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Proton exchange membranes based on sulfonated poly(arylene ether ketone) containing triazole group for enhanced proton conductivity



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ABSTRACT

Sulfonated poly(arylene ether ketone) (SPAEK) containing carboxylic acid groups at the pendant position was synthesized. The proton conductivity was enhanced over a wide range of humidity by grafting 1H-1,2,3-triazole (TRI), a heterocyclic protogenic reagent, on SPAEK via the pendant carboxylic acid. The proton conductivity, water uptake, and thermal and mechanical stability of the TRI-grafted SPAEK membranes (SPAEK–TRI) were measured and compared against those of a commercial Nafion[®] 117 membrane. The proton conductivity increased as the degree of sulfonation (DS) increased, and this effect was further enhanced by the introduction of TRI. The SPAEK–TRI membrane with 40% DS (SPAEK40–TRI) exhibited an even higher proton conductivity than Nafion[®] 117 over the entire range of relative humidity (RH). The SPAEK40–TRI membrane exhibited a tensile strength of 16.52 MPa, which was similar to that of Nafion[®] 117, and all of the membranes prepared in this study were thermally stable at up to 200 °C. The ion cluster dimensions for SPAEK40–TRI and SPAEK50–TRI were of 4.52 nm and 4.91 nm, respectively, which are larger than that of Nafion[®] 117, 3.36 nm. This difference is attributed to the higher water uptake in the SPAEK–TRI membranes than Nafion[®] 117.

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1. Introduction

Many alternative power sources to replace traditional fossil fuels have been proposed as a result of critical issues related to the increase in power consumption and the resulting pollution. A polymer electrolyte membrane fuel cell (PEMFC) has potential as an alternative source of energy due to its high energy conversion efficiency, green emissions, low-noise operation, and low maintenance costs [1–4].

A polymer electrolyte membrane is a core component of a PEMFC system. Nafion is a well-known commercial polymer electrolyte membrane for PEMFC that exhibits excellent chemical and mechanical stability in addition to high proton conductivity. Although its proton conducting properties are acceptable, its wider use is limited as a result of the inherent weakness associated with high purchasing cost and reduced conductivity in a condition with a reduced humidity [5–7]. Although a number of hydrocarbon-based polymer electrolytes have been proposed to replace Nafion, there is still a challenge for enhancement of proton conductivity for commercialization. The high proton conductivity can be established through a high DS [8,9]. Although the presence of water is a prerequisite not only to solvate protons but to promote their mobility, too high DS can sometimes lead to excessive

membrane swelling along with mechanical failure and a high fuel crossover [10–13].

An amphoteric material is an excellent proton carrier that exhibits both proton donating and accepting properties that are associated with a high degree of self-dissociation and a high dielectric constant. It shows high proton conductivity, even at a low humidity or water uptake (in a water deficiency condition). It operates in a stable manner over a wide range of temperatures [14,15], but it still possesses dynamic proton transporting properties that are similar to those of water [16,17]. Therefore, several amphoteric N-heterocycles, including pyrazole, benzimidazole, imidazole, and oxadiazole, have been studied as protogenic agents in PEMFC [18–20]. One of the major weaknesses for their utilization in fuel cells is that leakage occurs in the membranes after long-term operation, leading to a significant reduction in the proton conductivity of the membrane [21,22]. A couple of approaches have been developed to overcome this problem. One is to immobilize the heterocyclic molecules in the oligomers or macromolecules [23,24]. Large host molecules help the N-heterocyclic molecules become immobilized and support their aggregation through a rapid breaking and forming processes of the hydrogen bonds. Since the molecular mobility of the N-heterocycles is lessened, the ion conductivity of the immobilized systems is slightly lower than that of pristine N-heterocycles. The other approach involves bonding the N-heterocyclic molecules directly onto the polymer chain [25,26]. The confined number of N-heterocycle

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groups that are covalently bonded controls the proton transfer rate of the polymer membrane. Since the proton conductivity of a polymer membrane based on only N-heterocycle proton carriers cannot usually satisfy the requirements for PEMFC, the synthesis of polymers containing two types of proton carriers, sulfonic acid and N-heterocycle groups, may be an interesting approach to improve proton transport, even at a low humidity or low water uptake [27–29].

In our group, sulfonated poly(arylene ether ketone) (SPAEK) has been recently identified as one of the major concerns to prepare polyelectrolyte membranes for fuel cells as a result of its excellent physical properties and feasible processability [30–32]. PAEK has been frequently sulfonated through a simple post-sulfonation method. A long-term treatment with concentrated sulfuric acid at a high temperature, however, introduces some problems associated with polymer degradation and inaccurate control of the DS. The SPAEK with a precise DS was possibly established through a direct synthesis from an adjusted feed ratio of sulfonated monomer to nonsulfonated monomer [33,34]. TRI is a promising proton carrier among N-heterocycles. While its chemical structure is very similar to imidazole, its melting point, 120 °C is higher than that of imidazole, 89 °C because of its strong hydrogen bonds. It was reported that when it was tethered to a polymer, its strong self-dissociation property in acidic condition provided highly mobile proton charge carriers and thus increased the proton conduction property via structural diffusion (Grotthuss mechanism) in anhydrous condition [35–37]. Based on this background, the present study proposes the synthesis and characterization of a new PAEK proton exchange membrane that contains both sulfonic acid and TRI proton carriers. The SPAEK with the pendant carboxylic functional group was first synthesized from sulfonated and non-sulfonated monomers. TRI was possibly grafted onto the SPAEK through the amide coupling reaction. This grafted TRI is expected to enhance the proton transport via structural diffusion in association with the continuous proton defects [35]. Several important properties, such as the proton conductivity, water uptake, and thermal and mechanical stability, were investigated for the TRI-grafted SPAEK membranes (SPAEK–TRI), and the results were compared against those obtained for commercial Nafion[®] 117 membrane.

