

Short communication

Synthesis and characterization of sulfonated poly(ether sulfone) copolymer membranes for fuel cell applications

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Abstract

Sulfonated poly(ether sulfone) copolymers (PESs) are synthesized using hydroquinone 2-potassium sulfonate (HPS) with other monomers (bisphenol A and 4-fluorophenyl sulfone). A series of PESs with different mol% of hydrophilic group is prepared by changing the mole ratio of HPS in the polymerization reaction. The chemical structure and thermal stability of the polymers are characterized by using ¹H NMR, FT-IR and TGA techniques. The PES 60 membrane, which has 60 mol% of HPS unit in the polymer backbone, has a proton conductivity of 0.091 S cm⁻¹ and good insolubility in boiling water. The TGA showed that PES 60 is stable up to 272 °C with a char yield of about 29% at 900 °C under a nitrogen atmosphere. To investigate single-cell performance, a catalyst-coated PES 60 membrane is used together with hydrogen and oxygen as the fuel and the oxidant, respectively. Cell performance is enhanced by increasing the temperature. A current density of 1400 mA cm⁻² at 0.60 V is obtained at 70 °C.

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1. Introduction

Fuel cells are expected to be used as environmental friendly, reliable and decentralized power generation devices in the near future for mobile devices, residential buildings and automobiles [1,2]. Perfluorosulfonated polymer is widely employed as the proton-exchange membrane in polymer electrolyte fuel cells (PEFCs) due to its high proton conductivity and excellent chemical stability. Several companies, e.g., Dupont (Nafion[®]), Asahi Glass (Flemion[®]) and Asahi Chemical (Aciplex[®]) have developed similar membranes.

Perfluorosulfonated polymer electrolyte membranes tend to be expensive and possess disadvantages in terms of high methanol permeation and low proton conductivity at high temperature under low humidity [2,3]. To overcome these problems, studies have been conducted on non-fluorinated, hydrocarbon-based, polymer electrolyte membranes such as

poly(ether sulfone)s containing pendant sulfonate groups [4], sulfonated poly(ether ether ketone) [5], partially sulfonated poly(arylene ether sulfone) [6], poly(arylene ether sulfone) random statistical copolymers [7], sulfonated aromatic poly(ether ether ketone) [8], sulfoalkylated polysulfones [9], poly(ether ether ketone) and poly(4-phenoxybenzoyl-1,4-phenylene) [10], acid functionalized poly(arylene ether)s [11] and sulfonated poly(arylene ether) copolymers containing aromatic nitriles [12]. Most of this research has 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. [13] recently reported the performance of a direct methanol fuel cell (DMFC) that used a novel hexafluorobisphenol A-based disulfonated poly(arylene ether benzotrifluoride) copolymer [6FCN-35] or a biphenol-based disulfonated poly(arylene ether sulfone) copolymer [BPSH-40]. Membrane–electrode assemblies (MEAs) with the partially fluorinated hydrocarbon-based polymer membrane [6FCN-35] gave higher fuel cell performance than those with a Nafion[®] 115 or a non-fluorinated hydrocarbon-based polymer membrane [13].

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The hydrocarbon-based polymer electrolyte membrane offers the possibility of the wide-scale commercialization of PEFCs for future power generation systems. This paper describes an approach to the preparation of a hydrocarbon-based sulfonated 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 the sulfonated poly(ether sulfone) copolymers exhibits good PEFC performance under specific operating conditions.

2. Experimental

2.1. Materials

Hydrocarbon-based polymers were synthesized from commercially available 4-fluorophenyl sulfone (FPS), hydroquinone 2-potassium sulfonate (HPS), and bisphenol A (BPA). The HPS was purchased from Acros Organics and recrystallized from deionized water. The FPS and BPA were obtained from Aldrich Chemicals. Potassium carbonate, FPS, BPA and HPS were dried at 60 °C for 24 h under vacuum prior to polymerization. Dimethyl acetamide (DMAc), *N*-methylpyrrolidinone (NMP) (Sigma–Aldrich), dimethyl sulfoxide (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 functional groups of the sulfonated poly(ether sulfone) copolymer (PES). The measurements were recorded using a Nicolet Magma II FT-IR spectrometer. The ¹H NMR (300 MHz) spectrum was recorded on a Varian instrument at room temperature in DMSO-*d*₆ with a tetramethylsilane (TMS) internal standard. The thermal stability of the PES was analyzed by means of thermogravimetric analysis with a TGA 2950 instrument. The membrane sample was heated at a rate of 20 °C min⁻¹ in a nitrogen atmosphere. The proton conductivities of the PES membranes were measured using the method of Sumner et al. [12].

