions to environment [1–3]. The proton exchange membrane (PEM), which transfers protons produced at anode to cathode and acts as a barrier to avoid the crossover of fuel, is a key part of DMFCs. Perfluorosulfonated ionomers, such as Nafion®, are used as the main materials to prepare the PEM for DMFCs due to their good ionic conductivity as well as excellent chemical stability [4]. One disadvantage of Nafion® membranes is the high methanol permeability, which can result in significant loss of fuel cell performance. Though Nafion® membranes can be modified with some materials using sol–gel method [5], and such modification can reduce the methanol permeability [6], these membranes are still of high cost due to the Nafion® component. Therefore, the ideal PEM for DMFCs should be a membrane with high conductivity, low methanol permeability and low cost.

These have stimulated great efforts in developing cost-effective materials with low methanol permeability for DMFCs applications. In recent years, sulfonated poly(aryl ether ketone) [7–10] and sulfonated poly(aryl ether sulfone) [11–14] based membranes were shown to be of considerable promises as PEMs due to their high proton conductivity and good thermal stability. The microstructure difference between Sulfonated poly(ether ether ketone) (SPEEK) and Nafion® membranes was reported in Ref. [15], which demonstrated the advantages of SPEEK over Nafion® as PEMs for DMFCs. The methanol permeability of SPEEK was also reported in literatures [16,17], which showed reduction of methanol permeability in SPEEK membranes in comparison with Nafion® membranes. The proton conductivity, methanol permeability, water uptake and the swelling ratio of SPEEK membranes are all dependant on the degree of sulfonation (DS). Though the SPEEK membrane with a low DS shows good performance in blocking the crossover of methanol, obvious reduction of proton conductivity is also accompanied. And it is also difficult to process the SPEEK with a low DS due to its bad solubility in organic solvent. High DS results in too much water uptake and swelling ratio of the SPEEK membrane [18,19]. This can lead to mechanically less stable membranes, which are not suitable for DMFCs. Therefore, compromise may be reached by choosing SPEEK with a moderate DS.

Poly(vinylidene fluoride) (PVDF) is a kind of hydrophobic polymer and has been chosen as the base polymer to prepare fluorinated sulfonated PEMs by means of radiation grafting and subsequent sulfonation [20–22]. PVDF was also used to prepare blend and laminated membranes with Nafion® for

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DMFCs [23–25]. The results showed that the methanol permeability and the swelling ratio were effectively reduced in the PVDF based membranes, and good fuel cell performances were also found. This is very attractive for DMFCs applications. Despite these favorable qualities these membranes are still of high cost due to the Nafion® component. In a recent paper, the results of preliminary study showed that PVDF/SPEEK membranes were promising materials as candidates for DMFCs applications [26]. Therefore, more attention should be given to PVDF/SPEEK membranes. In present work, cost-effective membranes were prepared by blending PVDF with the SPEEK polymer of a moderate DS. The effect of PVDF content on water uptake, swelling ratio, proton conductivity and methanol permeability of the PVDF/SPEEK membranes were investigated to evaluate their potential applications in DMFCs.

2. Experimental section

2.1. Preparation of blend membranes

Victrex® PEEK extruded pellets were sulfonated using concentrated sulfuric acid (95–98 wt%) to obtain the SPEEK polymer. The reaction temperature was 38 °C. The SPEEK sample with moderate DS (DS = 0.78), which was determined using a Bruker Avance 600 MHz NMR spectrometer, was chosen to prepare the blend membranes. Detailed procedures for the sulfonation reaction and the determination of the DS can be found elsewhere [7,8]. Dried SPEEK polymer was dissolved in DMAc (10–15 wt%), then PVDF powder was added into the SPEEK polymer solution, which was stirred for several hours. After the PVDF powder was fully dissolved, the solution was cast onto a glass plate, then dried at ambient condition for several days, and kept under vacuum at 100 °C for 24 h.

