Sulfonated poly(ether sulfone) for universal polymer electrolyte fuel cell operations

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Abstract

The performances of the proton exchange membrane fuel cell (PEMFC), direct formic acid fuel cell (DFAFC) and direct methanol fuel cell (DMFC) with sulfonated poly(ether sulfone) membrane are reported. Pt/C was coated on the membrane directly to fabricate a MEA for PEMFC operation. A single cell test was carried out using H_2/air as the fuel and oxidant. A current density of 730 mA cm^{-2} at 0.60 V was obtained at 70 °C. Pt–Ru (anode) and Pt (cathode) were coated on the membrane for DMFC operations. It produced 83 mW cm^{-2} maximum power density. The sulfonated poly(ether sulfone) membrane was also used for DFAFC operation under several different conditions. It showed good cell performances for several different kinds of polymer electrolyte fuel cell applications.
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1. Introduction

Polymer electrolyte fuel cells (PEFCs) have been spotlighted because they are clean and highly efficient power generation systems. Proton exchange membrane fuel cells (PEMFCs), which use reformate gases or pure H_2 as the fuel, have been used in automotive and residential applications. Also, liquid feed fuel cells such as direct methanol fuel cell (DMFC) and direct formic acid fuel cell (DFAFC) have been studied as the energy source for portable devices.

The membrane electrode assembly (MEA) is one of the most important parts in PEFCs. Among the components of the MEA, the membrane is a key element and determines the performance of the fuel cell. At the moment, Nafion type perfluorosulfonated polymers have been used because of their high proton conductivity and chemical inertness. However, they have some problems such as a high liquid fuel permeability, low proton conductivity at high temperature under low humidity conditions and a high

manufacturing cost [1,2]. These are the principal drawbacks for commercialization of fuel cell membranes.

Recently, numerous researchers have synthesized several different kinds of hydrocarbon-based sulfonated polymers for a fuel cell membrane to overcome the problems of the perfluorosulfonated polymers. Sulfonated poly(ether sulfone)s [3–5], sulfonated PEEKs [6,7], sulfonated polyimides [8–10], sulfoalkylated polysulfones [11], sulfonated polyphthalazines [12,13] and sulfonated polybenzimidazoles [14,15] were prepared for fuel cell membranes. Also, several sulfonated polymers were tested for PEMFC [16–19] and DMFC [20–23] operations.

Hydrocarbon-based sulfonated polymers are very promising for fuel cell membranes because they can be synthesized relatively easily and inexpensively. Previously, we reported an easy preparation method of sulfonated poly(ether sulfone)s (PESs) [24]. They were synthesized using hydroquinone 2-potassium sulfonate (HPS) with other monomers (bisphenol A and 4-fluorophenyl sulfone). PESs with different mole% of hydrophilic group were prepared by changing the mole ratio of HPS in the polymerization reaction. As the HPS's portion increased in the polymer, the proton conductivity increased. However, when HPS was 70% in the polymer (PES 70), the polymer was dissolved in

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boiling water. The PES 60 membrane, which has 60 mole% of HPS unit in the polymer backbone, was not dissolved in boiling water. Also, it had a proton conductivity of 0.09 S cm^{-1} which is comparable to that of Nafion. Therefore, the PES 60 was used for PEMFC operation and showed good cell performance under specific conditions [24].

In this report, we present the possibility of the sulfonated poly(ether sulfone) (PES 60) for versatile PEFC applications. A lot of sulfonated polymers have been synthesized and characterized for fuel cell membranes. However, none of them have been successfully demonstrated for different kinds of polymer electrolyte fuel cell systems. We report PEMFC, DMFC and DFAFC performances of the sulfonated poly(ether sulfone) membrane. Even though the cell performances of the sulfonated polymer are lower than those of commercially available Nafion, the polymer remains a good candidate for universal PEFC operations.

