



Enhanced proton conductivity of sulfonated poly(arylene ether ketone sulfone) for fuel cells by grafting triazole groups onto polymer chains



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ABSTRACT

A series of triazole-grafted sulfonated poly(arylene ether ketone sulfone)s (SPTs) were fabricated via an amide coupling reaction between 3-amino-1,2,4-triazole and carboxylic acid group. The degree of sulfonation (DS) was set to 80% for preventing excessive swelling. The chemical structures of synthesized polymers were characterized by Fourier transform infrared spectroscopy (FT-IR) and ¹H NMR spectroscopy. The triazole group affected the properties of membranes dramatically. Increasing the triazole group content was conducive to promoting the thermal property and oxidative stability. And all SPT membranes retained above 92% of their weight after the test in Fenton's reagent at 80 °C for 1 h. The swelling ratio of SPT-3 membrane was only 12.66% and it was lower than that of C-SPAEEKS-3 membrane at 100 °C. It was also found that the proton conductivity was distinctly improved by introducing triazole groups and the SPT-4 membrane exhibited a proton conductivity of 0.166 S cm⁻¹ at 120 °C, which was larger than that of Nafion 117. In addition, all SPT membranes showed higher proton conductivity when compared with C-SPAEEKS-3 membranes over the range of relative humidity from 20% to 90% at 80 °C.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been extensively explored for the next generation of energy conversion device, largely due to their low pollution, high power density and high energy conversion efficiency [1]. However, there are still many important issues that have to be addressed for PEMFC. Perfluorosulfonic acid membranes, such as DuPont's Nafion, are the most widely used proton exchange membranes (PEMs), which have high proton conductivity and extraordinary chemical stability at a moderate temperature. But high cost, high methanol permeability, and reduced proton conductivity at higher temperatures (above 80 °C) have limited their more broad use for practical applications [2]. Therefore, a host of sulfonic acid functionalized materials with high proton conductivity and appropriate cost have been reported to alternate Nafion, including sulfonated poly(arylene ether sulfone) [3–5], sulfonated poly(arylene ether ketone) [6–8], sulfonated poly(phenylene oxide) [8,9], sulfonated poly-benzimidazole [10,11], sulfonated polyoxadiazole [12] and sulfonated polyimide [13,14]. However, those proton exchange

membranes with high proton conductivity generally have a high degree of sulfonation, leading to an excessive swelling ratio of membranes along with mechanical failure and a high fuel permeability [15,16].

Kreuer et al. [17] describes that the amphoteric N-heterocycles exhibit proton donor and acceptor properties, meanwhile show high degree of self-dissociation and high dielectric constant, such as pyrazole [18], imidazole [19], benzimidazole [20], oxadiazole [21] and triazole [22]. Among them, triazole groups acted as proton carrier have been widely developed for PEMs and the nitrogen atoms of triazole rings can interact with strong acid groups, including sulfonic and phosphonic acid [23]. Acid-doped triazole-based systems offer the possibility of high proton conductivity at high temperatures (above 100 °C) and exhibit less dependent on water content than sulfonic acid functionalized materials [24]. One of the major weaknesses for triazole-based systems is leakage during long-term fuel cell operation, which, in turn, leads to the significant decline of proton conductivity [25]. To overcome this issue, many strategies have been explored. Of all the strategies, immobilizing triazole groups in the oligomers or polymer backbones is a typical example [26]. Nevertheless, polymer backbones are so large that their mobility is poor. As a result, the triazole groups cannot transport protons effectively and perform reduced proton conductivity. The other approach is to bind the triazole groups onto polymer side-chain by using a covalent attachment

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reaction [24]. While, the PEMs containing only triazole groups could not meet requirements for PEMFC, synthesizing a new polymer electrolyte membrane based on both the sulfonic acid and triazole groups will enhance proton conductivity at high temperatures or low relative humidity operating conditions.

In this study, the sulfonated poly(arylene ether ketone sulfone)s with carboxylic acid pendant (C-SPAEEKS) were initially developed, and then the 3-amino-1,2,4-triazole was grafted onto C-SPAEEKS polymer chain by an amide coupling reaction, thus a novel sulfonated poly(arylene ether ketone sulfone) containing both triazole and sulfonic acid groups was obtained. The focus of this study was to immobilize triazole groups onto the sulfonated poly(arylene ether ketone sulfone) polymer chains, and the triazole group acted as a proton carrier was expected to promote proton conductivity according to Grotthuss mechanism at high temperatures or low relative humidity. Meanwhile, the degree of sulfonation (DS) was fixed at 80% for controlling the swelling ratio. To verify this idea, water uptake and swelling ratio, thermal property and mechanical property, ion exchange capacity and oxidative stability, proton conductivity of the triazole-grafted sulfonated poly(arylene ether ketone sulfone) (SPT) membranes were investigated respectively in this paper.