2.2. Characterization of blend membranes

The DSC measurements were carried out at a scanning rate of 10 °C/min using a Setaram DSC 141 calorimeter. XRD analysis was carried out for PVDF powder, SPEEK and blend membranes with a D/max-rB (Japan) diffractometer using a Cu Kα X-ray source operating at 50 kV and 50 mA. The XRD patterns were obtained at a scanning rate of 5° min^{-1} with an angular resolution of 0.05° of the 2θ scan.

2.3. Water uptake and swelling ratio

The membrane was vacuum dried at 100 °C for 24 h and weighed. Then the membrane was immersed into water at room temperature for 24 h. The wet membrane was quickly wiped to remove surface water and weighed again. Water uptake of the membrane was calculated by

$$\text{Water uptake} = \frac{W_\mathrm{w} - W_\mathrm{d}}{W_\mathrm{d}} \times 100\% \tag{1}$$

where W_w and W_d are the weights of wet and dry membranes, respectively. The swelling ratio of the membrane was calculated by

$$\text{Swelling ratio} = \frac{l_\mathrm{w} - l_\mathrm{d}}{l_\mathrm{d}} \times 100\% \tag{2}$$

where l_w and l_d are the lengths of wet and dry membranes, respectively.

2.4. Measurement of proton conductivity

Proton conductivities of the membranes were measured in transverse direction by AC impedance spectroscopy using an EG&G PARC Potentiostat/Galvanostat Model 273. A fully hydrated membrane sample was sandwiched between two stainless steel electrodes, which were put into a teflon cell. A spring, which was inserted between the bottom of the teflon cell and one stainless steel electrode, was used to keep constant pressure between the two stainless steel electrodes. The membrane dehydration from its edge was also reduced by sandwiching the edge of the membrane between two teflon rings. The teflon cell was placed in a temperature-controlled setup. The measurement temperature ranged from 30 to 80 °C. The conductivity was calculated from

$$\sigma = L/(RA) \tag{3}$$

where σ is the proton conductivity, L the thickness of the membrane, A the face area of the membrane, and R the bulk resistance value measured.

2.5. Measurement of methanol permeability

The methanol permeability was measured using a home-made glass diffusion cell, which consisted of two compartments. Initially one compartment (Cell A = 70 ml) was filled with a solution of methanol (10 vol%) and ethanol (0.5 vol%) in deionized water. The other (Cell B = 70 ml) was filled with an ethanol (0.5 vol%) solution in deionized water. The ethanol was used as an internal standard. The membrane was clamped between the two compartments. The solution in each compartment was continuously stirred to keep uniform concentration. The methanol concentration was detected by gas chromatography. The methanol concentration in Cell B as a function of time is given by [27]

$$C_\mathrm{B}(t) = \frac{A}{V_\mathrm{B}} \frac{DK}{L} C_\mathrm{A}(t - t_0) \tag{4}$$

where C_A and C_B are the concentrations of methanol in Cell A and Cell B, respectively. A, L and V_B are the area of membrane, the thickness of membrane and the volume of Cell B. D and K are the methanol diffusivity and partition coefficient between the membrane and the adjacent solution, respectively. The product DK is the methanol permeability (P), which was calculated from the slope of the straight-line plot of methanol concentration vs. permeation time. The measurement was carried out at 30 °C.

