

Short communication

Synthesis and characterization of cross-linked poly(ether sulfone) for a fuel cell membrane

K.-B. Heo^{a,b}, H.-J. Lee^b, H.-J. Kim^{b,*}, B.-S. Kim^{a,**}, S.-Y. Lee^b,
E. Cho^b, I.-H. Oh^b, S.-A. Hong^b, T.-H. Lim^b

^a Department of Chemical Engineering, Dongguk University, 3-ga Pil-dong, Chung-gu, Seoul 100-715, South Korea

^b Fuel Cell Research Center, Korea Institute of Science and Technology, 39-1 Hawolgok-dong, Sungbuk-gu, Seoul 136-791, South Korea

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Abstract

Cross-linkable sulfonated poly(ether sulfone) copolymer (PES) is synthesized using 4,4'-dihydroxystilbene, hydroquinone 2-potassium sulfonate (HPS) and 4-fluorophenyl sulfone. Cross-linked PES (c-PES) is obtained by UV irradiation of the cross-linkable membrane. The chemical structure and thermal stability of the copolymers are characterized by means of ¹H NMR, FT-IR and TGA techniques. The c-PES 70 membrane, which has 70 mol% of HPS units in the polymer backbone, has a proton conductivity of 0.12 S cm⁻¹ and good insolubility in boiling water. A catalyst-coated membrane is used to investigate single-cell performance for PEMFC applications. Humidified hydrogen and oxygen are employed as the fuel and oxidant, respectively. A current density of 1500 mA cm⁻² at 0.60 V is obtained at 70 °C.

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1. Introduction

Perfluorosulfonated polymers such as Nafion have been widely used as a polymer electrolyte membranes in polymer electrolyte fuel cells (PEFCs) due to their high-proton conductivity and excellent chemical stability. Nevertheless, the cost and performance limitations of present perfluorinated polymer electrolyte membranes have hindered the large-scale commercialization of PEFCs. This has stimulated research on less-expensive and more versatile polymer electrolytes. Therefore, there are many reports of alternative polymer electrolytes that have high-ionic conductivity and good thermal stability [1–5]. Recently, Kim et al. [6] examined the structure–property–performance relationships of sulfonated

poly(arylene ether sulfone) and its performance in a proton exchange membrane fuel cell (PEMFC) and a direct methanol fuel cell (DMFC) [6]. We have also studied the fuel cell performance of the mono-sulfonated poly(ether sulfone) membrane for PEMFC, DMFC and direct formic acid fuel cell (DFAFC) operations [7,8]. In that work, the sulfonation degree of the polymers was changed to synthesize polymer electrolytes that have good insolubility in boiling water without sacrificing proton conductivity.

When the sulfonation degree exceeds a certain level, the polymers are highly swollen and/or soluble to water. Cross-linking of the polymer is one way to overcome this problem. By cross-linking, the mechanical, chemical and thermal stabilities of the polymer improve. To date, very few reports are available for cross-linked (either ionic or covalent) polymer electrolytes. Mikhailenko et al. [9] investigated a cross-linking mechanism that involved elimination of the sulfonic acid groups. Covalently cross-linked sulfonated poly(ether ether ketone) (SPEEK) exhibited high-mechanical strength. However, its proton conductivity decreased slightly. Generally, UV

* Corresponding author. Tel.: +82 2 9585299; fax: +82 2 9585199.

** Corresponding author. Tel.: +82 2 22603364; fax: +82 2 22658808.

E-mail addresses: hjkim25@kist.re.kr (H.-J. Kim), bskim@dongguk.edu (B.-S. Kim).

irradiation-induced cross-linking is one of the most effective methods to obtain three-dimensional polymer networks [10–13]. Chen et al. [14] studied photochemically cross-linked polystyrene-ethylene-butylene sulfonate (PSEBS) copolymer membranes. They found that the UV cross-linking process did not change the ion-exchange capacity of the membrane and the sulfonic acid groups were stable during the UV irradiation. The cross-linked PSEBS exhibited lower water swelling, lower proton conductivity, and higher chemical stability. They also demonstrated that a photo cross-linked PSEBS was more stable than a PSEBS membrane during fuel cell operation. Recently, Zhong et al. [15] showed that a series of cross-linked sulfonated poly(ether ether ketone)s had proton conductivities that range from 0.0041 to 0.0235 S cm⁻¹ at room temperature. The cross-linked polymers displayed better hydrolytic and oxidative stabilities.

