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ORIGINAL PAPER

Fuel cell performance of polymer electrolyte membrane based on hexafluorinated sulfonated poly(ether sulfone)

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Abstract The potential-current fuel cell characteristics of membrane electrode assemblies (MEAs) using hexafluorinated sulfonated poly(ether sulfone) copolymer are compared to those of Nafion® based MEAs in the case of proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC). The hexafluorinated copolymer with 60 mol% of monosulfonated comonomer based acid form membrane is chosen for this study due to its high proton conductivity, high thermal stability, low methanol permeability, and its insolubility in boiling water. The catalyst powder is directly coated on the membrane and the catalyst coated membrane is used to fabricate MEAs for both fuel cells. A current density of 530 mA cm^{-2} at 0.6 V is obtained at 70 °C with H_2/air as the fuel and oxidant. The peak power density of 110 mW cm^{-2} is obtained at 80 °C under specific DMFC operating conditions. Other electrochemical characteristics such as electrochemical impedance spectroscopy, cyclic voltammetry, and linear sweep voltammetry are also studied.

Keywords Membrane electrode assembly · Electrolyte membrane · Polymer electrolyte fuel cell

Introduction

In recent years, the proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) have received much attention as alternative power sources because of their potential application in transportation, residential power sources, and portable electrical devices [1, 2]. In polymer electrolyte fuel cells

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(PEFCs), the membrane must display several characteristics, including transporting protons from the anode to the cathode, but prohibit the passage of electrons and heavier gases. The proton conductive ionomer membranes currently used in PEFCs are per-fluorinated polymers such as Nafion®, Asahi® and Dow®. Nafion® membranes are state-of-the-art for the PEMFC and DMFC due to their high conductivity when hydrated and chemical stability. Even though these membranes have exhibited good performance and long-term stability, their high cost, low performance at high temperature and high methanol crossover may limit their use in the mass production of fuel cells. As a result, key interests or challenges in the current fuel cell research is the development of an alternative membrane [3].

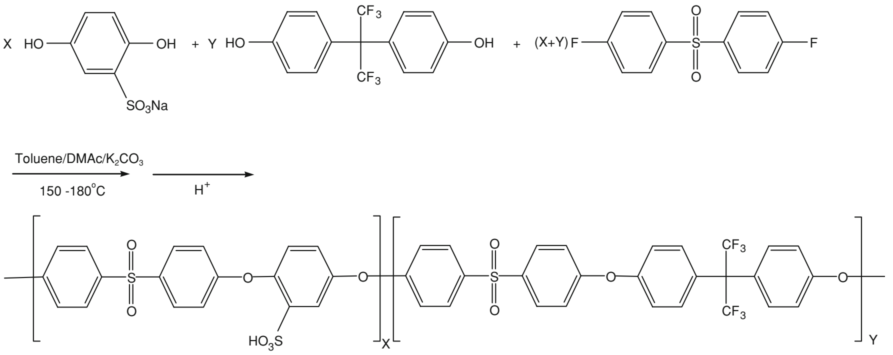
In the last two decades, several types of perfluorinated, partially fluorinated, non-fluorinated, acid-base blends, and other polymer based ionomer membranes have been studied as alternative membranes. The state-of-the-art advances in polymer electrolyte membranes have been described in detail by several recent reviews [4–10]. Although the alternative membranes have their own advantages, most of them have failed to meet the need for practical fuel cell applications. Nafion® has long served as a benchmark material when evaluating the performance of proton conducting membranes used in PEFCs. Therefore, the PEFCs performances of MEAs using some of those alternative membranes have been reported [11–21].

Several researchers observed both the membrane-electrode delamination failure and higher cell resistance due to the usage of dissimilar polymers with Nafion® bonded electrodes [22–24]. In our previous work, we reported an easy preparation method of hydrocarbon-based sulfonated poly(ether sulfone) (PES) copolymers and the PES 60's PEFCs performances due to its high proton conductivity and insolubility in boiling water [25, 26]. In this work, the chemical structure was modified to be more compatible with Nafion®-bonded electrode materials. We expect that the incorporation of fluorine moiety in the PES copolymer backbone may produce different membrane properties critical to fuel cell performance. The aim of this paper is to present the study of PEMFC as well as DMFC fuel cell performances of the hexafluorinated sulfonated poly(ether sulfone) copolymer (F-PES) membrane based MEAs.