3. Results and discussion

3.1. XRD and DSC measurements

Fig. 1 shows the XRD patterns of PVDF powder, SPEEK (DS = 0.78) and two PVDF/SPEEK membranes with various mass ratios. Two sharp diffraction peaks appeared at $2\theta \sim 18.4$ and 20.1° and illustrated the various crystalline forms of PVDF. It was reported that the PEEK was semicrystalline [28], but the SPEEK membrane was amorphous perhaps due to the introduction of sulfonic acid groups, which may induce disorder of the polymer structure. From the diffraction patterns, it was found that the sharp crystalline diffraction peaks in pure PVDF became less prominent in presence of the SPEEK. This may suggest that the addition of amorphous SPEEK induced significant disorder into the PVDF polymer. Fig. 2 shows the DSC thermograms for PVDF powder, pure SPEEK and PVDF/SPEEK membranes with different mass ratios. DSC results showed that the glass transition temperature (T_g) of pure SPEEK membrane was around 195 °C, which was consistent with results previously reported [8,29]. When the PVDF was introduced into the SPEEK membrane, the T_g of blend membranes may decrease to lower temperature because the –SO_3H interactions, which can hinder mobility of the polymer chain [8,30], were weakened due to the presence of PVDF [31]. No evident T_g was observed for PVDF/SPEEK membranes perhaps due to the overlap of the glass transition process of SPEEK with the melting process of PVDF. The melting temperature of plain PVDF, which appeared at 176.2 °C in the DSC curve, decreased upon the addition of SPEEK. The depression of the melting temperature for blend membranes in comparison with pure PVDF suggests the occurrence of intermolecular interactions between PVDF and SPEEK, which may perhaps suppress the formation of crystal of the crystalline component (PVDF) in the blend membrane. These data might also suggest that the PVDF and the SPEEK can mixed together with a high compatibility.

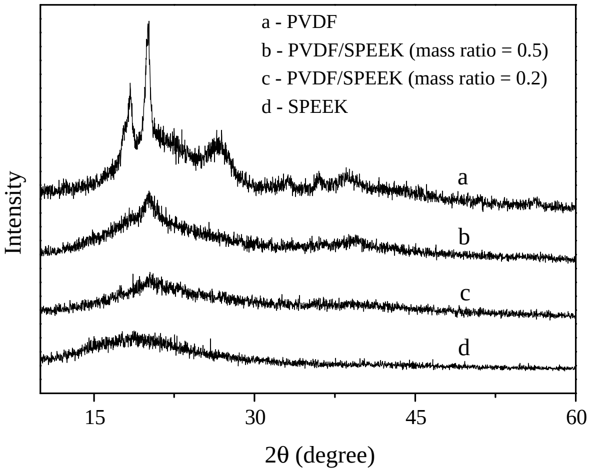

Fig. 1. XRD patterns of PVDF powder and PVDF/SPEEK blend membranes with various mass ratios.

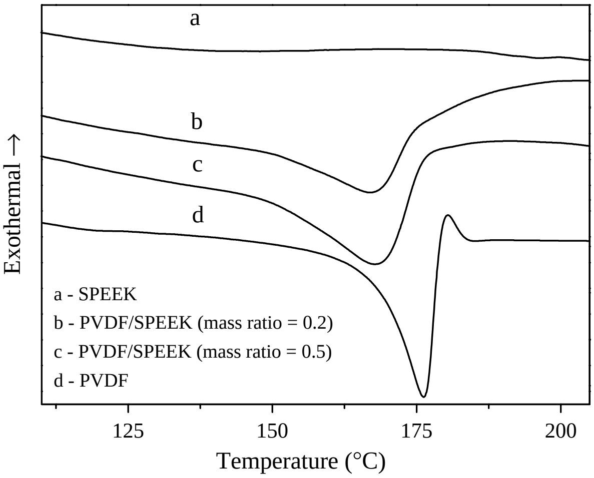

Fig. 2. DSC thermograms of PVDF powder and PVDF/SPEEK blend membranes with various mass ratios.

3.2. Water uptake and swelling ratio

The water content has great effects on the properties of PEMs. High water content can facilitate the transport of protons, but too much water absorption results in mechanically less stable membrane. For a membrane intended for DMFCs applications, the mechanical stability is very important due to its direct contact with the liquid methanol solution, which can enhance its swelling ratio. This may result in decrease in the mechanical stability. As can be seen in Fig. 3, the water uptake of the blend membranes decreased upon the addition of PVDF, which is hydrophobic in nature. When the content of hydrophobic PVDF increased, the content of the hydrophilic sulfonic functional groups, which were mainly responsible for the water uptake, decreased. Therefore, the water uptake in the membrane decreased. The introduction of hydrophobic PVDF can also suppress the swelling ratio of membranes, see Fig. 4. The water uptake and the swelling ratio of the blend membranes were lower than those of Nafion® 117 membrane, when the mass ratio of PVDF to SPEEK increased to 0.5 and