In this paper, we report the preparation of cross-linked poly(ether sulfone) (c-PES) using 4,4'-dihydroxystilbene with other commercially available monomers. This involved synthesized PES 70, which has 70 mol% of hydroquinone 2-potassium sulfonate units in the polymer backbone, and its cross-linked form, c-PES 70. By the cross-linking process, the insolubility of the polymer improves dramatically. Therefore, the c-PES could be used for PEMFC operation. The preparation of the polymer membrane and its single-cell performance is examined under specific conditions.

2. Experimental

2.1. Materials

Phenol and chloroacetaldehyde diethyl acetal, 4-fluorophenyl sulfone (FPS), hydroquinone 2-potassium sulfonate (HPS) were obtained from Aldrich Chemicals. The HPS was recrystallized from de-ionized water. Dimethyl acetamide (DMAc), dimethyl sulfoxide (DMSO), *N*-methyl pyrrolidone (NMP) (Aldrich), toluene, NaOH, KOH, HCl (J.T. Baker), glacial acetic acid (Aldrich HPLC grade), methanol and sulfuric acid (Daejung reagents and chemicals) were used as-received. Potassium carbonate, FPS, and HPS were dried at 60 °C for 24 h under vacuum before the polymerization.

2.2. Techniques

¹H NMR (300 MHz) spectrum was recorded on a Varian instrument at room temperature in DMSO-*d*₆ with tetramethylsilane (TMS) as an internal standard. FT-IR spectroscopy was used to confirm the functional groups of the PES and c-PES. The measurements were recorded using a Nicolet Magna II. The thermal stability of the c-PES was analyzed by thermogravimetric analysis with a TGA 2950 instrument. The specimens were preheated to 100 °C for 20 min to remove any residual moisture. Then, they were heated to 800 °C at a heating rate of 20 °C min⁻¹ in a nitrogen atmosphere. The proton conductivities of PES and c-PES membranes were measured using the method developed by Sumner et al. [16].

2.3. Synthesis of sulfonated poly(ether sulfone) (cross-linkable polymer PES 70)

The monomer 4,4'-dihydroxystilbene was prepared by following the procedure of Gao and Hay [17]. Sulfonated poly(ether sulfone) was synthesized by the modified method reported by Krishnan et al. [7]. 4,4'-Dihydroxystilbene (1.3 g, 6 mmol), 4-fluorophenyl sulfone (5.1 g, 20 mmol), hydroquinone 2-potassium sulfonate (HPS) (3.2 g, 14 mmol) and potassium carbonate (5.5 g, 40 mmol) were placed in a round-bottomed flask that contained DMAc (25 mL) and toluene (40 mL) and was equipped with a nitrogen inlet and a Dean-Stark trap. The reaction mixture was stirred at 150 °C for 3 h. Then, the azeotropic mixture was removed and the temperature was increased to 180 °C. The reaction mixture was stirred overnight at that temperature under a nitrogen atmosphere. The reaction mixture was cooled and diluted with a small amount of DMAc. Finally, the reaction mixture was precipitated in excess MeOH. The inorganic material was removed by Soxhlet extraction using de-ionized water. The polymer (PES 70) was then dried at 60 °C for 24 h in a vacuum oven. ¹H NMR (DMSO-*d*₆): δ 6.96–7.32 (m, 24H, ArH), 7.45–7.52 (s, 2.3H, ArH), 7.65–7.75 (m, 4H, ArH), 7.9–8.05 (m, 13.3H, ArH); FT-IR (cm⁻¹): 965, 1011, 1072, 1144, 1223, 1471, 1583.

