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Sulfonated poly(ether ether ketone) membranes for direct methanol fuel cell

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Abstract

Sulfonated poly(ether ether ketone) (SPEEK) membranes with various degrees of sulfonation (DS) were prepared. Their proton conductivity and methanol permeability as a function of temperature were investigated. It was found that the proton conductivity of SPEEK membranes exceeded 10^{-2} S/cm above 80 °C, which is close to that of Nafion® 115 membrane under the same condition. The methanol permeability of SPEEK membranes was about an order of magnitude lower than that of Nafion® 115 membrane. The direct methanol fuel cell (DMFC) performance of the SPEEK membranes was better than that of Nafion® 115 membrane at 80 °C.

Keywords: Poly(ether ether ketone) (PEEK); Proton conductivity; Methanol permeability; Direct methanol fuel cell (DMFC)

1. Introduction

Direct methanol fuel cells (DMFCs) have attracted considerable attention, since they offer numerous potential benefits, such as high efficiency, high power density, low or zero emissions and reliability [1–3]. However, the crossover of methanol through the electrolyte membrane in DMFC still restricts their performances and applications. The methanol crossover to the cathode not only reduces fuel efficiency, but also increases the overpotential of the cathode, thus resulting in lower cell performance [4].

Various efforts have been made in different directions aimed at membranes with high proton conductivity and low methanol permeability. Several methods for Nafion® modification were reported, such as substituting a part of H^+ in Nafion® 117 with Cs^+ ions [5], or treating the surface of ionomers using plasma etch and palladium sputter [6]. A methanol impermeable composite was proposed, which is composed of a Pd foil sandwiched between two layers of Nafion® 115 membrane [7]. Another direction is the development of polymer/inorganic mineral acid composite membranes. A well-known example of these is phosphoric acid doped polybenzimidazole (PBI) membrane [8]. Other efforts include works on membranes of partially fluorinated polymers, nonfluorinated polymers and their combinations [9,10].

In recent work [11–13], it has been shown that sulfonated poly(ether ether ketone) (SPEEK) is very promising for fuel cell application as it possesses a good thermal stability, mechanical strength and adequate conductivity. SPEEK membranes with good performance for hydrogen fuel cells are described in

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several reports [11]. Recently, Kreuer [12] reported that the absorptive amount of methanol in SPEEK membranes was lower than that of Nafion membranes, which may help to reduce the problems associated with high water drag and high methanol crossover in DMFC. It suggests that SPEEK membranes could be suitable for DMFC applications. In this paper, we report the proton conductivity and methanol permeability of SPEEK membrane and tested the performance of DMFC with this membrane.

2. Experimental

2.1. Sulfonated PEEK

Poly(ether ether ketone) (PEEK) was sulfonated as described [14,15]. PEEK was obtained from Jilin University, China in the form of powder. It was dried in a vacuum oven at 100 °C overnight. Therefore, about 20 g of polymers were dissolved in 1 l of concentrated sulfuric acid (95–98%) and vigorously stirred at room temperature for the desired time. Then, the polymer solution was gradually precipitated into ice-cold water under mechanical agitation. The polymer suspension was left to settle overnight. The polymer precipitate was filtered, washed several times with distilled water until pH was neutral and dried under vacuum at 60 °C for 24 h. The degree of sulfonation (DS) and ion-exchange capacity (IEC) of SPEEK was determined by titration: 1–2 g of SPEEK was kept in 0.5 M aqueous NaOH for 1 day and then was back titrated with 1 M HCl using phenolphthalein as an indicator.

2.2. Membrane preparation

The SPEEK was first dissolved in Dimethylformamide (DMF) to make a 10 wt.% solution, which was then cast onto a flat glass. The cast membranes were dried at 60 °C for 6 h to remove the solvents, and annealed at 100 °C for 4 h. After cooling to room temperature, the resultant membranes were peeled from the glass in deionized water. Finally, the membranes were treated with 1 M sulfuric acid solution for 1 day at room temperature and subsequently rinsed with deionized water several times. All the membranes were kept in deionized water before testing. The thickness of the dried SPEEK membranes was about 60 ± 2 μm.