2. Experimental

2.1. Materials

The hydrocarbon-based polymers used for this work were synthesized from commercially available 4-fluorophenyl sulfone (FPS), hydroquinone 2-potassium sulfonate (HPS) and bisphenol A (BPA). HPS was purchased from Acros Organics and recrystallized from deionized water. FPS and BPA were obtained from Aldrich Chemicals. Potassium carbonate, FPS, BPA and HPS were dried at 60 °C for 24 h under vacuum before used for polymerization. DMAc (Sigma–Aldrich), DMSO (Acros Organics), toluene, HCl (J.T. Baker), isopropyl alcohol (Aldrich HPLC grade) and methanol (Daejung Reagents & Chemicals) were used as received.

2.2. Synthesis of sulfonated poly(ether sulfone) (PES60) and membrane fabrication

4-Fluorophenyl sulfone (20 mmole, 5.09 g), bisphenol A (8 mmole, 1.83 g), hydroquinone 2-potassium sulfonate (12 mmole, 2.74 g) and potassium carbonate (40 mmole, 5.70 g) were added to the mixture of 25 mL of dimethyl acetamide (DMAc) and 40 mL of toluene in a 100 mL round bottom flask, equipped with a Dean-Stark apparatus, a nitrogen inlet and a thermometer. The flask was placed in an oil bath, and the reaction mixture was heated for 4 h at 150 °C. After the water was essentially removed from the reaction mixture by azeotropic distillation, toluene was distilled out and the temperature was raised to 180 °C. Then, it was allowed to stand overnight at the temperature under nitrogen atmosphere. When the reaction mixture was cooled to room temperature, it was poured to 1000 mL of MeOH to obtain the PES polymer. The crude product was filtered and dried in the vacuum oven at 60 °C for 1 h. The Soxhlet extraction was performed for the polymer using deionized water to remove inorganic material from the polymer. Then, the polymer was dried in the vacuum oven at 60 °C for overnight. The polymer was dissolved in DMSO (15%, w/v). The solution was poured on a glass plate and the thickness of the solution on the glass plate was controlled by doctor blade. The membrane was

dried at 60 °C under reduced pressure for 30 h. It was acidified with 10% HCl solution overnight and rinsed with water. Finally, it was dried at 60 °C under vacuum. ^{1}H NMR (DMSO-d_6) δ 1.65 (s, 6H, –CH$_3$), 6.96–7.35 (m, 21H, ArH), 7.37–7.52 (m, 1.5H, ArH), 7.80–8.02 (m, 10H, ArH); FT-IR (cm^{-1}) 712, 1020, 1078, 1107, 1146, 1225, 1476, 1584.

2.3. Methanol permeability measurement

Methanol permeability of membranes is measured using a cell which consists of two compartments that are separated by an electrolyte membrane [25]. Five percent aqueous methanol solution is fed into one compartment and deionized water is circulated through the other compartment. Each compartment is stirred continuously during the test. A differential refractive index detector is used to monitor the methanol concentration of the compartments to measure methanol permeability.

2.4. Membrane electrode assembly (MEA) preparation for PEMFC test

The catalyst slurry was prepared by mixing 40 wt% Pt/Vulcan XC 72 (E-Tek Inc.) with isopropyl alcohol and 5 wt% Nafion (EW1100) solution. It was sonicated for 1 h and sprayed on an electrolyte membrane (thickness: 30 μm). Finally, the catalyst-coated membrane was dried at 60 °C for 5 h. The active electrode area for a single cell test was 25 cm^2 with platinum loading of 0.2 and 0.4 mg cm^{-2} for anode and cathode, respectively.

The single cell was set up with the catalyst-coated membrane, gas diffusion media (SGL 10BC), Teflon gaskets and graphite blocks. The gases (fuel and oxidant) were passed through humidifiers before they (gas flow rate: 400 mL min^{-1} (anode) and 1000 mL min^{-1} (cathode) under ambient pressure) were allowed to enter the fuel cell inlets. i–V characteristics were evaluated using an electric load (Daegil Electronics, EL500P).