Experimental

Preparation of proton exchange membrane

The hexafluorinated sulfonated poly(ether sulfone) (F-PES) copolymers were prepared by direct aromatic nucleophilic substitution polycondensation of commercially available monomers such as 2, 2-Bis(4-hydroxyphenyl) hexafluoropropane, hydroquinone 2-potassium sulfonate, and 4-fluorophenyl sulfone under basic conditions in anhydrous dimethylacetamide at 180 °C. We previously reported the detailed synthesis procedure and characterization of sulfonated poly(ether sulfone) copolymer (PES 60) [25]. The similar experimental procedure was adapted by adjusting the mole ratio of the required monomer for the polymerization of F-PES copolymer, as shown in Scheme 1. Membranes were prepared by dissolving



Scheme 1 Synthesis of hexafluorinated sulfonated poly(ether sulfone) copolymers

the salt form copolymers in dimethyl sulfoxide (15% w/v) at room temperature. The solutions were filtered and directly cast onto clean glass plates. After drying at 60 °C under reduced pressure, the membranes were removed from the glass plates by submersing them in deionized water. The crude membranes in salt form were acidified with 10% HCl solution at 60–70 °C for 2 h. Then, the acid form membranes were treated with deionized water at 60–70 °C for 2 h and stored in deionized water at room temperature. All the membranes in acid form were obtained with a thickness of 45 ± 3 μm.

Proton conductivity

A four-point-probe home-made conductivity cell with two Pd plate outer current carrying electrodes and two Pt wire inner potential detecting electrodes was used. The distance between the potential probes were 1 cm apart and each of two current probes was at a distance of 1.6 cm. Membrane samples were cut into strips of 1 cm in width and 4 cm in length prior to the mounting in the cell. The proton conductivity measurements were performed on membranes after being soaked in deionized water for 48 h at room temperature. The measurements were performed by placing a conductivity cell in deionized water. Impedance measurements were performed using an IM6 (Zahner). The instrument was used in galvanostatic mode with AC current amplitude of 1 mA (current 0 A) over a frequency range of 5 MHz–1 Hz. The proton conductivity was calculated according to the following equation:

$$\text{Proton conductivity} \quad \sigma(\text{S/cm}) = \frac{l(\text{cm})}{R(\Omega) \times A(\text{cm}^2)} \tag{1}$$

where l is the distance between the two potential probes, R is ion conductive resistance of the membrane from the impedance spectra, and A is a membrane cross sectional area [thickness (t) × width (w)].

MEA fabrication for PEMFC test

Catalyst ink was prepared by mixing 40 wt% Pt/Vulcan XC 72 (E-Tek Inc.) catalyst powder with HPLC grade isopropyl alcohol and 5 wt% Nafion® (EW 1100) solution (Du Pont, Inc.). The catalyst ink was ultrasonicated for 1 h. The catalyst-coated membrane (CCM) was fabricated by spray-coating the freshly prepared catalyst ink on the membrane, i.e., acid form F-PES 60 membrane and Nafion® 112 membrane. The prepared CCM 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. Single cells were assembled with the prepared CCMs, gas diffusion media (Sigracet® SGL 10BC), Teflon gaskets and graphite blocks. Hydrogen and cathode gas was passed through a bubble humidifier before the gases were fed into the fuel cell inlets. The cell temperature was held at 70 and 80 °C. The potential-current (*i*–*V*) characteristics of the single cells were performed (Electric load—Daegil Electronics Inc., EL500P) using a fuel cell test station after 24 h activation under the fuel (H_2—400 mL min^{-1}) and oxidant (O_2/air—400/1200 mL min^{-1}) flow conditions maintained at a cell voltage of 0.6 V.

