Short communication

Synthesis and characterization of sulfonated polysulfone membranes for direct methanol fuel cells

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Abstract

Sulfonated polysulfones (SPSf) with different degree of sulfonation (DS) have been synthesized and evaluated as proton exchange membranes in direct methanol fuel cell (DMFC). The membranes have been characterized by ion exchange capacity (IEC), proton conductivity, liquid uptake, and single DMFC polarization measurements. The proton conductivities of the SPSf membranes increase with increasing sulfonation, but are lower than that of Nafion 115. Within the range of sulfonation of 50–70%, the SPSf membranes exhibit better performances in DMFC than Nafion 115 at lower methanol concentrations (1 M) despite lower proton conductivities due to suppressed methanol permeability and crossover. However, the performances of SPSf membranes at higher methanol concentrations (2 M) are inferior to that of Nafion 115 at current densities higher than about $50 \, \text{mA cm}^{-2}$ as the suppression in methanol crossover could not quite compensate for the lower proton conductivities.

1. Introduction

Polymeric Nafion is widely used as the membrane material at present for both proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) due to its high proton conductivity and good thermal and chemical stabilities. However, the high cost and the crossover of liquid methanol fuel from the anode to the cathode through the Nafion membrane have created interest in other non-fluorinated polymeric materials such as polyetheretherketone [1–4], polyimidazole [5,6], polyimide [7,8], and polysulfone [9–13] as membranes for PEMFC and DMFC. These materials are easier to synthesize and less expensive compared to Nafion. More importantly, they usually exhibit lower methanol permeability than that found with Nafion.

Membrane based on the aromatic polysulfone (PSf) is attractive for fuel cell applications due to its good thermal stability and mechanical property. Lufrano et al. [12,13] syn-thesized the sulfonated polysulfone (SPSf) by a mild sulfonation process at room temperature and compared the thermal stability of SPSf with that of PSf. They also compared the proton conductivity and performance in PEMFC of SPSf with those of Nafion membranes. However, no data are available on their performances in DMFC and the methanol crossover. Our group recently reported a comparison of the methanol crossover and electrochemical performance data in DMFC of the sulfonated polyetheretherketone (SPEEK) membrane with that of Nafion [4,14]. We present here the proton conductivity, methanol crossover, liquid uptake, and electrochemical performance in DMFC of the SPSf membranes with different degrees of sulfonation (DS) and compare the data with that of Nafion 115.

2. Experimental

The SPSf samples were prepared by sulfonating the commercial polysulfone (Udel 1700) at room temperature [12,13]. Five grams of polysulfone was dissolved in

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100 mL of chloroform at room temperature and treated with trimethylsilyl chlorosulfonate (Aldrich) to produce a silyl sulfonate polysulfone intermediate. The amount of intermediate produced depended on the mole ratio of the sulfonating agent to the polymer-repeat units (*x*). A slight excess sodium methoxide was then added to the solution to cleave the silyl sulfonate intermediates and to produce the final sulfonated product. All samples were washed thoroughly with methanol, rinsed several times with de-ionized water, and dried in a vacuum oven at 110 °C for 24 h. The degree of sulfonation (DS) was calculated from the ion exchange capacity (IEC) of the SPSf thus prepared. The IEC was determined by suspending 0.3 g of SPSf in 30 mL of 2 M NaCl solution for 24 h to liberate the H$^+$ ions and then titrating with standardized 0.1 M NaOH solution using phenolphthalein as an indicator. The membranes were obtained by casting onto to a glass plate an *N,N*-dimethylacetamide solution of the SPSf polymer (∼5 wt%) thus prepared and drying at 115 °C overnight. The thickness of the membrane was controlled by changing the amount of SPSf in the solution and all the membranes in this study had a thickness of 100–120 μm.

Proton conductivity values were obtained from the impedance data collected with an HP 4192A LF impedance analyzer in the frequency range of 5–13 MHz with an applied voltage of 10 mV after equilibrating the membranes with water vapor at 100% relative humidity (RH). The percent liquid uptake was determined from the weight gain found on equilibrating the dry membrane (dried at 100 °C for 24 h) in distilled water or methanol solution at different temperatures for 2 h followed by blotting carefully with a filter paper to remove the surface water droplets before weighing.

