



## Research Article

# Semi-interpenetrating Network Membrane from Polyethyleneimine-Epoxy Resin and Polybenzimidazole for HT-PEM Fuel Cells

**Chao Meng,<sup>1</sup> Sheng Huang,<sup>1</sup> Dongmei Han,<sup>2</sup> Shan Ren,<sup>1</sup> Shuanjin Wang<sup>1</sup>,<sup>✉</sup>  
and Min Xiao<sup>1</sup>**

<sup>1</sup>The Key Laboratory of Low-Carbon Chemistry & Energy Conservation of Guangdong Province/State Key Laboratory of Optoelectronic Materials and Technologies, School of Materials Science and Engineering, Sun Yat-sen University, Guangzhou 510275, China

<sup>2</sup>School of Chemical Engineering and Technology, Sun Yat-sen University, Zhuhai 519082, China

Correspondence should be addressed to Shuanjin Wang; wangshj@mail.sysu.edu.cn and Min Xiao; stsxm@mail.sysu.edu.cn

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In the present work, a semi-interpenetrating network (semi-IPN) high-temperature proton exchange membrane based on polyethyleneimine (PEI), epoxy resin (ER), and polybenzimidazole (PBI) was prepared and characterized, aiming at their future application in fuel cell devices. The physical properties of the semi-IPN membrane are characterized by thermogravimetric analysis (TGA) and tensile strength test. The results indicate that the as-prepared PEI-ER/PBI semi-IPN membranes possess excellent thermal stability and mechanical strength. After phosphoric acid (PA) doping treatment, the semi-IPN membranes show high proton conductivities. PA doping level and volume swelling ratio as well as proton conductivities of the semi-IPN membranes are found to be positively related to the PEI content. High proton conductivities of  $3.9 \sim 7.8 \times 10^{-2} \text{ S cm}^{-1}$  are achieved at  $160^\circ\text{C}$  for these PA-doped PEI-ER/PBI series membranes.  $\text{H}_2/\text{O}_2$  fuel cell assembled with PA-doped PEI-ER(1:2)/PBI membrane delivered a peak power density of  $170 \text{ mW cm}^{-2}$  at  $160^\circ\text{C}$  under anhydrous conditions.

## 1. Introduction

High-temperature ( $100\text{--}200^\circ\text{C}$ ) proton exchange membrane fuel cells (HT-PEMFCs) have been receiving increasing attention on account of their advantages over those operated at lower temperatures, including high tolerance to fuel impurities (e.g., CO and  $\text{H}_2\text{S}$ ), enhanced activity of the electrocatalysts on both anode and cathode, simplified water, and heat management [1, 2].

After nearly 20 years of development, a series of important advances have been made in the research of high-temperature proton exchange membranes. The research system has developed from the early doping modification of commercial perfluorosulfonic acid-type proton exchange membranes [3–5] to the present inorganic high-temperature proton exchange membrane [6–9], phosphoric acid-doped high-temperature proton exchange membrane

[1, 10–13], phosphonic polymer membrane [14], and other diverse membrane materials coexist. Phosphoric acid-doped high-temperature proton exchange membranes, such as phosphoric acid-doped polybenzimidazole (PBI), exhibit advantages such as high proton conductivity ( $4 \times 10^{-2} \sim 8 \times 10^{-2} \text{ S/cm}^{-1}$  @  $150^\circ\text{C}$ ) and good chemical stability under high temperature, low humidity, or no water conditions, which has become a research hotspot of high-temperature proton exchange membrane materials [15, 16], and are considered as one of the most promising high-temperature proton exchange membrane materials.

In addition to polybenzimidazole (PBI), there are other polymers that can be doped with phosphoric acid. As early as 1992, phospho-doped polyoxyethylene (PEO), polyacrylamide (PAAM), polyvinylpyrrolidone (PVP), polyethylenimine (PEI), and other phospho-doped polymer membranes

were prepared by Lassegues [17], but the proton conductivity of these membranes was generally not high (lower than  $10^{-3}$  S·cm $^{-1}$  at room temperature). One of the most important reasons is that the amount of phosphoric acid in the membrane is too low and cannot be effectively increased, because when the phosphoric acid is too high, these polymers are all paste due to the plasticization of phosphoric acid and cannot form a film at all.

Preparation of semi-interpenetrating polymer network (semi-IPN) is a facile approach to fabricate novel PEMs with specific and various morphology, enhanced mechanical performance, and reduced membrane swelling [18–20]. Tanaka et al. [21] prepared PEI-x H<sub>3</sub>PO<sub>4</sub> semi-IPN material by treating linear polyethylenimine (PEI) with H<sub>3</sub>PO<sub>4</sub> of different metering ratios. Their proton conductivity at a certain temperature is related to  $x$ . When the range of  $x$  is extended to 2.5~3.0, the proton conductivity reaches about 10 $^{-4}$  S·cm $^{-1}$  at 50°C. However, after such amount of phosphate is absorbed, the semi-IPN material will become a paste. To solve this problem, the crosslinked PEI (c-PEI) was synthesized by using ethylene glycol diglycidyl ether as the crosslinking agent and then compounded with H<sub>3</sub>PO<sub>4</sub>. No matter the matrix is PEI or c-PEI, the relationship between proton conductivity and  $x$  is very similar, but in the cross-linked system, the proton conductivity is smaller.

