



Durability of symmetrically and asymmetrically porous polybenzimidazole membranes for high temperature proton exchange membrane fuel cells



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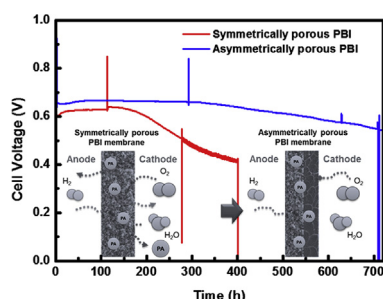
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HIGHLIGHTS

- Two types of Porous PBI membranes were fabricated via template-leaching process.
- Porous PBI membranes showed power densities high to 835 mW/cm² measured at 160 °C.
- Asymmetrically porous PBI as PEM showed a relatively improved FC durability.

GRAPHICAL ABSTRACT



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ABSTRACT

Two types of porous polybenzimidazole (PBI) membranes with symmetric and asymmetric morphologies were fabricated by the template-leaching method and characterized by scanning electron microscope (SEM). Their physicochemical properties were compared in terms of acid-doping level, proton conductivity, mechanical strength, and oxidative stability. The durability of fuel cell operation is one of the most challenging for the PBI based membrane electrode assembly (MEA) used in high-temperature proton exchange membrane fuel cells (HT-PEMFCs). In the present work, we carried out a long-term steady-state fuel cell test to compare the effect of membrane structure on the cell voltage degradation. It has also been demonstrated that the asymmetrically porous PBI could bring some notable improvements on the durability of fuel cell operation, the fuel crossover problem, and the phosphoric acid leakage.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) feature high power density, easy scale-up, and high electric efficiency, etc.

Thanks to these notable advantages, PEMFCs have huge commercial potential in transportation, stationary, and portable applications. However, the cost and durability issues remain the two major obstacles hindering PEMFC's widespread commercialization [1,2].

PEMFCs operating at elevated temperatures (100 °C–200 °C), namely high-temperature proton exchange membrane fuel cells (HT-PEMFCs), have been found capable to improve electrode

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reaction kinetics and enhance carbon monoxide tolerance [1–6]. These two benefits attributed to high temperature have the potential to allow non-noble metal catalyst to be used, simplification of both the water and heat managements, as well as no need for further hydrogen purification. This allows the possibility for the cost of fuel cells to be reduced accordingly.

Phosphoric acid doped polybenzimidazole (PBI) based HT-PEMFCs have received considerable attention for over two decades [7–11]. In the early stage of HT-PEMFC development, most studies focused on improving the proton conductivity of electrolyte membrane because it was considered as a crucial factor for fuel cell performance. For phosphoric acid doped PBI electrolyte membranes, high acid content is required for obtaining sufficient proton conductivity [7]. Since then, several studies have suggested preparing PBI membranes with the porous structure for filling excess phosphoric acid by capillarity [12–16]. For example, Mecerreyes et al. adopted a template-leaching method to fabricate porous PBI membranes with dibutyl phthalate (DBP) as a soft template [12]. One of their porous PBI membranes was reported to achieve a proton conductivity of $5 \times 10^{-2} \text{ S cm}^{-1}$ and a high acid content of 439 wt% (or acid doping level of 14.6 molecules per repeating unit), which were much superior to the dense one. Similarly, Weber and co-workers used silica nanoparticles as a hard template to fabricate porous PBI membranes for precisely controlling the pore size [13,14]. The conductivity of one of their porous PBI membranes with 66 wt% of phosphoric acid content was measured to be $1.1 \times 10^{-2} \text{ S cm}^{-1}$. Recently, Wang et al. who prepared a porous PBI membrane using the DBP template reached their highest proton conductivity of up to $4.8 \times 10^{-2} \text{ S cm}^{-1}$ [16].

Higher porosity probably renders porous PBI membrane to uptake more phosphoric acid. However, the fuel crossover and acid leakage problems may emerge while the connective pore structure is formed. These two problems are supposed to bring negative effect on the durability of HT-PEMFC for a long-term operation. We have suggested that an asymmetrically porous PBI membrane comprising a dense layer and a porous layer has the potential to solve them [17]. The dense layer can act as a barrier to hinder the fuel penetration from one side to another side. Also, the acid leakage possibly will be minimized if the dense layer faces the cathode side where the most water byproduct is being produced. This concept is schematically illustrated in Fig. 1.