To examine the ohmic and charge transfer resistance of the single cells, the impedance spectra (EIS) of single cells was carried out at 0.8 V after the H_2/air single cell tests. The applied frequency was varied from 10 kHz to 10 mHz with an ac amplitude of 5 mV. The humidified H_2 and air gases with the flow rate of 400 mL min^{-1} were fed to anode and cathode, respectively, at ambient pressure. The electrochemical active surface area (EAS) or Pt utilization was also estimated from cyclic voltammogram. A cyclic voltagram was performed with the range of 50 mV to 1.4 V at a scan rate of 50 mV s^{-1}. During the measurements of this experiment, humidified nitrogen and hydrogen were fed to the working electrode and counter electrode, respectively. H_2 cross over current density was measured by linear sweep voltammetry (LSV) with the above mentioned conditions.

MEA fabrication for DMFC test

The CCMs were prepared from standard catalyst inks using Pt–Ru (50:50 wt%) and Pt (Johnson Matthey) for anode and cathode, respectively. The catalyst ink with isopropyl alcohol and 5 wt% Nafion® (EW 1100) solution was sprayed directly on the membrane. The geometric active cell area was 10 cm^2 with a catalyst loading of 3 mg cm^{-2} for both electrodes. Toray carbon papers were placed on each side of the CCM and the five-layered cell was held between two graphite plates. The Nafion® 115 membrane based MEA was also prepared by the same procedure. The cell temperature was held at 60 and 80 °C. 1 M methanol solution was fed to the anode with a flow rate of 5 mL min^{-1} and the wet or dry air was fed at 1,250 sccm without back pressure. *i*–*V* Characteristics were obtained using an electric load (Daegil Electronics, EL200P).

Table 1 Ion exchange capacity (IEC), water uptake, proton conductivity and solubility of the acid from sulfonated poly(ether sulfone) membranes

Acid form membrane	IEC[a] (mequiv g^{-1})	Water uptake[b] (wt%)	Proton conductivity[c] [σ (S cm^{-1})]	Solubility[d]
F-PES 50	0.95	15	0.087	X
F-PES 60	1.28	23	0.094	X
F-PES 65	1.40	36	0.116	SW
PES 60	1.43	30	0.091	X

[a] IEC determined by titration

[b] Water uptake = $(W_{wet} - W_{dry})/W_{dry} \times 100$. W_{wet} and W_{dry} are the weights of the wet and dry membranes, respectively

[c] Proton conductivity at room temperature

[d] Solubility in boiling water (*X* not soluble, *SW* swollen)

Results and discussion

Membrane properties

The synthesized F-PES copolymers exhibited flexible membrane properties. The ion exchange capacity (IEC), water uptake, proton conductivity, and solubility in boiling water for F-PES membranes are summarized in Table 1, and the properties of PES 60 are also included for comparison. Both high proton conductivity and mechanical stability are important properties for proton exchange membranes. The above-mentioned properties are generally affected by IEC values. The IEC, water uptake, and proton conductivity for F-PES copolymer increased by increasing the mol% of sulfonated monomer. The F-PES 60 membrane has a lower water uptake than the PES 60 membrane. This is due to the presence of hydrophobic nature of the hexafluoroisopropylidene connecting unit in the polymer backbone. Harrison et al. [27] found the general trend of increasing water uptake by increasing IEC for different polymers. Kim et al. [17] reported the hydrocarbon based 25 mol% disulfonated poly(arylene ether sulfone) copolymer (BP-25, IEC 1.11 mequiv g^{-1}) and the partially fluorinated 25 mol% disulfonated poly(arylene ether sulfone) copolymer (6F-25, IEC 0.85 mequiv g^{-1}) showed the proton conductivity value 23 mS cm^{-1} and 26 mS cm^{-1}, respectively. A similar tendency in both IEC value and proton conductivity values for the two copolymer (PES 60 and F-PES 60) membranes were observed. Finally, the F-PES 60 membrane was chosen for fuel cell test due to its high proton conductivity, low methanol permeability, and good insolubility in boiling water.