2.4. Fabrication of cross-linked PES 70 (c-PES 70) membrane

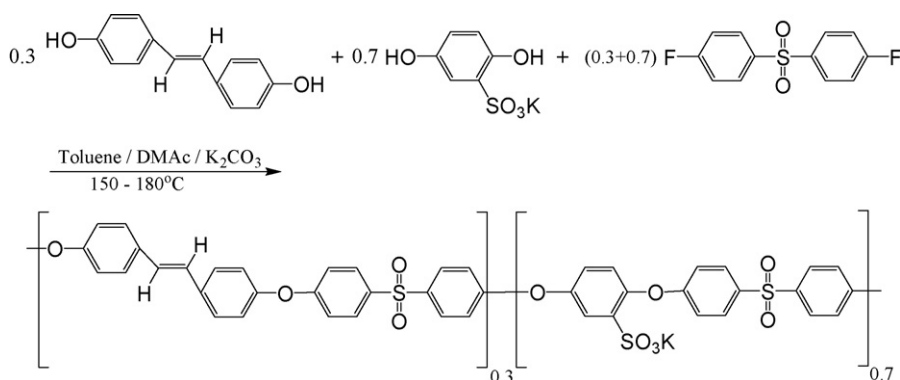
The cross-linkable PES 70 membrane was fabricated from 15% (w/v) DMSO solution with benzophenone (1 wt.% PES 70 solid content) as a photo-initiator. The polymer solution was poured on a glass plate and the thickness of the film was controlled by a doctor blade. To obtain the cross-linked membrane, UV was irradiated to the cross-linkable PES 70 cast solution (350 nm, 400 W) for 30 min under a nitrogen atmosphere. The UV irradiated membrane was dried at 60 °C under reduced pressure for 30 h. The membrane was placed in 10% HCl solution at 50 °C for 12 h and washed thoroughly with de-ionized water several times to obtain cross-linked PES 70 (c-PES 70) membrane. It was stored in de-ionized water at room temperature.

2.5. Membrane-electrode assembly (MEA) preparation

The MEA was fabricated with the cross-linked PES membrane (c-PES 70). 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 sprayed on the membrane directly. Finally, the catalyst-coated membrane was dried at 60 °C for 3 h. The active electrode area of the MEA for a single-cell test was 25 cm² with a platinum loading of 0.4 mg cm⁻² for both the anode and the cathode.

2.6. PEMFC test

The single cell was set up with the catalyst-coated membrane, a gas-diffusion layer (SGL 10BC), Teflon gaskets, and graphite bipolar plates. The gases (fuel and oxidant) were passed



Scheme 1. Synthesis of non-cross-linked poly(ether sulfone) copolymer (PESs).

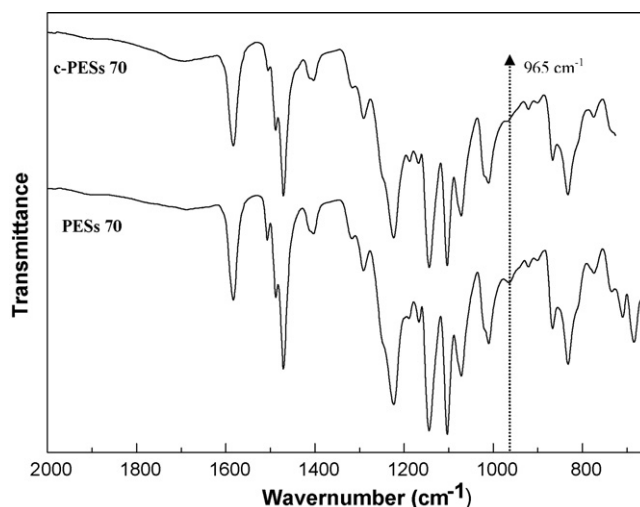
through humidifiers (gas flow rate: $400 \text{ cm}^3 \text{ min}^{-1}$ under ambient pressure) before entry into the fuel cell inlets. The I - V characteristics were evaluated with an electric load (Daegil Electronics, EL500P).

3. Results and discussion

3.1. Synthesis and characterization of cross-linked PES (*c*-PES)

Synthesis of sulfonated polymers using sulfonated monomers has been shown to be more advantageous than that from post-sulfonation [18]. Therefore, we used the former method. The cross-linkable PES was prepared by using hydroquinone 2-potassium sulfonate, 4,4'-dihydroxystilbene and 4-fluorophenyl sulfone 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. We synthesized PES 70, which has 70 mol% of hydroquinone 2-potassium sulfonate units in the polymer backbone. Also, to improve the insolubility of the polymer in water, the cross-linking method was employed. Benzophenone was used as a photo-initiator and UV was irradiated to fabricate cross-linked PES 70 (*c*-PES 70).

