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A facile method of asymmetric ether-containing polybenzimidazole membrane for high temperature proton exchange membrane fuel cell

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ABSTRACT

A facile method has been suggested for the preparation of poly [2,2'-(p-oxydiphenylene)-5,5'-benzimidazole] (OPBI) membrane that comprises of dense and porous layers for high temperature proton exchange membrane fuel cells (HT-PEMFCs). The porosity as well as the asymmetry of the membrane is formed by the use of component solvent at steadily increasing temperatures. This approach needs not to use any porogen, whereas the resultant asymmetric OPBI membrane indicates an improved phosphoric acid (PA) doping level together with mechanical strength. For instance, the PA doping level of the asymmetric OPBI membrane is almost twice as much as that of the homogenous dense OPBI membrane. The conductivity of asymmetric OPBI arrived at 0.072 S cm^{-1} at $180 \text{ }^\circ\text{C}$. The membrane electrode assembly (MEA) based on the asymmetric OPBI demonstrated an exceptional fuel cell functionality with a peak power density of 393 mW cm^{-2} at $160 \text{ }^\circ\text{C}$ under anhydrous conditions.

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Introduction

High temperature proton exchange membrane fuel cell (HT-PEMFC), based on phosphoric acid (PA) doped polybenzimidazole (PBI) membrane, is an effective and eco-friendly energy conversion [1]. HT-PEMFC possesses good performance even at high temperatures (typically between 120 and $200 \text{ }^\circ\text{C}$) and under anhydrous conditions with respect to that of PEMFC with Nafion[®] membrane as the electrolyte, which usually works below $100 \text{ }^\circ\text{C}$. This property provides

HT-PEMFC with attractive advantages including high tolerance to CO, improved chemical kinetics as well as simple management of water and heat [2–5]. It has been reported [6] that the HT-PEMFC based on mPBI membrane can achieve a power density of 240 mW cm^{-2} under dry hydrogen/air atmosphere and $160 \text{ }^\circ\text{C}$. Schmidt [7] have showed that HT-PEMFC using PBI, exposed on reformat environment containing $5 \text{ ppm H}_2\text{S}$ and $2\% \text{ CO}$, could run more than 3000 h only with a $20 \text{ } \mu\text{V h}^{-1}$ voltage degradation rate. Besides, PBI membrane also shows promising perspective on direct methanol fuel cells. For example, MEA based on PBI has been found [2,8]

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to exhibit higher open-circuit voltages (OCV) and better fuel cell performance than that using Nafion[®] 117 membrane with 1 M methanol.

Since the conductivity of PA-doped PBI membranes is greatly attributable to the transfer of protons along the hydrogen bond networks between PA molecules and protonated PBI, the PA content is a significant determinant factor for the output performance of HT-PEMFC [9–12]. There are several efforts [12–14] that have been taken to enhance the PA doping level for PBI membranes. Modification of the PBI monomer unit through grafting sulfonate groups or Lewis basic groups on the benzimidazole ring have presented improvement on the PA doping level for the resultant membranes. An alternative method [15,16] involves preparing PBI membranes with porous structure. For instance, Guo [17] applied SiO₂ solid spheres as a hard template in fabricating porous PBI membranes, in which the resultant membrane absorbed 350 wt% PA which is almost 1.5 times that of membrane without porosity. Nevertheless, the porous structure seems to worsen fuel crossover as well as PA leakage for proton exchange membranes, leading to the OCV deterioration as well as poor durability of HT-PEMFC. Moreover, porosity can enforce a negative impact on the mechanical properties of PBI membrane, which can also decline HT-PEMFC's durability [18].

However, asymmetric PBI membranes compromising dense and porous layers have also been found to solve these problems since dense layer can limit fuel penetration and acid leaching, whereas porous layer can help to dope more acid. Li-Cheng [19] reported an asymmetric PBI membrane with dense and porous layers fabricated by soft and hard templates. Results showed that the acid loss rate of the corresponding membrane was only about half that of symmetrically porous PBI membrane after fuel cell operating for 700 h. On the other hand, the dense layer of the asymmetric membranes helped to enhance the mechanical strength. For example, the mechanical strength of the membrane with 50% porosity declined by 45%, while that value for asymmetric membrane with similar porosity was about 34% [17,20].