Evaluation of PEMFC performance with F-PES 60 membrane

Figure 1 shows the H_2/O_2 potential-current (*i*–*V*) polarization curves of 25 cm^2 MEAs with F-PES 60 and Nafion® 112 membrane as a function of cell temperature. The MEAs were based on 0.2 and 0.4 mg Pt cm^{-2} for the anode and the cathode, respectively. The *i*–*V* performance of the MEA with F-PES 60 membrane is lower

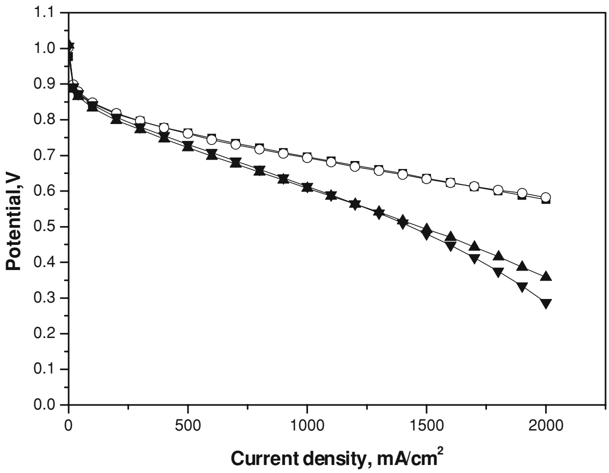


Fig. 1 PEMFC polarization curves for the membranes at different cell temperature in H_2/O_2 mode. Nafion® 112: 70 °C (*filled square*) and 80 °C (*open circle*); F-PES 60 (45 ± 3 μm): 70 °C (*filled triangle*) and 80 °C (*inverted filled triangle*). The other fuel cell parameter, i.e., catalyst loading, reactant flow, pressure, etc., are identical

than that of Nafion® 112 membrane at both 70 and 80 °C. The Nafion® 112 membrane based MEA did not show any significant loss in performance with temperature. But in the case of F-PES 60 based MEA, the cell performance at 70 °C was slightly improved in the high current density region. A high current density of 1,050 mA cm^{-2} (H_2/O_2) was obtained for F-PES 60 as shown in Fig. 1. When the fuel cell was operated with H_2/air, a significant decrease in *i–V* characteristics was observed shown in Fig. 2. A current density of 530 mA cm^{-2} (H_2/air) was obtained

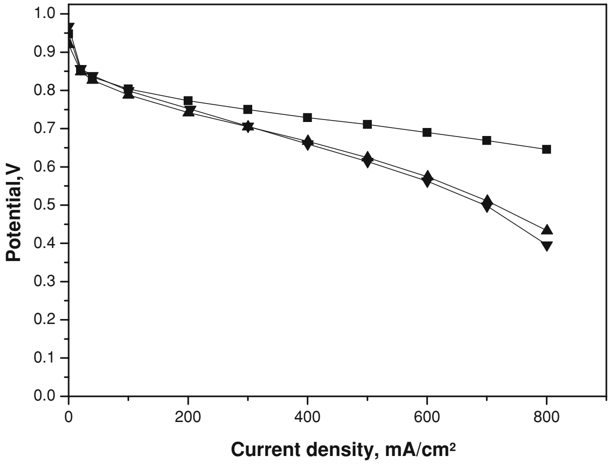


Fig. 2 PEMFC polarization curves of the membranes in H_2/air mode. Nafion® 112: 70 °C (*filled square*); F-PES 60 (45 ± 3 μm): 70 °C (*filled triangle*) and 80 °C (*inverted filled triangle*). The other fuel cell parameter, i.e., catalyst loading, reactant flow, pressure, etc., are identical

at 0.6 V with F-PES 60 membrane of thickness 45 ± 3 μm at 70°C, whereas 730 mA cm^{-2} (H_2/air) was obtained for PES 60 with a thickness 30 μm under the same operating conditions [26]. Kim et al. reported that the PEFC performance depends on the polymer backbone of sulfonated poly(arylene ether sulfone) copolymers. The author also found the difference in H_2/air fuel cell performance for non-fluorinated polymer backbone copolymer (BP-30) with partially fluorinated polymer backbone copolymer (6F-35). Even though the membranes (BP-30 and 6F-35) subjected to the fuel cell test have similar ion exchange capacity (IEC_V) and thickness, the 6F-35 exhibited superior performance than that of the BP-30 under specific fuel cell operating conditions, such as cell temperature, catalyst loading, reactant stoichiometry, and back pressure. The higher fuel cell performance of the 6F-35 membrane is due to its lower high frequency resistance (123 mΩ cm^2), which is approximately 25% lower than that of BP-30 [18]. Even though the presence of fluorine moiety in F-PES copolymer enhanced its adhesion with Nafion® bonded electrodes, the change in membrane thickness and IEC value may cause *i–V* performance loss in F-PES 60 membrane based MEAs compared to that of hydrocarbon based.