2.3. Water uptake

The membranes were dried in an oven at 60 °C for 48 h, weighed, soaked in deionized water overnight at room temperature, blotted dry with absorbent paper to remove any surface moisture, and reweighted. Water uptake was calculated from

$$\text{water uptake} = \frac{G_w - G_d}{G_d} \times 100\%$$

Here, G_w is the weight of the wet membranes and G_d the weight of the dry membranes.

2.4. Conductivity measurements

The proton conductivity of samples in the traverse direction was measured in a measurement cell using a frequency response analyzer (FRA) (Autolab PGSTAT20) [16,17]. Two stainless steel electrodes with a contacting area of 28.8 mm^2, connected from the FRA, horizontally pressed the membrane to be tested. The measured temperature was controlled from room temperature to 110 °C. The conductivity σ was calculated from the impedance data, using the relation $\sigma = l/RS$, where l and S are the thickness and area of the membrane, respectively, and R was derived from the low intersect of the high frequency semicircle on a complex impedance plane with the Re(z) axis.

2.5. Methanol permeability

The methanol permeability was determined using a diaphragm diffusion cell [16,17]. A glass cell ($V =$ 16.8 ml) containing solutions A and B in two identical compartments separated by the test membranes was utilized for permeability tests. The membranes were placed between the two compartments by a screw clamp. Solution A is 1 M methanol and solution B is deionized water. Both compartments were magnetically stirred during the permeation experiments. The concentration of methanol in solution B was estimated using a differential refractometer (WINOPAL LCD 201). The differential refractometer is highly sensitive to methanol, which can be continuously measured during the test. The methanol permeability P was calculated from the slope of the straight-line plot of methanol concentration versus permeation time. The measured temperature was controlled from room temperature to 80 °C.

2.6. Membrane-electrode assembly (MEA)

Unsupported Pt–Ru/C catalyst (20 wt.% Pt, 10 wt.% Ru, Johnson Matthey) was used in the anode. Pt/C (20 wt.% Pt, Johnson Matthey) was employed as the cathode catalyst. The platinum loading for all electrodes (anode and cathode) used in the experiments was 4.0 mg/cm^2. The reaction layer, for both anode and cathode, was prepared by direct mixing in an ultrasonic bath a suspension of Nafion ionomer in water with the catalyst powders, the obtained paste was spread on carbon cloth backings. The membrane-electrode assemblies (MEAs) were manufactured by pressing the electrode onto the membrane at 120 °C and 15.4 MPa for 2 min. The geometrical area of the electrode was 4 cm^2.

The single cell was assembled by mounting the MEA into a cell in which the anode and the cathode were contacted by a serpentine flow pattern machined into high-density graphite [18]. The operating temperature of the cell was 80 °C. Two molar methanol solution was pumped through the DMFC anode at a flow rate of 20 ml/min with atmosphere pressure, and humidified oxygen was fed to the cathode at 75 ml/min at a pressure of 0.1 MPa.

3. Results and discussion

Sulfonation of PEEK has been carried out using H_2SO_4, oleum or chlorosulfonic acid. When the sulfonation agent employed was 95–98% H_2SO_4, it can avoid polymer degradation and cross-linking reactions [19,20] which occur for sulfonation with oleum or with chlorosulfonic acid.

The PEEK was sulfonated for different reaction times ranging from 24 to 120 h to produce polymers of various DS. The IEC or DS of SPEEK polymer measured at room temperature is presented in Fig. 1 as a function of sulfonation reaction time. It can be seen that IEC (DS) of SPEEK increase continuously with the increment of reaction time. Upon sulfonation, PEEK reached an IEC close 2.4 meq./g (DS is about 85%) within 120 h.

