Journal of Membrane Science 476 (2015) 87–94

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Preparation and properties of the cross-linked sulfonated polyimide containing benzimidazole as electrolyte membranes in fuel cells

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ARTICLE INFO

Article history:
Received 16 April 2014
Received in revised form
27 October 2014
Accepted 15 November 2014
Available online 22 November 2014

Keywords:
Proton exchange membrane
Sulfonated polyimide
Benzimidazole
Cross-linked

ABSTRACT

Sulfonated polyimides containing benzimidazole (SPIBI) with varies sulfonation degree (DS) are synthesized by 1, 4, 5, 8-naphthalenetetracarboxylic dianhydride (NTDA), 5-amino-2-(4-aminophenyl) benzimidazole (APABI) and 4, 4′-diaminodiphenyl ether-2, 2′-disulfonic acid (ODADS). The cross-linked SPIBI membranes can be prepared with 3, 3′, 5, 5′-tetramethyl-diphenyl diglycidyl ether (TMBP) as cross-linker during the following thermal treatment process. By adjusting the DS of SPIBI and the weight ratio of the crosslinker, a series of the cross-linked membranes are obtained. All the obtained membranes exhibit good cross-linking densities for the gel fractions higher than 75%. Compared to pure SPIBI membranes, the mechanical properties, oxidative and hydrolytic stabilities of the cross-linked membranes are improved significantly. For instance, the tensile strength of the cross-linked membranes is in the range of 53.6–108.4 MPa, the anti-free oxidative stability of SPIBI-80-15 (with a cross-linker content of 15 wt% and DS of 80%) is almost four times of the data of the uncross-linked SPIBI-80 which is tested by Fenton′s reagent (3% H_2O_2, 3 ppm Fe^{2+}) at 80 °C. SPIBI-80-15 also exhibits much higher hydrolytic stability for more than 1440 h, while that of SPIBI-80 is 27 h in the same condition. The proton conductivity of the cross-linked membranes ranges from 10^{-3} to 10^{-2} S cm^{-1}.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been considered as the potential future power sources for portable uses including vehicles, mobile communication, and so on. As one of the key components of the PEMFC, proton exchange membrane (PEM) should have the merits of excellent stability and high proton conductivity [1–4]. Until now, the only practically used material as PEM is the perfluorinated sulfonic acid polymers, such as Nafion®, due to their high proton conductivity, excellent chemical stability, and good mechanical property. However, they still have some drawbacks, for instance, high costs, poor dimensional stability, as well as low mechanical property at high temperature and low humidity [5–7]. Several approaches for enhanced PEMs have been developed. Sulfonated aromatic hydrocarbon polymer is one of the alternative materials [8].

Several kinds of the sulfonated polymers have been investigated as proton-conducting membranes, including polystyrene copolymers, poly(arylene ether sulfone)s, poly(arylene ether ketone)s, polyimides and polybenzimidazoles, etc. [9–19]. Sufonated polyimides (SPI) are one of the most promising alternatives for PEM due to their high mechanical strength, unique thermal stability and excellent chemical stability [20,21]. Especially six-membered (naphthalenic) SPI have excellent chemical and thermal stability compared to those of five-membered ring polyimide. Polybenzimidazole (PBI) as a proton conducting material for PEMFC has also attracted much attention for their excellent oxidative stability, and good mechanical property, high proton conductivity at high temperature and low humidity when doped with acid [22]. In addition, cross-linking is one of the most important methods to enhance the chemical stability of the polymers. Therefore, the introduction of the benzimidazole group and cross-linking into the main chain of the SPI systems should be a good candidate to improve the performance of the SPI in PEMFCs.

In this paper, we synthesized a series of sulfonated polyimides containing benzimidazole group (SPIBI) with controlled sulfonation degree between 80% and 120% and prepared cross-linked membranes of SPIBI by TMBP through the N–H of the benzimidazole group in SPIBI reacted with the epoxy groups of the TMBP and formed the polymer network within the membranes during the membrane preparation. The mechanical properties, proton conductivities, oxidative and hydrolytic stabilities of these membranes were also investigated.

2. Experimental

2.1. Materials

3, 3′, 5, 5′-tetramethyl-diphenyl diglycidyl ether (TMBP) was provided by Gansu Research Institute of Chemical Industry; 4,4′-diaminodiphenyl ether (ODA) was purchased from Sinopharm

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http://dx.doi.org/10.1016/j.memsci.2014.11.023
0376-7388/© 2014 Published by Elsevier B.V.

Chemical Reagent Co., and was recrystalized in ethanol; NTDA was purchased from Alfa aesar Co.; 5-amino-2-(4-aminophenyl) benzimidazole (APBIA) was purchased from Zhejiang Dragon Chemical Group Co.; *m*-cresol was distilled under reduced pressure. Triethylamine, methanol (99.7 wt%, AR grade), Dimethylsulfoxide (DMSO, AR grade), Benzoic acid (CR grade) and acetone were supplied by Shanghai Chemical Reagent Co. 4,4′-diaminodiphenyl ether-2,2′-disulfonic acid (ODADS) was synthesized from ODA according to literature [23].