2.5. Membrane electrode assembly preparation for DMFC test

Unsupported Pt–Ru (50:50 wt%) and Pt (Johnson Matthey) were used for anode and cathode, respectively. Catalyst slurry which is composed of 5 wt% Nafion (EW1100) solution, isopropanol and catalyst was directly sprayed on an electrolyte membrane (thickness: 30 μm). The active electrode area for a single cell test was 10 cm^2 with catalyst loading of 3 mg cm^{-2} for anode and cathode. Carbon papers (Toray) were placed on each side of the catalyst-coated membrane and the 5-layered cell was held between two graphite plates. Polarization curves were obtained using an electric load (Daegil Electronics, EL200P).

2.6. Membrane electrode assembly preparation for DFAFC test

Unsupported Pt–Ru (50:50 wt%) and Pt (Johnson Matthey) were used for anode and cathode, respectively. Catalyst slurry was prepared and sprayed on an electrolyte membrane (thickness: 30 μm) as mentioned in Section 2.5. The catalyst loading

was $3\,mg\,cm^{-2}$ for anode and cathode and the active electrode area for a single cell test was $9\,cm^2$. Polarization curves were obtained at various temperatures after methanol treatment [26].

3. Results and discussion

3.1. PEMFC operations using sulfonated poly(ether sulfone)

Sulfonated poly(ether sulfone) was prepared by the modified method described in the paper [5]. It was synthesized using hydroquinone 2-potassium sulfonate (HPS) with other monomers (bisphenol A and 4-fluorophenyl sulfone) with different mole% of hydrophilic group by changing the mole ratio of HPS in the polymerization reaction [24]. The PES 60 membrane (Scheme 1), which has 60 mole% of HPS unit in the polymer backbone, has a reasonable proton conductivity and good insolubility in boiling water. So, we used the membrane for PEMFC operation with H_2 and O_2 gases as fuel and oxidant, respectively. It showed a current density of $1400\,mA\,cm^{-2}$ at $0.60\,V$ was obtained at $70\,°C$.

We operated a PEMFC with H_2/air using the PES 60 membrane. Firstly, a membrane electrode assembly was fabricated. The catalyst slurry, which was prepared by mixing 40 wt% Pt/Vulcan XC 72 (E-Tek Inc.) with isopropyl alcohol and 5 wt% Nafion (EW1100) solution, was sprayed directly on the PES 60 membrane. The same method was used for the MEA using Nafion 112 membrane for the comparison. The morphology of cross-section of the MEA using PES 60 membrane is shown in Fig. 1. From the cross-section of the membrane, the membrane thickness was about $30\,\mu m$.

The PEMFC performances of the PES 60 membrane and Nafion 112 are presented in Fig. 2. The cell performance of the MEA using the PES 60 membrane was $730\,mA\,cm^{-2}$ at $0.6\,V$. It is lower than that of Nafion 112. This could be related to the inappropriate interfacial contact between the PES 60 membrane and electrodes, because Nafion binder was used for the electrode fabrication [20]. We think that cell performance will be improved if we establish a better MEA fabrication method.
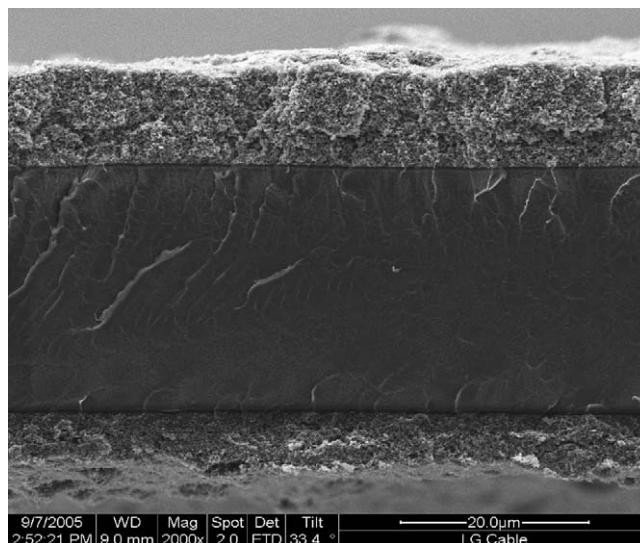