The electrodes (consisting of gas-diffusion and catalyst layers) for testing in DMFC were prepared as reported elsewhere [15]. The anode and cathode catalysts consisted of, respectively, commercial 40 wt% Pt–Ru (1:1) on Vulcan carbon (E-TEK) and commercial 20 wt% Pt on Vulcan carbon (Alfa Aesar). The electrodes prepared were impregnated with Nafion solution (5 wt% solution, DuPont Fluoro-products) by a spray technique and dried at 90 °C under vacuum for 30 min. The loadings for cathodes (Pt) and anode (Pt–Ru) were 1.0 and 0.6 mg cm^{-2}, respectively, and the Nafion loading for both the anode and cathode catalysts was 0.35 mg cm^{-2}.

The membrane-electrode assemblies (MEAs) were fabricated by uniaxially hot-pressing the anode and cathode onto a SPSf membrane at 140 °C for 3 min. For a comparison, an MEA consisting of pre-cleaned Nafion 115 was also prepared by a similar procedure. The electrochemical performances in DMFC of the MEAs thus fabricated were evaluated with a single-cell fixture having an active area of 5 cm^2 and feeding a preheated methanol solution into the anode at a flow rate of 2.5 mL min^{-1} by a peristaltic pump without back pressurization and humidified oxygen into the cathode at a flow rate of 200 mL min^{-1} with a back pressure of 20 psi.

Methanol crossover was evaluated by a voltammetric method [16] in which methanol solution was fed at a flow rate of 2.5 mL min^{-1} into the anode side of MEA while the cathode side was kept in an inert humidified N$_2$ atmosphere. By applying a positive potential at the cathode side, the flux rate of permeating methanol was determined by measuring the steady-state limiting current density resulting from complete electro-oxidation at the membrane/Pt catalyst interface at the cathode side.

3. Results and discussion

Table 1 summarizes the DS, IEC, proton conductivity (*σ*) at 65 and 80 °C and 100% RH of the SPSf membranes prepared with various mole ratios of the sulfonating agent to the polymer-repeat unit (*x*). For a comparison, the data for Nafion 115 membrane are also given in Table 1. As the value of *x* increases, the DS, IEC, and *σ* increase as expected. The conductivity of the SPSf membranes increase on increasing the temperature (from 65 to 80 °C) similar to that found with Nafion, but the *σ* values are lower than that of Nafion 115. For convenience, the SPSf membranes studied are hereafter designated as SPSf-28, SPSf-57, and SPSf-65 where the numbers refer to DS. Data of SPSf with DS > 65 are not presented as they exhibited severe swelling and consequent solubility in water [11].

Table 2 compares the percent liquid uptake at different temperatures and methanol concentrations for the SPSf membranes with various DS and for Nafion 115. The liquid uptake

Table 1
Ion exchange capacity (IEC), degree of sulfonation (DS), and proton conductivity (*σ*) of the SPSf membranes obtained with different mole ratios of the sulfonating agent to polymer-repeat units (*x*)

x	DS (%)	IEC (meq g^{-1})	*σ* at 100% RH (S cm^{-1})	
			65 °C	80 °C
2.3	28	0.60	1.3×10^{-4}	1.9×10^{-4}
3.2	57	1.17	4.9×10^{-4}	1.7×10^{-3}
3.7	65	1.32	2.2×10^{-3}	3.1×10^{-3}
Nafion 115	–	0.91	3.2×10^{-2}	3.5×10^{-2}

Table 2
Comparison of the liquid uptake of SPSf and Nafion 115 membranes in methanol solution at different temperatures

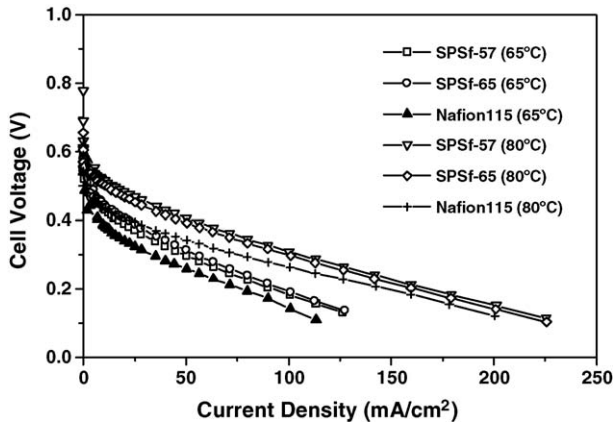| Membrane	Methanol concentration (M)	Liquid uptake (wt%)	
		65 °C	80 °C
SPSf-28	0	9.1	13.7
	1	15.2	16.0
	2	16.7	18.3
SPSf-57	0	25.7	31.0
	1	34.2	46.0
	2	47.1	50.3
SPSf-65	0	39.4	53.6
	1	46.4	55.2
	2	50.4	57.1
Nafion 115	0	24.0	26.6
	1	29.1	30.2
	2	32.2	33.7