In the recent years, HT-PEMFC made considerable progress toward the early stage of commercialization. Accordingly, the

importance of sufficient durability for the long-term operation of HT-PEMFC is growing. The insufficient stabilities of electrolyte membrane result from elevated working temperatures and acidic conditions have been explored in the literature [18–26]. However, few studies concerning the effect of the porous structure within electrolyte membranes on durability of fuel cell operation have been done. In this work, we attempt to compare the durability for two kinds of porous PBI membranes with symmetric and asymmetric morphologies respectively in terms of steady-state tests for a single cell. Also, the physicochemical properties required for an electrolyte membrane used for HT-PEMFC were studied.

2. Experimental

2.1. Materials

All chemical reagents and solvents were used as received. They are: 3,3'-diaminobenzidine (99%, Aldrich), 2,2-bis(4-carboxyphenyl)hexafluoropropane (98%, TCI), polyphosphoric acid (Sigma–Aldrich), phosphoric acid (85%, TCI), 1-ethyl-3-methylimidazoliumbis(trifluoromethylsulfonyl)imide (UniRegion Bio-Tech), dibutyl phthalate (Aldrich), *N,N*-dimethylacetamide (DMAC) (99.8%, Aldrich), methanol (>99.5%, Tedia), hydrogen peroxide aqueous solution (30%, Sigma–Aldrich), iron(II) sulfate heptahydrate (>99%, Sigma–Aldrich), and sodium hydroxide (97%, Showa).

The PBI used in this work was synthesized from 3,3'-diaminobenzidine and 2,2-bis(4-carboxyphenyl)hexafluoropropane according to our previous work. Carbon paper (GDL 24BC) and platinum catalyst (20 wt% Pt/C on Vulcan XC-72 carbon black) used for fabricating membrane electrode assemblies (MEAs) were purchased from SGL and E-TEK, respectively.

2.2. Preparation of membranes

Symmetrically and asymmetrically porous PBI membranes were prepared using different soft templates, DBP and 1-ethyl-3-methylimidazoliumbis(trifluoro-methylsulfonyl)imide ([EMIM][TFSI]), respectively [15,17]. The general procedure for preparing a porous PBI membrane is described as follows.

Before membrane casting, a PBI powder was dissolved in DMAC at 80 °C to obtain a 2 wt% solution. The batch of PBI used in this work has an inherent viscosity of 3.15 dL/g, which was measured at

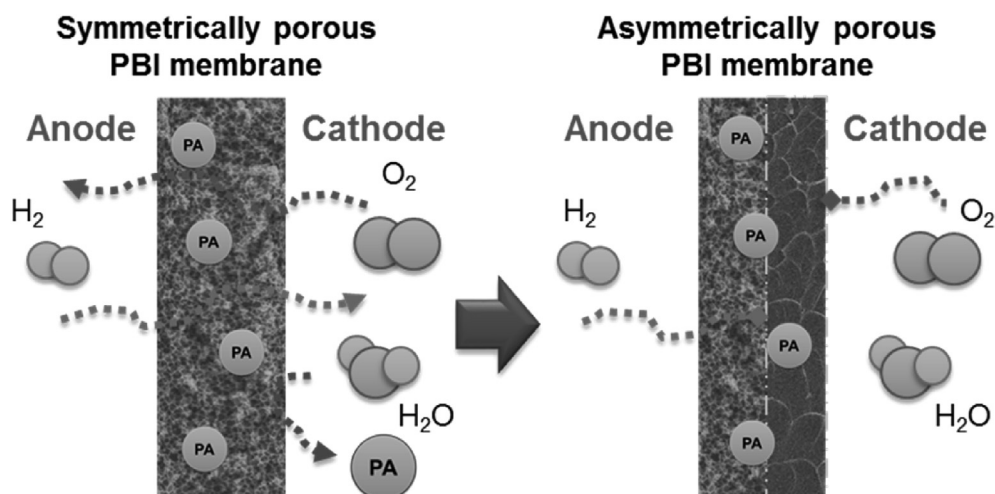


Fig. 1. Schematic illustration of how an asymmetrically porous PBI membrane has the potential to avoid fuel crossover and acid leakage issues.

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