Loureiro et al. [22] synthesized a semi-interpenetrating polymer network (semi-IPN) through the reaction of epoxy resin with 4,4-diamino-diphenylsulfone and polyethylenimine (PEI). The membrane was acidified by two methods: (i) absorption of H<sub>3</sub>PO<sub>4</sub> from aqueous solution and (ii) sulfonation to form covalently bonded -SO<sub>3</sub>H. The conductivity value of the film doped with H<sub>3</sub>PO<sub>4</sub> at 20% concentration (about 0.08 S cm $^{-1}$ , 80°C) was higher than that of the sulfonated samples.

The mechanical properties of the materials above, however, do not satisfy the requirement of PEM fuel cells. In recent years, various modification methods have been explored to balance the proton conductivity and mechanical properties of high-temperature proton exchange membranes. For instance, chemical crosslinking modification is an effective method to improve the chemical stability, mechanical properties, and long-term durability of proton exchange membranes [12, 23–28]. In addition, blending is a commonly used and effective method to improve the physical and chemical properties of polymer materials. The new materials obtained by blending not only have the properties of the raw materials themselves but also can overcome the defects of the original materials and produce excellent properties that cannot be matched by a single material.

In this study, we selected PEI, epoxy resin (ER), and PBI as constituent components for the new high-temperature PEM for fuel cells. Branched PEI is a weakly alkaline water-soluble polymer composed of several N-containing functional groups of primary, secondary, and tertiary amines, which can provide multiple active sites for crosslinking reactions and sites for the absorption of phosphoric acid [29, 30]. When PEI-ER and PBI are blended, an *in situ* crosslinking between ER and PEI in the presence of PBI can form a semi-interpenetrating network structure, which is expected

to improve the mechanical properties and heat resistance of the membrane. Moreover, the semi-IPN membrane should exhibit excellent proton conductivity at high temperature under anhydrous conditions, meeting the need of the application of HT-PEMFCs.

## 2. Experimental

**2.1. Materials and Reagents.** Polyethylenimine (PEI) ( $M_w = 25\,000$ , branched) was purchased from Sigma-Aldrich. Epoxy resin (ER) compound (E-51) was purchased from Macklin. Poly (4,4'-(diphenyl ether)-5,5'-bibenzimidazole) (OPBI) with a viscosity of 6000 Pa·S (tested as 10 wt% solution in N,N'-dimethyl acetamide) was purchased from Shanghai Shengjun Polymer Technologies Co. Ltd. Phosphoric acid (85 wt%) and N-methyl-2-pyrrolidone (NMP) were purchased from Aladdin.

**2.2. Membrane Preparation.** 80 wt% PEI, 80 wt% ER, and 5 wt% PBI solutions were prepared by dissolving PEI, ER, and PBI in pyrrolidone (NMP), respectively. The PEI, ER, and PBI solution with different volume ratios was mixed and stirred for 12 h at room temperature to obtain a transparent and homogeneous casting solution. Then, the PEI-ER-PBI blend solution was cast onto a glass plate and heated at 60°C for 12 h on a hot plate followed by drying at 140°C for 30 min to allow solidification and remove the solvent. PEI-ER/PBI semi-IPN membranes with PBI amount of 20 wt% and mass ratio of PEI to ER of 1:2, 2:3, 1:1, 3:2, and 2:1 were prepared, which are denoted as PEI-ER(1:2)/PBI, PEI-ER(2:3)/PBI, PEI-ER(1:1)/PBI, PEI-ER(3:2)/PBI, and PEI-ER(2:1)/PBI, in turn. The thickness of the PEI-ER/PBI semi-IPN membranes was controlled to be ~80 μm.

## 2.3. Characterization

**2.3.1. Thermal Analysis.** Thermogravimetric curves were recorded from room temperature up to 800°C at a heating rate of 10°C/min in nitrogen atmosphere with a flow rate of 100 mL/min by a Pyris1 TGA (Perkin Elmer). The samples were pretreated by heating to 100°C at a rate of 10°C/minute and kept for 30 minutes before cooling to room temperature.

**2.3.2. Mechanical Properties.** The mechanical properties of membranes were measured with a universal testing machine (New SANS, Shenzhen, China). The membranes were cut into long rectangular-shaped samples whose initial dimensions were 40 mm in length and 5 mm in width. Measurements were carried out at room temperature (RT) with a constant separating speed of 5 mm min $^{-1}$ .

**2.3.3. PA Doping Treatment.** For phosphoric acid (PA) doping, dried membranes were cut into 4 × 4 cm $^2$  size specimen and the weights of individual specimens were separately noted. The specimens were immersed into 85 wt% PA at 80°C for 2 h. The membranes were taken out from the PA, and excess PA was removed from the membrane surface by carefully wiping the specimens with dust-free paper. After drying at 100°C for 12 h, PA uptake and the size of each sample were measured immediately.

