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Pendant-sulfonated poly(arylene ether ketone) (PAEK) membranes cross-linked with a proton conducting reagent for fuel cells

Ji-eun Kim, Dukjoon Kim*

School of Chemical Engineering, Sungkyunkwan University, Suwon, Kyunggi 440-746, Republic of Korea

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ABSTRACT

Poly(arylene ether ketone) (PAEK) bearing a pendent sulfonic acid group was synthesized to prepare polymer electrolyte membranes for fuel cells. For preparation of this membrane, the precursor possessing the reactive carboxylic acid functional group was first synthesized to control the degree of sulfonation and cross-linking. A variety of essential properties for fuel cell membranes such as proton conductivity, water uptake, methanol permeability, and chemical, thermal, and mechanical stability were investigated. The proton conductivity was comparable to Nafion® 117 and it did not significantly decrease by addition of the cross-linker because of the sulfonic acid proton conducting group attached to it. Methanol permeability was very low and it decreases with cross-linking density – it decreased down to a fourth of that of Nafion® at 30% cross-linking density. Cross-linking reduced water uptake and thus enhanced dimensional stability of the membrane. The resistance to oxidation and hydration was also improved by cross-linking. Among a series of cross-linked membranes, the 20% cross-linked system exhibited the best cell performance associated with excellent membrane properties.

1. Introduction

Nafion® is known as an exceptional membrane with application in fuel cells as it has excellent proton conducting properties, along with high chemical stability. Proton conduction is provided by the presence of the hydrophilic, water-transportable ion clusters separated in the hydrophobic perfluorocarbon polymer matrix [1–4]. A few obstacles in Nafion® membranes, however, limit its wide application, namely high cost, high methanol permeability, and reduced conductivity at elevated temperature [5–16]. Methanol crossover is a serious problem in direct methanol fuel cell (DMFC) application as it causes considerable fuel loss and performance deterioration [5–10]. Reduction of conductivity is frequently found in high-temperature polymer electrolyte membrane fuel cell (PEMFC) operation where water is easily evaporated. A number of studies have been conducted to address these problems, including the synthesis of cost effective hydrocarbon-type polymer membranes such as polybenzimidazole (PBI), poly(ether sulfone) (PES), poly(ether ether ketone) (PEEK) [8,17–27], and blending of proton conducting or methanol impermeable materials with the aforementioned membranes [28–31].

PEEK is a typical engineering plastic with excellent chemical, thermal, and mechanical properties. It has received much attention regarding fuel cell membrane applications since it was reported that its ion cluster size is much smaller than Nafion® when sulfonated [8]. The small cluster size is very beneficial to methanol permeation reduction, as it diminishes the methanol transport *via* an electro-osmotic drag effect. Even though it bears such a positive property, it possesses a drawback associated with a low proton conductivity [22–26]. Compared to the acidity of Nafion®, that of sulfonated PEEK is low ($pK_a = -1$) because of the presence of abundant electrons within the benzene groups. This reduced polarity leads to less repulsion forces among the sulfonic acids, and thus a smaller cluster size. Another reason for this small cluster size arises from the rigid backbone structure of PEEK composed of phenyl groups. Those rigid chains are not flexible enough to render sulfonic acid groups to form large aggregates [8]. The weak polarity reduces the dielectric constant of the water present inside clusters and thus lessens ion conduction. Provision of high proton conductivity to PEEK membrane requires a high degree of sulfonation for this reason. In this lab's previous studies, sulfonated PEEK (SPEEK) membranes with a degree of sulfonation above 75% showed proton conductivity comparable to Nafion® 117, while still maintaining a very low methanol permeability [22,23,26]. However, those membranes confronted a problem associated with deterioration of dimensional stability caused by high swelling or variable dissolution when in contact with water, especially at elevated temperature. This impedes its utilization for long-time operation at high temperatures, mostly in PEMFC.

The objective of this research is to develop dimensionally stable sulfonated poly(arylene ether ketone) (SPAEK) membranes with the proton conductivity comparable to Nafion® but the methanol

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* Corresponding author. Tel.: +82 31 290 7250; fax: +82 31 290 7272.
E-mail address: djkim@skku.edu (D. Kim).

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permeability lower than it. In order to achieve this purpose, the pendant sulfonated-cross-linked systems were proposed. While sulfonation in the pendant position brings about more feasible aggregation of sulfonic acid groups with high acidity, cross-linking yields a more stable membrane dimension that is associated with reduced water uptake and enhanced thermal and mechanical properties.

2. Experimental

2.1. Materials

4,4-Bis(4-hydroxyphenyl)-pentanoic acid, 4,4′-difluorobenzophenone, and potassium carbonate were used for the synthesis of PAEK with a carboxylic acid pendant group. *N*-Hydroxysuccinimide (NHS) was used to link the taurine, 2-aminoethanesulfonic acid, which contains sulfonic acid group. *N*,*N*-Dicyclohexylcarbodiimide (DCC) was used as an eliminating agent of water, and 2,2′-benzidinedisulfonic acid (BDSA) a cross-linker. Toluene, methanol, dimethyl sulfoxide (DMSO), isopropanol (IPA), *N*,*N*′-dimethyl formamide (DMF), dimethylacetamide (DMAc), tetrahydrofuran (THF), and hydrochloric acid (HCl) were used as solvents for preparation the polymer and membrane. All chemicals mentioned herein were purchased from Aldrich (Milwaukee, WI).