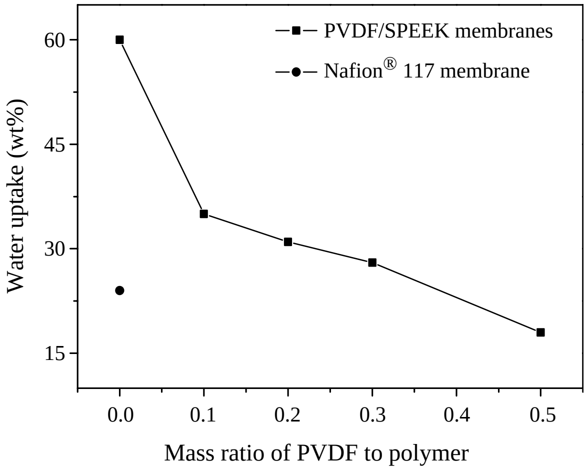

Fig. 3. Water uptakes of Nafion® 117 and PVDF/SPEEK blend membranes at room temperature.

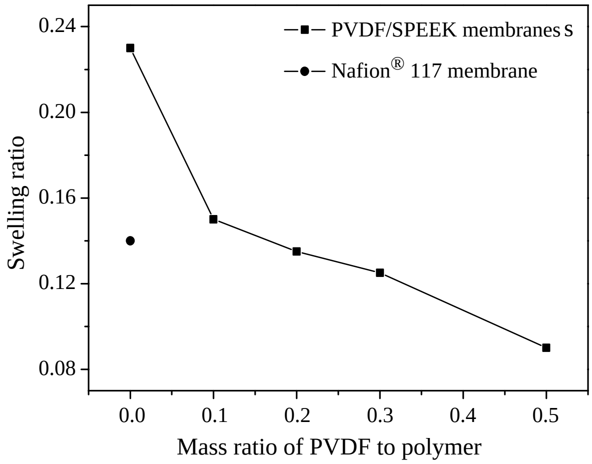

Fig. 4. Swelling ratios of Nafion® 117 and blend membranes at room temperature.

0.2, respectively. Therefore, the mechanical stability was enhanced upon the addition of PVDF.

3.3. Proton conductivity and methanol permeability

The proton conductivity can be obtained by a number of measurement techniques, any of which, however, has its own advantages and disadvantages [32]. It was also reported in Ref. [29] that the measurement technique had great effects on the proton conductivity, and nearly one order magnitude difference between transverse conductivity and longitudinal conductivity was found. Thus, for membranes intended for fuel cell applications, the measurement technique simulating the operational condition of an actual fuel cell is perhaps most appropriate. Since the proton transport current in a fuel cell is perpendicular to the membrane surface, in present study, proton conductivities of the PVDF/SPEEK membranes were measured in transverse direction. Prior to measurements, all membranes were hydrated in deionized water for 24 h at room temperature. As shown in Fig. 5, proton conductivities measured at 30 °C decreased with the increase in PVDF content. They were in the range of 3.6×10^{-3}–8.2×10^{-3} S/cm, which were comparable to that of Nafion® 117 membrane (1.1×10^{-2} S/cm) measured under the same condition. The proton transport in membranes requires well connected channels formed by ion clusters of hydrophilic sulfonated functional groups. The content and the diameter of the connected channels have significant effects on the proton transport rate in membranes. The phenomenon of percolation threshold has been observed for sulfonated polymers [30,33,34], when the density of sulfonic groups is low, the hydrophilic sulfonic groups form isolated ionic clusters in the continuous hydrophobic phase. When the density of sulfonic groups increases up to a certain value, the isolated ionic clusters form crosslinked channels with good connectivity and protons can transport fast in these channels [35]. The impedance study also suggests that the good connectivity of hydrophilic parts is important for proton transport in membranes [36].The introduction of hydrophobic PVDF reduced the density of sulfonic groups in the membrane. Therefore, the content of the ionic clusters and the well connected channels perhaps decreased. Since, the size of ionic clusters increase with the density of sulfonic groups [35], the diameter of the channels formed by ionic clusters may be also reduced upon the introduction of PVDF, which resulted in decrease of the density of sulfonic groups. The effect of temperature on the proton conductivity of blend membranes was shown in Fig. 6. As the proton conductivity is in general thermally motivated, it is natural for the proton conductivity to increase with the increase of temperature. When the temperature reached 60 °C, proton conductivities of all blend membranes surpassed 10^{-2} S/cm except for that of the membrane with a mass ratio of 0.5.