Ohmic and charge transfer resistance was estimated by measuring EIS spectra for the single cells. The plotted EIS spectra are presented in Fig. 3. Cyclic voltammogrames were measured for the single cells to evaluate Pt utilization, as shown in Fig. 4.

The H_2 cross-over current density was analyzed and shown in Fig. 5. The H_2 cross-over current density for F-PES 60 membrane based MEA is four times higher when compared to that of the Nafion® membrane based. The electrochemical characteristics of the F-PES 60 based MEA is shown in Table 2, and the characteristics of Nafion® 112 membrane based MEA is also included for comparison. The ohmic resistance and charge transfer resistance for MEA based on F-PES 60 membrane is higher than that of Nafion® under similar conditions. Unlike Nafion® 112 membrane based MEA, the F-PES 60 membrane based MEA was influenced greatly by the cell temperature. As shown in Fig. 3, the charge

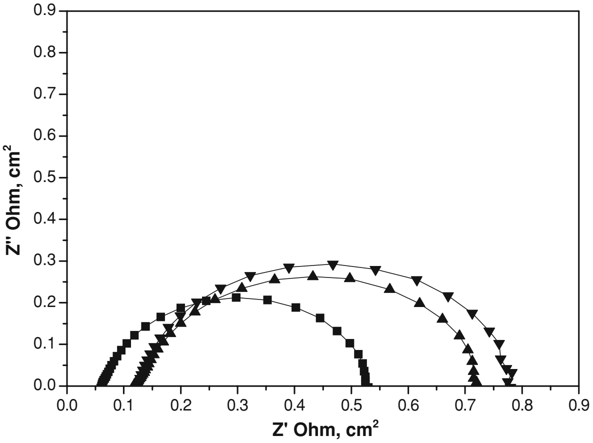


Fig. 3 Electrochemical impedance spectra for different proton exchange membrane based MEA with respect to temperature. Nafion® 112: 70 °C (*filled square*); F-PES 60 (45 ± 3 μm): 70 °C (*filled triangle*) and 80°C (*inverted filled triangle*)

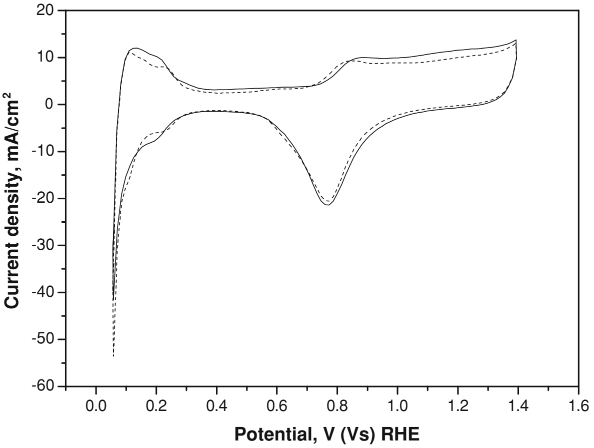


Fig. 4 Comparison of cyclic voltammograms obtained with the proton exchange membrane based MEA. Nafion® 112 (*solid line*), F-PES 60 (45 ± 3 μm) (*dash line*). The cell temperature is 70 °C with scan rate of 50 mV s^{-1}