Several properties such as proton conductivity, solubility in boiling water and aprotic solvents of PES 70 and *c*-PES 70, are shown in Table 1. The conductivity of *c*-PES is lower than that of PES 70 which is a similar trend to that shown by previous results [15]. The cross-linkable PES 70 was sufficiently hydrophilic to

Fig. 1. FT-IR spectrum of PESs 70 and *c*-PESs 70 membrane.

be dissolved partially in boiling water. By contrast, the *c*-PES 70 copolymer was not soluble in boiling water during Soxhlet extraction. Also, *c*-PES was not soluble in any aprotic solvents at room temperature, which confirms the cross-linking reaction.

The FT-IR technique was used to analyze the functional groups in the polymer structure. The FT-IR spectra of PES 70 and *c*-PES 70 are presented in Fig. 1. The absorption peak for $-\text{HC}=\text{CH}-$ of PES 70 appears at 965 cm^{-1} . This peak disappears in *c*-PES 70 and shows that the *c*-PES 70 was successfully obtained [19]. The peaks at 1583 and 1471 cm^{-1} are attributed to the vibration of the aromatic ring skeleton [20]. The characteristic absorption band for the aromatic sulfone group appears at 1144 cm^{-1} and the peak for aryl oxide occurs at 1223 cm^{-1} [3]. Two absorption peaks at 1072 and 1011 cm^{-1} are characteristic of the aromatic SO_3^- stretching vibrations [5]. The ^1H NMR spectrum of the PES 70 copolymer is shown in Fig. 2. The peak at 7.7 ppm corresponds to the aromatic hydrogens, which are *ortho*-position to $-\text{HC}=\text{CH}-$ group. Also, the peak for the aromatic hydrogens, which is in the *ortho*-position to sulfonic acid group, is observed at 7.5 ppm . Theoretically, the ratio of the peaks is 12 to 7 and the NMR shows the value. Therefore, it can be concluded that the polymer was synthesized as we expected.

The TGA curve of *c*-PES 70 is given in Fig. 3. It shows clearly that there are two weight-loss steps. The first weight loss

Table 1
Properties of PES 70 and *c*-PES 70

Polymers	Solubility				Conductivity (S cm^{-1}) ^b
	Water ^a	DMSO	DMF	NMP	
PES 70	Δ	○	○	○	0.15
<i>c</i> -PES 70	×	×	×	×	0.12
Nafion 112	–	–	–	–	0.11

(○) soluble; (Δ) partially soluble; (×) insoluble.

^a Boiling water.

^b At room temperature under 100% relative humidity.

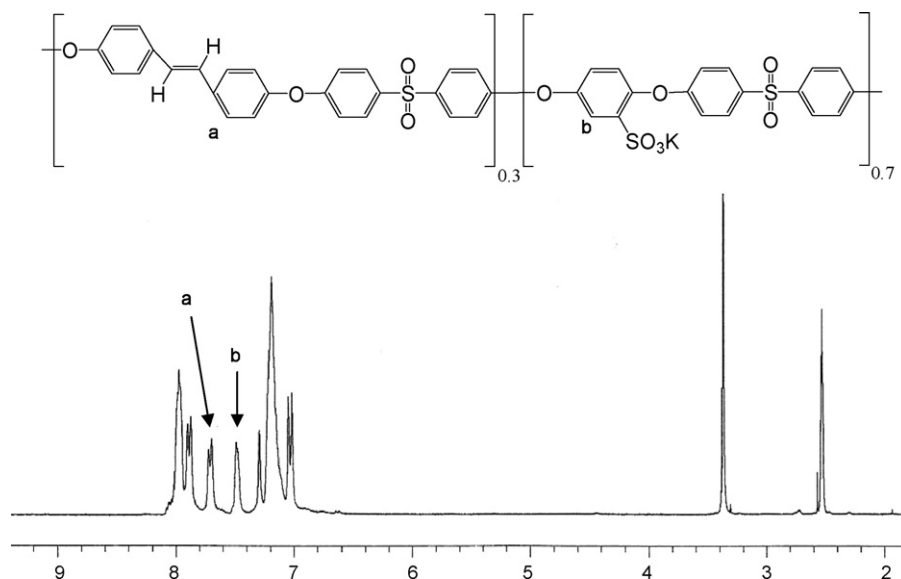
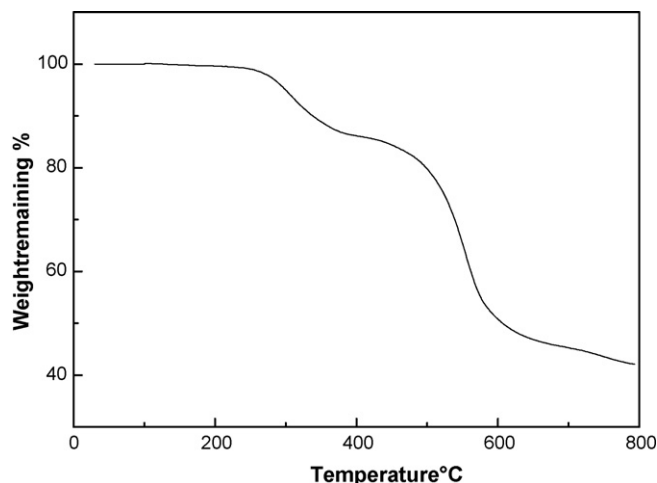
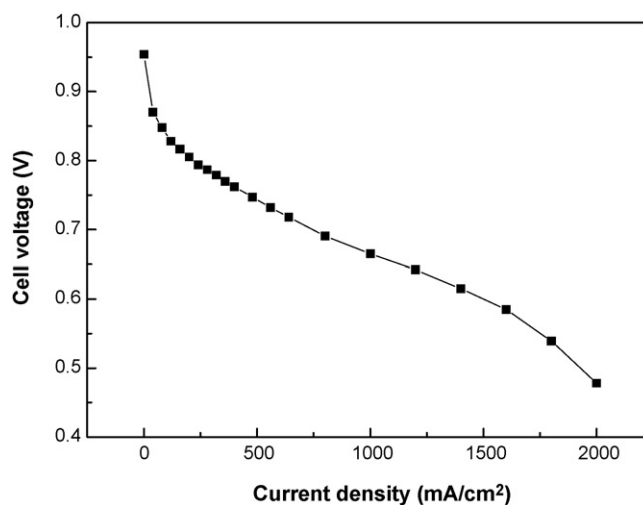
Fig. 2. ^1H NMR spectrum of PES 70.

