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Characterization of a soluble poly(ether ether ketone) anion exchange membrane for fuel cell application

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ABSTRACT

In this study, we synthesized a novel poly(ether-ether-ketone), containing di(quaternary ammonium) hydroxide groups in the polymer chain. Then we tested the alkaline-exchange properties of a membrane made from the novel polymer, for fuel-cell applications. First, we synthesized a di-hydroxide monomer with amine groups, which were then converted to ammonium functional groups by immersion in hydroxide solution. Then, we synthesized poly(ether-ether-ketone) using a synthesized monomer and bisphenol A. We controlled the mole ratio of the quaternary ammonium hydroxide groups in the polymer structure to evaluate the performance of the membrane. The performances of polymer-electrolyte membranes with differing degrees of amination were compared. The optimum composition of the membrane was determined based on the chemical and thermogravimetric analyses, mechanical properties, the behavior of water in the membrane, and the level of ion conductivity.

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Introduction

Fuel cells have attracted considerable attention as alternative power sources because of their numerous benefits, including high efficiency, high power density, and low-to-zero emissions compared to coal-fired power plants or internal combustion engines [1,2]. Proton exchange membrane fuel cells (PEMFC), in particular, have attracted much attention as a clean energy source for various applications [3,4]. These presently use perfluoro-based polymeric membranes, such as

Nafion, which assure high chemical stability and high proton conduction while dispersed platinum, which assures high catalytic efficiency for hydrogen at low temperatures, is used for the electrodes. However, PEMFC is limited for commercialization and large-scale applications because of the high cost of both membranes and catalyst [5]. Therefore, novel fuel cells are needed to resolve these limitations [6]. Alkaline-exchange-membrane fuel cells (AEMFCs) are expected to overcome the limitations of PEMFCs [7,8]. AEMFCs use a liquid alkaline solution such as potassium hydroxide (KOH) because it is the most conducting of all alkaline hydroxides. AFCs have

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advantages such as being easier to handle, because their operating temperature is relatively low, and because they exhibit higher reaction kinetics at the electrodes than occurs under acidic conditions [9,10]. One of the main drawbacks of the AFC is related to the use of liquid electrolyte. The KOH solution is very sensitive to the presence of CO₂. Carbonate or bicarbonate in the liquid alkaline solutions may be produced by CO₂ reactions with the oxidant-gas stream at the AFC cathodes. A major operating constraint is therefore the requirement for low CO₂ concentration in the oxidant feed-stream. However, when air is used instead of oxygen, the hydroxyl ions may react with CO₂ contained in the air [11,12]. Among the AEMFC components, the AEM is one of the key components in the system that determines the performance of the fuel cell [13]. Many different routes have been followed to develop more economical polymeric electrolyte fuel cells and considerable effort has been made to find membranes that are less expensive than Nafion. Creation of new AEM materials has been attempted by the introduction of quaternary ammonium groups to existing polymers. A number of hydrocarbon-based polymeric materials (e.g., poly(arylene ether sulfone)s [14,15], poly(vinyl alcohol) [16,17], poly(ether ketone) [18], poly(phthalazinone ether ketone) [19,20], poly(phenylene) [21,22] polybenzimidazole [23] and polystyrene (ethylene butylene) polystyrene [24]) have been developed for use as anion exchange membranes in fuel cells. However, most of the newly developed materials containing commercial membranes need to resolve problems such as chemical stability (nucleophilic displacement by the hydroxyl ions).