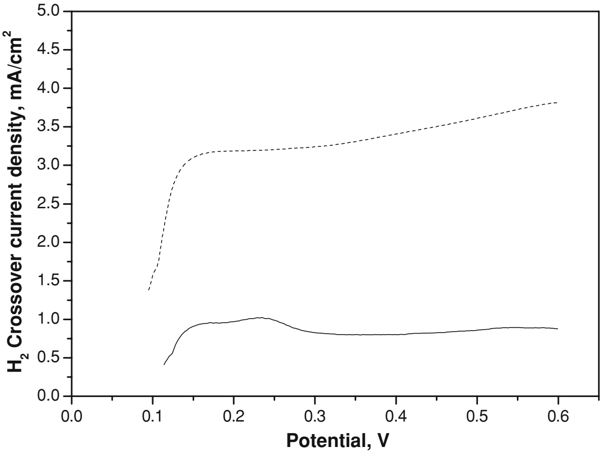


Fig. 5 Comparison of linear sweep voltagrams obtained for Nafion® 112 based MEA (*solid line*) and F-PES 60 membrane based MEA (*dash line*). The cell temperature is 70 °C with scan rate of 50 mVs^{-1}

transfer resistance is increased with F-PES 60 as proton exchange membrane (PEM) at 80 °C than that of the same PEM at 70 °C. Although the EAS and Pt utilization values for both the PEM based MEAs are almost similar under the same conditions, the EIS spectra varied with the PEM material used in the MEAs. The superior performance of the Nafion® based MEA is due to its lower ohmic and charge transfer resistance. The EIS results coincided with *i-V* curves, as shown in Fig. 2.

Evaluation of DMFC performance with F-PES 60 membrane

Pt–Ru (50:50 wt%) catalyst for the anode electrode and Pt for the cathode electrode was coated directly on the membrane (F-PES 60 and Nafion® 115). DMFC performance of the MEAs was measured with a function of temperature and cathode

Table 2 Electrochemical properties of the MEA based on hexafluorinated poly(ether sulfone) copolymer and Nafion® 112 membranes

MEA	Cell temperature (°C)	Ohmic Resistance (Ω cm^2)	Charge transfer resistance (Ω cm^2)	EAS m^2/g	Pt utilization (%)	H_2 crossover current density[a] (mA/cm^2)
F-PES 60	70	0.12	0.60	29.79	26.60	3.41
F-PES 60	80	0.13	0.65	–	–	–
Nafion® 112	70	0.06	0.46	31.66	28.26	0.80

[a] Potential at 0.4 V

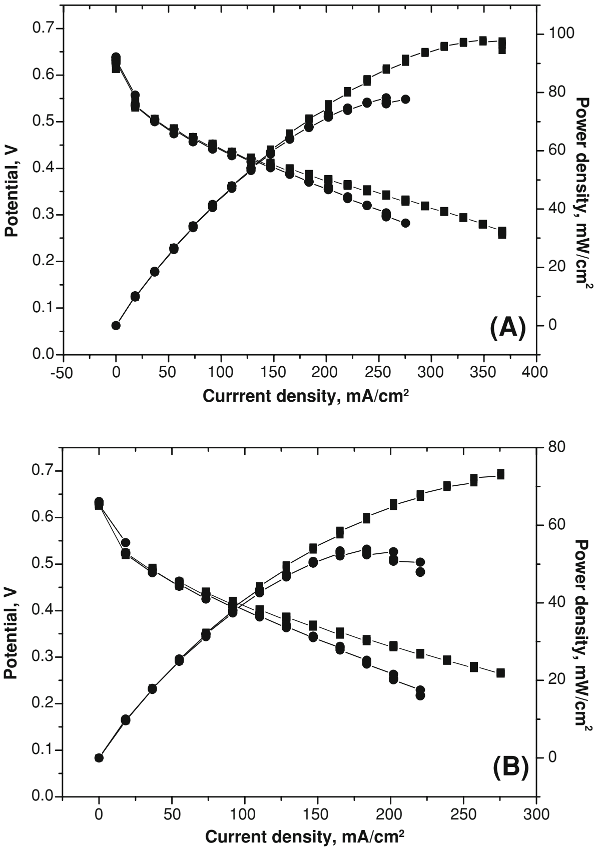


Fig. 6 DMFC polarization curves of the membranes with humidication (**a**) and without humidification (**b**) at the cathode under ambient pressure. Nafion® 115, 60 °C (*filled square*) and F-PES 60 (45 ± 3 µm), 60 °C (*filled circle*)

gas humidification. The polarization curves of MEAs at cell temperature of 60 °C are shown in Fig. 6a and b for humidified condition and non-humidified condition, respectively. Under humidified conditions, the peak power density value for the MEA based on F-PES 60 membrane and Nafion 115 membrane, was obtained as 78

