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Synthesis and properties of cross-linked poly(arylene ether ketone) electrolyte membranes containing hygroscopic proton conductors

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ABSTRACT

Sulfonated poly(arylene ether ketone) (SPAEK) fuel cell membranes were prepared in a cross-linked structure to enhance their dimensional and mechanical stability. Sulfonated mesoporous benzene-silica (SMBS) hygroscopic conductors were embedded in the membranes to lessen their dehydration in the low humid environment. Synthesis of the cross-linked SPAEK (CSPA EK) and its precursor was confirmed using ^1H NMR spectroscopy and FT-IR spectroscopy. The effects of sulfonation degree (SD) and hygroscopic conductors on the membranes properties such as proton conductivity, methanol crossover, and thermal and mechanical stability were analyzed. The prepared CSPA EK membranes were thermally stable up to 250 °C without any chemical degradation. While the CSPA EK membranes containing hygroscopic proton conductors exhibited superior conductivity to that of Nafion®117, those with a sulfonation percent of less than 20% showed lower methanol permeability. Although the water uptake of the composite membranes was higher than that of the pristine membranes, no mechanical failure was observed.

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Introduction

Fuel cells are environmentally safe and noiseless electrochemical devices for converting chemical energy to electrical energy by the oxidation of fuel. In contrast to secondary batteries, fuels are continuously supplied to the system, which renders the energy recharging process unnecessary. Fuel cells have a wide range of application fields, as they generate high power density and thus have high energy conversion efficiency [1,2]. Among several types of fuel cell that are basically classified according to fuel type, polymer electrolyte membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) use proton

conducting polymer membranes as electrolytes. Therefore, they are applied mostly for mobile and transportation energy sources operated at relatively lower temperatures than other types of fuel cell.

Nafion, a commercially available perfluorocarbon based polymer membrane, is one of the most widely used electrolytes in fuel cell operation, due to its excellent proton conducting, chemical and mechanical properties. Some polymer electrolyte membranes prepared from the partially fluorinated polymers such as poly(vinylidene fluoride-co-chlorotrifluoroethylene) graft copolymer also exhibit high proton conductivity without significant loss of mechanical properties [3]. The few drawbacks in the utilization of Nafion

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membranes, however, include fuel crossover through the membrane, reduced conductivity at low humidity, and high purchasing cost [4–9]. As protons are transported through the membrane in the hydrate state, its conducting ability is rapidly degraded when the membrane becomes dry. As water vaporizes at around 100 °C, the conductivity is usually significantly reduced when fuel cells are operated at high temperatures. In DMFC operation, the methanol crossover is also an important membrane property that affects the cell performance. As the ion cluster dimension of Nafion membrane is relatively large when percolated, the fuel (methanol) is easily permeated through the membrane, resulting in mixed potential, followed by poor fuel cell performance [10].

Although hydrocarbon-based membranes have a big advantage over Nafion membrane in low methanol permeation property in association with smaller ion cluster dimension, they suffer a big weakness in low proton conductivity [10–17]. Among several types of hydrocarbon-based polymer electrolyte membrane, sulfonated poly(ether ether ketone) has been reported as a promising polymeric material for replacing Nafion membranes, due to its superior properties such as low methanol permeability, excellent thermal, mechanical, and chemical stability, and inexpensive material price. Enhancing the proton conductivity, a typical weakness of sulfonated poly(ether ether ketone) membrane, necessitates increasing the sulfonation degree in the membrane. This, however, sometimes results in mechanical failure caused by high water uptake, swelling, and cracking at high temperature operation.

In our previous reports [18–23], highly sulfonated poly(arylene ether ketone) (SPAEK) was synthesized in a cross-linked structure and applied for the preparation of fuel cell membranes to enhance their dimensional and mechanical stability, even at high temperature operation. The proton conductive cross-linker was introduced to prevent conductivity loss by chemical cross-linking. Although the cross-linking effect on a variety of membrane properties was positive in the previous study, another important problematic property, i.e., reduced conductivity at low humidity, remained to be solved in these SPAEK membranes. In this study, the hygroscopic conductors were accommodated in cross-linked poly(arylene ether) membrane to lessen its dehydration behavior in a low humid environment. The hygroscopic conductors studied in this work, mesoporous benzene-silica beads, actually possess 2D-hexagonal cylinder-type pores with a diameter of about 3 nm. An anti-dehydration property was expected from their capillary condensation effect associated with their cylindrical mesoporous structure. In this study, the following essential membranes properties were analyzed for the hygroscopic conductor-embedded, cross-linked SPAEK (CSPA EK) membranes: proton conductivity, methanol crossover, and thermal and mechanical properties.

