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Crosslinked sulfonated poly(arylene ether sulfone) membranes for fuel cell application

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ABSTRACT

A series of sulfonated poly(arylene ether sulfone) with photocrosslinkable moieties is successfully synthesized by direct copolymerization of 3,3'-disulfonated 4,4'-difluorodiphenyl sulfone (SDFDPS) and 4,4'-difluorodiphenyl sulfone (DFDPS) with 4,4'-biphenol (BP) and 1,3-bis-(4-hydroxyphenyl) propenone (BHPP). The content of crosslinkable moieties in the polymer repeat unit is controlled from 0 to 10 mol% by changing the monomer feed ratio of BHPP to BP. The polymer membranes can be crosslinked by irradiating UV with a wavelength of 365 nm. From FT-IR analysis, it can be identified that UV crosslinking mainly occurs due to the combination reaction of radicals that occurs in conjunction with the breaking of the carbon–carbon double bonds (–CH = CH–) of the chalcone moieties in the backbone. Consequently, a new bond is created to form cyclobutane. The crosslinked membranes show less water uptake, a lower level of methanol permeability, and good thermal and mechanical properties compared to pristine (non-crosslinked) membranes while maintaining a reasonable level of proton conductivity. Finally, the fuel cell performance of the crosslinked membranes is comparable to that of the Nafion 115 membrane, demonstrating that these membranes are promising candidates for use as polymer electrolyte membranes in DMFCs.

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1. Introduction

Direct methanol fuel cells (DMFCs) that use polymer electrolyte membranes (PEMs) are promising candidates as power sources for portable electronics. In a DMFC, the PEM, located between the anode and the cathode, possesses important functions as a proton conductor, a methanol barrier and a mechanical separator between the anode and the cathode [1]. PEMs were first used in fuel cells in the 1960s in the form of a polystyrene sulfonic acid membrane [2]. Currently, DuPont's

Nafion[®] is the most common polymer electrolyte membrane used in the DMFC system. Nafion[®] is known for its excellent proton conductivity, good chemical stability and long-term durability. However, it also has several shortcomings, among which is its high cost, which presents a major obstacle to its widespread application to fuel cells. In addition, a loss of proton conductivity above 80 °C and high methanol crossover impose restrictions on the operating temperature and choice of possible fuels [3]. Consequently, a hydrocarbon membrane with high proton conductivity has been considered as an

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alternative PEM. The main approach, with this material, adopted by many researchers, has involved the attachment of sulfonic acid groups onto various aromatic polymers [4–11] with high thermal, chemical, and oxidative stability along with good mechanical properties and relative affordability. For example, sulfonated polymers such as sulfonated poly(ether ether ketone) (PEEK) [4–7], poly(ether sulfone) (PES) [8–10], polyimides (PI) [11–15], and poly(arylene ether nitriles) [16] have been investigated for fuel cell membranes due to their high proton conductivity and good processability with simple polycondensation. These polymers are non-fluorinated membranes, unlike Nafion, and it is well known that these wholly aromatic polymers have a thermally and chemically stable structure. However, the water uptake and methanol permeability of these polymers are relatively high.

Generally, a crosslinking reaction between polymer chains is considered to be an efficient means of limiting methanol permeability and water uptake and enhancing the stability and mechanical properties of the membranes [17–19]. Thus far, many ionically crosslinked membranes using acid-base blend systems [20,21] and covalently crosslinked membranes using various functional groups [22–24] have been developed. Specifically, Zhong et al. [24] reported crosslinked membranes containing a crosslinkable group comprised of diallyl bisphenol A moieties in the polymer backbone. The water uptake value of the crosslinked membrane was only ~50% of that of the non-crosslinked membranes, while their proton conductivities were decreased by only 90%. In addition, Lee et al. [22,25] reported the synthesis and crosslinking reaction of precursor polymers containing ethynyl moieties at the both ends of the polymer chain as a thermally crosslinkable group. The water uptake decreased by approximately 50% compared to the non-crosslinked membrane without a marked decline in the value of proton conductivity. In addition, the methanol permeability of the membranes showed a lower value ($0.88 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) than that of Nafion 117 ($1.54 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) [25]. These results indicate that the crosslinking of the polymers can be a useful methodology when seeking to improve the physical and electrochemical properties of PEMs.