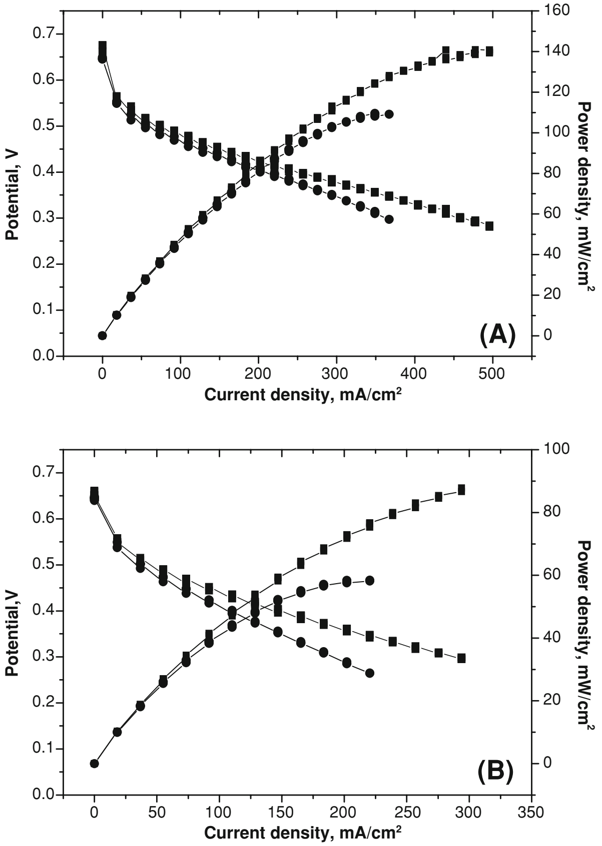


Fig. 7 DMFC polarization curves of the membranes with humidication (**a**) and without humidification (**b**) at the cathode under ambient pressure. Nafion® 115, 80 °C (*filled square*) and F-PES 60 (45 ± 3 μm), 80 °C (*filled circle*)

and 98 mW cm^{-2}, respectively. Whereas, in case of non-humidified conditions, their peak power density value for F-PES 60 and Nafion 115 membrane was obtained as 54 and 76 mW cm^{-2}, respectively.

Figure 7a and b shows the humidified and non-humidified condition of DMFC performance at 80 °C. Under humidified conditions at 80 °C, the peak power density value for the MEA with F-PES 60 membrane was obtained as 110 mW cm^{-2}, which is comparable to that of Nafion® 115 membrane (141 mW cm^{-2}). Similarly, under non-humidified conditions, 58 and 88 mW cm^{-2} was obtained for F-PES 60 and Nafion 115, respectively. The results exhibited that the increase in cell temperature enhances the fuel cell performance of MEAs under humidified and/or non-humidified conditions.

The incorporation of the hexafluorinated isopropylidene unit instead of the isopropylidene unit in the polymer backbone is significantly affecting IEC and water uptake properties of F-PES 60 without sacrificing the proton conductivity. Therefore, the DMFC performance of MEA with F-PES 60 was superior to that of MEA based on PES 60 [26]. The fluorine moiety could lead to good interfacial contact between the membrane and Nafion® bonded catalyst layer. From the results, it is clear that the performance of the F-PES 60 membrane in the case of DMFC is better than that of the PEMFC application.