Experimental

Materials

5,5-Carbonylbis(2-fluorobenzene-sulfonate) (99%) was purchased from Yan Jin Technology Co., Ltd. (Tianjin, China) and

2,2'-benzidine disulfonic acid (BDSA) and 3-amino-1,5-naphthalene disulfonic acid salt were from Tokyo Chemical Industry (TCI, Japan). 4,4-Bis(4-hydroxyphenyl)-valeric acid, 4,4'-difluorobenzophenone, potassium carbonate (K_2CO_3), dimethylsulfoxide (DMSO), toluene, N,N'-dicyclohexylcarbodiimide (DCC), N-hydroxysuccinimide (NHS), N,N-dimethylacetamide (DMAc), hydrochloric acid (HCl), dimethylformamide (DMF), sodium hydroxide (NaOH), methanol, sodium hydroxide (NaOH), isopropanol, and tetrahydrofuran (THF) were purchased from Aldrich (Aldrich, Milwaukee, WI, USA) and used without purification. Cetyltrimethylammonium chloride solution (CTAC) (25 wt%, Aldrich), 1,4-bis(triethoxysilyl)benzene (BTEB) (Aldrich), (3-Mercaptopropyl)trimethoxysilane (MPTMS) (95 wt%, Aldrich), sodium hydroxide (99%, Duksan Reagents & Chemicals, Korea), hydrogen peroxide (30 wt%, Duksan Reagents & Chemicals, Korea), hydrochloric acid (37 wt%, Aldrich), and sulfuric acid (Duksan Reagents & Chemicals, Korea) were used to synthesize mesoporous benzene silica (MBS).

Synthesis of sulfonated poly(arylene ether ketone) (SPA EK) precursor

An SPAEK precursor containing carboxylic acid pendant group was first synthesized to prepare the cross-linked polymer electrolyte membranes. The SPAEK precursor was synthesized from 5,5-carbonyl bis(2-fluorobenzene-sulfonate), 4,4-bis(4-hydroxyphenyl)-valeric acid, and 4,4'-difluoro-benzophenone. The sulfonation degree (SD) of SPAEK was determined by the feed ratio of sulfonated to nonsulfonated monomers. The pendant carboxylic acid was modified to N-hydroxysuccinimide (NHS) for more feasible cross-linking reaction. The synthetic procedure and method are described in more detail below.

Anhydrous DMSO (45 g), 4,4-bis(4-hydroxyphenyl)-valeric acid (0.01 mol), toluene (40 g), and K_2CO_3 (0.25 mol) were introduced in a 250 mL 3-neck flask occupied with nitrogen gas. The reactants were stirred for 8 h at room temperature, and then the reaction was further conducted for 4 h at 145 °C. The intermediate reactants were cooled down to room temperature, and then 4,4'-difluorobenzophenone (0.009 mol) and 5,5-carbonylbis(2-fluorobenzene-sulfonate) (0.001 mol), DMSO (10 mL) were added for further reaction at 150 °C for 12 h. The byproduct of water was removed by refluxing via azeotropic distillation. The water-eliminated mixture was heated to 165 °C, and maintained at this temperature for 24–36 h to obtain polymer precipitates. The precipitates were dissolved in THF (25 mL) and concentrated HCl (6 mL) solution. After elimination of unreacted monomer and impurities using filtration, the polymer solution was dropped into 500 mL IPA solvent to obtain white colored SPAEK precipitate. After filtration, the polymer product was washed consecutively with 600 mL IPA and 600 mL distilled water several times, followed by drying at 80 °C for 24 h in vacuum. The yield of final product was 90%.

The carboxylic acid group in SPAEK precursor was reformed to NHS group via DCC NHS and DCC were used in excess amounts for high conversion into SPAEK-NHS. SPAEK 2.34 g (0.005 unit-mol) and NHS 0.69 g (0.006 mol) were homogeneously mixed in DMF 25 mL, while DCC 1.235 g (0.006 mol) was dissolved in 4 mL DMF. The two mixtures were

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