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고분자 전해질 연료전지용 Sulfonated Poly(ether sulfone)의 합성 및 특성 평가

N. N. Krishnan, 김형준*, M. Prasanna, 조은애, 오인환, 홍성안, 임태훈

Synthesis and Characterization of Mono-sulfonated Poly(ether sulfone) for a Fuel Cell Application

N. N. Krishnan, H.-J. Kim*, M. Prasanna, E. Cho, I.-H. Oh, S.-A. Hong, T.-H. Lim

Key words : Hydrocarbon-based electrolyte membrane, Membrane electrode assembly, Poly(ether sulfone), Polymer electrolyte fuel cell.

Abstract : Sulfonated poly(ether sulfone) copolymers (PESs) 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. The chemical structure and the thermal stability of these polymers were characterized by using ^{1}H-NMR, FT-IR and TGA techniques. The PES 60 membrane, which has 60 mole% of HPS unit in the polymer backbone, has a proton conductivity of 0.091 S/cm and good insolubility in boiling water. The TGA showed that PES 60 was stable up to 272 °C with a char yield of about 29% at 900 °C under N_2 atmosphere. To investigate the single cell performance, the catalyst coated PES 60 membrane was used and a single cell test was carried out using H_2/O_2 gases as fuel and oxidant at various temperatures. We observed that the cell performance was enhanced by increasing the cell temperature. A current density of 1400 mA/cm^2 at 0.60 V was obtained at 70 °C.

* Corresponding author: hjkim25@kist.re.kr

1. Introduction

Fuel cell power systems have been expected to be one of the most environmental friendly, reliable, decentralized power generation in the near future for mobile devices, residential usages and automobiles(1). Perfluorosulfonated membrane is the most widely used proton exchange membrane due to its high proton conductivity and excellent chemical stability. Several companies have developed similar membranes such as Dupont (Nafion®), Asahi Glass (Flemion®) and Asahi Chemical (Aciplex®).

Perfluorosulfonated polymer electrolyte membranes tend to be expensive and possess several disadvantages like high methanol permeation and low proton conductivity at high temperature under low humidity(2,3). To overcome these problems, the non-fluorinated hydrocarbon-based polymer electrolyte membranes have been studied as an alternative(4-12). However, most researches have been limited to the polymer synthesis and/or membrane characterization. Very few hydrocarbon-based polymers have been tested in fuel cells(13,14). Kim et al. recently reported the direct methanol fuel cell performance of hydrocarbon-based polymer electrolyte. The membrane electrode assemblies (MEAs) with the polymer membrane showed the fuel cell performance comparable to that of Nafion® 117(13).

The hydrocarbon-based polymer electrolyte membrane will bring the possibility of commercializing PEFCs for future power generation systems. This paper describes our approach to prepare sulfonated hydrocarbon-based polymer (sulfonated poly(ether sulfone)s) for PEFC applications. The monomers for polymerization are commercially available and relatively cheap. A new class of proton exchange membranes with well-defined structures of the sulfonated poly(ether sulfone) copolymers showed good PEFC performance under specific operating conditions. We report the possibility of the polymer for PEFC applications.

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, NaOH, KOH, HCl (J.T. Baker), isopropyl alcohol (Aldrich HPLC grade) and methanol (Daejung reagents & chemicals) were used as received.

2.2 Techniques

FT-IR spectroscopy was used to confirm the copolymer PES's functional groups. Measurement was recorded using a Nicolet Magma II FT-IR spectrometer. ^{1}H-NMR (300 MHz) spectrum was recorded on a Varian at room temperature in DMSO-d_6 with tetramethylsilane (TMS) internal standard. The thermal stability of the PES was analyzed using thermo gravimetric analysis instrument TGA 2950. Membrane sample was heated at the rate of 20 °C/min in N_2 atmosphere. Proton conductivities of PES membranes were measured using the same method as reported in the literature(12).