In Fig. 2, the water uptake of SPEEK membranes is plotted against the number of sulfonic acid groups. The water uptake increased with DS and reached 120 wt.% for a SPEEK membrane with 85% DS (0.85 SO_3H groups per repeat unit). These results show that the water uptake of SPEEK membranes increased linearly up to a DS of 70% and thereafter very rapidly above 75%. In addition, it can be found that the water uptake of our SPEEK membranes is higher than that of Nafion® 115 membrane.

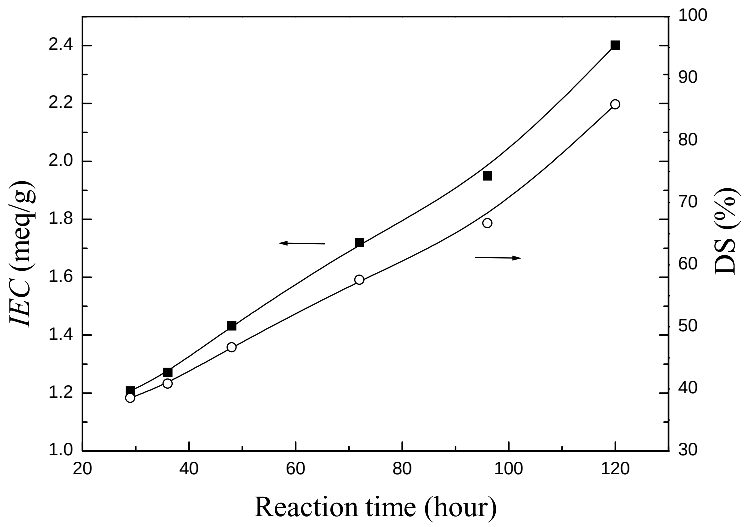

Fig. 1. Influence of reaction time on the DS and IEC values of PEEK sulfonated at room temperature.

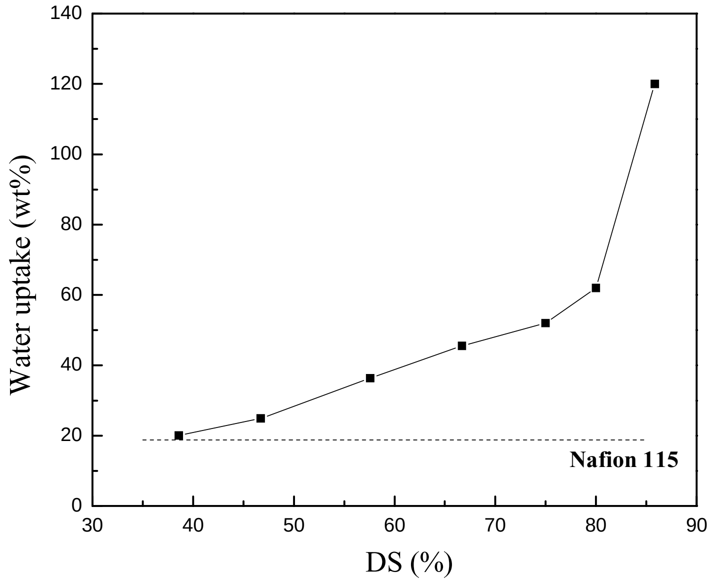

Fig. 2. DS as a function of water uptake for SPEEK polymer at room temperature.