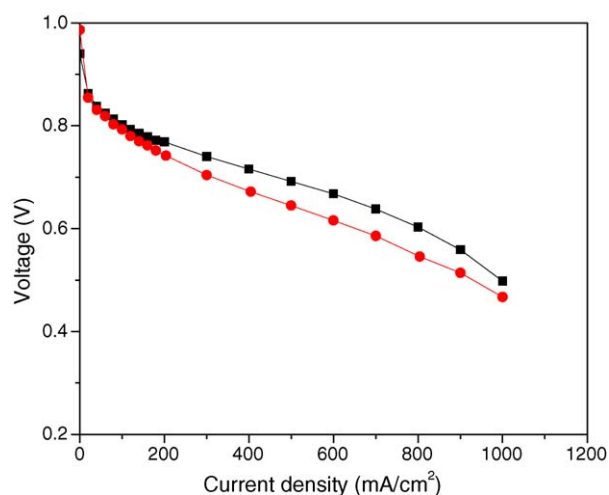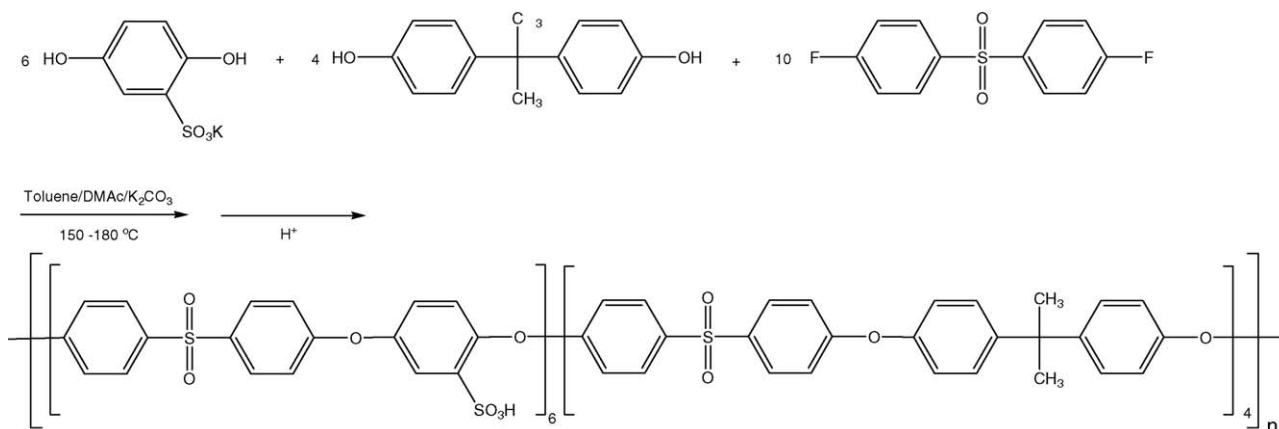Fig. 1. SEM image of cross-sectional view of MEA with PES 60 membrane.

Fig. 2. Polarization curves for MEAs using PES 60 (●) and Nafion 112 (■) with the H_2/air (65–70% relative humidity) at $70\,°C$ under ambient pressure. Flow rate: $400\,mL\,min^{-1}$ (anode), $1000\,mL\,min^{-1}$ (cathode).
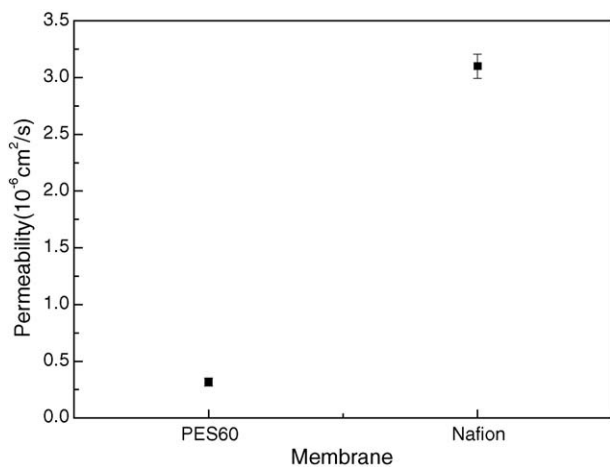

Scheme 1. Synthesis of PES 60.