2.2. Synthesis of PAEK

4,4-Bis(4-hydroxyphenyl)-pentanoic acid (0.01 mol) and K_2CO_3 (0.02 mol) were placed in a mixture of dry DMSO (50 g) and toluene (30 g) in a 250 mL three-neck round bottom flask, under nitrogen gas, equipped with a Dean-stark trap. The reactants were stirred at room temperature for 2 h, followed by reaction at 145 °C for 4 h. After the product was cooled down to room temperature, 0.01 mol of 4,4′-difluorobenzophenone was added. The reaction was conducted at slowly increasing temperatures to 148 °C for 4 h, and then 160 °C for another 2 h until precipitates were produced. The precipitates were collected at room temperature and then dissolved in 50 mL of THF/HCl mixture (40/50). White precipitates were obtained when the solution was poured into 1000 mL of DI water. The product was washed several times with DI water and methanol consecutively. The pure samples were dried in a vacuum oven at 80 °C for at least 48 h. Fig. 1 shows the synthetic route of PAEK possessing the carboxylic acid pendant group.

2.3. Synthesis of sulfonated PAEK (SPAEK) and cross-linked SPAEK (CSPAEK)

After the PAEK (2.32 g, 0.005 mol) was dissolved in 30 mL of DMF, NHS (0.58 g, 0.005 mol) was added and stirred for 4 h. DCC (1.02 g) was then added in the mixture and stirred for 24 h at room temperature to remove any precipitates by filtration. The solution remaining was placed in 500 mL of ethanol to yield precipitation. The precipitates were washed with ethanol several times and dried at 40 °C for 12 h.

The dry PAEK-NHS sample (1.4 g, 0.0025 mol) was dissolved in 25 mL of DMAc. After taurine was added and stirred at room temperature for 4 h, the mixture was reacted at 90 °C for 12 h. The product was obtained after precipitation in 300 mL of IPA several times, followed by drying at 60 °C. The amount of taurine fed was from 70 mol% to 100 mol% stoichemically calculated based on all reactive sites in polymer repeating units.

SPAEK-NHS (0.4 g) and cross-linker BDSA (0.026 g) were dissolved in 6 mL of DMSO and the solution cast on a glass slide. The cross-linking reaction was conducted in a vacuum oven at 90 °C for 12 h, followed by drying at 95 °C for 24 h. The film was detached from a glass slide, and then immersed in 1.5 M HCl of aqueous solution for 24 h. The unreacted reagents and excess HCl solution were removed by heating the membrane in DI water. pH was measured to check whether HCl had been completely removed. Washing process was repeated until its neutralization.

The solid membrane obtained was flexible, and transparent-to-grey in color. Its thickness was 150–180 μm. The synthetic pathway of SPAEK and CSPAEK is shown in Fig. 2.

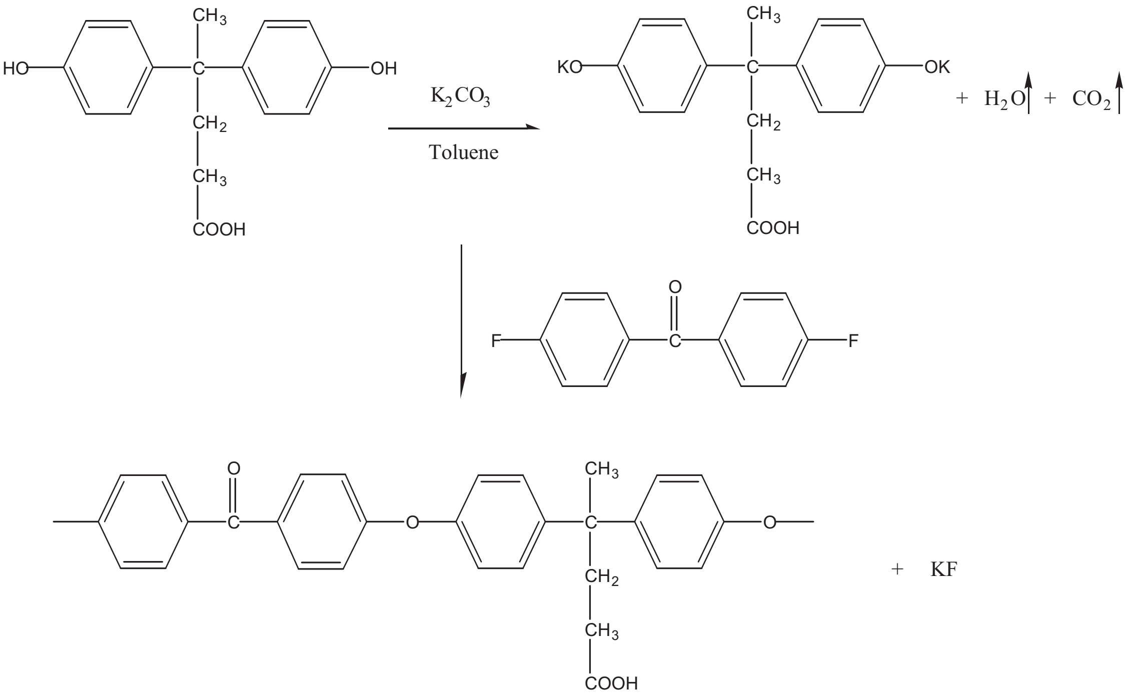

Fig. 1. Synthetic pathway of PAEK with carboxylic acid groups.