2.3 Synthesis of mono sulfonated Poly(ether sulfone) copolymer (PES 60)

Sulfonated poly(ether sulfone)s were synthesized by the modified method described in the paper previously reported(12). Typical process for synthesizing PES (PES 60): 4-Fluorophenyl sulfone (20 mmol, 5.09 g), bisphenol A (8 mmol, 1.83 g), hydroquinone 2-potassium sulfonate (12 mmol, 2.74 g) and potassium carbonate (40 mmol, 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 that, 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. The reaction mixture was cooled to room temperature and poured into the mixture of HCl (500 mL) and MeOH (500 mL) to precipitate the polymer. The crude product was filtered and dried in the vacuum oven at 60 °C for 24 h. The polymer was dissolved in 50 mL of DMSO and precipitated again in the mixture of HCl (500 mL) and MeOH (500 mL). The polymer was collected by filtration and the residual HCl in the polymer was extracted by deionized water in a Soxhlet extractor. The polymer was filtered and dried at 60 °C under vacuum. Other copolymers were prepared with different molar ratio of monomers using same method. ^{1}H-NMR (DMSO-d_6) δ 1.65 (s, 6H, -CH_3), 6.90 - 7.40 (m, 21H, Ar*H*), 7.40 - 7.44 (m, 1.5H, Ar*H*), 7.80 - 8.00 (m, 10H, Ar*H*); FT-IR (cm^{-1}) 712, 1020, 1078, 1107, 1146, 1225, 1476, 1584.

2.4 Membrane electrode assembly (MEA) preparation

PES 60 (acid form) was dissolved in dimethyl sulfoxide (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. MEA was fabricated with the membrane. 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 the membrane. 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.

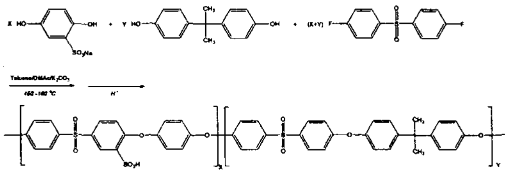
2.5 PEFC single cell test

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 were allowed to enter the fuel cell inlets (gas flow rate: 400 cc/min under ambient pressure). I-V characteristics were evaluated using an electric load (Daegil Electronics, EL500P).

3. Results and Discussion

3.1. Synthesis and characterization of PESs

The direct synthesis of sulfonated polymer using sulfonated monomers has been proven to be more advantageous than that of post-sulfonation(7). The post-sulfonation causes some problems such as cross-linking reaction. Also, the direct synthesis controls the degree of sulfonation leading to the higher thermal stability as well as mechanical properties. Therefore, we synthesized sulfonated polymer electrolyte by the direct synthesis using hydroquinone 2-potassium sulfonate (HPS). 4-Fluorophenyl sulfone (FPS) was reacted with stoichiometric amounts of hydroxyl group terminated monomers (HPS and bisphenol A (BPA)) in the presence of potassium carbonate in DMAc (Scheme 1). Toluene was used for azeotropic removal of water during the reaction. After the water was removed from the reaction mixture, toluene was distilled out and the temperature was raised to 180 °C to complete the polymerization.



Scheme 1. Synthesis of mono sulfonated poly(ether sulfone) copolymer.

The sulfonation degree of a polymer electrolyte influences the conductivity of the electrolyte membrane as well as the solubility in water. Those are the two competitive factors which should be considered for synthesis of sulfonated polymer electrolyte. Three sulfonated poly(ether sulfone)s (PESs) were synthesized in order to find new materials that have good conductivity and water insolubility. PESs with different mole% of hydrophilic group were prepared by changing the mole ratio of HPS in the polymerization reaction. Table 1 shows the composition, proton conductivity and solubility in boiling water of the polymers. 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 boiling water. Therefore, PES 60 membrane was used for a single cell test.

The polymer structure was confirmed by FT-IR and ^{1}H-NMR analyses. The FT-IR spectrum of PES 60 is presented in Fig. 1. The two peaks at 1584, 1476 cm^{-1} are attributed to the vibration of the aromatic ring skeleton. Characteristic absorption band for aromatic sulfone group appears at 1106 cm^{-1} and the peak for aryl oxide appears at 1225 cm^{-1}. The two absorption peaks appear at 1078 and 1020 cm^{-1}, which are the characteristics of the aromatic SO_3^- symmetric and asymmetric stretching vibrations, respectively. Also, the S-O stretching vibration appears at 712 cm^{-1}. The copolymer composition was confirmed from the integral value in ^{1}H-NMR of PES 60. The aromatic hydrogen labeled as "a" in the repeating unit of PES 60 in Fig. 2 appears at 7.40 - 7.44 ppm. The methyl hydrogen "b" in the polymer appears at 1.65 ppm confirming the formation of the polymer. Theoretically, the peak integration ratio of two peaks (a/b) should be 1.5/6 and peak integration in the ^{1}H-NMR spectrum is almost the same value. We can conclude that PES 60 was synthesized as expected with the NMR and IR analyses.