2.3. Synthesis of mono-sulfonated poly(ether sulfone) copolymer (PES 60)

Sulfonated poly(ether sulfone) was synthesized by the modified method reported by Sumner et al. [12]. The typical process for synthesizing PES (PES 60) was as follows. 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 a mixture of 25 mL of dimethyl acetamide and 40 mL of toluene in a 100 mL round-bottom flask that was 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 tem-

perature was raised to 180 °C. Then, the mixture was allowed to stand overnight at that temperature under a nitrogen atmosphere. After cooling to room temperature, the mixture was poured into 1000 mL of methanol to obtain the PES polymer. The crude product was filtered and dried in the vacuum oven at 60 °C for 1 h. The polymer was subjected to Soxhlet extraction using deionized water to remove inorganic material. The polymer was then dried overnight in a vacuum oven at 60 °C. The polymer was dissolved in 50 mL of DMSO and precipitated in a mixture of HCl (500 mL) and methanol (500 mL). The polymer was collected by filtration and the residual HCl in the polymer was extracted by treatment with deionized water. The polymer was filtered and dried at 60 °C under vacuum. Other copolymers were prepared with different molar ratios of monomers using the same method. ¹H NMR (DMSO-*d*₆) δ 1.65 (s, 6H, -CH₃), 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.

2.4. Membrane–electrode assembly (MEA) preparation

The membrane was prepared by dissolving the acid form of PES 60 in DMSO (15%, w/v). The solution was poured on a glass plate and the thickness of the film was controlled by means of a doctor blade. The membrane was dried at 60 °C under reduced pressure for 30 h. A 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. The slurry 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 cm² with a platinum loading of 0.2 and 0.4 mg cm⁻² for the anode and the cathode, respectively.

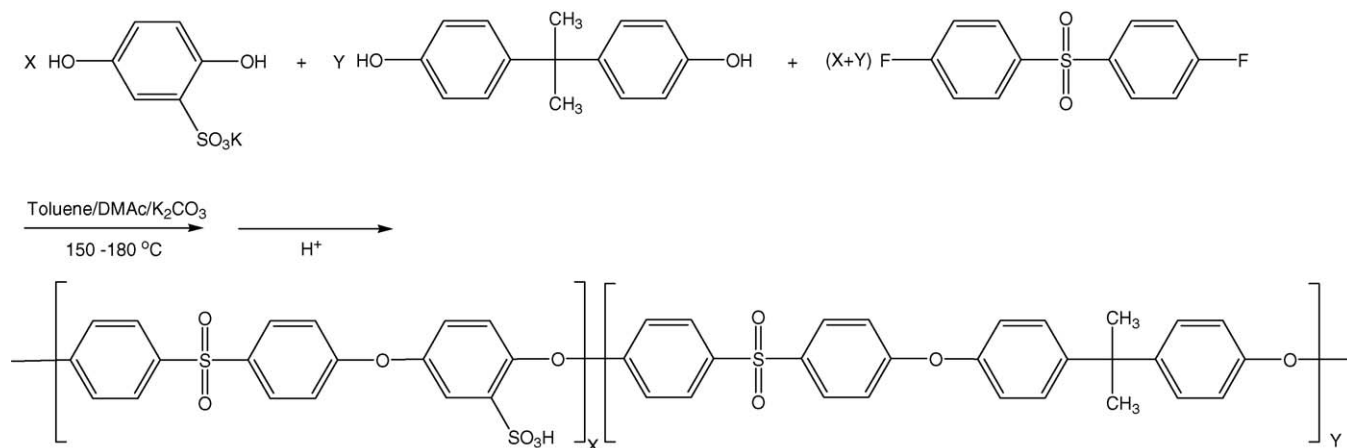
2.5. Single-cell PEFC test

A 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 (gas flow rate: 400 mL min⁻¹ under ambient pressure) before entry via the fuel cell inlets. Current–potential (*I*–*V*) characteristics were evaluated using an electric load (Daegil Electronics, EL500P).

