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Dimensionally-stable phosphoric acid-doped polybenzimidazoles for high-temperature proton exchange membrane fuel cells

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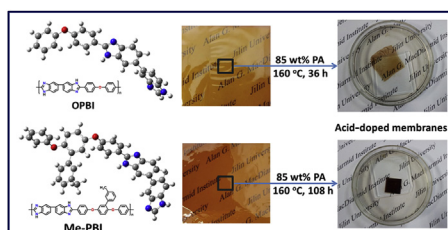
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HIGHLIGHTS

- Ether-linked PBIs were prepared with high molecular weight and good solubility.
- Free volume was increased by incorporating bulky pendent groups.
- The highly PA-doped PBI membranes exhibited excellent dimensional-mechanical stability.
- The high temperature membranes had good fuel cell performance without humidification.

GRAPHICAL ABSTRACT



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ABSTRACT

Phosphoric acid-doped polybenzimidazole (PA-*m*-PBI) membranes are widely investigated for high temperature proton exchange membrane fuel cells because of their low cost and high performance. For this system, a major challenge is in achieving a good compromise between the phosphoric acid doping level and the membrane dimensional-mechanical stability. Different from the established PA-*m*-PBI system, the present work investigates two types of PA-PBI membranes incorporating flexible ether linkages and asymmetric bulky pendants (phenyl and methylphenyl), which exhibit much better dimensional-mechanical stability after immersing in PA solution, even at high temperature for an extended period. This superior stability allowed higher acid doping levels (20.6 and 24.6) to be achieved, thus increasing proton conductivity (165 and 217 mS cm^{-1} at 200 °C under anhydrous conditions) as well as significantly improving fuel cell performance. The peak power densities in hydrogen/air fuel cell were 279 and 320 mW cm^{-2} at 160 °C, without humidification. Molecular simulation, density and fractional free volume, and wide-angle X-ray diffraction were used to investigate their structure-property relationships.

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1. Introduction

There is currently increasing interest in operating proton exchange membrane fuel cells (PEMFCs) at high temperature and low humidity conditions. Compared with low temperature PEMFCs (≤ 80 °C), intermediate and high temperature proton exchange

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membrane fuel cells (HT-PEMFCs) operating at 100–200 °C are more desirable for a number of reasons, such as a higher tolerance of the anode to CO poisoning, increased catalyst efficiency, simplified water/thermal management and improved resistance to fuel impurities [1]. Polybenzimidazole (PBI) has been widely studied as a high temperature proton exchange membrane (HT-PEM) material because of its excellent mechanical and thermal stability, as well as its basic heterocyclic structure, which acts as a proton donor and acceptor simultaneously. However, PBI cannot be used in isolation as a solid electrolyte due to its inherently low conductivity of 10^{-9} mS cm⁻¹ [2]. Phosphoric acid (PA) is a good electrolyte with high thermal stability and was first doped into PBI by Wainright et al., and the resulting HT-PEM exhibited many attractive properties [3]. With this landmark study in the 1990s, and considerable ensuing research, PA-PBI membranes have evolved as one of the most promising candidates for HT-PEMFCs.

In the past two decades, the most widely investigated PBI has been the commercially available poly[2,2'-m-(phenylene)-5,5'-bibenzimidazole] (*m*-PBI). To avoid insoluble residues when preparing homogenous membranes, PBI polymers with a relatively low linear molecular weight (M_w) ranging from about 23 to 40 kDa, corresponding to an inherent viscosity of 0.5–1 dL g⁻¹, were synthesized [4], but this allows only a moderate doping of PA (typically 6–10 mol of PA per mole PBI repeat unit), resulting in low proton conductivity (<100 mS cm⁻¹) [5,6]. Therefore, many strategies including grafting [6,7], crosslinking [8,9], inorganic doping [10–13], polymer blending [14,15], introducing porosity [16,17], and sol-gel membrane formation [5,18] have been adopted to enhance the membrane performance. While this previous work has resulted in significant enhancements in improving acid doping levels (ADL) and thereby increasing conductivity, higher ADLs sacrifice membrane dimensional-mechanical stability leading to greatly reduced HT-PEMFC performance and durability. Thus, the trade-off between ADL and membrane stability is still a difficult and unresolved challenge.

Recently, noncommercial PBIs with novel chemical structures have been explored as an avenue to tailor performance. Until now, this work has been focused primarily on the incorporation of functional groups into the PBI structures; some notable examples are as follows: (1) PBIs containing nitrogen heterocycles (e.g. pyridine and imidazole) were synthesized to increase ADL and proton conduction [19–22]. (2) Sulfonated PBIs were investigated to determine the effect of strongly acidic groups on the ADLs and proton conductivity [5,23–25]. (3) The incorporation of other functional groups, such as hydroxyl and amino groups, to improve properties or allow further chemical modifications (e.g. grafting and crosslinking) [20,26–29]. While these approaches have indeed yielded improvements in membrane performance, some persistent challenges remain, such as tedious synthetic procedures, crosslinking during polymerization, poor solubility and processability, and low mechanical integrity.