2.2. Synthesis of sulfonated copolyimide

The sulfonated polyimides containing benzimidazole (SPIBI) with various sulfonation degree were synthesized by ODADS, APBIA and NTDA via "one-step" polymerization. A synthetic procedure of the SPIBI is described below using starting monomers of NTDA/ODADS/APBIA (6/3/3, mol/mol) as an example: in a 100 mL of dried 3-necked flask with a mechanical stirring device, 3.0 mmol ODADS, 24 mL *m*-cresol and 1.0 mL Et_3N were successively added under nitrogen flow. After ODADS was completely dissolved, 3 mmol of APBIA, 6.0 mmol NTDA and benzoic acid were added. The mixture was stirred at room temperature for 10 min and then heated at 80 °C for 4 h and 180 °C for 20 h. When the solution viscosity apparently increased during the dehydration, several of *m*-cresol was added to dilute the solution and the reaction was continued for a further 4 h. After cooling to 100 °C, additional 10 mL of *m*-cresol was added to dilute the highly viscous solution, which was then poured into 200 mL of acetone. The fiber-like precipitate was filtered off, washed with acetone by the soxhlet extraction to remove the solvent thoroughly, and dried in vacuum at 60 °C for 24 h.

The chemical structure of the SPIBI and TMBP are shown in Fig. 1. Fig. 1 shows the ^{1}H-NMR spectrum of SPIBI-100. The peak at δ13.3 ppm is attributed to the acidic proton of benzimidazole. Based on DS, the SPIBIs are named as SPIBI-*X*, in which *X*% (*X*=80, 100, and 120). The inherent viscosity (determined by the Ubbelohde viscometer in H_2SO_4 at 25 °C) of the SPIBI-80, SPIBI-100 and SPIBI-120 is 0.44 dL g^{-1}, 1.34 dL g^{-1} and 1.99 dL g^{-1}, respectively.

2.3. Membrane preparation and proton exchange

The pure and cross-linked SPIBI membranes were prepared by casting of the SPIBI (in Et_3N salt form) solution in DMSO (5 wt%) on clean glass plates and stand at 80 °C for 24 h in the vacuum. The preparation procedure of the cross-linked membrane is described below using SPIBI-80-15 as an example. 0.6 g of SPIBI-80 and 0.09 g of TMBP were dissolved in 12 mL of DMSO, and the mixture was stirred at room temperature to get a homogenous solution, then it was cast on the glass plate with 8 × 8 cm^2 to control the thickness of the membrane. After kept at 80 °C for 6 h in the vacuum to evaporate the solvent, it was heated at 150 °C for 10 h to complete the reaction of epoxy in TMBP and N–H in imidazolyl sections. The membrane can be obtained easily by putting the plate into the deionized water. After washing by boiled water and methanol several times, all the as-cast films were soaked in 1.0 mol L^{-1} HCl solution at room temperature for 24 h successively to free the sulfonic acid and to get rid of Et_3N. These membranes were thoroughly washed with deionized water and then dried in vacuo at 150 °C for 24 h. The thickness of the films was in the range of 40–60 μm.

To SPIBI-80, the cross-linked membranes can be assigned as SPIBI-80-*Y*, in which *Y* represents the content of the cross-linker in the membrane. To SPIBI-100 and SPIBI-120, the cross-linked membrane can be assigned as SPIBI-100-*T* and SPIBI-120-*T*. The feed content of the TMBP in the SPIBI-100 and SPIBI-120 is a fixed value according to the content of the N–H in imidazolyl group as that of the best addition of the SPIBI-80-*Y*.

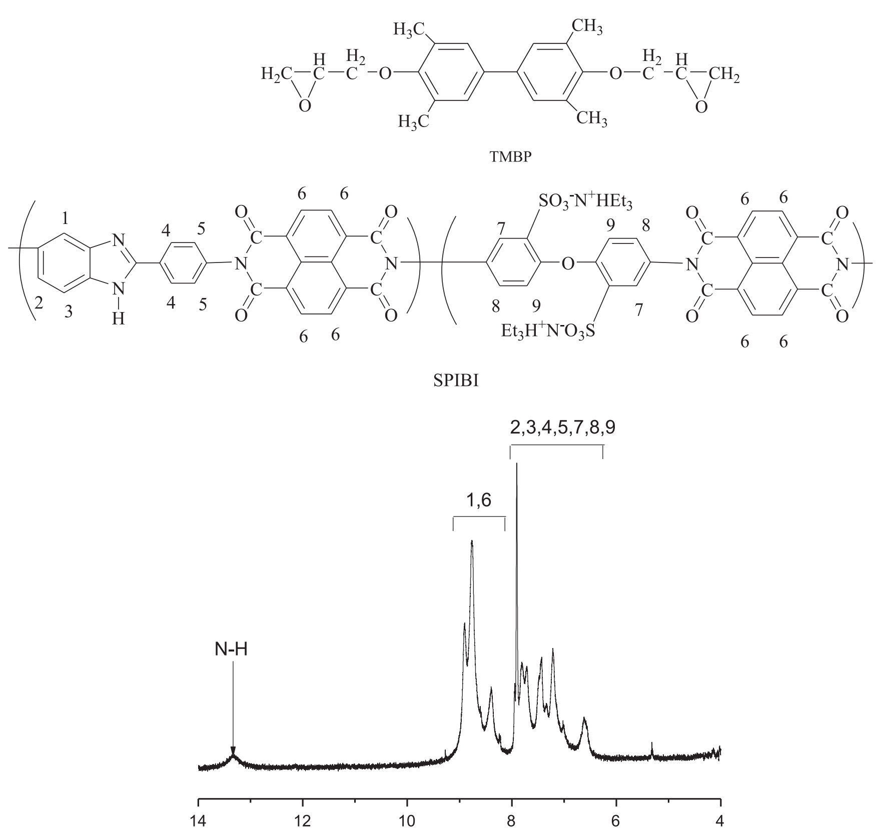

Fig. 1. The chemical structure of the sulfonated polyimide containing benzimidazole and 3, 3′, 5, 5′-tetramethyl-diphenyl diglycidyl ether (TMBP).

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