



Phosphoric acid-doped poly(ether sulfone benzotriazole) for high-temperature proton exchange membrane fuel cell applications

Kaili Wang^a, Li Yang^{a,*}, Wenxuan Wei^a, Lin Zhang^b, Guanjun Chang^{a,*}

^a State Key Laboratory Cultivation Base for Nonmetal Composite and Functional Materials & School of Material Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, PR China

^b Research Center of Laser Fusion, China Academy of Engineering Physics, 621900 Mianyang, PR China



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ABSTRACT

A novel proton exchange membrane poly(ether sulfone benzotriazole) (PESB) was synthesized by polycondensation of 4,4-difluorodiphenylsulfone and 4-Hydroxy-1H-benzotriazole. The polymer structure was characterized by FT-IR, NMR and elemental analysis. The results were well consistent with the proposed structure. We introduced large amounts of benzotriazole into the polymer main chains by facile nucleophilic reaction, and proton transfer could be achieved through acid-base interactions of benzotriazole with phosphoric acid (PA). Compared with PA-doped m-PBI, the PA-doped PESB membrane showed higher proton conductivity due to the strong acid-base interactions between the benzotriazole and PA. The PA uptake of 221% PESB membrane displayed the proton conductivity of 0.073 S cm^{-1} at $160 \text{ }^\circ\text{C}$, which was higher than that of m-PBI. The fuel cell performance of the PA-doped PESB was evaluated and was obtained a maximum peak power density of 427 mW cm^{-2} with an open cell voltage of 0.91 V at $160 \text{ }^\circ\text{C}$.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have drawn people's much attention due to high efficiency and cleanliness compared with traditional energy sources, and it is acknowledged as the best candidate for next generation electrical vehicles [1]. The proton exchange membrane (PEM) is the crucial materials of the PEMFCs, due to its dual role of conducting protons and separating fuel and oxidizing agent [2–7]. PEM must possess a few characteristics such as high proton conductivity, outstanding oxidative stability, excellent thermal stability and so on. Nafion, which is widely used in perfluorosulphonic acid membrane, has outstanding performance. Despite considerable effort, the availability of Nafion is limited to a certain extent for some reasons, including high costs and low proton conductivity at high operating temperatures above $80 \text{ }^\circ\text{C}$ due to the dehydration of the membrane [8]. Accordingly, the development of a new strategy for construction of alternate membranes with high proton conductivity, outstanding mechanical, excellent thermal and chemical properties at high operating temperature still remains an attractive and promising goal [9–11].

Phosphoric acid (PA) doped Poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole] (m-PBI) PEM for used in high temperature PEMFCs has some advantages of the high proton conductivity, good fuel cell performance in no humidification above $80 \text{ }^\circ\text{C}$ and its unique heterocyclic structure,

which could act as a proton donor and acceptor simultaneously [9,12–15]. Recently, benzotriazole in the polymer side chains has been used in PEMFCs. The -N=N- of benzotriazole group can be considered as a new base site, and this base site could accelerate proton transfer more easily through the Grotthuss mechanism. Meanwhile, proton transfer can be achieved through strong acid-base interactions between the PA and the -N=N- base sites of benzotriazole at high temperature [16,17]. In this article, we introduce large amounts of benzotriazole units into the polymer main chains by a facile nucleophilic substitution polycondensation reaction. We expect that proton migration and transfer processes take place within the hydrogen bond network, which is formed by PA with -N=N- base sites or PA because of the strong acid-base interactions between PA and the -N=N- base sites at high temperature, as shown in Fig. 1.

2. Experimental

Materials, measurements, acid doping measurements, proton conductivity measurements, oxidative stability measurements and Membrane Electrode Assembly (MEA) fabrication and fuel cell test are included in Supporting information.

* Corresponding authors.

E-mail addresses: yanglichem628@126.com (L. Yang), gjchang@mail.ustc.edu.cn (G. Chang).

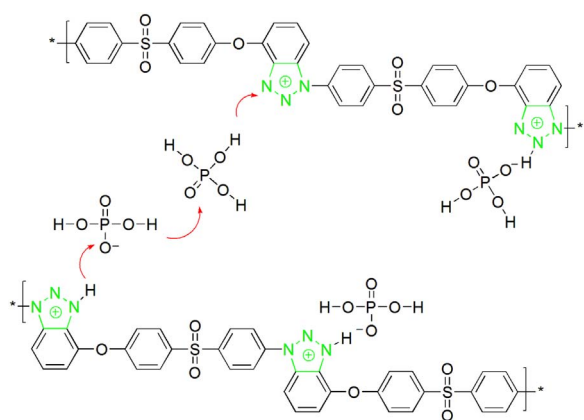


Fig. 1. Schematic illustration of proton conduction between poly(ether sulfone benzotriazole) (PESB) and PA.

2.1. Synthesis of Poly(ether sulfone benzotriazole) (PESB)

A three-necked flask was evacuated and backfilled with a magnetic stirrer, an argon, and a water-cooled condenser. The flask was charged 4,4-difluorodiphenylsulfone (2.0 mmol), 4-Hydroxy-1H-benzotriazole (2.0 mmol), K_2CO_3 (4 mmol). The reaction was stirred in the reaction flask for about 10 min. Then N-Methylpyrrolidinone (NMP 6 mL) was added under argon atmosphere. The reaction mixture was evacuated and flushed with high-purity argon. This procedure was repeated three times. The flask was immersed in a 160 °C oil bath under stirring for 3 h, and then the temperature was increased to 190 °C under stirring for 3 h. The polymer solution was cooled to room temperature, then the polymer solution was dropped into water, filtered, washed with water and methanol and dried 100 °C under vacuum yield (yield: 96%). Anal. calcd. for $(C_{18}H_{11}N_3O_3S)_n$ (349.05) $_n$: C, 61.88; H, 3.17; N, 12.03; found: C, 61.68; H, 3.20; N, 11.98.