Table 1. The composition and properties of sulfonated poly(ether sulfone) (PES)

Polymer	X*	Y*	Solubility**	Conductivity (S/cm)
PES 50	0.5	0.5	X	0.08
PES 60	0.6	0.4	X	0.09
PES 70	0.7	0.3	O	0.12

* Ratio in Scheme 1

** Solubility in boiling water

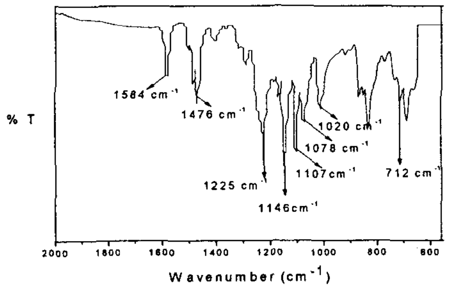


Fig. 1. FT-IR spectrum of PES 60 membrane.

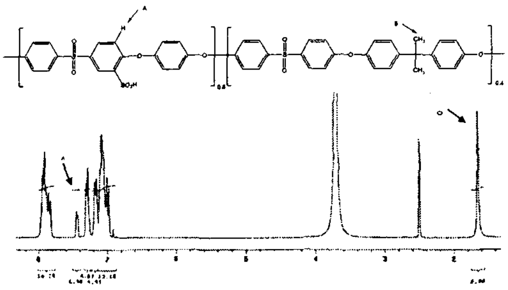


Fig. 2. ^{1}H-NMR spectrum of PES 60.

The Fig. 3 shows the TGA curve for PES 60. From this figure, it is evident that there are three weight loss steps in the TGA curve. The first weight loss appeared in the temperature range of 70-140 °C which is caused by the loss of water. The degradation of the sulfonic group is found in the temperature range of 270-440 °C. The onset of the weight loss is at 448 °C which is due to the polymer back bone decomposition. Based on the result, the PES 60 membrane is thermally stable in the temperature range applicable for PEFC.

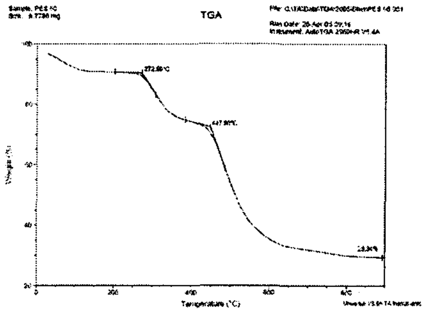


Fig. 3. TGA curve of PES 60 membrane.

3.2. PEFC performance

Membrane electrode assembly (MEA) was fabricated with PES 60 membrane. Pt/C slurry was sprayed directly on the membrane and the Pt loading was 0.2 and 0.4 mg/cm^2 for anode and cathode, respectively. The cell test was carried out at 60 and 70 °C. The result is shown in Fig. 4. The cell performance at 70 °C was higher than that at 60 °C. Nafion 112 was also used for the single cell test with same MEA fabrication method as for PES 60 membrane for comparison (Fig. 4). 1800 mA/cm^2 of current density was obtained at 0.6 V with Nafion 112 at 70 °C, whereas 1400 mA/cm^2 of current density was obtained for PES 60 under the same operation condition. If high proton conducting PES is synthesized and its MEA fabrication method is established, the cell performance will be improved.

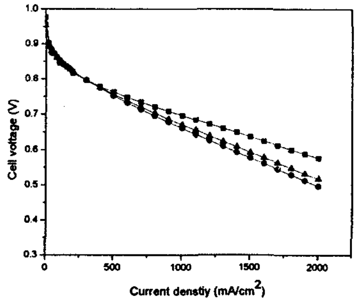


Fig. 4. Polarization curves for PES 60 based MEA and Nafion 112 based MEA in the H_2/O_2 mode. Cell temperature: PES 60 membrane 60 °C (●), 70 °C (▲) and Nafion 112 membrane 70 °C (■).

4. Conclusions

Sulfonated poly(ether sulfone)s (PESs) were synthesized with different molar ratio of hydroquinone 2-potassium sulfonate (HPS), 4-fluorophenyl sulfone (FPS) and bisphenol A (BPA). PESs with different mole% of hydrophilic group were prepared by changing the mole ratio of HPS in the polymerization reaction. The PES 60 membrane, which has 60 mole% of HPS unit in the polymer backbone, has a proton conductivity of 0.091 S/cm and good insolubility in boiling water. To investigate the single cell performance of PES 60 membrane, the membrane electrode assembly was fabricated with the membrane. The cell was operated with H_2/O_2 gases as fuel and oxidant at different cell temperature. The cell performance increased as the cell temperature increased. A current density of 1400 mA/cm^2 at 0.60 V was obtained at 70 °C.

5. References

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