3. Results and discussion

3.1. Synthesis and characterization of PESs

Direct synthesis of sulfonated polymers from sulfonated monomers has been shown to be more advantageous than that of post-sulfonation [7]. Post-sulfonation causes problems with respect to the cross-linking reaction. Also, direct synthesis controls the degree of sulfonation and this leads to higher thermal stability as well as better mechanical properties. Therefore, in this study, sulfonated polymer electrolyte was prepared by direct synthesis using hydroquinone 2-potassium sulfonate. 4-Fluorophenyl sulfone was reacted with stoichiometric amounts



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

of hydroxyl-group-terminated monomers (HPS and bisphenol A) in the presence of potassium carbonate in DMAc (Scheme 1). Toluene was used for azeotropic removal of water during the reaction. The toluene was then distilled out and the temperature was raised to 180 °C to complete the polymerization.

The degree of sulfonation of a polymer electrolyte influences the conductivity of the electrolyte membrane as well as its solubility in water. Two competitive factors should be considered for the synthesis of sulfonated polymer electrolyte. Three sulfonated poly(ether sulfone)s (PESs) were synthesized in order to find new materials that have good proton conductivity and water insolubility. PESs with different mol% of hydrophilic groups were prepared by changing the mole ratio of HPS in the polymerization reaction. The composition, proton conductivity and solubility in boiling water of the polymers are listed in Table 1. As the proportion of HPS in the polymer is increased, the proton conductivity also increases. When the HPS content is 70% (PES 70), however, the polymer dissolves in boiling water. Therefore, a PES 60 membrane was used for single-cell testing.

The polymer structure was confirmed by FT-IR and ¹H NMR analyses. The FT-IR spectrum of PES 60 is presented in Fig. 1. The peaks at 1584 and 1476 cm⁻¹ are attributed to vibration of the aromatic ring skeleton [15]. The characteristic absorption band for the aromatic sulfone group appears at 1146 cm⁻¹ and the peak for aryl oxide appears at 1225 cm⁻¹ [4]. Two absorption peaks appear at 1078 and 1020 cm⁻¹ and are characteristic of the aromatic SO₃⁻ stretching vibrations [8]. The copolymer composition was confirmed from the integral values in the ¹H NMR analysis of PES 60. Aromatic hydrogen, labeled as 'a' in the repeating unit of PES 60 in Fig. 2, appears at 7.37–7.52 ppm and the methyl hydrogen 'b' in the polymer appears at 1.65 ppm

conform the formation of a polymer. Theoretically, the peak integration ratio of two peaks (a/b) should be 1.5/6 and the peak integration in the ¹H NMR is almost the same value. It is therefore concluded that PES 60 was synthesized as expected.

The TGA curve for PES 60 are given in Fig. 3. It is evident that there are three weight-loss steps in the TGA curve. The first weight loss appears in the temperature range 70–140 °C and is caused by the loss of water. The degradation of the sulfonic group is found in the temperature range 270–440 °C. The third weight loss occurs at about 448 °C and is due to decomposition of the polymer backbone. Based on the results, the PES 60 membrane is thermally stable within the temperature range applicable for application in PEFCs.

3.2. PEFC performance

A membrane–electrode assembly (MEA) was fabricated with a 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 the anode and the cathode, respectively. The cell test was carried out at 60 and 70 °C. The results are shown in Fig. 4. The cell performance at 70 °C is higher than that at 60 °C. Nafion 112 was also used for single-cell tests with the same MEA fabrication method as that for the PES 60 membrane (Fig. 4). A current density of 1800 mA cm⁻² was obtained at 0.6 V with Nafion

Table 1
Composition and properties of sulfonated poly(ether sulfone) (PES)

Polymer	X ^a	Y ^a	Solubility ^b	Conductivity (S cm ⁻¹)
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

^a Ratio in Scheme 1.

^b Solubility in boiling water.