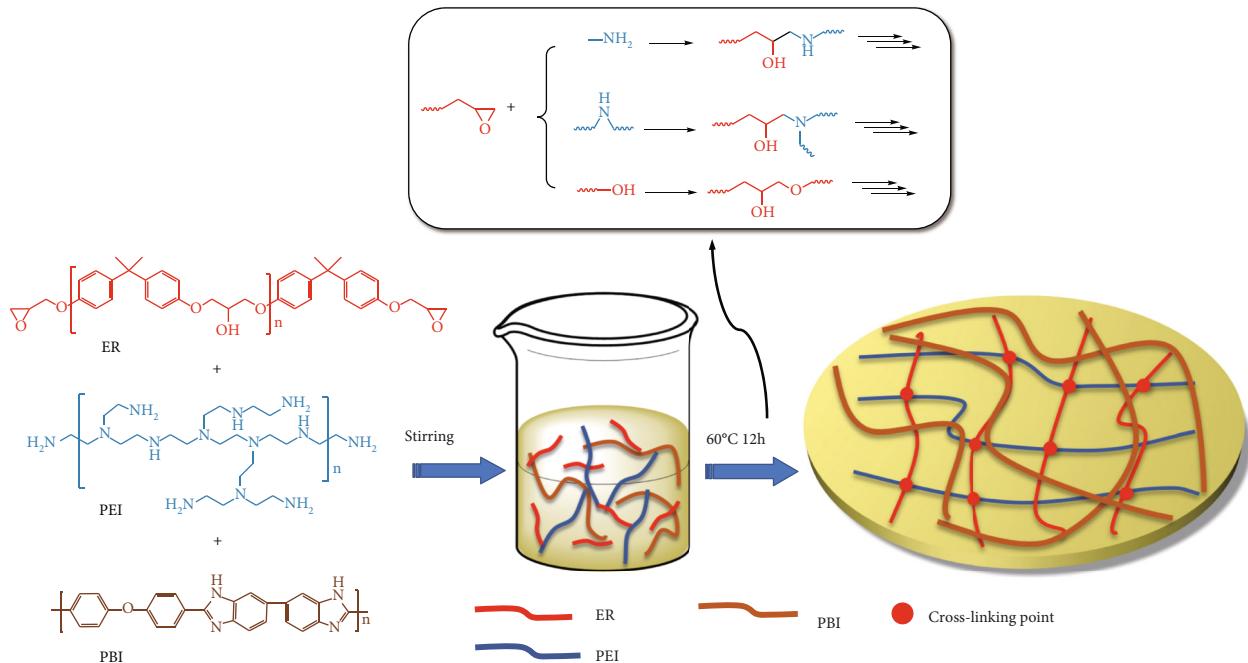


FIGURE 1: In situ step-growth polymerization of polyethylenimine (PEI) and epoxy resin (ER) in the presence of polybenzimidazole (PBI) to form a PEI-ER/PBI semi-IPN membrane, where PBI and PEI-ER crosslinked networks form a semi-interpenetrating network structure.

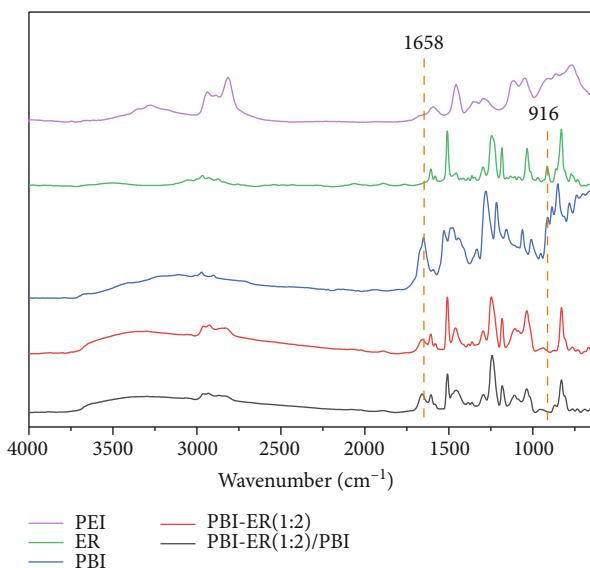


FIGURE 2: FT-IR spectra of PEI, ER, and PBI membranes, PEI-ER(1:2) membrane, and PEI-ER(1:2)/PBI semi-IPN membrane.

The PA uptake ratio of the membrane (acid doping content (ADC)) was calculated by the following equation:

$$\text{Acid doping content (ADC)}(\%) = \frac{W_2 - W_1}{W_1} \times 100, \quad (1)$$

where  $W_1$  is the initial weight of dried membrane and  $W_2$  is the weight of PA-doped membrane.

The volume swelling ratio and area swelling ratio are defined as the percentage of the membrane volume augment and membrane area augment, respectively, after PA doping treatment and are calculated by the following equation:

$$\begin{aligned} \text{Volume Swelling (\%)} &= \frac{V_2 - V_1}{V_1} \times 100, \\ \text{Area Swelling (\%)} &= \frac{S_2 - S_1}{S_1} \times 100, \end{aligned} \quad (2)$$

where  $V_2$  and  $S_2$  are the volume and area of the PA-doped membrane, respectively.  $V_1$  and  $S_1$  are the volume and area of the undoped dry membrane.

**2.3.4. Structural Characterization.** IR spectra of PEI, ER, and film samples were recorded on a NICOLET 6700 Fourier-Transform Infrared Spectrometer (FT-IR).

**2.3.5. Gel Fraction Test.** The effect of crosslinking was determined by gel fraction test. The membrane samples were immersed in NMP at 80°C for 12 h and then removed from the solvent and dried. The gel fraction was calculated by comparing the weight of the dried sample before and after solvent extraction.

