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Synthesis of sulfonated poly(arylene ether ketone) block copolymers for proton exchange membrane fuel cells

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ABSTRACT

Sulfonated poly(arylene ether ketone) (SPAEK) block copolymers were synthesized through nucleophilic aromatic substitution polymerization. Compared with a Nafion (NRE-212), state-of-the-art proton conducting membrane, the block copolymer membrane showed a well separated phase morphology and high proton conductivity under fully hydrated condition at 80 °C. The fuel cell operated with a SPAEK membrane showed a current density of 1617 mA cm^{-2} at 0.6 V under 100% relative humidity (RH), whereas a NRE-212 membrane exhibited a current density of 1238 mA cm^{-2}, which is about 30% lower than newly prepared SPEAK membrane. In addition, the maximum power density of 1160, and 800 mW cm^{-2} was observed for SPAEK, NRE-212 membranes, respectively at 80 °C under 100% RH condition. The SPEAK membrane exhibited 1.4-folds enhancement in the maximum power density in comparison with NRE-212 membrane.

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1. Introduction

Polymer electrolyte membranes fuel cells (PEMFCs) have considered one of the promising energy conversion devices because of their high efficiencies and wide range of applications such as power stations, electric vehicles, and electronic applications [1]. Fuel cell powered electric vehicles have been commercialized. However, some technical issues for full scale commercializing PEMFCs powered vehicle still remain. The most important challenge is the cost of present fuel cell materials. The commercialized membrane such as Nafion has high production cost, low durability, low glass transition temperature and environmental concerns of fluorine present in the membrane [2–4]. To overcome these technical issues, one of the most important problems is to develop alternative membranes with enhanced proton conductivity as well as excellent fuel cell performance with respect to the state-of-the-art polymer electrolyte membrane (PEMs) such as perfluorosulfonic acid (PFSA) ionomer.

Hydrocarbon based PEMs were investigated in the last decade because of their low gas permeability, low production cost, and good thermal-stability. Especially, non-fluorinated aromatic membranes have received considerable attention due to the environmental compatibility [5,6]. Although, the hydrocarbon membranes have certain good properties, however they exhibit

several drawbacks such as weak mechanical properties, low proton conductivity, and low fuel cell performance [7,8]. To overcome these inferior properties, block copolymers composed of hydrophobic and hydrophilic blocks with sulfonic acid groups were developed to achieve the well-developed phase separation with interconnected ionic channels [9–16]. Bae et al. reported block copolymers composed of rigid and robust chemical structure as a hydrophobic component to improve the proton conductivity [17]. By introducing asymmetric chemical structure into the polymer, the phase separation of the block copolymer was well established in the membrane [17]. The ether (–O–) linkage, sulfide groups (–S–), ketone groups (–C=O–), and sulfoxide groups (–O=S=O–) were introduced for membrane flexibility and sulfonic acid groups would be attached on benzene. However, all of these groups can be easily susceptible from the oxidative degradation. Miyatake et al. synthesized block copolymers with sulfonated benzophenone groups as hydrophilic blocks through coupling reaction to improve oxidative stability of membrane, as decreasing ether linkage [18].

In this study, we introduce the rigid and robust hydrophobic oligomer as our block copolymer component to achieve high proton conductivity. In addition, we have developed block copolymers composed of a new hydrophilic oligomer with bi-phenol and sulfonated difluorobenzophenone in order to improve the oxidative stability of the membrane. The synthesis and characteristics of the oligomer and block copolymer are presented in supporting information.

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2. Experimental

2.1. Materials

4,4′-Difluorobenzophenone (DFBP), 4,4′-biphenol (BP), bis(4-fluorophenyl)sulfone (FPS), and 2,7-dihydroxynapthalene (DHN) were purchased from TCI Inc, Tokyo, Japan. N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), 30% oleum and toluene were purchased from Sigma-Aldrich, Korea. Isopropyl alcohol, H_2O_2, and H_2SO_4 were purchased from Daejung Chemicals, Korea and were used as received. Nafion 212 (NRE-212) membrane was purchased from Aldrich, Korea.

2.2. Synthesis of sulfonated DFBP

A 100 mL round-bottom flask was charged with 5.0 g of DFBP and 30% oleum was added to the flask. The sulfonation reaction was carried out at 115 °C for 8 h with reflux and then the mixture was poured into the crushed ice. After filtration, the solution was neutralized with 1 M NaOH solution. Addition of NaCl into the mixture gave a slightly yellow precipitate. The product was dissolved in water and purified with dialysis tube for 1 h. Then, the mixture was evaporated and dried in vacuum oven overnight to give SDFBP in 68% yield.

2.3. Synthesis of hydrophilic oligomer

A 100 mL round-bottom flask was charged with BP (2.3 g, 12.6 mmol), SDFBP (6.6 g, 15.7 mmol), potassium carbonate (2.9 g, 21 mmol), 32 mL of DMSO, and 16 mL of toluene. The reaction mixture was heated at 145 °C for 3 h with a Dean Stark trap and then the reaction temperature was increased to 170 °C and held for 3 h to obtain viscous solution. The solution was cooled to 25 °C and dropwise into 500 mL of IPA to precipitate a light yellow powder. The product was dissolved in water and purified for 1 h to achieve pure hydrophilic oligomer. Then, evaporating and drying in vacuum oven at 100 °C gave hydrophilic oligomer in 83% yield.