In the current work, a high molecular weight OPBI was synthesised and used as the polymer matrix in preparing asymmetric membranes. The chemical structure of the OPBI was approved through the ¹H NMR analysis. The asymmetric OPBI membrane consisting of dense as well as porous layers was formed without the use of porogen, instead by controlling the evaporation of solvents at a range of temperatures for a certain time. The asymmetric structure was formed through two steps. Firstly, the high molecular weight OPBI was dissolved into the mixture of DMSO and DMAc. Then secondly, the mixture was casted into a petri dish, and heated at gradient increasing temperatures for some period of time. The PA doped asymmetric OPBI membranes including PA doping level, and proton conductivity and mechanical strength were then examined and characterised. The performance of membrane electrode assembly (MEA) based on asymmetric OPBI has also been demonstrated with dry H₂ along with air at elevated temperatures. The aim of the present work includes two subjects: one is that high temperature proton exchange membrane with asymmetric structure is formed by using mixed solvents and gradient gradually increasing temperature, the method of which is not necessary to use porogen.

The other is that high molecular OPBI is applied as the membrane matrix material to provide good mechanical strength and toughness for the resultant membranes.

Experiment

Materials

4,4'-Oxybis(benzoic acid) (OBBA, 99%), 3,3'-diaminobenzidine (DAB, 99%), together with polyphosphoric acid (PPA, 85%) were obtained from the Energy Chemical Co., Ltd. (China). Dimethylacetamide (DMAc), Dimethyl sulfoxide (DMSO), ethanol as well as sodium bicarbonate were purchased from the Tianjin Fu Chen Chemical Reagents Factory. DMAc and DMSO were further dried by the use of 4 Å molecular sieves. All the other chemicals were used as received.

Synthesis of OPBIs

A 100 mL three-necked round bottom flask was equipped with nitrogen gas purging. Then, 40.0 g PPA was added into the flask and heated at 100 °C under magnetic stirring for about 30 min. After the PPA melted, 4 mmol DAB was put into the flask and stirred until the DAB was completely dissolved. Then, 4 mmol OBBA was added into the flask; the mixture was continuously stirred until the monomer was absolutely dispersed. Then, the mixture was heated at 140 °C for around 5 h. Subsequent to this procedure, the temperature was increased to 160 °C and additional 3.0 g PPA was added into the flask. The mixture was heated and stirred for another 10 h to obtain higher molecular weight OPBI. The reaction product was poured into a saturated sodium bicarbonate solution to neutralise the PPA. The precipitate was soaked in saturated sodium solution for 12 h to further remove the residual acid. Afterwards, the precipitate was washed with deionised water and ethanol for several times and dried under vacuum at 100 °C for 12 h. OPBI, with a low to high molecular weight of 24.2 (L-OPBI) and 83.5 kDa (H-OPBI), correspondent to the inherent viscosities of 0.58 and 1.39 d L g⁻¹, were prepared.

Membrane preparation

For preparation of asymmetric OPBI membranes, the OPBI was first dissolved in DMSO and DMAc (V_{DMSO}:V_{DMAc} = 1:1) mixture at 140 °C to produce a 2 wt% solution. The solution was casted into a dish and heated in an oven at 80 °C for 5 h. During this process, most of the solvents were evaporated. The clear solution turned into sticky and opaque mixture. Next, the sticky residual mixture was dried at 100 °C for more than 12 h to form the porous layer. The resultant membrane was then peeled off and soaked in deionised water as well as ethanol for a long time at 80 °C, then further dried at 140 °C for 10 h. After drying, the asymmetric OPBI membrane was acquired. To compare them, OPBI membranes were also formed by adjusting the choice of solvents and heating temperature, as shown in Table 1.

Phosphoric acid doping

Before doping of the PA, all the membranes were cut into rectangular specimens (5.0 cm × 5.0 cm). They were then

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