Fig. 1. Comparison of the polarization curves of the SPSf membranes with that of Nafion 115 in DMFC. The data were collected with a methanol flow rate of 2.5 mL min^{-1} at the anode and an O$_2$ flow rate of 200 mL min^{-1} with a pressure of 20 psi at the cathode. The humidifier temperature for O$_2$ was same as the cell temperature. Anode: 0.6 mg PtRu cm^{-2}; cathode: 1.0 mg Pt cm^{-2}, methanol concentration: 1 M.
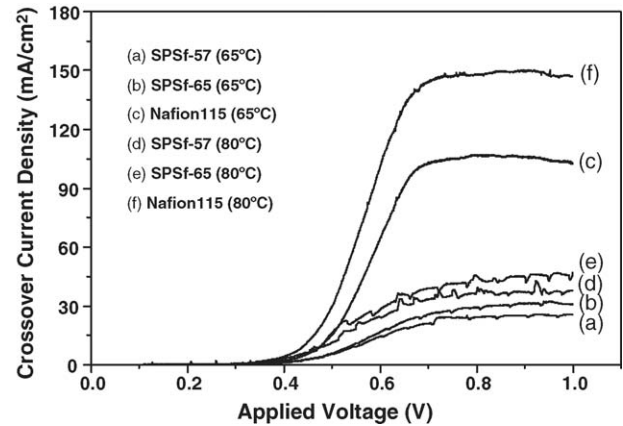

Fig. 2. Comparison of the variations of the methanol crossover current density for the SPSf and Nafion 115 membranes in DMFC. Methanol concentration: 1 M.

increases as (i) the temperature or the methanol concentration increases with a given DS and (ii) the DS increases at a given temperature and methanol concentration. The liquid uptake generally reflects the trend in swelling, which is a critical issue for the MEA stability in fuel cells. At a DS of around 50%, the liquid uptake, irrespective of water or methanol is being used, reaches the level generally found with the Nafion membrane. As the DS increases above 50%, the increase in the number of sulfonic acid groups in SPSf leads to a higher absorption of water than that in Nafion 115. Interestingly, as the DS increases further, but below 70%, the liquid uptake does not increase too much even at 80 °C, unlike in the case of the SPEEK membranes [4].

Fig. 1 compares the electrochemical performance data of the SPSf and Nafion 115 membranes in DMFCs at 65 and 80 °C that were collected with 1 M methanol solution at the anode side. The SPSf-28 membrane with a DS of 28% showed poor performance in DMFC due to its low σ arising from a lower DS and so it is not presented in Fig. 1. We can see from Fig. 1 that both the SPSf-58 and SPSf-65 membranes show better performances with lower polarization losses at 65 or 80 °C than the Nafion 115 membrane despite lower proton conductivities. Particularly at low current densities, the performances of the SPSf membranes are much better than that of Nafion 115 with higher open circuit voltages (OCV). The better performance despite lower proton conductivities could be attributed to the lower methanol crossover, as indicated by a lower methanol crossover limiting current density compared to that for the Nafion 115 membrane in Fig. 2. Although the thickness of SPSf-56 and SPSf-64 membranes is similar to that of Nafion 115, the methanol crossover limiting current densities are only one-third of that found with Nafion 115, indicating much lower methanol permeability [4].

