Journal of Membrane Science 501 (2016) 220–227

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Phosphoric acid-doped cross-linked sulfonated poly(imide-benzimidazole) for proton exchange membrane fuel cell applications

Zhouying Yue [a], Yang-Ben Cai [a], Shiai Xu [a,b,*]

[a] Shanghai Key Laboratory of Advanced Polymeric Materials, Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China
[b] The Chemical Engineering College of Qinghai University, Xining 810016, China

ARTICLE INFO

Article history:
Received 21 July 2015
Received in revised form
17 November 2015
Accepted 29 November 2015
Available online 3 December 2015

Keywords:
Sulfonated poly(imide benzimidazole)
Phosphoric acid-doping
Cross-linking
Proton exchange membrane

ABSTRACT

A series of covalently cross-linked sulfonated poly(imide benzimidazole)s (CBrSPIBIs) were synthesized using 4,4′-bibromomethenyl diphenyl ether as a cross-linker. However, the cross-linked structure results in a reduction of ion conductivity due to the blockage of the hydrophilic channel. Thus, the alkaline imidazole ring was used as a cross-linking site and a basic site to absorb phosphoric acid (PA) molecules. Even at a low humidity and PA-doping level, the proton conductivity of the resulting PA-doped CBrSPIBI (PA-CBrSPIBI) membranes is one to two orders of magnitude higher than that of CBrSPIBI and Nafion due to the formation of a new proton transport pathway between PA and sulfonic acid groups. In addition, these membranes display excellent mechanical strength and chemical stability because of the cross-linked structure. The tensile strength of PA-doped cross-linked membranes ranges from 47.2 to 55.5 MPa, and they can maintain their integrity and mechanical strength in water for more than two months, which is superior to the corresponding sulfonated polyimide and polybenzimidazole blend membranes.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are among the most promising energy conversion devices for transportation and stationary applications due to their high efficiency and low emission [1]. Nafion (DuPont), a poly(tetrafluorethylene)-based polymer with sulfonic acid (SA) groups arranged at intervals along the backbone, is the state-of-the-art material for the proton exchange membranes (PEMs). The key to proton transport in Nafion is thought to be nanochannels of SA groups, through which 'hydrated' protons can pass efficiently [2,3]. Although Nafion is a good proton conductor for hydrated protons, it suffers from poor conductivity in unassisted proton transfer such as Grotthuss and anhydrous proton transfer [4], thus resulting in low conductivity at temperatures above the boiling point of water. Sulfonated aromatic hydrocarbon-based PEM copolymers have emerged as an attractive alternative due to their excellent mechanical strength, film-forming ability, and chemical and thermal stability [5]. However, aromatic PEMs often exhibit poor ion transport properties under the desired electrochemical condition, such as insufficient proton conductivity under relative low humidity ($<50\%$) in hydrogen fuel cells [6]. In recent years, considerable efforts have been devoted to the development of hydrocarbon membranes for wider temperature ranges and lower humidity or even completely dry conditions [7], because operating a PEMFC without humidification could simplify the water/thermal management [8].

Compared with sulfonated acid groups, the PA groups show lower energy penalty in transferring protons (37.2 and 69.9 kJ mol^{-1}, respectively) and slightly higher water bonding energy (47.3 and 44.4 kJ mol^{-1}, respectively), where the former promotes the proton transport and the latter renders enhanced water retention properties [9]. PA-doped polybenzimidazole (PA-PBI) membranes have been extensively studied for high temperature (100 to 200 °C) PEMs under anhydrous conditions. However, for the PA-PBI membranes, higher doping level could lead to higher proton conductivity but poorer mechanical properties.

Heteropoly acids-doped sulfonated or PA-polymers have been reported recently [10,11], but there are few reports about PA-

---

[*] Corresponding author at: Shanghai Key Laboratory of Advanced Polymeric Materials, Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China.
E-mail address: saxu@ecust.edu.cn (S. Xu).

http://dx.doi.org/10.1016/j.memsci.2015.11.045
0376-7388/

doped sulfonated polymers, probably due to the difficulty in preparing a polymer containing both SA and alkaline groups. The most widely studied PA-doped sulfonated polymer is the PA-doped sulfonated polybenzimidazoles [12,13]. The main purpose of the incorporation of SA is to improve the solubility of PBI [14,15]. PA-doped blend membranes, such as PA-PBI/sulfonated poly(ether ether ketone) [16] and PBI/sulfonated polyimide [17] membranes, have also been extensively investigated. However, the effect of the amount of SA and PA on the proton conductivity of membranes and the underlying mechanism remain poorly understood. Suzuki et al. [18] prepared a series of PA-doped sulfonated polyimide and polybenzimidazole blend membranes (PA-SPI/PBI) and investigated the effects of PA-doping level and SA content on the proton conductivity. It was found that the proton conductivity of membranes containing both acid groups was significantly higher than that of neat sulfonated polymer membranes or PA-doped membranes under high temperature and low humidity conditions due to the formation of a new proton transport pathway between PA and SA. However, the stability of the blend membrane was poor because of the weak ionic bond, and its durability decreased rapidly after aging because of the competition between intermolecular interaction and self-association of the components [19]. This highlights the need for the preparation of a material containing both basic benzimidazole rings and sulfonated imide groups with good stability.

