



Highly proton-conductive thermally rearranged polybenzoxazole for medium-temperature and low-humidity polymer electrolyte fuel cells



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HIGHLIGHTS

- Acid doped thermally rearranged polybenzoxazole membranes for medium temperature fuel cell.
- Cavity control in TR-PBO membrane impregnates acid dopants.
- Doped TR-PBO results in fast proton conduction behavior and excellent tolerance to acid leaching.

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ABSTRACT

Here a new membrane design concept to improve proton conductivity and to maintain a constant acid doping level for an extended period of time for medium-temperature and low-humidity polymer electrolyte fuel cells (MT/LH-PEFC) is presented. A polymer electrolyte membrane is prepared via thermal rearrangement of hydroxyl-containing polyimide (HPI) precursor membranes over 350 °C, followed by subsequent acid-impregnation. The thermal treatment for 1 h converts HPI into a thermally rearranged polybenzoxazole (TR-PBO) membrane with high surface area, similar to zeolites. The microporous structure and the basic sites (–C=N–) in benzoxazole moieties contribute to the stable impregnation of small acidic molecules (e.g., HCl, HNO₃, H₃PO₄, and HPF₆) in large quantities within the polymer matrix. The acid-doping level decreases with the increasing size of acidic dopants. TR-PBO impregnated using HCl with the smallest radius has a much higher doping level and excellent proton conductivity ($1.60 \times 10^{-1} \text{ S cm}^{-1}$ at 130 °C and RH 28%) when compared with PBI ($6.59 \times 10^{-2} \text{ S cm}^{-1}$ at the same conditions). Different from a common acid-doped PBI system, the acid-doped TR-PBO membranes do not exhibit a severe acid leaching even in repeated heating and cooling cycles between 90 and 130 °C.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) have been perceived as a promising electrochemical device producing renewable energy with high efficiency [1]. Among them, the medium-temperature and low-humidity PEFCs (MT/LH-PEFCs) operate in a dry state under a temperature range between 120 and 180 °C. MT/LH-PEFCs have a variety of advantages such as relatively fast kinetics of electrode reaction, better heat utilization, favorable integration of fuel processing units, and improved resistance to carbon monoxide (CO) poisoning onto platinum (Pt) catalyst [2].

There have been great efforts to develop desirable polymer electrolytes for MT/LH-PEFCs. One approach is to fabricate sulfonated polymer-inorganic composites containing hygroscopic inorganic oxides [3,4] and heteropolyacids [5–8] in order to enhance water retention levels and to compensate proton conductivity reduced as a result of membrane dehydration at a temperature higher than 100 °C, respectively. Another is to replace water molecules as proton transport media in sulfonated polymers with non-aqueous and low-volatile heterocyclic compounds (e.g., imidazole and imidazolium salt, pyrazole, and benzimidazole solution) [9–11]. Both membrane materials, however, are still not free from severe losses in proton conduction in conjunction with thermal decomposition of their sulfonic acid groups [12].

The most successful MT/LH-PEFC membrane study is observed in the impregnation of strong inorganic acids (e.g., phosphoric acid (H₃PO₄) [13–16], hydrochloric acid (HCl) [17], and nitric acid

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(HNO₃) [17] into basic polymers bearing electron-donating groups (e.g., ether, alcohol, imine, amide, or imide). The basic polymers form hydrogen bonds with the acids which undergo spontaneous dissociation to some extent even under water-free conditions. The self-ionization enables protons to be transported in the acid-doped polymers [18]. A representative acid-doped polymer is polybenzimidazole (PBI, pKa = ~5.5) impregnated with H₃PO₄ in which two protons per repeating unit delocalize its electron density for forming a stable polymer system through the resonance stabilization [19]. The acid–base complexation is made by treating PBI in the membrane state with highly concentrated H₃PO₄ solution for a given time [9,13–17] or by polymerizing PBI in polyphosphoric acid used as both a solvent and a dopant [20–23]. In spite of much effort, it is still difficult to meet electrochemical performance requirements owing to their relatively low proton conductivities (e.g., <4 × 10⁻² S cm⁻¹) under MT/LH-PEFC operation conditions. The PBI membranes, particularly with high H₃PO₄ contents, also suffer from the acid leaching; the dopants leach out with a small amount of water molecules produced as a result of the redox reaction. It hinders the MT/LH PEFC system from exhibiting a high technical reliability for an extended period of time.