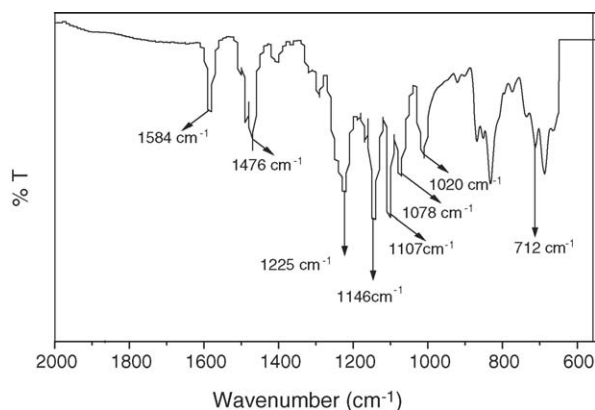


Fig. 1. FT-IR spectrum of PES 60 membrane.

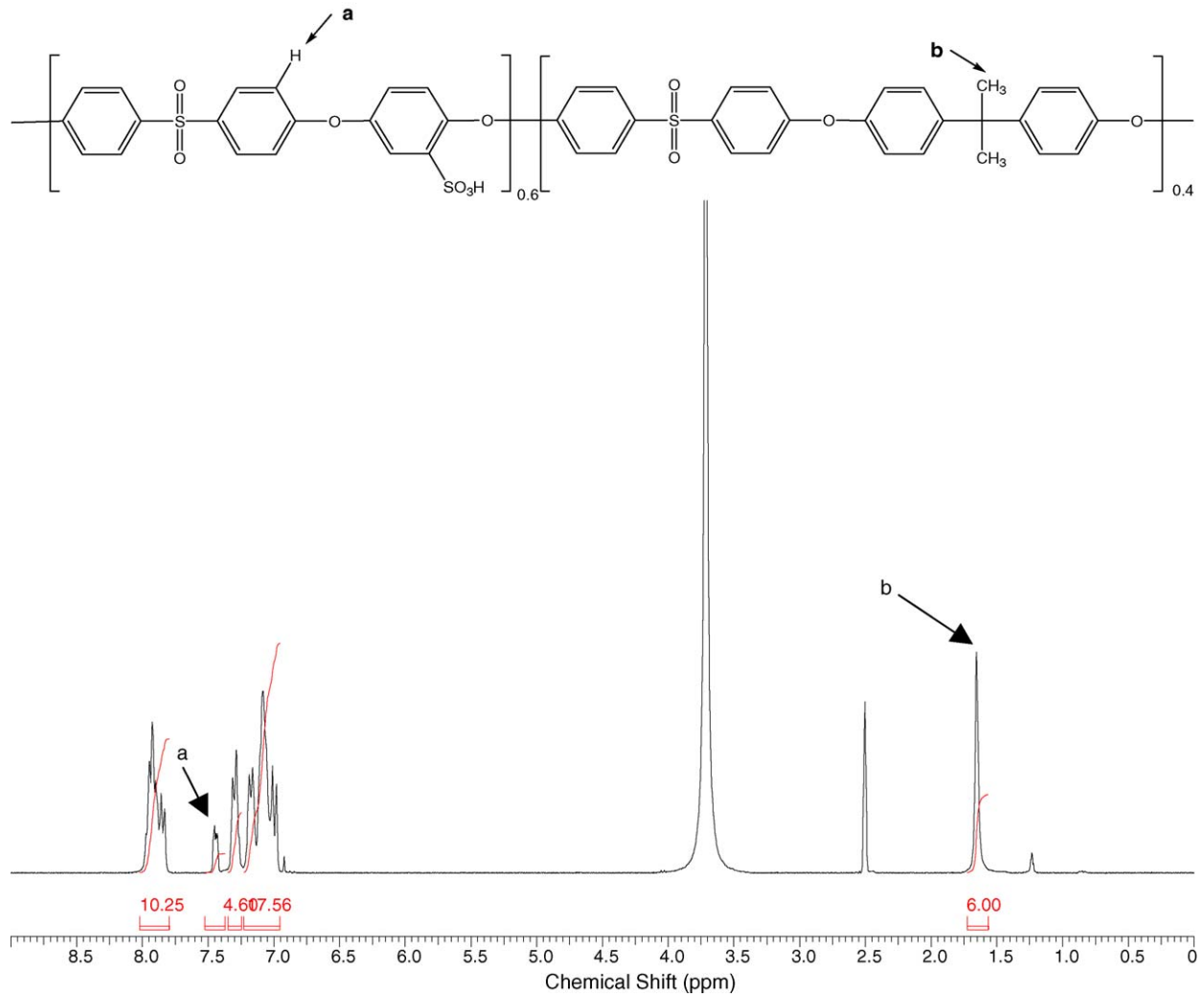


Fig. 2. ¹H NMR spectrum of PES 60.