2.4. Synthesis of hydrophobic oligomer

A 100 mL round-bottom flask was charged with FPS (4.0 g, 15.7 mmol), DHN (3.58 g, 16.7 mmol), potassium carbonate (4.62 g, 33.4 mmol), 32 mL of DMAc, and 16 mL of toluene. The mixture was heated at 145 °C for 2 h with a Dean Stark trap and then the reaction temperature increased to 170 °C for 2 h. The obtained viscous mixture was diluted with 20 mL of DMAc for lowering viscosity and poured into 1 L of DI water to achieve light green product. The cured product was washed with methanol several times and then dried in vacuum oven gave hydrophobic oligomer in 80% yield.

2.5. Synthesis of block copolymer

A 100 mL round-bottom flask was charged with hydrophilic oligomer (0.25 g, 0.07 mmol), hydrophobic oligomer (0.31 g, 0.07 mmol), potassium carbonate (0.029 g, 0.21 mmol), calcium carbonate (0.0701 g, 0.7 mmol), 4 mL of DMSO, and 1 mL of toluene with vigorous magnetic bar stirring. The mixture was heated at 145 °C for 20 h. After finishing the polymerization, the reaction temperature decreased to room temperature and then a small amount of DMSO was added in the mixture solution for lowering viscosity. The polymer solution was poured into 1 M HCl solution. Then, the light brown fiver was washed with 3 M NaCl solution to change sorting form and washed again with DI water to remove remaining sodium chloride. Drying in vacuum oven gave block copolymer in 89% yield.

2.6. Preparation of membrane

The block copolymer (0.32 g) was dissolved into 10 mL of DMAc or NMP solvent. The membrane was casted by casting this solution onto a glass petri dish and dried in a vacuum oven at 60 °C for 2 h, followed by at 80 °C for 4 h. After membrane casting, the membrane was peeled off using small amount of DI water and dried again to check thickness of the membrane. The average thickness of membrane, measured by a digital micrometer, was 50 ± 5 μm. Finally, the membrane was treated by boiling in 1 M H_2SO_4 aqueous solution and washed with DI water several times.

2.7. ^1H NMR spectra and gel permeation chromatography

To confirm the chemical structures of the hydrophobic, hydrophilic oligomer, and block copolymer, ^1H NMR spectra were obtained with a 400 MHz Bruker AV 400 spectrometer using DMSO-d_6 as a solvent. Molecular weight of each samples was measured by gel permeation chromatography (GPC) with THF and $NaNO_3$ solution. Two different columns were used for hydrophobic and hydrophilic oligomer, respectively. Standard polystyrene was used for calibration of molecular weight.

2.8. Water uptake and ion exchange capacity

Water uptake of the membrane was investigated by using the dry and wet membranes. The membrane was dried in vacuum oven at 90 °C for overnight and then measured the weight. After that, the membrane was soaked in water for 24 h and checked the weight. Water uptake was calculated by the following equation

$$\text{Water uptake}(\%) = \frac{W_{\text{swollen}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

W_{swollen} is the weight of the membrane which was soaked in water for 24 h and W_{dry} is the weight of dry membrane.

Ion exchange capacity (IEC) was measured by titration. The membrane was dried in the oven at 100 °C for overnight and then immersed in 3 M NaCl solution for exchanging H^+ to Na^+. The solution was titrated with 0.01 M NaOH solution. IEC was calculated based on the following equation

$$\text{IEC} = \frac{V_{\text{NaOH}} \times C_{\text{NaOH}}}{W_{\text{dry}}}$$

V_{NaOH} is the added volume of NaOH at the equivalence point (mL), C_{NaOH} is the concentration of NaOH (M) and W_{dry} is the weight of dry membrane.

2.9. Bound water analysis

The amount of bound water absorbed in the membranes was determined using a differential scanning colorimeter (DSC, TA instrument) [19,20]. In DSC measurement, the freely absorbed water on the surface of the hydrated membranes were removed first and then the membranes were frozen at −80 °C and hold for 5 min. After that, the membranes were heated from −80 to 80 °C with a heating rate of 1 °C min^{-1} [19,20]. The amount of bound water in the hydrated membrane was determined following the equation.

$$W_b = WU - (W_f + W_{fb}) = WU - (\frac{Q_{\text{endo}}}{Q_{\text{pure}}} \times 100)$$

where W_b was the amount of bound water, and WU was the water uptake, W_f and W_{fb} were the amounts of free water and freezable loosely bound water, respectively. Q_{endo} was the endothermic fusion enthalpy of hydrated membrane calculated by DSC from −40 to 10 °C (J g^{-1}) and Q_{pure} was the enthalpy of deionized water