Fig. 3. Permeabilities of Nafion 115 and PES 60 membranes.

3.2. DMFC operations using sulfonated poly(ether sulfone)

Methanol permeabilities of the PES 60 membrane and Nafion 115 are presented in Fig. 3. It was found that methanol permeability of the PES 60 membrane was lower than that of Nafion 115. It showed similar results to previously reported review papers [27,28]. According to the papers, most sulfonated poly(ether sulfone)-like polymer membranes have a lower methanol permeability than Nafion. Nafion has a hydrophobic flexible polymer backbone and sulfonic acid groups on long flexible side chains, which form distinct hydrophilic and hydrophobic domains. Through the hydrophilic domain, methanol is transported very easily. Unlike Nafion, the sulfonated poly(ether sulfone)s have stiff polymer backbones which are less hydrophobic than Nafion. Also, sulfonic acid groups are attached directly to poly(ether sulfone) backbone. Because of those reasons, the sulfonated poly(ether sulfone) has a less distinct phase separated structure which causes less methanol cross-over.

A MEA was fabricated with the PES 60 membrane. Pt–Ru (50:50 wt%) and Pt were coated on the anode and cathode sides of the membrane, respectively. Fig. 4 shows impedance analysis and DMFC performances of the MEA at 60 °C with different methanol feed concentration (1 and 2 M). High methanol feed (2 M) generated higher resistance, resulting in lower cell performance than low methanol feed (1 M), which could be related to higher methanol cross-over for higher methanol feed concentration [29]. Also, a cell test was carried out at 70 °C (Fig. 5). It showed a similar trend to that at 60 °C and cell performance was higher than that at 60 °C. It produced 83 mW cm^{-2} power density.

The DMFC test was carried out without humidification at the cathode. This is presented in Fig. 6. The cell performance decreased when the cathode was not humidified. According to the result, humidification at the cathode is essential to achieve a maximum power density.

The DMFC performances of the PES 60 membrane and Nafion 115 are presented in Fig. 7. The cell performance of the MEA using the PES 60 membrane was lower than that of Nafion 115. This could be bad interfacial contact between the hydrocarbon membrane and fluorocarbon binder. Recently, Kim et al. reported DMFC performance using new disulfonated poly(arylene ether sulfone) [20]. The polymer contains trifluoromethyl group which promotes the interfacial contact between the membrane and electrodes, resulting in high DMFC performance. We think that a new MEA fabrication method for the sulfonated polymer membrane has to be established for better cell performance and long term operation.

3.3. DFAFC operations using sulfonated poly(ether sulfone)

Direct formic acid fuel cell (DFAFC) is one of the good candidates for portable power generation systems. It has several advantages over DMFC [30]. It has a low fuel cross-over and produces a low amount of catalyst poisoning intermediates compared to DMFC. Decrease of fuel cross-over allows the use of a high fuel feed concentration and improves overall cell efficiency, resulting in higher cell performance than DMFC. Also, formic acid is more environmentally friendly than methanol.

