INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 43 (2018) 3299–3307

Available online at www.sciencedirect.com

ScienceDirect

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

Fabrication of crosslinked polybenzimidazole membranes by trifunctional crosslinkers for high temperature proton exchange membrane fuel cells

*Jingshuai Yang, Haoxing Jiang, Liping Gao, Jin Wang, Yixin Xu, Ronghuan He**

Department of Chemistry, College of Sciences, Northeastern University, Shenyang 110819, China

ARTICLE INFO

Article history:
Received 15 September 2017
Received in revised form
11 December 2017
Accepted 25 December 2017

Keywords:
Crosslinking
Polybenzimidazole
Mechanical strength
Conductivity
High temperature
Fuel cell

ABSTRACT

Two trifunctional bromomethyls containing crosslinkers, 1,3,5-tris(bromomethyl)benzene (B3Br) and 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (Be3Br), are employed to covalently crosslink polybenzimidazole (PBI) membranes for the high temperature proton exchange membrane fuel cell. The presence of three bromomethyl groups in each crosslinker molecule is expected to create more free volume for acid doping while enhancing the adhesive strength of the PBI chains. In addition, the influence of the two crosslinker structures on the property of the crosslinked membranes is compared and analyzed. All the crosslinked PBI membranes exhibit longer morphology durability over the pristine PBI membrane toward the radical oxidation. Moreover, the crosslinked PBI membranes with the crosslinker Be3Br containing three ethyl groups display superior acid doping level, high conductivity and excellent mechanical strength simultaneously, over those with the crosslinker B3Br and the pristine PBI membrane. Single cell measurements based on the acid doped membrane with a crosslinking degree of 7.5% by Be3Br demonstrate the technical feasibility of the prepared membranes for high temperature proton exchange membrane fuel cells.

Introduction

High temperature proton exchange membrane fuel cells (HT-PEMFCs) have attracted much attention as clean energy conversion devices for automotive, stable and portable applications because of suppressed CO poisoning, simple water and better thermal managements, resulting from their operating temperature above 100 °C [1]. The widely investigated phosphoric acid (PA) doped polybenzimidazole (PBI) membrane has been developed to be one of the most promising electrolytes for HT-PEMFC [2,3]. Furthermore, the PBI-based HT-PEMFCs exhibit several advantages, including high CO or SO_2 tolerance, nearly anhydrous working conditions, better heat utilization and possible integration with fuel processing units [1,3,4]. So far, one of the critical issues for attaining a superior performance of the PBI-based HT-PEMFCs is the trade-off between the conductivity and mechanical strength. As a class of heterocyclic polymers, PBI contains two imide groups per repeat unit. These alkaline groups can be easily doped with phosphoric acid (PA) molecules. The abundant doped PA

* *Corresponding author.*
E-mail address: herh@mail.neu.edu.cn (R. He).
https://doi.org/10.1016/j.ijhydene.2017.12.141

molecules could bring in the PBI membrane superiorly high proton conductivity. The sol-gel method is an alternative approach to fabricate PBI membranes with acid doping levels (ADLs) as high as 20–40, as proposed by Benicewicz et al. [5,6]. The obtained membranes exhibited quite high conductivities of around 0.2 S cm^{-1} above 160 °C. As an expense, however, the mechanical strength of PA doped PBI membranes dramatically deteriorates as the increase of ADL, due to the decreased interaction force between PBI polymer chains [2,7]. Therefore, various modified approaches for PBI electrolytes have been developed in order to improve the mechanical strength without or with less sacrifice of the proton conductivity. Up to now, various kind of explorations have been employed such as increasing molecular weight of the PBI polymer [8], fabricating composite membranes with nano inorganic compounds such as TiO_2 [9], HfO_2 [10], silica [11], clay [12] and heteropolyacids [13,14], synthesis of PBI variants [5,15–18] or highly branched PBIs [19], crosslinking the PBI ionically or covalently [20–26], and thermal curing of PBI membranes [27,28].