In this study, we synthesized a series of sulfonated poly(arylene ether sulfone) copolymers containing the chalcone moiety, which possesses high photoreactivity as a photo-crosslinkable functional group and which is randomly located in the polymer backbone. Due to the presence of BHPP as a chalcone moiety, these copolymers could be easily cross-linked by UV irradiation. The properties of pristine and crosslinked membranes were characterized in terms of their proton conductivity, water uptake, methanol permeability, and thermal and mechanical stability. In addition, the cross-linking effects of the resulting membranes are discussed here in detail in terms of their future application as PEM candidates.

2. Experimental

2.1. Materials

4,4'-biphenol (BP) obtained from TCI chemical was recrystallized with ethanol and dried. 4,4'-difluorodiphenyl sulfone

(DFDPS) was purchased from Richem and recrystallized with ethanol. 1,3-bis-(4-hydroxyphenyl)propanone (BHPP) obtained by Claisen–Schmidt condensation of benzaldehyde and acetophenone use either basic or acidic catalysis [26,27]. Anhydrous potassium carbonate (K_2CO_3) was obtained from Aldrich and dried under vacuum at 200 °C before polymerization. A reaction solvent N-methyl-2-pyrrolidinone (NMP) was distilled with calcium hydride onto molecular sieves in vacuum before use.

2.2. Synthesis of the 3,3'-disulfonated 4,4'-difluorodiphenyl sulfone (SDFDPS)

An optimized procedure from previously approaches was developed and used for the synthesis of 3,3'-disulfonated 4,4'-difluorodiphenyl sulfone (SDFDPS) from DFDPS [10]. A typical procedure was as follows: DFDPS (28.7 g, 99 mmol) was dissolved in 60 mL of 30% fuming sulfuric acid in a 100 mL three-neck flask equipped with a mechanical stirrer and a nitrogen inlet/outlet and heated to 120 °C for 6 h. Then, the dark colored reaction mixture was added to deionized ice water. Next, 180 g of sodium chloride was added, which produced a white precipitate identified as the disodium salt of SDFDPS. The powder was filtered and redissolved in 400 mL of deionized water. Then, neutralization to a pH of 7.0 with 2 N sodium hydroxide, filtration, drying and recrystallizing using ethanol : water (2:1) followed the salting out process. Final drying in a vacuum oven at 150 °C for 12 h produced the monomer grade disulfonated compound [10]. The resulting SDFDPS is purified by recrystallization with the mixture of IPA and water (6:1), followed by drying in a vacuum oven at 120 °C for 24 h.

2.3. Typical procedure for the synthesis of the sulfonated poly(arylene ether sulfone) with chalcone moieties (for SPAES-5)

The SPAES-X (X means the mol% of chalcone moieties in the polymer repeat unit) was synthesized by aromatic nucleophilic polymerization which is similar polymerization procedures to those reported previously as shown in Scheme 1 [28]. The typical polymerization procedure for SPAES-5 is as follows: A 4-neck round bottom flask was equipped with a mechanical stirrer, nitrogen inlet and Dean Stark trap fitted condenser. The flask was charged with BP (3.2446 g, 0.95 mol), BHPP (0.2203 g, 0.05 mol), SDFDPS (4.2034 g, 0.50 mol), DFDPS (2.3317 g, 0.50 mol) and potassium carbonate (3.0674 g, 1.21 mol) and NMP (48 mL) was introduced to afford a 20% (w/v) solid concentration. Toluene (24 mL) was used as an azeotropic agent. The reaction mixture was heated to 150 °C in an oil bath and the toluene was allowed to reflux for 4 h to remove any water present from hydrated monomers. After 4 h, toluene was removed and the reaction temperature was slowly increased to 190 °C. The reaction was allowed to proceed for 10 h. By the end of the reaction, the solution was cooled down to room temperature and diluted with NMP enough to allow easy filtering. The copolymer was precipitated with deionized water and washed with deionized water several times. After, the copolymer was vacuum-dried at 120 °C for 24 h.

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