The effect of the DS on the proton conductivity of SPEEK membranes at room temperature is shown in Fig. 3. For comparison, the conductivity of Nafion® 115 membrane was also measured under the same conditions. It was found that the conductivity of SPEEK membranes increased with DS and reached a value of 5.05×10^{-3} S/cm for 85% DS. With increments of DS, the polymer becomes more hydrophilic and absorbs more water, which facilitates proton transport. Hence, the sulfonation raises the conductivity of PEEK

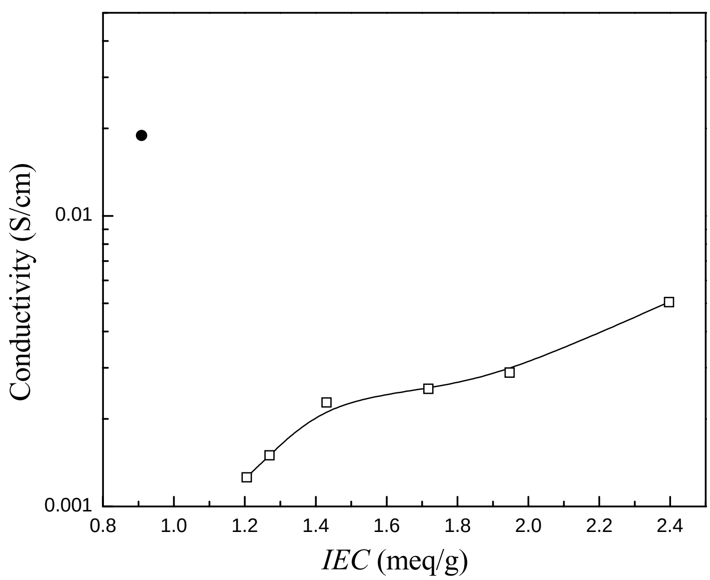

Fig. 3. Proton conductivity of SPEEK membranes at room temperature: (●) Nafion® 115 membrane; (□) SPEEK membranes.

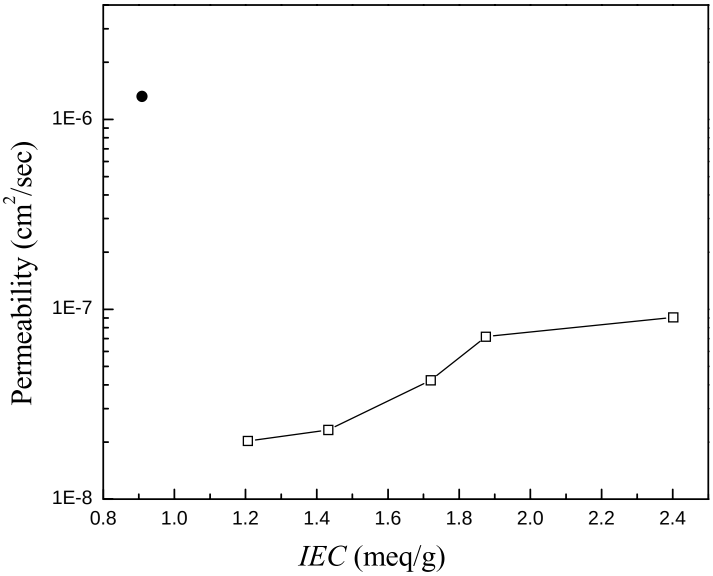

Fig. 4. Methanol permeability of SPEEK membranes at room temperature: (●) Nafion® 115 membrane; (□) SPEEK membranes.

not only by increasing the number of protonated sites (SO_3H), but also through formation of water mediated pathways for protons. Compared with Nafion® 115 membrane at room temperature, however, these SPEEK membranes have lower conductivity.

Prior to methanol permeability measurements, all the membrane samples were soaked in water for hydration. Fig. 4 shows the methanol permeability of these SPEEK membranes and Nafion® 115 membrane at room temperature. The measured methanol permeability of Nafion® 115 membrane is 1.32×10^{-6} cm^2/s at room temperature, which corresponds with the literature result of 1.17×10^{-6} cm^2/s [21]. It can be seen that the methanol permeability of SPEEK membranes increases with the increment of DS and reached a value of 9.07×10^{-8} cm^2/s for 85% DS. It is important to note that the methanol permeability of SPEEK membranes is considerably smaller than that of Nafion® 115 membrane.

