Partially Fluorinated and Tetrasulfonated Poly(arylene biphenylsulfone) Block Coploymers for Fuel Cell Membranes and Their Major Characteristics

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Abstract

The proton exchange membrane is one of the key materials of a polymer electrolyte membrane fuel cell (PEMFC). Among the different types of membranes, Nafion has been primarily used as a standard PEMFC membrane. However, the high cost, low glass transition temperature, and environmental incompatibility of the membranes have impeded the widespread commercialization of PEMFCs. In order to overcome these demerits, a number of alternative membranes have been developed for use in PEMs.[1]

Recently, to improve physical and electrochemical properties the precise control of morphology has been suggested as a strategy. Mutiblock copolymer containing hydrophilic and hydrophobic segments were developed to mimic the nano-separated morphology of Nafion.[2,3] These membranes produced higher conductivity than their randomly sulfonated analogs due to the formation of well-connected water domains. There have recently been many reports of sulfonated block copolymers produced by copolymerization of sulfonated monomers and/or postsulfonation method.[4,5] Related to these reports, we synthesized newly designed and highly sulfonated block copolymers. Here, we report the sulfonated poly(arylene biphenyl ether sulfone) block copolymers and their major characteristics.

We prepared directly a new series of tetrasulfonated perfluorinated poly(biphenylsulfone) block copolymers as proton exchange membrane materials from hydrophilic and hydrophobic polymer via a nucleophilic aromatic substitution reaction. First, hydrophilic oligomers were synthesized through polymerization of tetrasulfonated 4,4'-bis[(4-chlorophenyl)sulfonyl]-1,1'-biphenyl monomer and 4,4'-(hexa-fluoroisopropylidene) diphenol. Second, hydrophobic oligomers were synthesized from decafluorobiphenyl and 4,4'-(hexafluoroisopropylidene) diphenol. Finally we synthesized the block copolymers from hydrophilic and hydrophobic oligomers. The copolymers were characterized by proton NMR, FT-IR, GPC, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) thermograms. ^{1}H-NMR, FT-IR and GPC were used for DS determination and structural analysis. The membranes showed excellent thermal and oxidative stability; e.g., TGA and DSC demonstrated that all sulfonated block copolymers exhibited good thermal stability with an initial weight loss at temperatures above 200℃. The performance of the membranes was measured in terms of water uptake, ion exchange capacity, proton conductivity and single cell test.[6] The conductivity is greatly influenced by ion exchange capacity, temperature, and water activity. The proton conductivity of the block copolymer-70 was 129 mS cm^{-1} at 90□ and 100% relative humidity (Figure 1). The new copolymers, which contain ion conductivity sites on the deactivated positions of the arylene sulfone ether backbone rings, are candidates as new polymeric electrolyte materials for PEMFC.[7,8]

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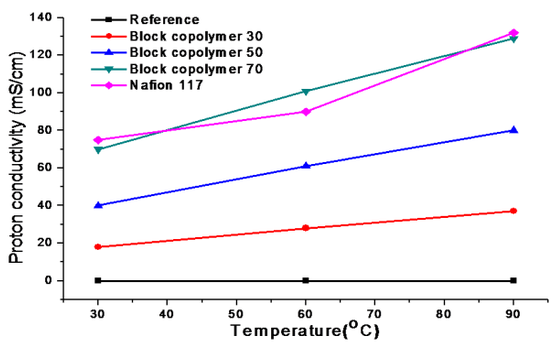

Figure 1. Proton conductivity of polymers for various temperatures at 100% RH.

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