Since the N-H groups in the benzimidazole rings of PBIs are chemically reactive, the covalent crosslinking of PBI membranes can be achieved via a S_N2 reaction between the PBI and a cross-linker containing two or more electrophilic active groups, such as halides [2] and epoxides [25]. As a result, covalent crosslinking has been demonstrated as an effective method to reinforce the PBI membranes with high ADLs. The macromolecule cross-linkers of chloromethylated polysulfone (CMPSU) [22] and poly(vinylbenzyl chloride) [23] have been employed to fabricate covalently multi-crosslinked hexafluoropropylidene containing PBI (F_6PBI) and sulfone PBI (SO_2PBI) membranes, respectively. The macromolecule multi-crosslinked F_6PBI and SO_2PBI membranes display better fuel cell performance and long term fuel cell durability, resulting from the superior mechanical strength at elevated temperatures while sustaining high PA contents. Besides, other macromolecule cross-linkers including polybenzoxazine [21] and bromomethylated poly (aryl ether ketone) [24] have been used to prepare the multi-crosslinked PBI membranes as well. Due to more compact structures, multi-crosslinked PBI membranes generally displayed lower ADLs than the neat PBI membranes under the same acid doping condition [22,24–26]. Previously, we observed that the silane multi-crosslinked PBI membranes showed superior ADLs comparing to the pristine PBI membrane [29]. This phenomenon probably resulted from the introduction of the siloxane network, which might create a more free volume for adoption of PA molecules [11,20,30]. For better understanding the influence of the crosslinking structure on the properties of the membrane, we tried to crosslink PBIs by using novel cross-linkers with adjustable structures.

In the present work, two typical crosslinkers, 1,3,5-tris(bromomethyl)benzene and 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene, were used to prepare covalently crosslinked PBI. Each crosslinker molecule has three bromomethyl groups, which are expected to create more free volume for acid doping and increase the conductivity of membranes without or less weaken their mechanical properties. Through a facile S_N2 reaction as mentioned previously [22,31], the crosslinkers with and without the flexible groups of triethyl were grafted onto the PBI backbones, respectively. The degree of cross-linking was optimized by controlling the additive amount of the crosslinker in order to make a comparison on the properties of the fabricated membranes simply and effectively. The physicochemical properties and premier fuel cell performance were investigated.

Experimental

Fabrication of crosslinked PBI membranes

The PBI polymer was synthesized by condensation polymerization of 3,3′-diaminobenzidine tetrahydrochloride dehydrate (Applichem, USA) and isophthalic acid (Sigma-Aldrich), with a molar ratio of 1:1 in polyphosphoric acid (Sinopharm Chemical Reagent Co., Ltd), as reported previously [8]. The obtained polymer has an inherent viscosity of around 0.73 dL g^{-1} (5 g L^{-1} in 98 wt% sulfuric acid at 30 °C). As shown in Fig. 1, the crosslinked PBI membranes were fabricated from PBI and two different crosslinkers, i.e. 1,3,5-tris(bromomethyl)benzene (B3Br, Sigma-Aldrich) and 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (Be3Br, Sigma-Aldrich), respectively. The detailed procedure is as follows. A PBI solution of 2 wt% in *N,N*-dimethylacetamide (DMAc, J&K Scientific) was prepared by dissolving PBI in DMAc at 160 °C under refluxing. The crosslinker, i.e B3Br or Be3Br, was added to the PBI solution. The resulted mixture was ultrasonicated for 1 h at room

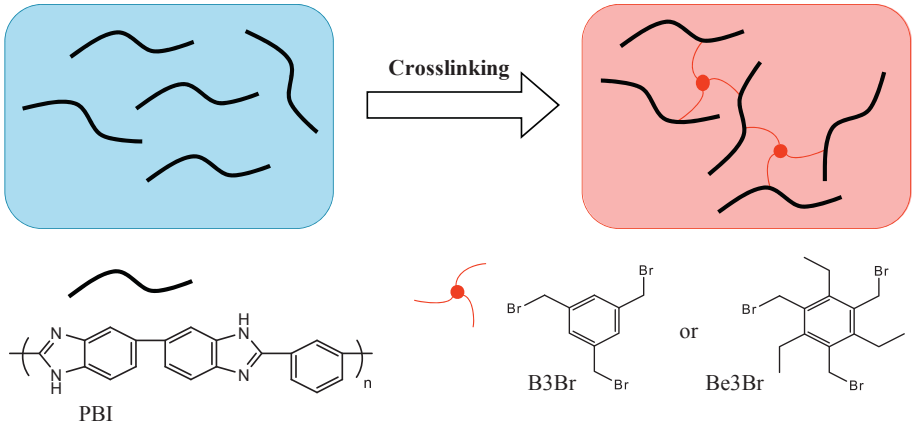

Fig. 1 – Schematic illustration of the crosslinked PBI membranes.