Fig. 3 compares the electrochemical performance data of the SPSf-58 and SPSf-65 membranes with that of Nafion 115 at 65 and 80 °C that were collected with 2 M methanol solution. For both the SPSf and Nafion 115 membranes, the performances are better than those found with 1 M methanol solution in Fig. 1 due to higher methanol flux. However, although the SPSf membranes show better performance than the Nafion 115 membrane with higher OCV at lower current densities due to lower methanol crossover as indicated by the data in Fig. 4, the performances of the SPSf-58 and SPSf-65 membranes at higher current densities are lower than that of Nafion 115 due to the lower proton conductivities. Both the SPSf-58 and SPSf-65 membranes show similar performances (with both 1 and 2 M methanol solutions) despite the differences in the DS and higher proton conductivity for the SPSf-65 membrane. This is because of an increase in the methanol crossover as well with increasing DS as indicated by the data in Figs. 2 and 4. The higher methanol crossover encountered with the SPSf-65 membrane offsets the improvement gained with the higher proton conductivity. In Fig. 4,
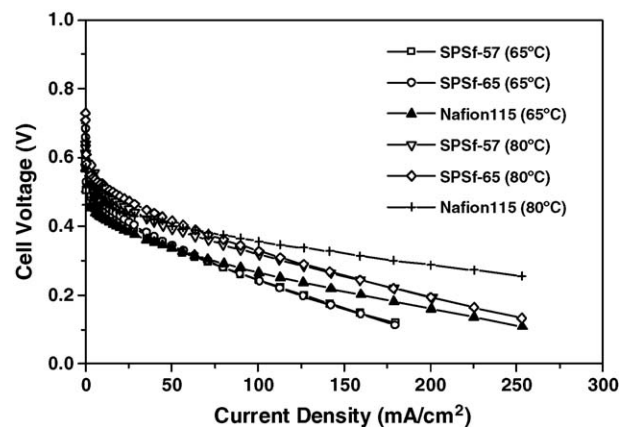

Fig. 3. Comparison of the polarization curves of the SPSf membrane with that of Nafion 115 in DMFC. The experimental conditions were same as those in Fig. 1 excepting the methanol concentration was 2 M.
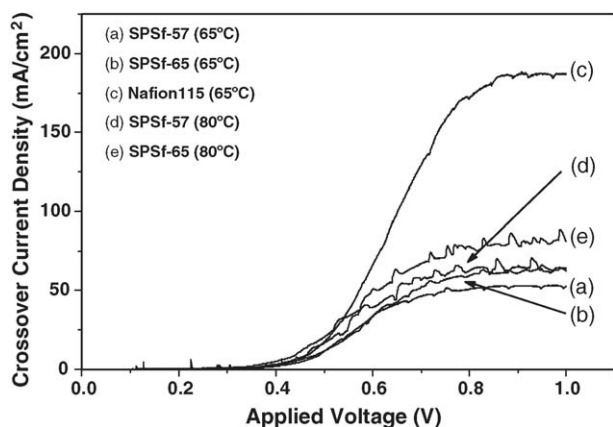
Fig. 4. Comparison of the variations of the methanol crossover current density for the SPSf and Nafion 115 membranes in DMFC. Methanol concentration: 2 M. Since the current exceeded the limit of our equipment, the data for Nafion 115 at 80 °C is not given.

the plot of methanol crossover current of Nafion 115 at 80 °C is not shown because it exceeded the current limit of our equipment.

The lower methanol crossover observed with the SPSf membranes compared to that with the Nafion 115 membrane could be attributed to the narrower pathways for methanol/water permeation in the former. It has been found that the smaller separation between the hydrophobic and hydrophilic groups in SPEEK compared to that in Nafion leads to narrower, less connected hydrophilic channels, resulting in a stronger confinement of water/methanol in the narrow channels and significantly lower water/methanol permeation [2,3,17]. SPSf has an aromatic backbone similar to that in SPEEK, and so SPSf can also be expected to have a smaller separation between the hydrophobic and hydrophilic groups, resulting in a lower methanol permeation.

Although the SPSf membranes exhibit lower methanol crossover than Nafion 115 membrane in DMFC, separation of the MEAs from the SPSf membranes were observed after 2 days of operation. This finding is similar to that found before for the SPEEK membranes in PEMFC and DMFC [4,18]. The separation of the MEAs is due to the poor adhesion properties of the SPSf membranes [19]. Modifications in the MEA fabrication such as the use of SPSf solution instead of Nafion solution to spray onto the electrodes as bonding resin could help in this regard.

4. Conclusions

The electrochemical performances of SPSf membranes with different degrees of sulfonation have been investi-gated in DMFC. SPSf membranes with 50–70% sulfonation exhibit performances comparable to that of Nafion 115 due to lower methanol crossover, but the performances at high current densities with high concentrations of methanol (2 M) are lower than that of Nafion 115 due to the lower proton conductivity. However, separations of the electrodes from the SPSf membranes were observed after 2 days of operation in DMFC due to the poor adhesion and bonding properties. Further work is needed to overcome this problem and fully assess the long term stability. Nevertheless, the lower cost and methanol crossover compared to that of Nafion make the SPSf membranes promising alternatives for DMFC.

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