We have recently prepared a series of covalently cross-linked sulfonated poly(imide benzimidazole) membranes (CBrSPIBIs) with good stability and toughness using a new cross-linker, 4,4′-bibromomethenyl diphenyl ether [20]. In the present study, these membranes were further doped with PA with the aid of the alkaline imidazole ring in the sulfonated poly(imide benzimidazole) chain. The doping effect of PA on proton conductivity and mechanical properties was investigated. In addition, the chemical stability and mechanical properties of PA-doped CBrSPIBIs were also characterized and compared with the blend membranes. The results show that these PA-doped CBrSPIBI membranes have good long-term durability and high proton conductivity.

2. Experimental

2.1. Materials

1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA) and PA were obtained from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. 3,3′-bis(4-sulfophenoxy) benzidine (BSPOB), 6,6′-bis [2-(4-aminophenyl) benzimidazole] (BAPBI), and 4,4′-bibromomethenyl diphenyl ether were synthesized as described previously [21–23]. Triethylamine (Et_3N; Lingfeng Chemical Reagent Co. Ltd., Shanghai) were purified by distillation under reduced pressure and dehydrated with 4 Å molecular sieves prior to use. Benzoic acid (Lingfeng Chemical Reagent Co. Ltd., Shanghai) was used as the catalyst, and *m*-Cresol and dimethyl suloxide (DMSO, Lingfeng Chemical Reagent Co. Ltd., Shanghai) was used as the solvent. Other reagents were obtained from commercial sources, all of which were reagent grade and used as received.

2.2. Synthesis of sulfonated poly(imide benzimidazole)s (SPIBIx)

SPIBI80 was synthesized from BSPOB (3.2 mmol, 1.6918 g), BAPBI (0.8 mmol, 0.3332 g) and NTDA (4.0 mmol, 1.0720 g) by a solution-thermal imidization method [24]. IR (KBr, cm^{-1}): 1680–1712 (C=O), 1390 (C–N–C), 715 (O=C–N), 3201 (NH of benzimidazole), 1450 (in-plane vibration of 2,6-disubstituted benzimidazole ring), 1246 (imidazole ring breathing).

In the nomenclature of SPIBI*x*, *x*(80, 70 and 60) denotes the molar fraction of the sulfonated diamine monomer. The intrinsic viscosity of SPIBI-80, SPIBI-70 and SPIBI-60 is 2.47 dL g^{-1}, 2.26 dL g^{-1} and 1.62 dL g^{-1}, respectively, indicating they have high molecular weight.

2.3. Fabrication of CBrSPIBIx

CBrSPIBI*x* membranes were fabricated using 6 wt% SPIBI solution in DMSO and a certain content of the cross-linker (4,4′-bibromomethenyl diphenyl ether). The molar ratio of the benzyl bromide in the cross-linker to the amino group in the imidazole ring is 1. The mixture was casted on a clean glass plate and dried at 80 °C for 24 h and then at 160 °C for 3 h in a vacuum oven to remove the solvent and proceed the cross-linking reaction. All Et_3N salt-formed membranes were converted into the protonated form by immersing in 1.0 M HCl solution at room temperature for 2 d. The thickness of the cross-linked CBrSPIBIx membranes ranges from 40 to 60 μm.

2.4. Doping procedure

PA-doped membranes were obtained by immersing the membranes in an 85 wt% PA aqueous solution at 80 °C for 48 h. Then the membranes were taken out and wiped. The amount of PA doped was determined by titration using standardized sodium hydroxide solution (0.1 M, using thymolphthalein as titration indicator). The membrane was then rinsed with water and dried in a vacuum oven at 130 °C for 24 h to obtain the dry weight of polymer. The amount of PA doped was calculated from:

$$PA\,wt\% = \frac{V_{NaOH}C_{NaOH}M_{PA}/2}{W_{dry} + V_{NaOH}C_{NaOH}M_{PA}/2} \times 100\% \qquad (1)$$

where W_{dry} is the weight of dry membrane, V_{NaOH} and C_{NaOH} are the volume and molar concentration of NaOH consumed, and M_{PA} is the molecular weight of PA, respectively.

2.5. Characterization and measurements

Structural analysis was carried out using a Nicolet 6700 Fourier transform infrared (FTIR) spectrometer in the range of 400–4000 cm^{-1}. The ion exchange capacity (IEC, mequiv g^{-1}) of the membrane was determined using a classical titration method. Dry membranes in the protonated form were immersed in 1.0 M NaCl solution for 2 d to liberate H^+ ions and then titrated with 0.01 M NaOH and phenolphthalein (titration indicator). The thermal degradation behaviors were measured using a TG 209 thermogravimetric analyzer (Netzsch, Germany) in a nitrogen atmosphere. Before measurement, samples were preheated to 120 °C and maintained at this temperature for 15 min to remove absorbed moisture and residual solvent, then cooled to 80 °C and reheated to 750 °C at a heating rate of 10 °C min^{-1}. The oxidative stability was measured by immersing the membranes (0.5 cm × 1.0 cm) with a thickness of ~50 μm in Fenton's reagent (3 ppm Fe^{2+}, 3% H_2O_2) at 80 °C, and evaluated by the elapsed time when the membrane dissolved completely (τ) and the weight change after soaking for 1 h. The hydrolytic stability was measured by soaking a small piece of samples in deionized water at 80 °C, and evaluated by the elapsed time when the membrane began to lose its mechanical properties, i.e., the membrane was broken after bending.

The proton conductivity was measured using the four-point probe technique by a Autolab CHI660E electrochemical analyzer with an AC current amplitude of 0.1 mA in a frequency range of 10^6–1 Hz. The membrane was held between the two electrodes of the PTFE mould. The in-plane proton conductivity (σ, S cm^{-1}) was