In this report, we used the PES 60 membrane as an electrolyte for DFAFC operation. Pt–Ru (50:50 wt%) and Pt were coated onto the anode and cathode sides, respectively. Fig. 8 shows DFAFC performance dependence on formic acid feed
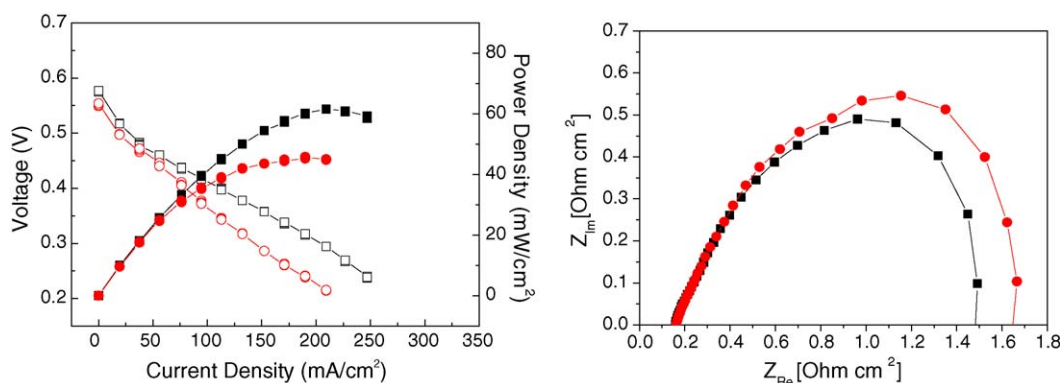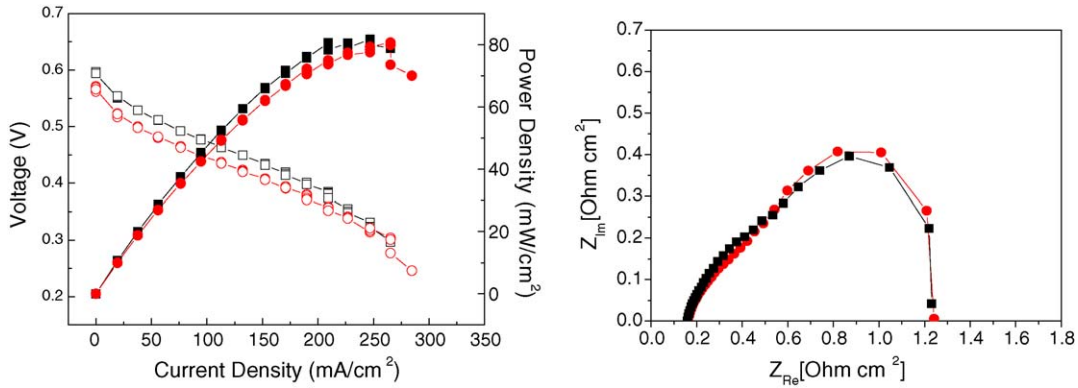

Fig. 4. Polarization curves and impedance of direct methanol fuel cell based on the PES 60 membrane with different methanol feed concentration (1 M (■) and 2 M (●)) under ambient pressure. Electrode: Pt–Ru loading of 3 mg cm^{-2} (anode) and Pt loading 3 mg cm^{-2} (cathode); active area: 10 cm^2; temperature: 60 °C; flow rate: 5 mL min^{-1} (anode), 1250 mL min^{-1} (cathode); oxidant: air (90–95% relative humidity).

Fig. 5. Polarization curves and impedance of direct methanol fuel cell based on the PES 60 membrane with different methanol feed concentration (1 M (■) and 2 M (●)) under ambient pressure. Electrode: Pt–Ru loading of 3 mg cm^{-2} (anode) and Pt loading 3 mg cm^{-2} (cathode); active area: 10 cm^2; temperature: 70 °C; flow rate: 5 mL min^{-1} (anode), 1250 mL min^{-1} (cathode); oxidant: air (90–95% relative humidity).
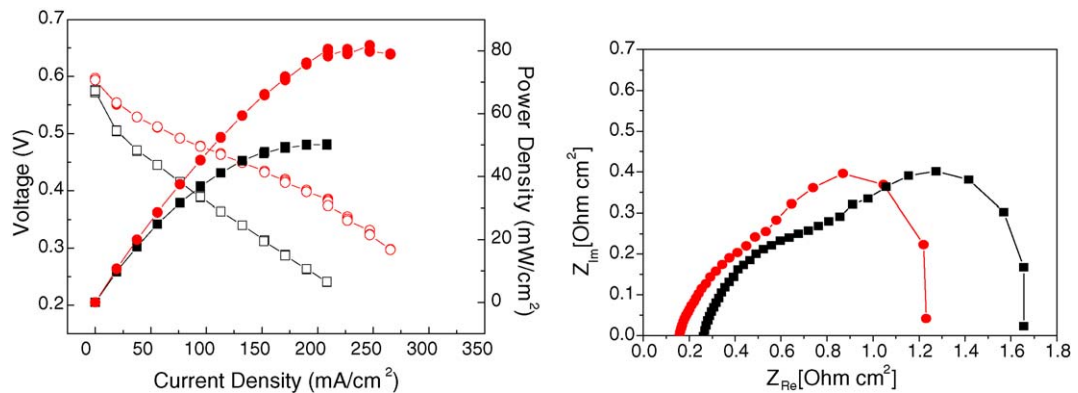