The concentration gradient, pressure gradient and electro-osmotic drag coefficient all have effects on the methanol permeability. In present study, the later two factors are absent, and the methanol concentration gradient is the only driving force for methanol permeability. The transport of methanol in membranes also requires channels with good connectivity. As discussed above the content of well connected channels

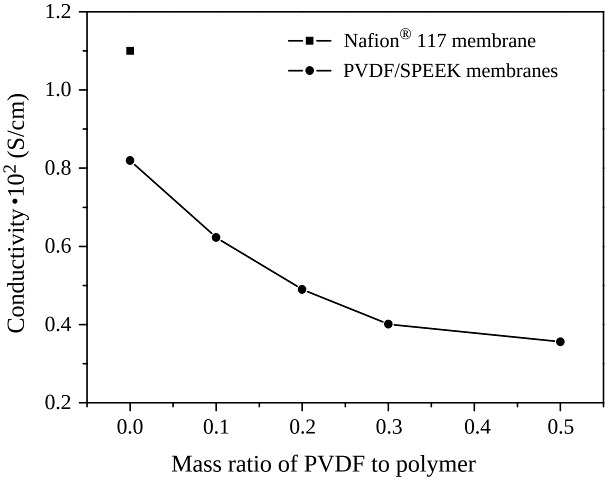

Fig. 5. Proton conductivities of Nafion® 117 and blend membranes at 30 °C.

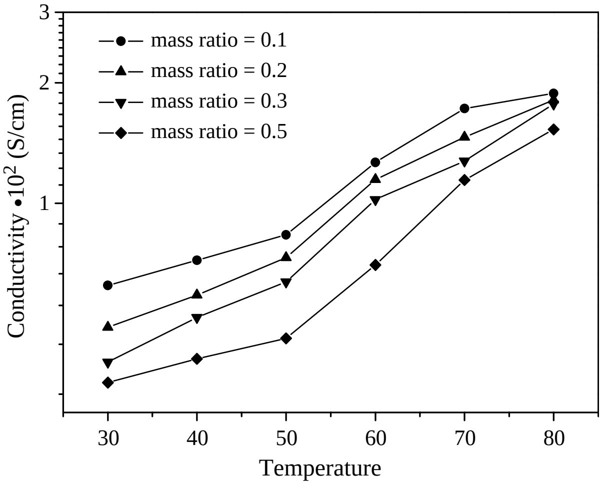

Fig. 6. Proton conductivities of blend membranes as a function of temperature.

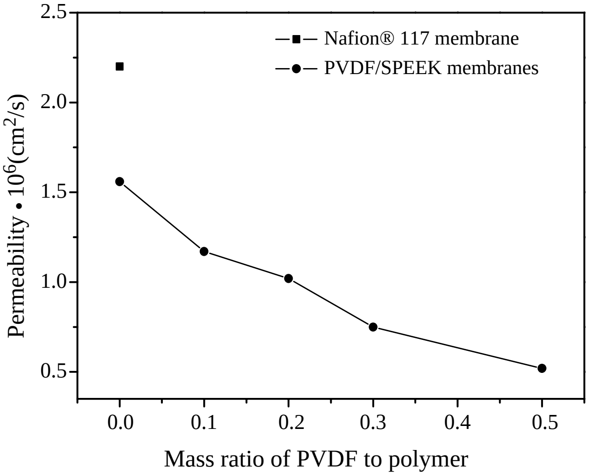

Fig. 7. Methanol permeabilities of blend membranes at 30 °C.