112 at 70 °C, whereas 1400 mA cm⁻² was obtained for PES 60 under the same operation conditions. The lower cell performance of PES 60 could be related to membrane-electrode delamination in the MEA [13]. If a PES with a higher proton conductivity is

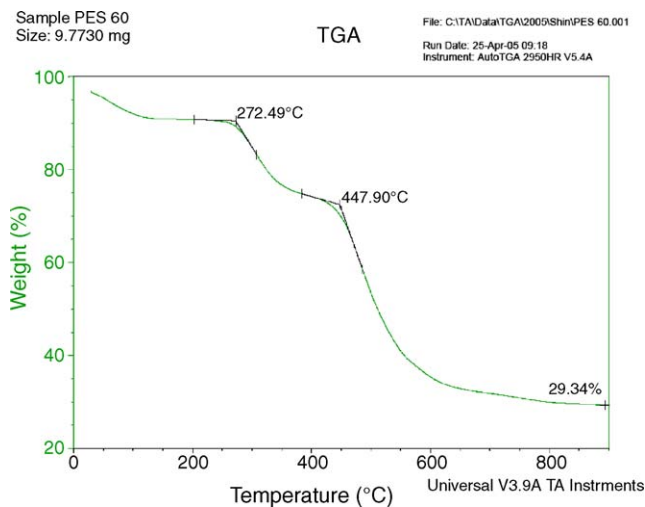


Fig. 3. TGA curve of PES 60 membrane.

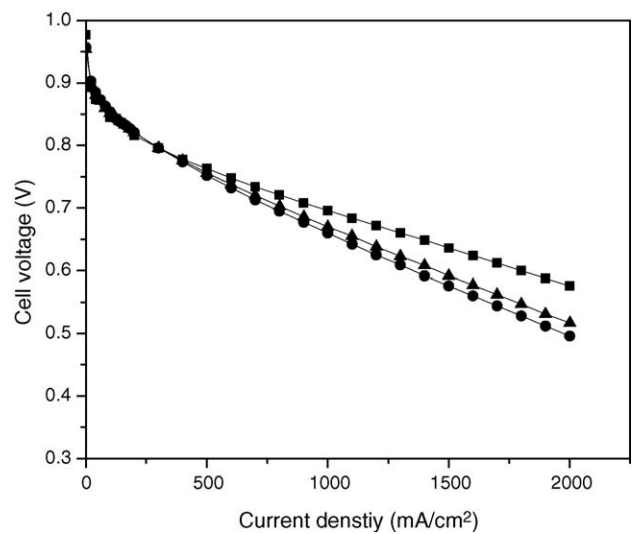


Fig. 4. Polarization curves for PES 60-based MEA and Nafion 112-based MEA in H₂/O₂ mode. Cell temperature: PES 60 membrane 60 °C (●), 70 °C (▲) and Nafion 112 membrane 70 °C (■).

synthesized and its MEA fabrication method is established, then the cell performance will be improved.

4. Conclusions

Sulfonated poly(ether sulfone)s have been synthesized with different molar ratios of hydroquinone 2-potassium sulfonate, 4-fluorophenyl sulfone and bisphenol A. PESs with different mol% of hydrophilic groups have been prepared by changing the mole ratio of HPS in the polymerization reaction. The PES 60 membrane, which has 60 mol% of HPS units in the polymer backbone, has a proton conductivity of 0.091 S cm^{-1} and good insolubility in boiling water. To investigate the single-cell performance of a PES 60 membrane, a membrane-electrode assembly has been fabricated. The cell is operated with H_2/O_2 gas as fuel and oxidant at different temperatures. The cell performance increases as the cell temperature increases. A current density of 1400 mA cm^{-2} at 0.60 V is obtained at 70°C .

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