2. Experimental

2.1. Material

5,5-Carbonylbis(2-fluorobenzene-sulfonate) was obtained from Yan Jin Technology Co., Ltd. (Tianjin, China) and was used without further purification. Dimethyl sulfoxide (DMSO), 4,4-bis(4-hydroxyphenyl)valeric acid, 4,4'-difluorobenzophenone, potassium carbonate (K₂CO₃), toluene, N-hydroxysuccinimide (NHS), N,N'-dicyclohexylcarbodiimide (DCC), 1 H-1,2,3-triazole (TRI), N,N-dimethyl acetamide (DMAc), dimethylformamide (DMF), hydrochloric acid (HCl), methanol, isopropanol, and tetrahydrofuran (THF) were purchased from Aldrich (Milwaukee, WI, USA) and used without further purification.

2.2. Synthesis of SPAEK

5,5-Carbonylbis(2-fluorobenzene-sulfonate), 4,4'-difluorobenzophenone, and 4,4-bis(4-hydroxyphenyl)valeric acid were reacted together via the nucleophilic aromatic substitution reaction to obtain SPAEK containing carboxylic groups at the pendant sites. The number of sulfonated groups per repeating unit was controlled by adjusting the molar ratio of the sulfonated monomer (m) to the nonsulfonated monomer (n). In this work, the SPAEK

samples were synthesized with three different mole percentages of sulfonated monomer of 40%, 50%, and 60%. The resulting DS thus were 40%, 50%, and 60%, correspondingly. As an example, SPAEK40 (DS=40%) was prepared as follows: a Dean Stark trap, a nitrogen gas inlet, dry DMSO (45 g), 4,4-bis(4-hydroxyphenyl)valeric acid (2.95 g, 10 mmol), toluene (40 g), and K₂CO₃ (3.5 g, 0.25 mol) were added at room temperature to a 250 mL four-necked round bottom flask equipped with a mechanical stirrer and stirred for 8 h. The reaction mixture was slowly heated to 145 °C for 4 h. The water byproduct was removed from the reaction mixture through azeotropic distillation with toluene. After cooling the mixture to room temperature, 4,4'-difluorobenzophenone (1.309 g, 6 mmol), 5,5-carbonylbis(2-fluorobenzene-sulfonate) (1.689 g, 4 mmol) were placed into the mixture, followed by heating to 150 °C for 2 h to remove the residual water. The temperature was then raised to 168 °C and stirring continued for 24 h until the precipitate appeared in the solution. A solid-liquid phase separation occurred after the product mixture had been cooled down to room temperature. The solid was filtrated and then completely dissolved in a mixture of THF (25 mL) and concentrated HCl solution (7 mL). The polymer solution was dropped into an excess amount of isopropanol to form white precipitates. The solid precipitate was collected via vacuum filtration, washed twice with 500 mL of isopropanol and 500 mL of distilled water consecutively, and then dried in a vacuum at 80 °C for 24 h to obtain the final SPAEK powder. The average yield of the final product was of 88%.

2.3. Synthesis of SPAEK–NHS

The SPAEK–NHS was synthesized to activate the pendant carboxylic groups using an excess amount of DCC and NHS. The SPAEK–NHS was then reacted with amine to form an amide linkage with a much higher yield. The details of the procedure used to synthesize SPAEK40–NHS are as follows: 2.64 g (0.005 unit mol) SPAEK40 and 0.69 g (0.006 mol) NHS were added into a 25 mL DMF and stirred for 4 h to obtain a homogeneous solution. 1.235 g (0.006 mol) of DCC were then added to the reaction mixture and stirred at room temperature for 12 h, and then at 40 °C for another 12 h. A clean polymer solution was obtained after removing all of the suspended solids via filtration, and the polymer solution was dropped into 500 mL of isopropanol to form a white precipitate. This precipitate was then washed twice with isopropanol and methanol to consecutively remove all unreacted reagents. A dry SPAEK–NHS product was obtained after vacuum drying at 40 °C for at least 48 h. The reaction yield was of about 95%. The SPAEK–NHS intermediates with different DS were synthesized using the same procedure, as shown in Fig. 1.

2.4. Preparation of membrane

A series of SPAEK–TRI membranes with different DS were prepared. The TRI were fully grafted on the pendant site. SPAEK–NHS (6.75 × 10⁻⁴ unit mol) was added to a 10 mL vial and dissolved completely with 5 mL DMAc for 5 h. 4.3 × 10⁻² mL of TRI (7.43 × 10⁻⁴ mol) were added to the solution under vigorous stirring for 24 h at room temperature. The mixture was then cast on a glass plate, and the membranes were fabricated by removing the solvent at 85 °C for 12 h in an oven. The membrane was then placed in a vacuum oven at 85 °C for 24 h to completely remove the solvent. The SPAEK–TRI membrane was then immersed in 2.0 N HCl solution at room temperature for 12 h to change the membrane into an acidic form. A clean membrane was then obtained by washing out the HCl and NHS by immersing it in hot deionized (DI) water for 5 h. This process was repeatedly conducted until a neutral pH had been reached. The membranes that were

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