decreased in blend membranes upon the introduction of PVDF, which is hydrophobic and have not sulfonic functional groups required for the formation of ion clusters and methanol transport channels. As shown in Fig. 7, methanol permeabilities of the PVDF/SPEEK membranes decreased with the increase of PVDF content and ranged from 1.6×10^{-6} to 5.2×10^{-7} cm^2/s, which were lower than that of Nafion® 117 membrane (2.2×10^{-6} cm^2/s) measured under the same condition. This is favorable for DMFCs. The effect of methanol concentration on the methanol permeability was investigated for blend membranes with mass ratios of 0.3 and 0.5. As can be seen in Table 1, when the methanol concentration increased from 5 to 20 vol%, their methanol permeabilities increased from 7.0×10^{-7} and 4.8×10^{-7} cm^2/s to 1.1×10^{-6} and 7.0×10^{-7} cm^2/s, respectively. The effect of methanol concentration on the solution uptake and swelling ratio properties was also studied for Nafion® 117, pure SPEEK and blend membranes at room temperature. As shown in Figs. 8 and 9, the solution uptake and swelling ratio of the membranes increased with the increase of methanol concentration. It might be caused by the increased compatibility between solution and membranes, which results from difference in solubility parameters. A little increase of solution uptake and swelling ratio was observed for Nafion® 117 membrane, which still possessed good mechanical stability. When the methanol concentration reached 20 vol%, the pure SPEEK membrane turned to a gel, therefore, its solution uptake and swelling ratio could not be measured. For blend membranes with mass ratios of 0.3 and 0.5, when the methanol concentration reached 30 vol%, the solution uptake and the swelling ratio of the membranes were much high, and the membranes turned opalescent and began to lose their mechanical stability. Generally, the concentration of methanol used for DMFCs is about 8 vol%, therefore, the PVDF/SPEEK blend membranes are still promising for DMFCs. It was reported that the porosity of the sulfonated polymer membranes equilibrated in methanol solutions increased with the increase of methanol concentration [37]. This is perhaps the reason for the increase of the methanol permeability, when the methanol concentration increased. The selectivity, which is defined as the ratio of proton conductivity to methanol permeability [38,39], is often used to evaluate the possibility of using membranes in DMFCs. A membrane with higher selectivity is desired for DMFCs. Fig. 10 shows the selectivities of Nafion® 117 and PVDF/SPEEK membranes, which were based on the conductivities and methanol permeabilities measured at 30 °C. Among all the membranes investigated in this paper, the blend membrane with a mass ratio of 0.5 possessed the highest selectivity value, and all other blend membranes showed similar selectivities to that of Nafion® 117 membrane. This is very attractive for DMFCs.

Table 1
Methanol permeabilities of PVDF/SPEEK membranes with mass ratios of 0.3 and 0.5 as a function of methanol concentration

Mass ratios of membranes	Methanol permeability (cm^2/s) with various methanol feed concentrations		
	5 vol%	10 vol%	20 vol%
0.3	7.0×10^{-7}	7.5×10^{-7}	1.1×10^{-6}
0.5	4.8×10^{-7}	5.2×10^{-7}	7.0×10^{-7}

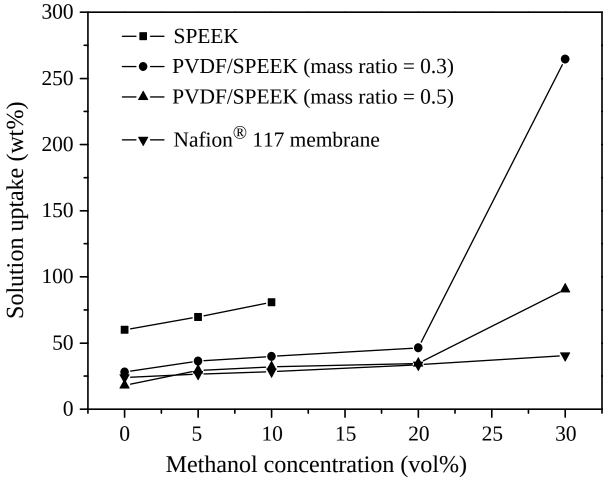

Fig. 8. Solution uptakes of Nafion® 117 and PVDF/SPEEK membranes as a function of methanol concentration.