The physical and chemical properties of SPEEK depend on the concentration of sulfonic groups and the nature of counter ions. Sulfonation modifies the chemical character of PEEK, reduces the crystallinity and consequently affects solubility. Thus, when the DS is over 30%, the SPEEK polymers are soluble in dimethylformamide (DMF), dimethylsulfoxide (DMSO), or *N*-methylpyrrolidone (NMP), above 70% they are soluble in methanol and at 100% sulfonation in hot water [19,20]. In addition, when the DS is above 60%, these polymers were highly swollen in methanol water solution (1 M) at 80–90 °C in our experiments. For these reasons, the SPEEK polymers with the DS above 60% are not suitable for the DMFC application. Thus, we prepared SPEEK with the DS of 39 and 47% for a DMFC test in our experiments.

Fig. 5 is an Arrhenius plot of proton conductivity as a function of temperature at 100% RH (relative humidity) for the SPEEK membranes and Nafion® 115 membrane. It can be found that the relation between conductivity and temperature basically accords with the Arrhenius equation. From the Arrhenius equation, the apparent activation energy of membrane can be calculated. The apparent activation energies of proton migration are reported in Table 1 along with the conductivity at 80 °C. The activation energy of Nafion® 115 membrane is 9.04 kJ/mol, which is in reasonable agreement with the literature value of 9.45 kJ/mol [22]. As can be seen, the conductivity of SPEEK membranes increases continuously with the increment of temperature. When the temperature is above 80 °C, the conductivity of these SPEEK membranes exceeds 0.01 S/cm, which is close to that of Nafion® 115 membrane.

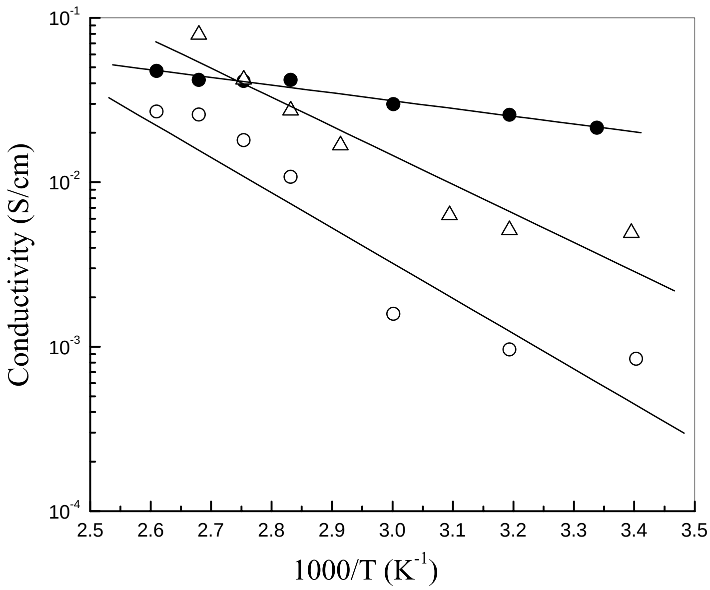

Fig. 5. Arrhenius plots of proton conductivity for samples: (●) Nafion® 115 membrane; (△) SPEEK membrane (DS = 47%); (○) SPEEK membrane (DS = 39%).

In addition, we note that the activation energy for SPEEK membranes is higher than that of Nafion® 115 membrane. May be there exist other variables affecting the measured activation energy in the experiments, besides the temperature factor. For SPEEK membranes, two other variables are also present in the experiments. The first variable is water content. The water uptake of the SPEEK membranes increases with temperature. The second is the ion content of the polymers. The dissociation constants of weak acids vary with temperature, so the ion contents in the SPEEK polymers will also vary. These will affect the conductivity measurements and therefore the measured activation energies. However, these effects likely did not influence the activation energy determined for Nafion® membrane. Nafion® 115 membrane is fully ionized at room temperature, so an increase in temperature will have no effect on the ion density. In addition, the Nafion® 115 membrane was pretreated in boiling water, so the water uptake likely did not increase with the increment of temperature [23]. Thus, the activation energy of SPEEK membranes is higher than that of Nafion® membrane.

