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# Poly(benzimidazole)-epoxide crosslink membranes for high temperature proton exchange membrane fuel cells

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## ABSTRACT

The crosslinked polybenzimidazole (PBI) proton exchange membrane is prepared by blending the epoxy (diglycidyl ether bisphenol-A) resin in the PBI with an imidazole–NH/epoxide Eqv. no. ratio ranging from 20/1 to 6/1. We show that the mechanical properties of the PBI membrane are improved by introducing a small quantity of crosslinks in the membranes (i.e., an imidazole–NH/epoxide Eqv. no. ratio of 15/1–10/1). Due to its high mechanical strength, the thinner crosslinked PBI membrane (thickness ~50 μm) has a similar H<sub>2</sub>/O<sub>2</sub> gas barrier property to the thicker PBI membrane (thickness ~80 μm). Thus, the proton transport resistance across the membrane thickness direction of the thinner crosslinked PBI membrane is lower than that of the thicker non-crosslinked PBI membrane. We show that the crosslinked PBI membrane has a better fuel cell performance than the non-crosslinked PBI membrane at 160 °C with a non-humidified H<sub>2</sub> gas.

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## 1. Introduction

It is generally accepted that polyelectrolyte membrane fuel cells (PEMFCs) present an attractive alternative to traditional power sources, due to their high efficiency and non-polluting nature. In the past decade, researchers [1–7] had made efforts to develop hydrocarbon membranes for PEMFCs working at high temperatures (100 °C < Temp < 200 °C). One of the most prominent proton exchange membranes (PEMs) is the polybenzimidazole (PBI) doped with phosphoric acid [2], in which phosphoric acid acts as the proton's conducting carrier and no water is needed for the conduction of protons in the membranes. Thus PEMFCs using PBI doping phosphoric acid membranes as proton-conducting separators are available to work at high temperatures (140 °C < Temp < 200 °C) and low humidity environment [2,6,7]. Besides high conductivity at

temperatures above 140 °C, PBI membranes also show good thermal stability, high mechanical strength, excellent chemical stability etc. [8–10,11]. The high temperature operation fuel cells offer many advantages such as fast electrode kinetics, high tolerance to fuel impurities such as CO, and simple thermal and water management for cell operations and designs [12].

It had been shown that the mechanical properties of the PBI membrane can be improved by introducing a proper quantity of inter-polymer crosslinks in the membranes. Two series of crosslinked PBI membranes had been reported in literature. One is ionically crosslinked PBIs and the other is covalently crosslinked PBIs. The ionically crosslinked PBIs were prepared according to the Lewis acidic–basic complexes polymer concept developed by Kerres et al. [13], these blended polymers, such as PBI/Nafion [14–16], PBI/sulfonated-

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polysulfone [13,17–19], and PBI/sulfonated-poly(ether ether ketone) [20] membranes etc. showed high phosphoric acid doping levels, high proton conductivity, moderate swelling behavior, and suitable mechanical strength due to the interaction of the Lewis acid  $-\text{SO}_3\text{H}$  groups bonded on the polymers with the Lewis base imidazole  $>\text{NH}$  and  $-\text{N}=\text{C}$  groups of PBI. The covalently crosslinked PBIs were usually prepared by blending PBI with crosslinkers, such as divinyl sulfone [21] and dichloromethyl phosphoric acid [22] etc., which had functional groups for reacting with the imidazole groups of PBI to form covalently crosslinked structures. Comparing with ionically crosslinked PBIs, it has been shown that covalently crosslinked PBIs have better thermal stabilities than ionically crosslinked PBIs [23]. However, fewer papers have reported the fuel cell performance data of covalently crosslinked PBIs.

In the present work, we prepared the crosslinked PBI membranes by blending the PBI with an epoxy resin (diglycidyl ether bisphenol-A, i.e. Epon-828) with a [imidazole-NH]/[epoxide] equivalent no. ratio ranging from 20/1 to 6/1 and curing the blend membrane at 135 °C. We have shown that the mechanical strength of the PBI membranes was improved by introducing a suitable quantity of crosslinks (i.e., [imidazole-NH]/[epoxide] equivalent ratio =  $\sim 20/1-10/1$ ) in the PBI membranes. The high mechanical strength of the crosslinked PBI membranes allows them to have a thinner thickness than the neat non-crosslinked PBI membranes when they are used for PEMFC applications without lowering the membrane's  $\text{H}_2/\text{O}_2$  gas barrier property. The thinner thickness of the membrane causes a lower proton transport resistance across the membrane thickness direction and a better PEMFC performance. We have shown that the crosslinked PBI membrane (thickness  $\sim 50 \mu\text{m}$ ) has a better fuel cell performance than the non-crosslinked PBI membrane (thickness  $\sim 80 \mu\text{m}$ ) at 160 °C with a non-humidified  $\text{H}_2$  fuel gas.