Here, we explore a different approach: to determine whether the properties of PA-PBI can be significantly improved by simply altering the configuration and stacking of PBI molecular chains. High molecular weight PBIs containing flexible ether linkages and asymmetric bulky pendants (phenyl and methylphenyl) were synthesized and their PA-doped membranes were fabricated for HT-PEMFC tests. A wide performance comparison between these new ether-linked PA-PBIs and a standard OPBI (poly[2,2'-(*p*-oxydiphenylene)-5,5'-bibenzimidazole]) found that the present membranes exhibit quite different PA-doping behaviors, dimensional-mechanical stability, proton conductivity, and fuel cell performance to PA-OPBI. Molecular simulation, density and fractional free volume (FFV), and WAXD were used to investigate their structure-property relationships.

2. Experimental section

2.1. Materials

(3-Methyl)-phenylhydroquinone was synthesized according to our previous work [30]. Phenylhydroquinone (97%, Sigma-Aldrich Ltd.), 4-fluorobenzonitrile (99%, Energy Chemical Co.), 3,3'-diaminobenzidine (DAB) (97%, Aladdin Reagent) and 4,4'-oxybis(benzoic acid) (98%, Alfa Aesar Reagent) were used as received without purification. Phosphorus pentoxide-methanesulfonic acid (PPMA) [31] solution was prepared by dissolving phosphorus pentoxide (Beijing Chemical Reagent, China) into methane sulfonic acid (Aladdin Reagent) in the mass ratio of 1:10. *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were purchased from Tianjin Tiantai Fine Chemicals Co. Ltd. Sodium bicarbonate (NaHCO₃), potassium hydroxide (KOH), potassium carbonate (K₂CO₃), ethanol, acetone and toluene were obtained from Beijing Chemical Reagent, China.

2.2. Synthesis of ether-linked PBIs and preparation of PA-PBI membranes

As shown in Fig. 1, the dicarboxylic acid monomers (Ph-COOH and Me-COOH) and PBIs (Ph-PBI, Me-PBI and OPBI) were synthesized according to previous work [32,33]. A typical synthesis procedure of Me-PBI was as follows: 2.2000 g (5 mmol) of Me-COOH, 1.0714 g (5 mmol) of DAB and 10 mL PPMA were added into a 50 mL three-necked flask with a mechanical stirrer, a nitrogen inlet and a drying tube. The mixture was kept at 100 °C for 2 h and 140 °C for 2 h in nitrogen atmosphere under mechanical stirring. Thereafter the temperature of the system was raised to 180 °C, and kept for 5–6 h. The high viscosity mixture was poured into a large excess of deionized water with stirring. After washing the obtained product several times with deionized water, the precipitated polymer was immersed in 10 wt% NaHCO₃ solution at 40 °C for 48 h. Me-PBI was washed thoroughly with deionized water until the wash water pH reached 7.0, and then dried at 120 °C for 24 h under vacuum. Ph-PBI derived from Ph-COOH and DAB, and OPBI derived from 4,4'-oxybisbenzoic acid and DAB, were prepared using a similar procedure.

¹H NMR of Me-PBI (300 MHz, DMSO-*d*₆): δ(ppm) 12.94 (s, 2 H), 8.21 (dd, 4 H), 7.85 (d, 2 H), 7.74–7.26 (m, 11 H), 7.25–7.03 (m, 4 H), 2.30 (s, 3 H).

Me-PBI, Ph-PBI and OPBI membranes were prepared by solution casting procedures. Polymer powder (1.0 g) was dissolved in DMSO (10 wt%) by stirring at room temperature for 24 h. The resulting homogeneous solution was cast onto clean glass plates and dried at 80 °C for 12 h and then at 100 °C for 12 h. The resulting membranes were peeled off after drying in a vacuum oven at 120 °C for 24 h, the thickness of membranes was in the range of 60–70 μm.

The PA-PBI membranes were prepared by immersing Me-PBI, Ph-PBI and OPBI membranes in dishes containing 85 wt% PA at 160 °C. Five doping membranes of each type of PBI membrane were prepared by immersing in PA for different time: 3 h, 12 h, 36 h, 72 h, and 108 h. After treatment, the PA-doped membranes were removed from the dishes, wiped dry with tissue, and dried under vacuum at 100 °C for 5 h. However, OPBI membranes that were doped for 36 h or longer could not be tested due to excessive dimensional swelling and insufficient mechanical strength. The resulting membranes are denoted as Me-3, Me-12, Me-36, Me-72, Me-108, Ph-3, Ph-12, Ph-36, Ph-72, Ph-108, and O-3, O-12, where the numerical suffix refers to the doping time.

2.3. Measurements

¹H NMR spectrum of Me-PBI was measured with Bruker 510

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