2. Experimental

2.1. Materials

Disodium-3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS) and 4-carboxyphenyl hydroquinone (4C-PH) were prepared in laboratory on the basis of a similar method described by Na and Li et al. [27]. 4,4'-difluorodiphenylmethane (99% purity) and 2,2-Bis(4-hydroxyphenyl)propane (bisphenol A) (99%, GC grade) were purchased from Shanghai Macklin Biochemical Co. Ltd. N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDCI) (98% purity), N-Hydroxysuccinimide (NHS) (98% purity), 3-amino-1,2,4-triazole (96% purity) were all received from Aladdin Chemical Reagent Co. Ltd., China. Tetramethylenesulfone (TMS), dimethyl sulfoxide (DMSO) (AR grade), toluene (AR grade), HCl, anhydrous K_2CO_3 (AR grade) were provided by Beijing Chemical Reagent Company. All these solid chemicals were dried under vacuum at 60 °C for 24 h prior to their use and all experiments were performed in deionized water.

2.2. Synthesis of C-SPAEEKS copolymers

The C-SPAEEKS copolymers were synthesized by nucleophilic aromatic substitution reaction based on the works of Xu et al. [28]. The degree of sulfonation (DS) which was the number of sulfonic groups per repeating unit, was fixed at 80% by setting the ratio between 4,4'-difluorodiphenylmethane and SDCDPS. The copolymers were named as C-SPAEEKS-*x*, where *x* referred to the mole fraction of 4C-PH in the total feed ratio. For example, C-SPAEEKS-3 was synthesized as follows:

SDCDPS (0.008 mol), 4,4'-difluorodiphenylmethane (0.012 mol), 4C-PH (0.006 mol), bisphenol A (0.014 mol) and anhydrous K_2CO_3 (0.025 mol) were added to a 100 mL three-necked flask equipped with a mechanical stirrer, and reflux condenser under nitrogen atmosphere. Next, TMS (20 ml) and toluene (15 ml) were added and here the toluene was used as the azeotropic agent. The reaction mixture was refluxed at 130 °C for 4 h to remove the water produced in reaction. Then, the toluene was evaporated completely at 150 °C. Moreover, the temperature of the reaction mixture was raised gradually and maintained at 190 °C for 20 h. After the polymerization, the resulting viscous mixture was poured into deionized water. The obtained copolymers were

washed with boiling water for several times to remove the water-soluble salts and residual solvents. Then the copolymers were dried at 80 °C for 24 h in a drying oven. Note that in this case C-SPAEEKS-5 was mechanically very weak and it was hard to satisfy testing requirements for PEMs.

2.3. Synthesis of SPT copolymers

Triazole-grafted polymers were synthesized by grafting 3-amino-1,2,4-triazole to C-SPAEEKS-*x* polymer chain through an amide coupling reaction. The formulations of triazole-grafted polymers were denoted as SPT-*y*. Here, *y* was the mole content of 3-amino-1,2,4-triazole in the SPT-*y* copolymers. For example, SPT-3 was synthesized as follows:

Firstly, C-SPAEEKS-3 (0.01 mol) and DMSO (30 ml) were added into a 100 mL three-necked flask equipped with a mechanical stirrer, kept stirring until C-SPAEEKS-3 dissolved completely. Then, EDCI (0.0045 mol) was added and waited for 30 min to activate the carboxyl at 3 °C by ice bath. Next, 3-amino-1,2,4-triazole (0.0045 mol), NHS (0.0045 mol) were added to the flask and continued to stir for 12 h at ambient temperature. The resulting viscous solution was purified by dialyzing in the deionized water for 72 h to remove the micromolecule impurities. The dialysate was regarded as SPT-3, and it was dried in a vacuum oven at 80 °C for 24 h. The synthesis route of SPT-*y* is shown in Fig. 1.

2.4. Membrane preparation

The C-SPAEEKS-*x* and SPT-*y* membranes were obtained based on the solvent casting method. The SPT-*y* copolymers were casted onto a glass plate from their DMSO solution (10 wt%) and dried at 60 °C for 48 h in a vacuum oven. After that, the membranes were acidified in 2 M HCl for 24 h to obtain the acid-type membranes. Then the acid-type membranes were washed by deionized water for several times to remove any excess acid. Finally, the membranes were dried in a vacuum oven at 60 °C for 24 h. The thickness of the membranes ranged from 40 μm to 80 μm.

2.5. Characterization

Fourier transform infrared spectroscopy (FT-IR) analyses were recorded on a Nicolet Avatara-360 spectrometer, the scan range ranged from 4000 cm^{-1} to 650 cm^{-1} . 1H NMR spectra were performed using a 400 MHz Bruker Avance III spectrometer with deuterated dimethyl sulfoxide (DMSO- d_6) as the solvent and tetramethylsilane as the internal standard at 298 K. Thermogravimetric analyses (TGA) were employed to evaluate thermal stability of membrane with a Pyris 1TGA (Perkin-Elmer) analyzer at a heating rate of 10 °C min^{-1} from 40 °C to 600 °C in nitrogen atmosphere. Transmission electron microscopy (TEM) images of the membranes were obtained using a JEM-1011 electron microscope. The TEM samples were cut into small pieces and stained by soaking in silver nitrate solution at room temperature for 24 h. Then the stained samples were washed repeatedly by deionized water and dried under vacuum at 60 °C for 24 h. Finally, the stained samples were dissolved into DMSO and placed on a copper grid for observation.

2.6. Characterization of membranes

2.6.1. Water uptake and swelling ratio

The water uptake and swelling ratio of membranes were measured by using the following method: the sample films (1 cm × 1 cm) were all dried in a vacuum oven at 80 °C for 24 h prior to the measurements. The dried films were soaked in deionized water at the desired temperature for 48 h until the

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