Synthesis and Characterization of Ionic Cross-linkable Sulfonated Poly(arylene ether sulfone)s for Direct Methanol Fuel Cells

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1.INTRODUCTION

Proton exchange membrane (PEM) is one of key components in the direct methanol fuel cell (DMFC), functioning as an electrolyte, transferring protons from the anode to the cathode and providing a barrier for electrons and for fuel and oxygen between the electrodes. Nafion® is the most commonly used PEM materials because of their excellent chemical and mechanical stabilities as well as high proton conductivity. However, they are very expensive and shows high methanol permeability and dramatic decrease of proton conductivity at high temperature above 80℃. Recently, considerable research has been focused on hydrocarbon-based PEM materials. Many sulfonated polymers, such as sulfonated poly(ether sulfone), poly(ether ether ketone), polyimides, poly(arylene ether nitriles), have been prepared for fuel cell membranes due to high proton conductivity, and good processability by simple polycondensation. However, those sulfonated polymers exhibited rather poor performance caused by high methanol permeability and water uptake compared with the Nafion®.

In this study, ionic cross-linkable sulfonated poly(arylene ether sulfone)s (SPAESs) were synthesized by direct polymerization of dihalide and diphenoxide monomers which contained sulfonated groups in dihalide and ionic cross-linkable moieties in diphenoxide monomer,

respectively. The novel copolymers were characterized by NMR and FT-IR, and their thermal stability, mechanical property and inherent viscosity were investigated. In addition, the effects of crosslinking of ionic crosslinked copolymer membranes were evaluated by determining the ion-exchange capacity, water uptake, methanol permeability, and proton conductivity.

2.EXPERIMENTAL

Ionic-crosslinkable SPAES was synthesized by direct copolymerization of 3,3′-disulfonated-4,4′-dichlorodiphenyl sulfone (SDFDPS), 4,4′-dichlorodiphenyl sulfone (DFDPS), and biphenol (BP), 5,5′-bis{2,4-(hydroxyphenyl)benzimidazole] (BHPB) by varing ratio of BP to BHPB.

The reaction mixture was stirred for a few minutes and then refluxed at 150~160℃ for 4 h to remove toluene and water by azeotropic distillation. After refluxing, the reaction temperature was raised to 190℃ and maintained for 1~4h. After cooling the solution to room temperature, the solution was filtered, followed poured into water in order to precipitate. Finally, the polymer was dried under vacuum at 120℃ for 48 h.

The ionic-crosslinkable SPAES membranes in the sodium form were prepared by redissolving the sodium-form copolymer in NMP to afford 7% (w/v), casting directly onto clean glass plate, and drying at 60℃ under a constant purge of N_2 for 24 h and under vacuum at 120℃ for 24 h. The membranes were converted into the acid form by addition into boiling 0.5M H_2SO_4 for 2 h, and then in boiling water another 2 h to remove any residual acid.

3. RESULTS AND DISCUSSION

Novel ionic cross-linkable sulfonated poly(arylene ether sulfone) were synthesized and investigated. The copolymers possess excellent mechanical and thermal stability, which inherent viscosity is higher than 2.0 dL/g. Proton conductivities and IEC values of the ionic crosslinking

copolymers were appeared similar with conventional SPAES copolymers, while water uptake and methanol permeability of the ionic crosslinking copolymers were exhibited significantly low due to formation of the crosslinked polymer network derived from physical interaction of the copolymer chains.

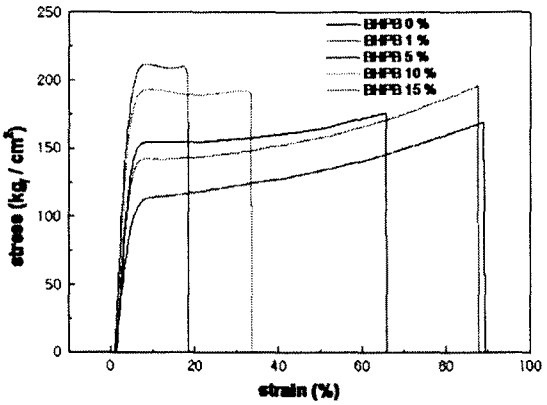

Fig. 1. Influence of BHPB contents on the Tensile test

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