Conclusion

The effect of fluorine moiety in the copolymer composition, such as proton conductivity, water uptake, ion exchange capacity, and solubility in boiling water, was studied. The fuel cell performance of the hexafluorinated sulfonated poly(ether sulfone) (F-PES 60) was demonstrated in PEMFC and DMFC under specific operating conditions. A current density of 1,050 mA cm^{-2} (H_2/O_2) and 530 mA cm^{-2} (H_2/air) was obtained at 0.6 V with a F-PES 60 membrane of thickness 45 ± 3 μm at 70 °C. EIS spectra revealed the performance loss of the F-PES 60 based MEA. The lower EAS and higher H_2 cross-over current density also affected the fuel cell performance. The DMFC performance of the F-PES 60 MEA was comparable to that of the Nafion® 115 membrane. The maximum peak power density value at 80 °C for F-PES 60 membrane was obtained as 110 mW cm^{-2}, which is only 20% lower than that of Nafion® 115 membrane and still higher than PES 60 membrane.

References

1. Acres GJK (2001) J Power Sour 100:60
2. Aricò AS, Srinivasan S, Antonucci V (2001) Fuel Cells 1:133
3. Steele BCH, Heinzel A (2001) Nature 414:345
4. Rikukawa M, Sanui K (2000) Prog Polym Sci 25:1463
5. Rozière J, Jones DJ (2003) Annu Rev Mater Res 33:503
6. Hickner MA, Ghassemi H, Kim YS, Einsla BR, McGrath JE (2004) Chem Rev 104:4587
7. Smitha B, Sridhar S, Khan AA (2005) J Membr Sci 259:10
8. Rusanov AL, Likhatchev D, Kostoglodov PV, Müllen K, Klapper M, Schmidt M (2005) Adv Polym Sci 179:83
9. Hamrock SJ, Yandrasits MA (2006) J Polym Sci C Polym Chem 46:219
10. Dobrovol'skii YA, Volkov EV, Pisareva AV, Fedotov YA, Likhachev DY, Rusanov AL (2007) Russ J Gen Chem 77:766
11. Bae JM, Honma I, Murata M, Yamamoto T, Rikukawa M, Ogata N (2002) Solid State Ion 147:189
12. Kim YS, Sumner MJ, Harrison WL, Riffle JS, McGrath JE, Pivovar BS (2004) J Electrochem Soc 151:A2150
13. Einsla BR, Kim YS, Hickner MA, Hong YT, Hill ML, Pivovar BS, McGrath JE (2005) J Membr Sci 255:141
14. Tian SH, Shu D, Chen YL, Xiao M, Meng YZ (2006) J Power Sour 158:88
15. Yin Y, Yamada O, Hayashi S, Tanaka K, Kita H, Okamoto KI (2006) J Polym Sci A Polym Chem 44:3751
16. Asano N, Aoki M, Suzuki S, Miyatake K, Uchida H, Watanabe M (2006) J Am Chem Soc 128:1762
17. Kim YS, Einsla B, Sankir M, Harrison W, Pivovar BS (2006) Polymer 47:4026
18. Sankir M, Kim YS, Pivovar BS, McGrath JE (2007) J Membr Sci 299:8
19. Heo KB, Lee HJ, Kim HJ, Kim BS, Lee SY, Cho E, Oh IH, Hong SA, Lim TH (2007) J Power Sour 172:215

20. Li Y, Roy A, Badami AS, Hill M, Yang J, Dunn S, McGrath JE (2007) J Power Sour 172:30
21. Kim DS, Kim YS, Guiver MD, Ding J, Pivovar BS (2008) J Power Sour 182:100
22. Jörissen L, Gogel V, Kerres J, Garche J (2002) J Power Sour 105:267
23. Carter R, Wycisk R, Yoo H, Pintauro PN (2002) Electrochem Solid State Lett 5:A195
24. Scott K, Taama WM, Argyropoulos P (2000) J Membr Sci 171:119
25. Krishnan NN, Kim HJ, Prasanna M, Cho E, Shin EM, Lee SY, Oh IH, Hong SA, Lim TH (2006) J Power Sour 158:1246
26. Kim HJ, Krishnan NN, Lee SY, Hwang SY, Kim D, Jeong KJ, Lee JK, Cho E, Lee J, Han J, Ha HY, Lim TH (2006) J Power Sour 160:353
27. Harrison WL, Wang F, Mecham JB, Bhanu VA, Hill M, Kim YS, McGrath JE (2003) J Polym Sci A Polym Chem 41:2264