**2.3.6. Proton Conductivity Measurements.** Proton conductivity was measured via a standard four-probe AC impedance method using a PGSTAT204 N electrochemical workstation (AUT86925, AUTOLAB). All samples were cut into 1 cm × 4 cm size, and the average thickness of the samples was obtained by a thickness tester. The PA-doped membranes were stuck in a four-probe clamp and placed in a temperature-controlled chamber. The impedance

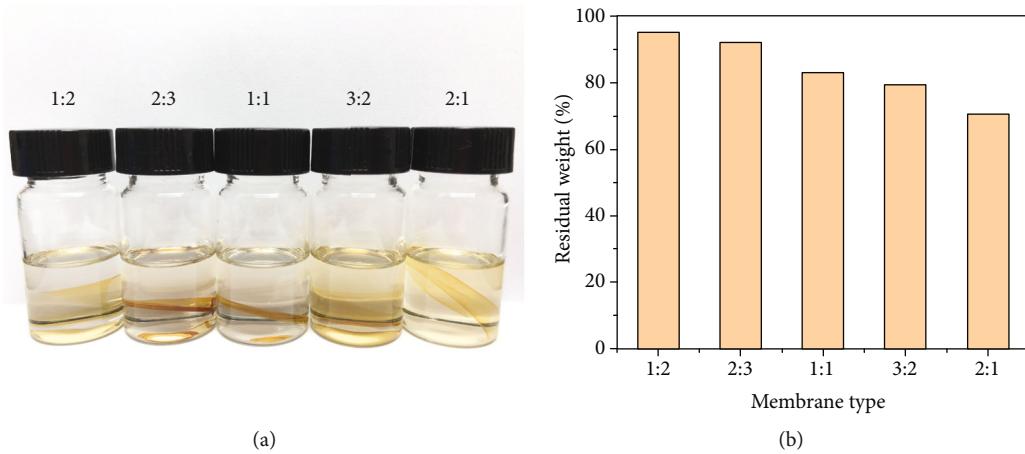


FIGURE 3: Gel fraction test of PEI-ER/PBI membranes performed in NMP at 80°C for 12 h. (a) The membrane samples in NMP at 80°C after 12 h and (b) the residual weight of the membranes after solvent treatment.

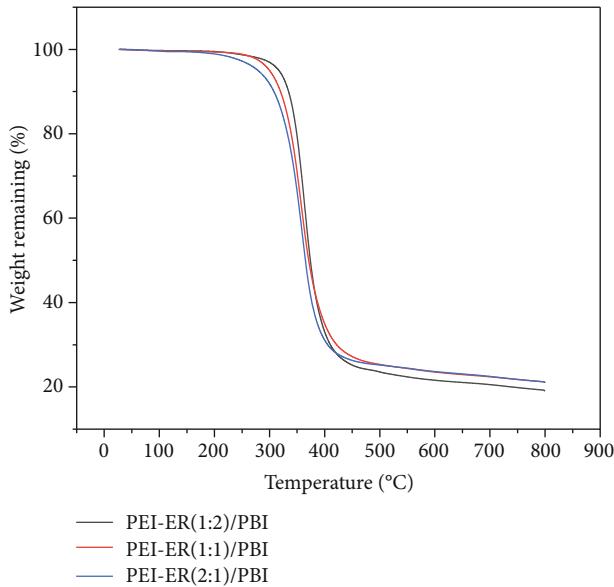


FIGURE 4: TGA curves of different PEI-ER/PBI semi-IPN membranes.

TABLE 1: Acid doping content (ADC) and swelling rate of different semi-IPN membranes.

Membrane	ADC %	Swelling in area %	Swelling in volume %
PEI-ER(1:2)/PBI	101.9	27.0	48.2
PEI-ER(2:3)/PBI	134.7	62.1	68.6
PEI-ER(1:1)/PBI	169.6	77.8	74.7
PEI-ER(3:2)/PBI	272.1	88.7	116
PEI-ER(2:1)/PBI	302.4	107	121

measurement was performed from 80 to 160°C, under anhydrous conditions, in the frequency range of 100 mHz to 100 kHz. The conductivity was calculated by the following formula:

$$\text{Proton conductivity } \sigma = \frac{L}{R \times W \times T}, \quad (3)$$

where  $L$  is the distance between reference electrodes,  $R$  is the membrane resistance, and  $W$  and  $T$  are the width and thickness of the samples, respectively.

**2.3.7. Fuel Cell Tests.** The fuel cell property was assessed using single-cell stacks. Hydrogen and oxygen without prehumidification were applied to the fuel cell at flow rates of 80 mL min<sup>-1</sup> and 160 mL min<sup>-1</sup>, respectively. The area of each of the membrane electrode assemblies (MEAs) was 2.3 × 2.3 cm<sup>2</sup>. The electrodes, 1.0 mg cm<sup>-2</sup> Pt/C for the anode and the cathode, were purchased from Hensen Company. The membranes and electrodes were bonded together by PA without hot pressing, and the active area of the membrane electrode assembly (MEA) was 5 cm<sup>2</sup>. Polarization curves were obtained using current-step potentiometry.

### 3. Results and Discussion

**3.1. Fourier-Transform Infrared (FT-IR) Spectroscopy.** The step-growth polymerization of ER and PEI to form a cross-linked network (PEI-ER) (Figure 1) involves the reactions of epoxide (or glycidyl) groups of ER with the primary ( $-\text{NH}_2$ ) and secondary ( $-\text{NH}-$ ) amine groups of PEI and the hydroxyl ( $-\text{OH}$ ) groups of the intermediate products formed through ring opening of the epoxide groups. To gain insight into the reaction between PEI and ER, Fourier-transform infrared (FT-IR) spectroscopy was used to characterize the PEI-ER(1:2) membrane and PEI-ER(1:2)/PBI membrane with curing time of 12 h. As a comparison, the FT-IR spectra of pure PEI, ER, and PBI membrane were also collected.

As shown in Figure 2, C–O stretching of epoxide at 916 cm<sup>-1</sup> totally disappeared and a wide O–H stretching peak

TABLE 2: Mechanical properties of different semi-IPN membranes before and after phosphoric acid doping.