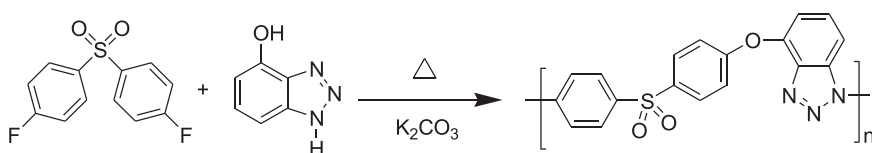
2.2. Membrane preparation

The polymer PESB was dissolved in N-Methylpyrrolidinone (NMP) to form a 5–10 wt% solution at 60 °C. Then the solution was filtered and cast on a clean glass sheet by dropper. The solvent was evaporated in a vacuum oven at 90 °C for 12 h. Dried PESB membrane was immersed in the water and removed from the glass plate automatically. The membrane was then dried to a constant weight at 100 °C for 12 h in the vacuum oven. Thickness of the PESB membranes was the 48 μ m.

3. Results and discussion

3.1. Characterization of polymer

A novel proton exchange membrane poly(ether sulfone benzotriazole) (PESB) was synthesized by polycondensation of 4,4-difluorodiphenylsulfone and 4-Hydroxy-1H-benzotriazole. (Scheme 1). The polycondensation proceeded smoothly with a high yield (96%). The molecular weight of the resulting PESB was measured by gel permeation chromatography (GPC). The M_n and M_w values were shown in Table S1. The M_n value was 126,000 and the M_w value was 273,000. The polydispersity was 2.17. Moreover, the achieved polymer was characterized spectroscopically. The 1H NMR spectrum of PESB was



Scheme 1. The synthetic route for the poly(ether sulfone benzotriazole) (PESB).

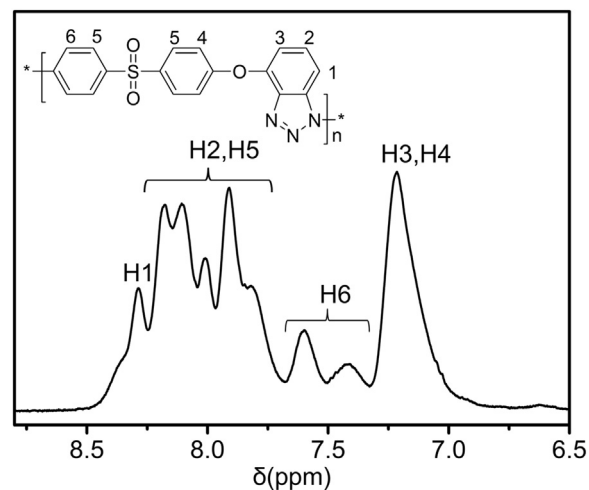


Fig. 2. 1H NMR spectrum of the poly(ether sulfone benzotriazole) (PESB) recorded in $DMSO-d_6$.

given in Fig. 2 ($DMSO-d_6$). The signal appearing at 8.33 ppm was assigned to H_1 , which was attached close to triazole ring. The peaks at around δ 7.75–8.30 ppm were assigned to the aromatic protons (i.e. H_2 and H_5), which were shifted downfield due to the electron-withdrawing nature of sulfone and triazole units. Fig. 3 showed the FT-IR spectrum of PESB. The absorption band around 1590 cm^{-1} was assigned to a $C=C$ stretching vibrations of benzene ring. The bands at 1036 cm^{-1} and 1244 cm^{-1} could be identified as symmetrical and asymmetric of the C-O stretching vibration, respectively. In addition, the 1H - 1H COSY and ^{13}C NMR spectra also demonstrated the precise structure of the polymer and were in good agreement with the results from IR and 1H NMR analyses (Figs. S1 and S2).

3.2. Phosphoric acid (PA) uptake

The PA doped PESB membranes were obtained by completely immersing the membranes in a concentration range of 60–80 wt% at room temperature for 120 h (Fig. 4). The results indicated that PA uptake increased with the PA concentration of 60–80 wt%. PA could be steadily absorbed by the alkaline groups of benzotriazole in the polymer chain. Thus, the acid uptake of PESB was slightly higher than m-PBI under the same doping acid concentration. The PESB membranes had capability to retain the acid molecules via the interactions of PA and $-N=N-$ base sites (i.e. H_2PO_4-H and $-N=N-$ groups in PESB) [18–21]. The large amounts of $-N=N-$ base sites of the PESB main chains could enhance the acid-base interactions between the PA and the base sites, and therefore increase its acid uptake. After 120 h, the PA uptake of the PESB membranes achieved equilibrium, and PA uptakes of the PESB and m-PBI membranes could reach maximum content of 221% and 215% in 80% PA concentration, respectively. PA uptake of PESB membrane was higher than m-PBI because of the strong acid-base interactions between $-N=N-$ and PA.

3.3. Thermal and mechanical properties

Thermal stability has major effect on the application of polymer materials, especially polymer materials are used in high temperature environments. The thermal stability of the PESB polymer was evaluated

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