## 2. Experimental

### 2.1. Synthesis of PBI

PBI was synthesized from 3,3'-diamino benzidine (Aldrich) and isophthalic acid (Aldrich) using polyphosphoric acid (Aldrich) as a solvent. The polymerization procedures were same as those reported by Iwakura et al. [24]. 25.68 g (0.12 mol)

3,3'-diamino benzidine and 19.92 g (0.12 mol) isophthalic acid were mixed with 500 g polyphosphoric acid and polymerized under  $\text{N}_2$  atmosphere at 200 °C for 36 h and then at 210 °C for another 24 h. The molecular weight of PBI was determined using a gel permeation chromatography (GPC, Jasco PU-2080 plus) with a RI detector (Jasco RI-2031 plus). The mobile phase was *N,N'*-dimethyl acetamide (DMAc) and the concentration of PBI in the elution solution was  $1.0 \text{ mg mL}^{-1}$ .  $1.0 \text{ mg mL}^{-1}$  of LiCl was mixed in the PBI/DMAc elution solution to avoid aggregation of PBI molecules via inter-polymer imidazole hydrogen bonding [25]. The measurement was carried out at 40 °C with a solution flow rate of  $0.8 \text{ mL min}^{-1}$ . The average PBI molecular weight obtained using narrow molecular weight distribution polystyrene ( $M_w/M_n < 1.1$ , Aldrich) calibration was  $\langle M_w \rangle = 2.3 \times 10^5$  and  $\langle M_n \rangle = 1.1 \times 10^5$ .

### 2.2. Preparations and characterizations of neat PBI and epoxy modified PBI crosslinked membranes

#### 2.2.1. Membrane preparations

Two non-crosslinked PBI membranes with two different thicknesses and five PBI/epoxy (Epon-828, diglycidyl ether bisphenol-A) crosslinked membranes with similar thickness but various imidazole-NH/epoxide equivalent (Eqv.) no. ratios were prepared. The PBI solution and the PBI/epoxy blend solutions with the imidazole-NH/epoxide Eqv. no. ratios ranging from 20/1 to 6/1 (where the imidazole-NH Eqv. wt. of the PBI and the epoxide Eqv. wt. of the Epon-828 were 154 g/NH Eqv. and 193 g/epoxide Eqv., respectively) were prepared using DMAc solvent. The polymer concentration of each solution was around 5.0 wt.%. Each solution was cast onto a glass plate with a blade coater to prepare the membrane. The cast solution film was then dried under vacuum at 80 °C for 24 h and then at 135 °C for 1 h to remove the solvent and proceed with epoxide-PBI crosslink reaction. The designations and thicknesses (*L*) of the two PBI membranes and the five PBI/epoxy crosslinked membranes are listed in Table 1.

#### 2.2.2. Phosphoric acid doping level

The membranes were doped with phosphoric acid by immersing the membrane in an 85 wt.% phosphoric acid aqueous solution at 70 °C for 48 h. The phosphoric acid doping level ( $\text{PA}_{\text{dop}}$ ) of a membrane was defined as the moles of

**Table 1 – The phosphoric acid doping levels and conductivities (at 160 °C and 0%RH) of PBI/epoxy crosslinked membranes.**

Membrane	NH/epoxide (Eqv. no. ratio)	<i>L</i> ( $\mu\text{m}$ )	$\text{PA}_{\text{dop}}$ (mol $\text{H}_3\text{PO}_4$ /mole BI) <sup>a</sup>	$\sigma$ ( $10^{-2} \text{ S cm}^{-1}$ )	$L/\sigma$ ( $\text{cm}^2 \text{ S}^{-1}$ )
PBI-1	1/0	82 ± 3	6.20 ± 0.31	1.82 ± 0.08	0.45
PBI-2	1/0	52 ± 3	6.11 ± 0.34	1.80 ± 0.08	0.29
PBI-Ep-201	20/1	51 ± 3	6.06 ± 0.42	1.54 ± 0.05	0.33
PBI-Ep-151	15/1	52 ± 2	5.97 ± 0.28	1.49 ± 0.06	0.34
PBI-Ep-101	10/1	51 ± 2	5.80 ± 0.30	1.35 ± 0.04	0.37
PBI-Ep-081	8/1	52 ± 2	5.55 ± 0.26	1.02 ± 0.04	0.51
PBI-Ep-061	6/1	50 ± 1	5.10 ± 0.25	0.82 ± 0.05	0.61

<sup>a</sup> BI = a repeat unit of PBI.

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