Membrane	Tensile strength (MPa)		Elongation at break (%)	
	PA undoped	PA doped	PA undoped	PA doped
PEI-ER(1:2)/PBI	60	4.2	8.6	14
PEI-ER(2:3)/PBI	49	2.2	8.0	4.4
PEI-ER(1:1)/PBI	37	1.4	18	1.4
PEI-ER(3:2)/PBI <sup>a</sup>	22	—	43	—
PEI-ER(2:1)/PBI <sup>a</sup>	13	—	98	—

<sup>a</sup>These membranes swelled significantly in PA solution.

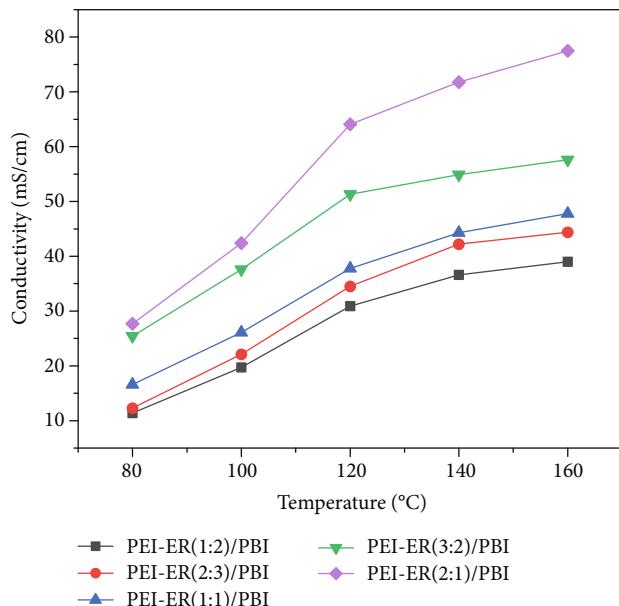


FIGURE 5: Proton conductivities of PA-doped PEI-ER/PBI membranes in anhydrous condition.

appeared at  $3200\text{-}3700\text{ cm}^{-1}$  in the spectra of PEI-ER(1:2) membrane and PEI-ER(1:2)/PBI membrane, indicating that the epoxy resin was crosslinked successfully with polyethyleneimine. The absorption band at  $1658\text{ cm}^{-1}$  is attributed to the imidazole ring C=N absorption of PBI.

**3.2. Gel Fraction Test.** Gel fraction test was carried out to further ascertain that crosslinking was successful. As shown in Figure 3, all the membrane samples maintained the structural integrity after immersing in NMP at  $80^\circ\text{C}$  for 12 h. The residual weight of the samples after solvent treatment was over 70% of the original weight. Among them, the gel fraction of PEI-ER(1:2)/PBI, PEI-ER(2:3)/PBI, and PEI-ER(1:1)/PBI membranes was more than 80%, indicating that the semi-interpenetrating network structure may reduce the solubility of PBI in NMP.

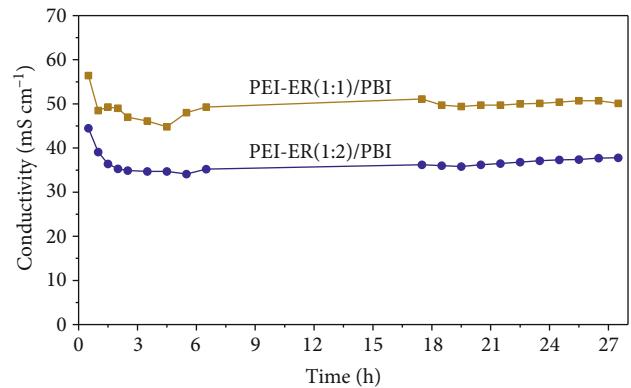


FIGURE 6: Variation of proton conductivity of PA-doped PEI-ER(1:1)/PBI membrane and PA-doped PEI-ER(1:2)/PBI membrane at  $140^\circ\text{C}$  in anhydrous condition with time.

**3.3. Thermal Properties.** Thermal stability of polymer electrolytes is one of the most critical features for long-term durability of fuel cells, especially in high-temperature operation. The thermal stability of PEI-ER/PBI semi-IPN membranes was investigated by TGA under nitrogen atmosphere. The TG curves were recorded after pretreating the samples at  $100^\circ\text{C}$  for 30 minutes. Therefore, even though PEI has strong water absorption, the evaporation of water cannot be seen in the spectrum.

As shown in Figure 4, the degradation of PEI-ER/PBI semi-IPN membranes begins at around  $300^\circ\text{C}$ , which is much higher than the operation temperature ( $\leq 200^\circ\text{C}$ ) of HT-PEMFCs. Thus, the PEI-ER/PBI semi-IPN membranes have sufficient thermal stability for their application in HT-PEMFCs.

**3.4. PA Doping Level.** Acid doping treatment was performed by immersing the PEI-ER/PBI semi-IPN membranes in 85 wt% PA solution at  $80^\circ\text{C}$  for 2 h. As shown in Table 1, PA uptake increased with the increase of PEI content since the more N-containing functional groups could absorb more phosphoric acid via the acid-base interaction. In addition, the higher the ratio of PEI to ER, the lower the degree of crosslinking and thus the higher phosphoric uptake because the less crosslinked membrane has larger voids for containing the PA. Accordingly, the area and volume swellings of the membranes also increase with the increase of ADC as shown in Table 1, which has been widely reported for PA-doped membranes [31–33].