Fig. 6. Polarization curves and impedance of direct methanol fuel cell based on the PES 60 membrane with humidification (90–95% relative humidity) (●) and without humidification (■) at the cathode under ambient pressure. Electrode: Pt–Ru loading of 3 mg cm^{-2} (anode) and Pt loading 3 mg cm^{-2} (cathode); active area: 10 cm^2; temperature: 70 °C; flow rate: 5 mL min^{-1} (anode), 1250 mL min^{-1} (cathode); oxidant: air.

concentration (6, 10 and 15 M) at 30 °C. The cell performance decreased as the feed concentration increased, which is a similar trend to DMFC operation [31]. Fig. 9 shows cell dependence on operation temperature (30, 60 and 70 °C) at a fixed formic acid

feed concentration (6 M). The cell performance improved as the temperature increased.

The DFAFC performances of PES 60 membrane and Nafion 115 are presented in Fig. 10. The cell performance of the MEA
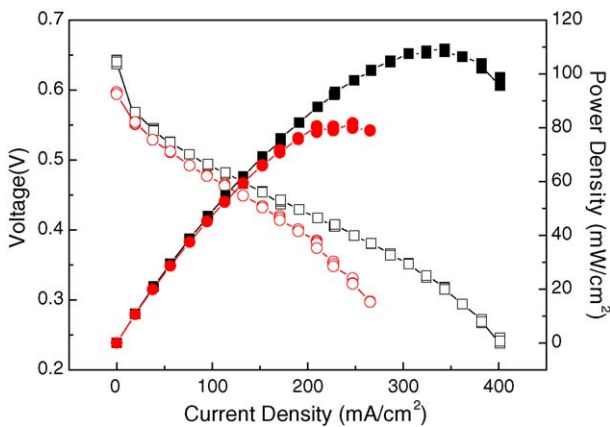

Fig. 7. Polarization curves and impedance of direct methanol fuel cell based on the PES 60 membrane (●) and Nafion 115 (■) with humidification (90–95% relative humidity) at the cathode under ambient pressure. Electrode: Pt–Ru loading of 3 mg cm^{-2} (anode) and Pt loading 3 mg cm^{-2} (cathode); active area: 10 cm^2; temperature: 70 °C; flow rate: 5 mL min^{-1} (anode), 1250 mL min^{-1} (cathode); oxidant: air.
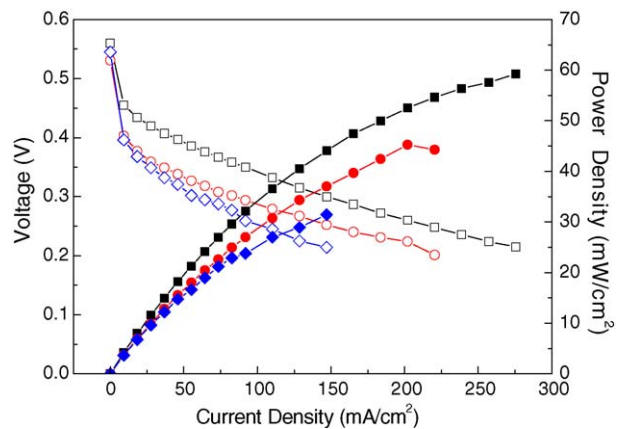