Poly(ether-ether-ketone) (PEEK) is a thermostable polymer with an aromatic, non-fluorinated backbone, in which 1,4-disubstituted phenyl groups are separated by ether (–O–) and carbonyl (–CO–) linkages. PEEK is a widely investigated candidate for use in PEMFC materials due to its high chemical and thermo-oxidative stability, good mechanical properties, and lower cost [25]. Thus, aminated PEEK have been examined as alternative AEM materials. This anion exchange membrane (AEM) is usually prepared by chloromethylation and quaternary amination. However, the chloromethyl methyl ether used in chloromethylation is highly toxic and potentially harmful to human health [26]. To avoid the use of such a toxic material for synthesis of the polymeric material, membranes were prepared directly from available chloromethylated polymers, and novel alternative synthetic routes such as bromination or benzylmethylation have been developed [21]. However, it is difficult to confirm the final structure of a polymer after the bromination reaction [27]. One of the methods for the preparation of the membrane, attaching ammonium groups onto polymer backbones, can be achieved by direct copolymerization of monomers with an ammonium moiety [28]. Also, the degree of modification can be controlled by changing the composition of the monomer used for synthesis. In this study, we aimed to develop a series of anion exchange membranes. First, we synthesized a monomer with amine groups and then converted them to ammonium groups. PEEK containing amine functional groups in the repeating unit of the polymer backbone was prepared directly synthesized from modified monomer evaluated for possible fuel cell applications. Also, it is difficult for PEEK to be used as membrane because of their poor solubility. The PEEK with bisphenol-A

moiety has been successfully synthesized to obtain the desired solubility and processability. The membrane was tested to determine the effect of the degree of amination of the membrane, on the membrane properties (e.g., water uptake, IEC, ion conductivity).

Experimental

Materials

The substance 4,4'-dihydroxydiphenyl ether (DHDPE) was obtained from Tokyo Chemical Industry Co., Ltd. Dimethylamine solution (33 wt%), formaldehyde solution (37 wt%), 4,4'-difluorobenzophenone, bisphenol A, cesium carbonate and iodomethane were purchased from Aldrich Chemical Corp. Chloroform and sulfuric acid were purchased from Daejung Chemical. All reagents were used as received. DHDPE was dried under vacuum at 60 °C over 24 h before synthesis. Deionized water was produced with Aquamax™ equipment (Younglin Instruments, Korea).

Synthesis of 2,2'-di(trimethylaminemethylene)-4,4'-dihydroxydiphenylether (ADHDPE)

A measured amount (30.0 g–0.145 mol) of 4,4'-Dihydroxydiphenyl ether was dissolved in 90 mL of ethanol. The synthesis of ADHDPE was done in 2-neck flasks equipped with reflux condensers and nitrogen gas inlets. Dimethylamine (3.0 equiv.) and formaldehyde (4.0 equiv.) solutions were added to the flask. The reaction was maintained at 25 °C for 24 h [29]. The samples were filtered and washed several times with deionized water to remove residual reagents, and then were dried in a vacuum oven for at 60 °C for 1 d. The dried powder was re-crystallized in ethanol to yield a light yellow powder. Finally, the recrystallized product was dried in a vacuum oven at 60 °C for 24 h before being used in the synthesis: ¹H NMR (CDCl₃, ppm): 6.62 (s, 2H, ArH), 6.78 (s, 2H, ArH), 3.5 (s, 4H; –CH₂–N–), 2.32 (s, 12H; –N–CH₃).

Synthesis of poly(ether-ether-ketone) containing tertiary amine groups

The procedure for polymerization of AD10, where 10 designates the mole percent of ADHDPE in the polymer, was carried out as follows: 4,4'-difluorobenzophenone (9.46 g, 43.4 mmol) ADHDPE (1.51 g, 4.8 mmol), bisphenol A (9.02 g, 39.5 mmol), anhydrous DMAc (180 mL), and potassium carbonate (11.83 g, 85.6 mmol) were added to a 4-neck flask equipped with a reflux condenser and nitrogen gas inlet. The mixture was then vigorously stirred for 3 h at 25 °C. After dissolving the mixture, the temperature was raised slowly from 30 to 100 °C. Then, the mixture was stirred at 120 °C for 12 h. After the synthesis process, the solution was poured into DI water to yield the fibrous polymer. Finally, precipitated polymer was washed with methanol and water (1:4 v/v) several times to remove residual monomer and catalyst. The experimental series of relative composition ratios of ADHDPE and BPA (0:1.0; 0.1:0.9; 0.2:0.8; 0.3:0.7; 0.4:0.6) are referred to as AD0, AD10, AD20, AD30, and AD40, respectively.

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