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Characterization of highly sulfonated PEEK based membrane for the fuel cell application

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ARTICLE INFO

Article history:

Received 15 November 2016

Received in revised form

12 April 2017

Accepted 17 April 2017

Available online xxx

Keywords:

Polymer electrolyte membrane

Cation exchange

Fuel cell

Sulfonation degree

ABSTRACT

In this study, poly(bisphenol-A-ether ketone) (PBAEK) is synthesized via nucleophilic aromatic substitution poly condensation between bisphenol A and 4,4-difluorobenzophenone, and the synthesized polymers are sulfonated using chlorosulfuric acid and suitable synthesis conditions for the temperature and sulfonating reagent content. The sulfonation degree of polymer is calculated using element analyses. The prepared sulfonated polymers are characterized for potential fuel cell applications through determining their water uptake, proton conductivity, and thermal stability. The significant advantage of the synthesized sulfonated PBAEK (SPBAEK) is its better solubility relative to commercial PEEK in various solvents, because SPBAEK backbones contain bisphenol A. The water uptake of the membrane increases with increases in the sulfonation degree. The SPBAEK membrane exhibits increased proton conductivity compared with the PBAEK membrane at 100% relative humidity conditions. As the sulfonation degree increases, the proton conductivity increases due to the increasing content in the hydrophilic domain. This property allows the prepared membranes to be potential candidates for proton exchange membrane fuel cells.

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Introduction

Proton exchange membrane fuel cells (PEMFCs) are considered to be one of the most promising clean energy technologies because these fuel cells can generate electrical energy directly from chemical energy with a highly efficient, eco-friendly system compared with coal combustion engines [1–3]. The key constituent of a PEMFC is the protonexchange membrane (PEM), which is responsible for proton transfers from the anode to the cathode, and it prevents fuel crossover [4,5]. Furthermore, the PEM must have excellent properties including high ionic conductivity, low fuel permeability, and mechanical

stability [6]. Nowadays, perfluorinated sulfonic acid membranes such as Nafion are widely used as proton exchange membranes due to their excellent mechanical properties, chemical stability, and high proton conductivity in the fully hydrated state. However, Nafion membranes have significant disadvantages of complex synthesis, high manufacturing cost, and loss of conductivity at low humidity and high temperature [7–9]. For these reasons, many researchers have focused on developing new materials for proton exchange membranes (PEMs) based on several aromatic hydrocarbons [10–13]. A number of hydrocarbon-based polymeric materials such as polyimide (PI) [14], poly(arylene ether ketone) (PAEK) [15], polybenzimidazole (PBI) [16], and poly(etheretherketone) (PEEK)

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<http://dx.doi.org/10.1016/j.ijhydene.2017.04.082>

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[17,18] have garnered attention in recent years due to their high thermal and chemical stability, and ease of synthesis processing [19]. Among the aromatic hydrocarbon electrolyte membranes, poly(etheretherketone) (PEEK) has received particular attention over the past few years due to its high mechanical properties and chemical durability. In particular, sulfonated PEEK membranes have been demonstrated to exhibit stable performance comparable with commercial perfluorosulfuric acid membranes in fuel cells. Furthermore, hydrocarbon-based membranes can achieve high proton conductivities through the copolymerization of sulfonated monomers and post-treatment processes of polymers using various sulfonation reagents such as sulfuric acid and chlorosulfuric acid [20]. This method can easily fabricate highly sulfonated polymer materials. However, the control of the sulfonation degree of the polymer is difficult as a result of their undesirable side reactions, such as chain scissions and cross-linking, and the degradation of the polymer due to the strongly acidic conditions [21]. In order to overcome these problems, this study focuses on the optimization of the sulfonation conditions of PEEK for PEMFC applications.

In this study, highly sulfonated PEEK is achieved without polymer degradation and membranes are obtained with optimum properties for use as PEMs. For this purpose, a bisphenol A-based PEEK polymer is synthesized and then sulfonated using chlorosulfuric acid as the sulfonation agent [22–25]. The effect of the reaction temperature on the degree of sulfonation is also investigated in detail. Finally, the PEEK membranes directly prepared from the sulfonated monomer are evaluated for potential fuel cell applications through determining the degree of sulfonation, water behavior, proton conductivity, and chemical and thermal stabilities.