Fig. 6 shows the methanol permeability as a function of temperature for SPEEK membranes and Nafion® 115 membrane. It can be found that an Arrhenius-type dependency of methanol permeability on temperature exists for all these membranes. The apparent activation energies for methanol permeation through the three membranes are also reported in Table 1 along with the methanol permeability at 80 °C. It is important to note that the methanol permeability

Table 1
Conductivity and methanol permeability at 80 °C of SPEEK and Nafion® 115 membranes[a]

Sample	DS (%)	Thickness (μm)	Conductivity (S/cm)	Permeability (cm^2/s)	E_m (kJ/mol)	E_p (kJ/mol)	β[b]
SPEEK	39	78	0.0108	1.321×10^{-7}	41.02	30.34	4.91
SPEEK	47	82	0.0168	1.453×10^{-7}	33.49	27.87	5.06
Nafion	–	152	0.0418	4.935×10^{-6}	9.04	22.44	3.93

[a] The activation energies of proton migration E_m and of methanol permeation E_p are also reported.
[b] $\beta = \log(\sigma/P)$.

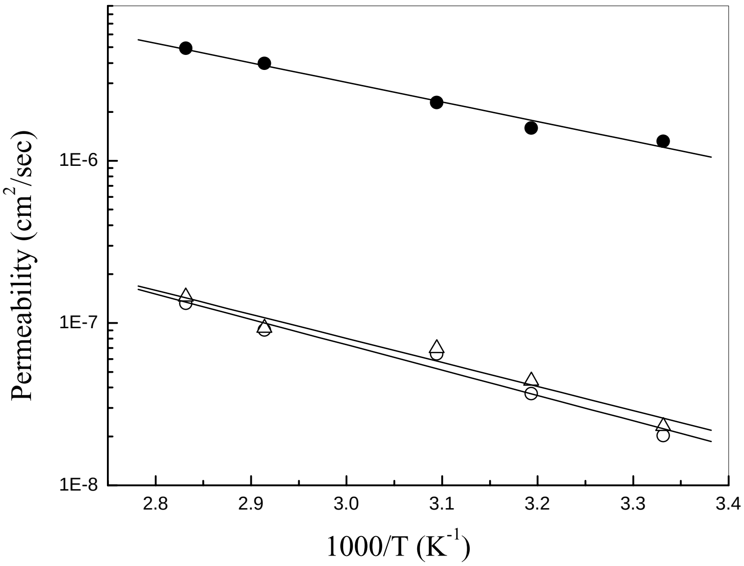

Fig. 6. Arrhenius plots of the methanol permeability for samples: (●) Nafion® 115 membrane; (△) SPEEK membrane (DS = 47%); (○) SPEEK membrane (DS = 39%).

of the SPEEK membranes is considerably smaller than that of Nafion® 115 membrane over the temperature range 25–80 °C. The different methanol permeation of SPEEK and Nafion® membranes can be explained by the difference in their microstructures. In Nafion® membranes, because of their high hydrophobicity perfluorinated backbone and their high hydrophilicity of the sulfonic acid functional groups, it would give rise to form hydrophobic/hydrophilic domains, especially in the presence of water. The sulfonic acid groups aggregate to form a hydrophilic domain. These hydrophilic domains are interconnected in Nafion® membranes. Not only proton and water can transport through these domains, but a smaller polar molecule such as methanol can also permeate through these domains [5]. This will lead to the methanol crossover. However, the microstructure of SPEEK membranes was found to be distinctly different compared with Nafion® membranes. As a result of the smaller hydrophobic/hydrophilic difference (the backbone is less hydrophobic, and the sulfonic acid functional group is less acidic and therefore, also less polar and lower conductivity) and the lesser flexibility of the polymer backbone, the separation into a hydrophilic and a hydrophobic domain is less pronounced. One important consequence of the less hydrophobic/hydrophilic separation in the SPEEK membranes is that the methanol permeability is lower than that of Nafion® 115 membrane.