**3.5. Mechanical Properties.** An assessment of the mechanical strength of the polymer electrolyte membranes is essential to fabricate membrane electrode assembly. It is well known that high acid doping level usually provides high proton conductivity but results in a large volume swelling ratio and at the expense of mechanical strength. The mechanical properties of PEI-ER/PBI semi-IPN membranes before and after PA doping treatment are summarized in Table 2. The pristine semi-IPN membranes show outstanding mechanical properties and dimensional stability. With the increase of PEI content, the tensile strength decreases from 60 MPa for PEI-

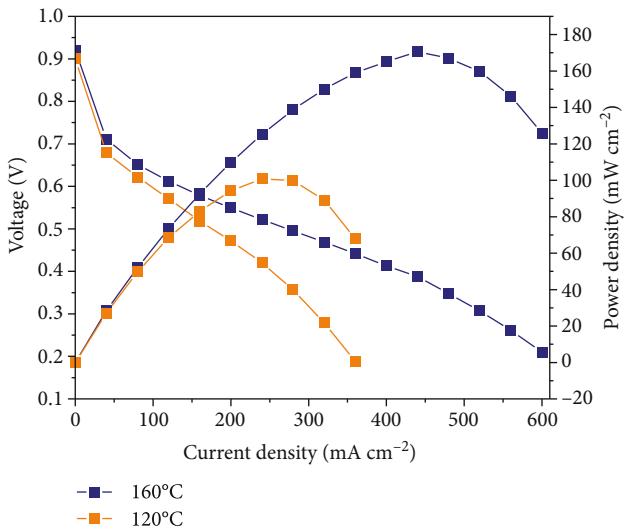


FIGURE 7: Single cell performance of PA-doped PEI-ER(1:2)/PBI at 120°C and 160°C.

ER(1:2)/PBI to 13 MPa for PEI-ER(2:1)/PBI while the elongation at break increases from 8.6% to 98%. It is apparent that more rigid aromatic groups in the backbone and higher crosslinking contribute to higher strength and lower elongation. After PA doping treatment, the mechanical properties of the semi-IPN membranes reduced sharply, especially for PEI-ER(3:2)/PBI and PEI-ER(2:1)/PBI. As He et al. [34] pointed out, high PA doping level will lead to large volume swelling, which will reduce the intermolecular force and thus reduce the mechanical strength of the membrane. However, for the doped membranes with PEI:ER lower than 1:1, the tensile strength is still higher than 1.4 MPa, which is strong enough for membrane electrode assembly.

**3.6. Proton Conductivity.** The proton conductivities of PA-doped PEI-ER/PBI semi-IPN membranes were measured from 80°C to 160°C without extrahumidification (Figure 5). As expected, the proton conductivities increase with the content of PEI in the membranes increasing because more PA was doped with the increase of the alkaline groups. For the same kind of membrane, the proton conductivity increases sharply with the temperature increases from 80 to 120°C and then level off from 140 to 160°C. The PEI-ER(2:1)/PBI semi-IPN membrane shows the highest proton conductivity of  $7.8 \times 10^{-2}$  S cm⁻¹ at 160°C, and all the membranes exhibit proton conductivity higher than  $3.5 \times 10^{-2}$  S cm⁻¹ at temperatures higher than 140°C, which is sufficient for their application as electrolyte membranes in HT-PEMFCs. A comparison of the proton conductivity of PA-doped PEI-ER/PBI membrane with some of the reported PA-doped PBI membranes is shown in Table S1. The proton conductivity of PEI-ER/PBI series membranes is higher than or comparable to that of PBI and related crosslinked PBI membranes.

Taking both proton conductivity and mechanical strength into consideration, the PA-doped PEI-ER(1:1)/PBI membrane and PEI-ER(1:2)/PBI membrane show good comprehensive performance and were chosen for stability

testing. The variation of proton conductivity with time was tested at 140°C for 27 h. The conductivities were recorded every hour for the first 7 h and the last 10 h with an interval of 10 h in the oven at 140°C overnight. As shown in Figure 6, the proton conductivity first decreased due to the evaporation of adsorbed water and then remained stable. After 27 h, the proton conductivity could still maintain about  $4.9 \times 10^{-2}$  S cm⁻¹ and  $3.8 \times 10^{-2}$  S cm⁻¹, respectively, demonstrating excellent proton conductivity durability in high-temperature and anhydrous environments.

**3.7. Fuel Cell Performance.** PA-doped PEI-ER(1:2)/PBI membrane was chosen and assembled to perform the fuel cell tests. Figure 7 shows the polarization and power density curves of H<sub>2</sub>/O<sub>2</sub> fuel cells obtained at 120°C and 160°C under anhydrous conditions. Open circuit voltages of 0.90 V and 0.92 V were achieved at 120°C and 160°C, respectively, suggesting dense membrane with good gas penetration resistance [35]. Since the reaction kinetics and proton conductivity can be effectively improved by increasing the temperature, as expected, the maximum power density increases with increasing temperature. The highest power density was measured to be 170 mW cm⁻² at 160°C. The cell performances shown in Figure 7 are very encouraging and demonstrate a promising application of PEI-ER/PBI semi-IPN membrane for HT-PEMFCs.