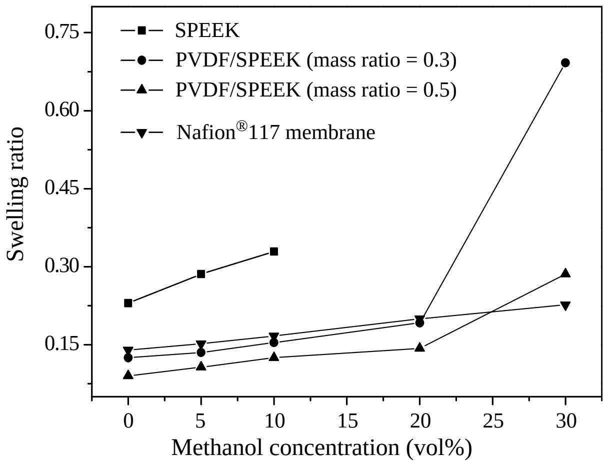

Fig. 9. Swelling ratios of Nafion® 117 and PVDF/SPEEK membranes as a function of methanol concentration.

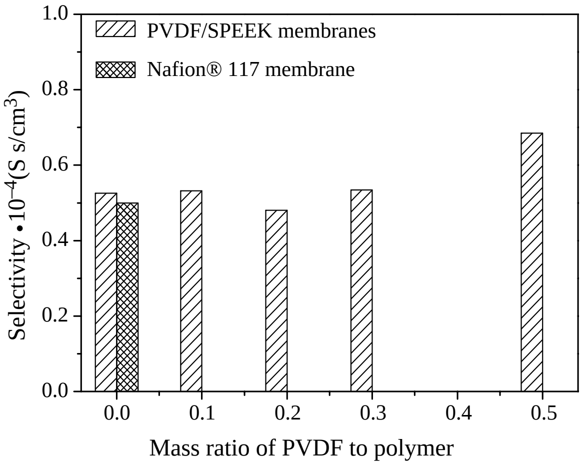

Fig. 10. Selectivities of Nafion® 117 and blend membranes.

4. Conclusions

Cost-effective PVDF/SPEEK blend membranes with high compatibility were prepared using solution casting method. The mechanical stability of SPEEK membrane was improved upon the introduction of hydrophobic PVDF. The water uptake and the swelling ratio of PVDF/SPEEK membranes decreased with the increase of PVDF content and ranged from 60 to 18% and 23 to 9%, respectively. When the mass ratio of PVDF to SPEEK was higher than 0.3, the water uptake and the swelling ratio of the blend membrane were lower than those of Nafion® 117 membrane (24 and 14%), respectively. Though the proton conductivity decreased upon the addition of PVDF, they were still comparable to that of Nafion® 117 membrane measured under the same condition. Methanol permeabilities of the blend membranes also decreased with the increase of PVDF content and ranged from 1.6×10^{-6} to 5.2×10^{-7} cm^2/s, which were lower than that of Nafion® 117 membrane. In addition, higher selectivity values were found for most blend membranes in comparison with Nafion® 117 membrane. The methanol permeability increased with the increase of methanol concentration. When the methanol concentration reached 30 vol%, the blend membranes started to be mechanically less stable. If high concentration of methanol is required for specific use of DMFCs, SPEEK with lower DS may be tried to prepare PVDF/SPEEK blend membranes, which may show higher mechanical stability. Therefore, the PVDF/SPEEK blend membranes are promising for DMFCs, such as DMFCs for laptop, mobile phone and other applications due to their low cost, low methanol permeability and comparable conductivity to Nafion® 117 membrane.

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