This paper describes a new membrane material design concept to improve proton conduction capability and to minimize severe acid leaching by controlling characteristics of cavities in the polymer matrix, which are believed to be used as acid reservoirs. Polybenzoxazole (PBO) was employed as a polymer matrix for doping acids. PBO has excellent thermal and chemical stability, and good hydrolytic resistance. When treated with acids, the basic polymer forms ionic complexes in the form of counter anions bound to its protonated benzoxazole groups in which protons are mainly located on its nitrogen atoms, maintaining the same distance as the usual N–H bond length in the orientation bisecting the –C=N–C– bond angle on the heterocyclic rings. Different from conventional PBO synthesized by polycondensation reaction of a bisaminohydroxyphenyl compound and a dicarboxylic acid, microporous PBO (TR-PBO) used in this study was prepared from hydroxyl-containing polyimide (HPI) precursor in the membrane state via thermal rearrangement reaction over 350 °C [24]. The resulting TR-PBO membranes exhibited a large surface area over HPI precursor. The cavity in TR-PBO was narrowly distributed in bimodal shape with the mean size of about 3.8 Å and 9 Å. The connectivity of the cavity was much improved after the thermal rearrangement [25]. Here, it was noticed that the small cavity size of the basic polymer is similar to thermodynamic diameters of acidic dopants and the cavities are connected each other. It means that a large portion of the dopants may exist in the cavities stably regardless of water generation during MT/LH-PEFC operation and the cavity network may be utilized as an effective proton transport pathway, respectively.

The goal of this study is to systematically investigate acid-doping effects on basic polymer matrices from HPI precursor to TR-PBO prepared under different thermal protocols. The ultimate objective of this study is to disclose the importance of cavity characteristics for both proton conduction and the acid preservation. Finally, thermo-oxidative resistance and electrochemical reliability of acid-doped TR-PBO membranes were observed under thermal aging histories and during repeated heating and cooling cycles, respectively.

2. Experimental

2.1. Materials

2,2-Bis(3-amino-4-hydroxy-phenyl)hexafluoropropane (APAF, FW = 366.26 g mol⁻¹) as a diamine was purchased from Tokyo

Kasei Co., and used as received. 4,4-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA, 99 wt.%, FW = 444.24 g mol⁻¹) and 1-methyl-2-pyrrolidinone (NMP, anhydrous) were purchased from Aldrich Chemical Co. (WI, USA), and used as a dianhydride and a solvent, respectively. Hexafluorophosphoric acid (HPF₆), HCl, HNO₃, and H₃PO₄ (Aldrich Chemical Co., WI, USA) were purchased, and used as dopants.

2.2. Synthesis of polyimide precursor (HPI), and membrane formation

HPI precursor was synthesized via thermal imidization following synthetic procedures in Fig. 1 [24,25]. APAF (10 mmol) with hydroxyl functional groups was dissolved in NMP solution under a nitrogen atmosphere using mechanical stirrer, until a clear solution was obtained. 6FDA in the powder state was slowly added into APAF solution. The reaction mixture was stirred for one day at ambient temperature to yield a transparent viscous poly(amic acid) (HAA) solution. Then, HPI membrane was prepared by casting HAA solution onto the glass plate and thermally treating in vacuum with stepwise imidization protocols: 100 °C for 1 h, 150 °C for 1 h, 200 °C for 1 h, and 250 °C for 1 h. After imidization, the vacuum oven was cooled to ambient temperature.

2.3. Preparation of thermally rearranged polybenzoxazole (TR-PBO) membranes

TR-PBO membranes were fabricated from HPI in the membrane state via the thermal rearrangement (see Fig. 1). Prior to the thermal treatment, the membrane samples were dried at 110 °C in vacuum to remove any residual NMP, water molecules, and dust. For thermal rearrangement, HPI membrane on an alumina holder plate was placed in the middle of a quartz tube of the muffled tubular furnace where argon gas flowed at a rate of 150 ml min⁻¹. An isothermal annealing was carried out at 300 °C for 1 h to finish thermal imidization. Then, the HPI membrane was thermally treated at three different temperatures (350, 400, and 450 °C) for 1 h. The furnace was cooled to ambient temperature at the rate of 10 °C min⁻¹. The resulting TR-PBO films are denoted as TR-PBO_{temperature} (°C). For example, TR-PBO₄₀₀ means a TR-PBO film obtained after the thermal treatment at 400 °C. Before treated in acids, each membrane was kept in a desiccator to be isolated from any moisture sources.

2.4. Acid-impregnation of TR-PBO membranes

TR-PBO membranes were doped by immersing them in 10 M HCl, HNO₃, H₃PO₄, and HPF₆ solution at room temperature for one day. The increase in the weight of the acid-doped membranes is associated with both water and dopant molecules. In order to minimize the effect of water uptake, acid-doped TR-PBO membranes were sufficiently dried at 110 °C in vacuum until their weights reached unchangeable levels. The acid uptake was defined as the mole number of acid molecules per benzoxazole unit using Eq. (1).

$$\text{Acid uptake [mol. \%]} = \frac{W_{\text{dopant}} / MW_{\text{dopant}}}{(W_{\text{polymer}} / MW_{\text{repeating unit}})} \times 100 \quad (1)$$

where W_{dopant} and W_{polymer} are the weight of an acidic dopant and a basic polymer, respectively. MW_{dopant} and $MW_{\text{repeating unit}}$ denote the molecular weight of the dopant and the polymer repeating unit. The acid-doped membranes were washed in methanol for three days to remove “free acids,” and dried at 80 °C in vacuum [16]. The

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