Experimental

Materials

The 4,4'-difluorobenzophenone (DFBP), bisphenol A (BPA), potassium carbonate, anhydrous *N,N*-dimethylacetamide (DMAc), and toluene were purchased from Aldrich Chemical (USA). The chlorosulfuric acid (98%) was purchased from Kanto Chemical (Japan). Sodium hydroxide and sodium chloride were purchased from Daejung Chemical (Korea). All reagents were used as received and dried under vacuum at 60 °C for 24 h prior to synthesis. Deionized water was produced with Aquamax™ equipment (Younglin Instruments, Korea).

Synthesis of sulfonated poly(bisphenol-A-ether ketone) (sPBAEK)

The synthesis of sPBAEK copolymers was performed using the aromatic nucleophilic substitution step copolymerization method. The polymerization procedure was conducted as follows: DFBP (13.57 g, 0.124 mol), bisphenol A (14.20 g, 0.124 mol), anhydrous DMAc (170 mL), toluene (85 mL), and potassium carbonate (17.28 g, 0.25 mmol) were added to a 4-neck flask equipped with a reflux condenser, dean stark, and nitrogen gas inlet. The mixture was vigorously stirred for 3 h in order to

obtain a homogeneous solution. After dissolving the mixture, the temperature was raised slowly from 25 °C to 120 °C. Finally, the mixture was stirred at 150 °C for 20 h. After the synthesis process, the solution was poured into methanol in order to yield the fibrous polymer. Finally, the precipitated polymer was washed with methanol and water (1:4 v/v) several times to remove the residual monomer and catalyst. The fibrous polymers were filtered after the washing process and were then dried in a vacuum oven for 24 h. Various polymers were prepared through controlling the reaction temperature and amount of sulfonating reagent. An amount of 5 g of PBAEK polymer was dissolved with an equivalent amount of chlorosulfuric acid while stirring for 20 min in the temperature range of 0–25 °C. After this reaction time, the reacted polymer solution was precipitated in cold ice water and washed until a neutral pH was reached in the rinse water. The prepared sPBAEK samples were filtered and washed several times again. The final products were dried in a vacuum oven for a minimum of 24 h at 80 °C. The degree of sulfonation (DS) of the sPBAEK polymer was determined via elemental analyses using the ratio between the sulfur and carbon (Sulfur/Carbon ratio).

Membrane preparation

The sPBAEK was dissolved in DMAc in order to obtain a 3 wt% solution. The solution was poured into a petri dish and then dried slowly at 60 °C for 24 h. Next, the prepared membrane was dried in a vacuum oven at 100 °C for 48 h in order to remove the residual solvent. The membranes were immersed in a 1 M H₂SO₄ boiling solution for 3 h in order to obtain high acidity and then washed in boiling deionized water for 12 h. The membrane was washed with deionized water several times in order to remove the residual sulfuric acid. The prepared membrane was stored in deionized water at room temperature until use. All membranes had an average thickness of 50 μm.

Characterization

Chemical structure of the polymer

The Fourier transform infrared (FT-IR) spectra of the membrane were collected using a Nicolet IR-200 (Thermo Electron Corp., USA) and were scanned between the wavelengths of 500 and 4000 cm⁻¹ with a resolution of 8 cm⁻¹ and a scan condition of 32 cm⁻¹. The elemental analyses (EA) were performed using an EA1110 (CE Instruments, UK). The degree of sulfonation of the sPBAEK was calculated through measuring the sulfur/carbon ratio obtained from the elemental analyses results.

Water uptake of the membrane

The water uptake was determined through calculating the change in the weight of the membrane before (W_{dry}) and after (W_{wet}) immersion in the deionized water. The water uptake was determined as follows. First, the weight of the dry membrane was measured. Then, the membranes were soaked in deionized water at different temperatures (20, 40, 60, and 80 °C) for 48 h. The membranes were subsequently removed

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