Fig. 3. TGA curve of c-PESs 70 membrane.

appears above $260\text{ }^\circ\text{C}$ and is due to degradation of the sulfonic acid group. The second weight loss occurs at about $480\text{ }^\circ\text{C}$ and results from decomposition of the copolymer backbone. Based on these results, the c-PES 70 membrane is thermally stable for PEMFC application.

3.2. PEMFC performance of c-PES 70-based MEA

A membrane-electrode assembly (MEA) was fabricated with the c-PES 70 membrane. A Pt/C slurry was sprayed directly on the membrane and the Pt loading was 0.4 mg cm^{-2} for both side electrodes. A cell test was carried out at $70\text{ }^\circ\text{C}$. The polarization curve for c-PES 70 is shown in Fig. 4. A current density of 1500 mA cm^{-2} at 0.6 V is obtained with humidified oxygen and hydrogen. It produces relatively low-cell performance [7,8]. A Nafion binder was used for the electrode fabrication. Therefore, the interaction between the Nafion binder and c-PES 70 membrane is not concrete. This could generate membrane-

Fig. 4. Polarization curves for c-PESs 70-based MEA in H_2/O_2 mode at $70\text{ }^\circ\text{C}$.

electrode de-lamination in the MEA [21]. Kim et al. [6] operated a PEMFC with a hydrocarbon-based membrane (BP-30) and with a partially fluorinated membrane (6F-35) using a Nafion binder in the electrodes under identical operating conditions [6]. The 6F-35 membrane showed high performance due to a low-ohmic losses compared with the BP-30. It is considered that incompatibility between the c-PES 70 membrane and the Nafion binder in the electrode causes high-interfacial resistance, and thereby results in low-cell performance. If a fluorinated c-PES with high-proton conductivity is synthesized and its MEA fabrication method is established, the cell performance will be improved.

4. Conclusions

A cross-linked sulfonated poly(ether sulfone) has been synthesized successfully with 4,4'-dihydroxystilbene and other commercially available monomers. The c-PES 70 membrane,

which has 70 mol% of HPS units in the polymer backbone, has a proton conductivity of 0.12 S cm^{-1} and good insolubility in boiling water. To examine single-cell performance, a c-PES 70-based MEA has been fabricated. The cell is operated with humidified H_2 and O_2 gas as fuel and oxidant at 70°C . A current density of 1500 mA cm^{-2} is obtained at 0.60 V .

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