## 4. Conclusions

A series of novel PEI-ER/PBI semi-IPN membranes with excellent thermal stability and mechanical strength were prepared by in situ crosslinking of ER and PEI in the presence of PBI. Thanks for the abundant alkaline N-containing functional groups, the PEI-ER/PBI semi-IPN membranes show high PA doping level. Acid doping amount and swelling rate as well as proton conductivities of the PEI-ER/PBI membranes increase with increasing PEI content. The highest proton conductivity of  $7.8 \times 10^{-2}$  S cm⁻¹ at 160°C is achieved for PA-doped PEI-ER(2:1)/PBI membrane, and the PA-doped series membranes with PEI:ER lower than 1:1 show good mechanical strength (1.4~4.2 MPa) and high and stable proton conductivity (higher than  $3.5 \times 10^{-2}$  S cm⁻¹) at temperatures higher than 140°C. The H<sub>2</sub>/O<sub>2</sub> fuel cell performance of the PA-doped PEI-ER(1:2)/PBI membrane gave a peak power density of 170 mW cm⁻² at 160°C under anhydrous conditions, demonstrating promising potential of these PA-doped PEI-ER/PBI membranes as alternative PEMs for HT-PEMFC application.

## Data Availability

The authors confirm that the data supporting the findings of this study are available within the article.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

## Acknowledgments

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## Supplementary Materials

Table S1: comparison of the proton conductivity of PA-doped PEI-ER/PBI membrane with some of the reported PA-doped PBI membranes. (*Supplementary Materials*)

## References

- [1] S. Bose, T. Kuila, T. X. H. Nguyen, N. H. Kim, K. T. Lau, and J. H. Lee, "Polymer membranes for high temperature proton exchange membrane fuel cell: recent advances and challenges," *Progress in Polymer Science*, vol. 36, no. 6, pp. 813–843, 2011.
- [2] A. Chandan, M. Hattenberger, A. El-Kharouf et al., "High temperature (HT) polymer electrolyte membrane fuel cells (PEMFC) - a review," *Journal of Power Sources*, vol. 231, pp. 264–278, 2013.
- [3] Z. G. Shao, P. Joghee, and I. M. Hsing, "Preparation and characterization of hybrid Nafion-silica membrane doped with phosphotungstic acid for high temperature operation of proton exchange membrane fuel cells," *Journal of Membrane Science*, vol. 229, no. 1-2, pp. 43–51, 2004.
- [4] A. Saccà, A. Carbone, E. Passalacqua et al., "Nafion-TiO<sub>2</sub> hybrid membranes for medium temperature polymer electrolyte fuel cells (PEFCs)," *Journal of Power Sources*, vol. 152, pp. 16–21, 2005.
- [5] A. Saccà, I. Gatto, A. Carbone, R. Pedicini, and E. Passalacqua, "ZrO<sub>2</sub>-Nafion composite membranes for polymer electrolyte fuel cells (PEFCs) at intermediate temperature," *Journal of Power Sources*, vol. 163, no. 1, pp. 47–51, 2006.
- [6] S. M. Haile, D. A. Boysen, C. R. I. Chisholm, and R. B. Merle, "Solid acids as fuel cell electrolytes," *Nature*, vol. 410, no. 6831, pp. 910–913, 2001.
- [7] W. Zhou, A. S. Bondarenko, B. A. Boukamp, and H. J. M. Bouwmeester, "Superprotic conductivity in MH PO<sub>3</sub>H M = Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, NH<sub>4</sub><sup>+</sup>," *Solid State Ionics*, vol. 179, no. 11-12, pp. 380–384, 2008.
- [8] S. Lu, D. Wang, S. P. Jiang, Y. Xiang, J. Lu, and J. Zeng, "HPW/MCM-41 phosphotungstic acid/mesoporous silica composites as novel proton-exchange membranes for elevated-temperature fuel cells," *Advanced Materials*, vol. 22, no. 9, pp. 971–976, 2010.
- [9] J. Zeng and S. P. Jiang, "Characterization of high-temperature proton-exchange membranes based on phosphotungstic acid functionalized mesoporous silica nanocomposites for fuel cells," *Journal of Physical Chemistry C*, vol. 115, no. 23, pp. 11854–11863, 2011.
- [10] Z. Zhou, R. Liu, J. Wang, S. Li, and J. L. Brédas, "Intra- and intermolecular proton transfer in 1H(2H)-1,2,3-triazole based systems," *Journal of Physical Chemistry A*, vol. 110, no. 7, pp. 2322–2324, 2006.
- [11] Y. Chen, M. Thorn, S. Christensen et al., "Enhancement of anhydrous proton transport by supramolecular nanochannels in comb polymers," *Nature Chemistry*, vol. 2, no. 6, pp. 503–508, 2010.
- [12] W. Ma, C. Zhao, J. Yang et al., "Cross-linked aromatic cationic polymer electrolytes with enhanced stability for high temperature fuel cell applications," *Energy & Environmental Science*, vol. 5, no. 6, pp. 7617–7625, 2012.
- [13] Q. Li, R. He, J. O. Jensen, and N. J. Bjerrum, "PBI-based polymer membranes for high temperature fuel cells - preparation, characterization and fuel cell demonstration," *Fuel Cells*, vol. 4, no. 3, pp. 147–159, 2004.
- [14] B. Lin, L. Qiu, J. Lu, and F. Yan, "Cross-linked alkaline ionic liquid-based polymer electrolytes for alkaline fuel cell applications," *Chemistry of Materials*, vol. 22, no. 24, pp. 6718–6725, 2010.
- [15] S. Subianto, "Recent advances in polybenzimidazole/phosphoric acid membranes for high-temperature fuel cells," *Polymer International*, vol. 63, no. 7, pp. 1134–1144, 2014.
- [16] D. J. Jones and R. Jacques, "Recent advances in the functionalisation of polybenzimidazole and polyetherketone for fuel cell applications," *Journal of Membrane Science*, vol. 185, no. 1, pp. 41–58, 2001.
- [17] J. C. Lassegues, *Proton Conductors: Solids, Membranes and Gels-Materials and Devices*, P. Colombari, Ed., Cambridge University Press, 1992.
- [18] C. W. Lin, Y. F. Huang, and A. M. Kannan, "Semi-interpenetrating network based on cross-linked poly(vinyl alcohol) and poly(styrene sulfonic acid-co-maleic anhydride) as proton exchange fuel cell membranes," *Journal of Power Sources*, vol. 164, no. 2, pp. 449–456, 2007.
- [19] C.-H. Lee and Y.-Z. Wang, "Synthesis and characterization of epoxy-based semi-interpenetrating polymer networks sulfonated polyimides proton-exchange membranes for direct methanol fuel cell applications," *Journal of Polymer Science Part A: Polymer Chemistry*, vol. 46, no. 6, pp. 2262–2276, 2008.
- [20] Y. F. Huang, L. C. Chuang, A. M. Kannan, and C. W. Lin, "Proton-conducting membranes with high selectivity from cross-linked poly(vinyl alcohol) and poly(vinyl pyrrolidone) for direct methanol fuel cell applications," *Journal of Power Sources*, vol. 186, no. 1, pp. 22–28, 2009.
- [21] R. Tanaka, H. Yamamoto, A. Shono, K. Kubo, and M. Sakurai, "Proton conducting behavior in non-crosslinked and cross-linked polyethylenimine with excess phosphoric acid," *Electrochimica Acta*, vol. 45, no. 8-9, pp. 1385–1389, 2000.
- [22] F. A. M. Loureiro, R. P. Pereira, and A. M. Rocco, "Polyethylenimine-based semi-interpenetrating network membranes for fuel cells," *The Electrochemical Society*, vol. 45, no. 23, pp. 11–19, 2013.
- [23] N. N. Krishnan, D. Joseph, N. M. H. Duong et al., "Phosphoric acid doped crosslinked polybenzimidazole (PBI-OO) blend membranes for high temperature polymer electrolyte fuel cells," *Journal of Membrane Science*, vol. 544, pp. 416–424, 2017.