Fig. 8. Polarization curves of direct formic acid fuel cell based on the PES 60 membrane with different formic acid feed concentration ((6 M (■), 10 M (●) and 15 M (♦)) under ambient pressure. Electrode: Pt–Ru loading of 3 mg cm^{-2} (anode) and Pt loading 3 mg cm^{-2} (cathode); active area: 9 cm^2; temperature: 30 °C; flow rate: 5 mL min^{-1} (anode), 250 mL min^{-1} (cathode); oxidant: O$_2$ (90–95% relative humidity).
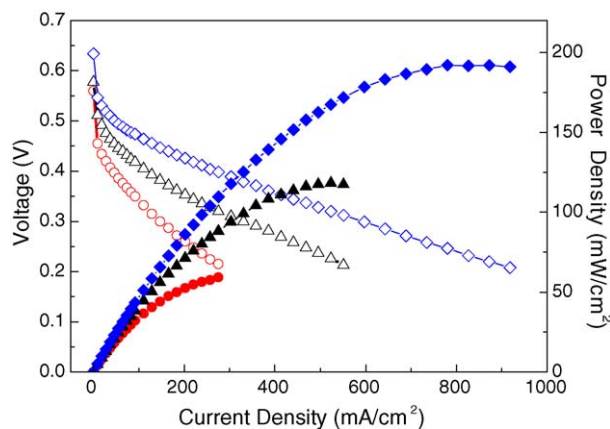
Fig. 9. Polarization curves of direct formic acid fuel cell based on the PES 60 membrane at different operation temperature (30 (●), 60 (▲) and 70 (♦)) under ambient pressure. Electrode: Pt–Ru loading of 3 mg cm^{-2} (anode) and Pt loading 3 mg cm^{-2} (cathode); formic acid feed concentration: 6 M; active area: 9 cm^2; flow rate: 5 mL min^{-1} (anode), 250 mL min^{-1} (cathode); oxidant: O$_2$ (90–95% relative humidity).
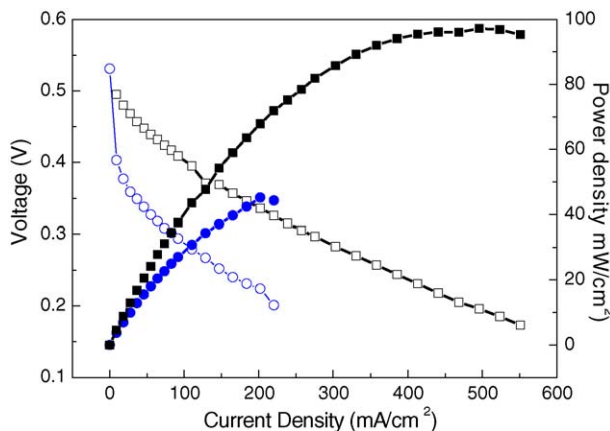

Fig. 10. Polarization curves of direct formic acid fuel cell based on the PES 60 membrane (●) and Nafion 115 (■) with humidification (90–95% relative humidity) at the cathode under ambient pressure. Electrode: Pt–Ru loading of 3 mg cm^{-2} (anode) and Pt loading 3 mg cm^{-2} (cathode); formic acid feed concentration: 3 M; active area: 9 cm^2; temperature: 30 °C; flow rate: 5 mL min^{-1} (anode), 250 mL min^{-1} (cathode); oxidant: O$_2$.

using the PES 60 membrane was lower than that of Nafion 115, which is similar to the DMFC operation reported in Section 3.2.

4. Conclusions

A sulfonated poly(ether sulfone) membrane was used for three different kinds of polymer electrolyte fuel cells (PEMFC, DMFC and DFAFC). It generated 730 mA cm^{-2} at 0.60 V for PEMFC operation with H$_2$ and air. Also, the sulfonated mem-

brane was used for DMFC and DFAFC operation under different operation temperatures, feed concentrations and humidification conditions. The cell performance improved as the temperature increased and feed concentration was lowered. We believe that the sulfonated poly(ether sulfone) is one of the best candidates for a fuel cell membrane.

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