High proton conductivity (σ) and low methanol permeability (P) are two of the essential characteristics, which a polymer electrolyte membrane must possess in order to be validly proposed for use in DMFC. We combined the two into a factor β (=$\log(\sigma/P)$) as the characteristic parameter of a membrane, so that different membranes can be more easily compared. The practical significance of this parameter is explained in quantitative terms as in [24]. In Table 1, it can be found that SPEEK membranes show remarkably low methanol permeability compared to Nafion® 115 membrane, whereas their proton conductivity are close to that of Nafion® 115 membrane. Then, the β value of both SPEEK membranes is higher than that of Nafion® 115 membrane at 80 °C. Maximum β value is reached for SPEEK membrane with the DS 47%.

The polarization curves of MEAs made from the SPEEK membranes are shown together with the respective curves of a Nafion® 115 MEA in Fig. 7. It can be seen that the open circuit voltage for the SPEEK membranes (0.632–0.645 V) is higher than that of Nafion® 115 membrane (0.595 V). This reason is that the methanol permeability of SPEEK is lower

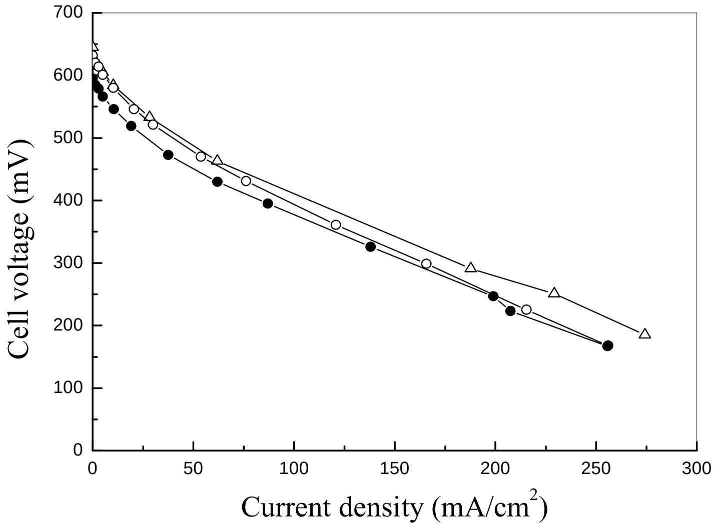

Fig. 7. Polarization curves for the various MEA equipped with different membranes (operating conditions: 80 °C, oxygen feed, methanol 2 M): (●) Nafion® 115 membrane; (△) SPEEK membrane (DS = 47%); (○) SPEEK membrane (DS = 39%).

than that of Nafion® 115 membrane (Fig. 5). Because of high conductivity and low methanol permeability, the DMFC performance of the SPEEK membranes was better than that of Nafion® 115 membrane.

4. Conclusion

SPEEK membranes with various DS were prepared. With the increment of DS, the proton conductivity and methanol permeability of SPEEK membranes increase at room temperature. Allowing for the need to DMFC application, the SPEEK membranes with the DS 39% and 47% were tested in a single DMFC. The proton conductivity of two SPEEK membranes exceeded 10^{-2} S/cm above 80 °C, which was close to that of Nafion® 115 membrane under the same condition. The activation energy of SPEEK membranes was higher than that of Nafion® 115 membrane. Because of the different microstructure, the methanol permeability of SPEEK membranes was considerably lower than that of Nafion® 115 membrane over the temperature range 25–80 °C. It is proposed that the β parameter can be used to evaluate the performance of membranes for DMFC. The β values of two SPEEK membranes are higher than Nafion® 115 membrane at 80 °C. And the DMFC performances of the SPEEK membranes were better than that of Nafion® 115 membrane.

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