- [24] F. Mack, K. Aniol, C. Ellwein, J. Kerres, and R. Zeis, "Novel phosphoric acid-doped PBI-blends as membranes for high-temperature PEM fuel cells," *Journal of Materials Chemistry A*, vol. 3, no. 20, pp. 10864–10874, 2015.
- [25] D. Joseph, N. N. Krishnan, D. Henkensmeier et al., "Thermal crosslinking of PBI/sulfonated polysulfone based blend membranes," *Journal of Materials Chemistry A*, vol. 5, pp. 409–417, 2016.
- [26] S. K. Kim, K. H. Kim, J. O. Park et al., "Highly durable polymer electrolyte membranes at elevated temperature: cross-linked -copolymer structure consisting of poly(benzoxazine) and poly(benzimidazole)," *Journal of Power Sources*, vol. 226, pp. 346–353, 2013.
- [27] B. Singh, N. M. H. Duong, D. Henkensmeier et al., "Influence of different side-groups and cross-links on phosphoric acid doped radel-based polysulfone membranes for high temperature polymer electrolyte fuel cells," *Electrochimica Acta*, vol. 224, pp. 306–313, 2017.
- [28] J. Jiang, E. Qu, M. Xiao, D. Han, S. Wang, and Y. Meng, "3D network structural poly (aryl ether ketone)-polybenzimidazole polymer for high-temperature proton exchange membrane fuel cells," *Advances in Polymer Technology*, vol. 2020, 13 pages, 2020.
- [29] S. Wang, Z. Li, and C. Lu, "Polyethyleneimine as a novel desorbent for anionic organic dyes on layered double hydroxide surface," *Journal of Colloid & Interface Science*, vol. 458, pp. 315–322, 2015.
- [30] X. S. Song, S. Xing, H. P. Li et al., "An antibody that confers plant disease resistance targets a membrane-bound glyoxal oxidase in Fusarium," *New Phytologist*, vol. 210, no. 3, pp. 997–1010, 2016.
- [31] J. Yang, J. Wang, C. Liu et al., "Influences of the structure of imidazolium pendants on the properties of polysulfone-based high temperature proton conducting membranes," *Journal of Membrane Science*, vol. 493, pp. 80–87, 2015.
- [32] Q. Li, R. He, R. W. Berg, H. A. Hjuler, and N. J. Bjerrum, "Water uptake and acid doping of polybenzimidazoles as electrolyte membranes for fuel cells," *Solid State Ionics Diffusion & Reactions*, vol. 168, no. 1-2, pp. 177–185, 2004.
- [33] J. Yang, D. Aili, Q. Li et al., "Benzimidazole grafted polybenzimidazoles for proton exchange membrane fuel cells," *Polymer Chemistry*, vol. 4, no. 17, p. 4768, 2013.
- [34] R. H. He, Q. F. Li, A. Bach, J. O. Jensen, and N. J. Bjerrum, "Physicochemical properties of phosphoric acid doped polybenzimidazole membranes for fuel cells," *Journal of Membrane Science*, vol. 277, no. 1-2, pp. 38–45, 2006.
- [35] J. Yang, Q. Li, L. N. Cleemann et al., "Crosslinked hexafluoropropylidene polybenzimidazole membranes with chloromethyl polysulfone for fuel cell applications," *Advanced Energy Materials*, vol. 3, no. 5, pp. 622–630, 2013.