

Synthesis and Characterization of H₃PO₄ Doped Poly(benzimidazole-co-benzoxazole) Membranes for High Temperature Polymer Electrolyte Fuel Cells

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Poly(benzimidazole-co-benzoxazole)s (PBI-co-PBO) are synthesized by polycondensation reaction with 3,3'-diaminobenzidine, terephthalic acid and 3,3'-dihydroxybenzidine or 4,6-diaminoresorcinol in polyphosphoric acid (PPA). All polymer membranes are prepared by the direct casting method (*in-situ* fabrication). The introduction of benzoxazole units (BO units) into a polymer backbone lowers the basic property and H₃PO₄ doping level of the copolymer membranes, resulting in the improvement of mechanical strength. The proton conductivity of H₃PO₄ doped PBI-co-PBO membranes decrease as a result of adding amounts of BO units. The maximum tensile strength reaches 4.1 MPa with a 10% molar ratio of BO units in the copolymer. As a result, the H₃PO₄ doped PBI-co-PBO membranes could be utilized as alternative proton exchange membranes in high temperature polymer electrolyte fuel cells.

Key Words : High-temperature polymer electrolyte fuel cell, Membrane electrode assembly, Polybenzimidazole, Poly(benzimidazole-co-benzoxazole)

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) which can operate at high temperatures are particularly desirable fuel cells due to their capacity to increase catalyst activity while decreasing catalyst poisoning by CO.¹⁻³ Perfluoro-sulfonic acid polymers are the most widely used polymer electrolyte membranes for fuel cells because they promote high proton conductivity and good chemical, mechanical and thermal stability. However, they have high proton conductivity only when sufficiently hydrated with water. Since their proton conduction strongly depends on water content, their conductivity decreases with the evaporation of water above 100 °C, resulting in poor cell performance.^{4,5} Therefore, there is a tremendous demand to develop novel materials possessing high ionic conductivity under low or non humidifying conditions at high temperatures.

Achieving a desirable operating temperature without water requires a completely different type of membrane material. Recently, several electrolytes that can conduct proton under dry conditions have been investigated. Cesium hydrogen sulfate and cesium dihydrogen phosphate undergo a transformation phase of high conductivity around 110 °C and have been investigated by Haile *et al.*⁶ Heteropolyacid has also been explored as fuel cell electrolytes, and shows high proton conduction at room temperature under low relative humidity.⁷ Angell *et al.* have found that ammonium bifluoride and various ammonium salt mixtures can be used as

protic electrolytes for proton conduction over a wide temperature range.⁸ Watanabe *et al.* reported that acid-base complex protic ionic liquids constituting strong acid incorporated into ionic liquids or organic amines showed high proton conductivities without humidification.^{9,10}

Phosphoric acid (H₃PO₄) has been an attractive material for fuel cell applications because of its unique properties such as thermal stability and high proton conductivity. H₃PO₄ shows high proton conductivity without water at temperatures higher than 100 °C because it has a similar proton conduction route to the Grotthuss mechanism.¹¹

H₃PO₄ doped poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (polybenzimidazole, PBI) membranes have been extensively investigated for high-temperature PEMFCs.¹²⁻¹⁹ The first attempt of H₃PO₄ doped PBI membranes for a PEMFC was carried out by Litt *et al.* They showed that H₃PO₄ doped PBI does not require water for proton conduction. In particular, an acid-base complex incorporating basic polymer, such as PBI, and strong acid, such as H₃PO₄, shows high proton conductivity. This occurs as a consequence of the hop and turn conduction mechanism of proton and phosphoric acid molecules.^{12,16}

Xiao *et al.* prepared gel state H₃PO₄ doped PBI membranes by the polyphosphoric acid (PPA) process.^{19,20} In this process, a PBI membrane was obtained *in-situ* from a polymerization solution mixture. The membrane showed high proton conductivity due to a high acid-doping level. However, it had low mechanical strength because of the high doping level. The mechanical strength dropped significantly when these membranes were prepared as a gel state polymer matrix due to the decrease of tensile strength.^{18,21,22}

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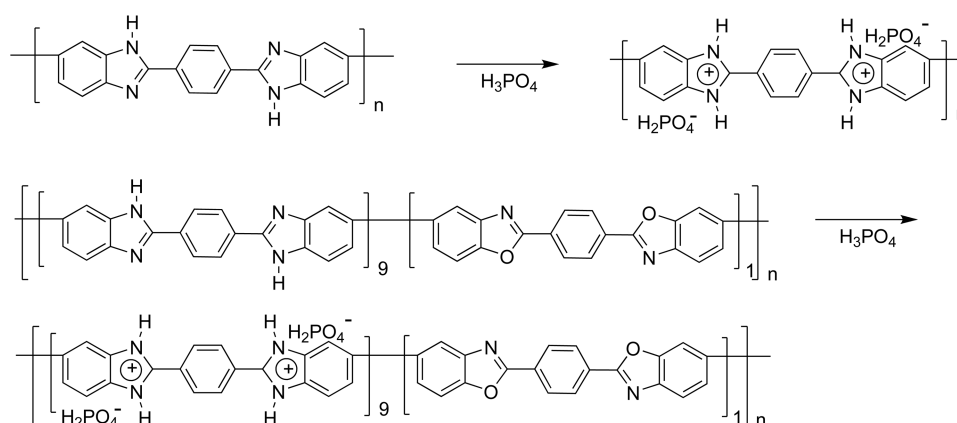


Figure 1. Comparison of doped states of PBI and PBI-co-PBO.

Highly acid-doped PBI has high proton conductivity but low mechanical strength, whereas low acid-doped PBI has low proton conductivity but high mechanical strength. This research focused on *in-situ* fabricated proton-conducting PBI membrane with a good mechanical property without significant proton conductivity loss for high temperature PEMFC applications. We prepared novel poly(benzimidazole-co-benzoxazole) (PBI-co-PBO) based polymer electrolyte membranes. We synthesized two types of the copolymers: poly(2,2'-(1,4-phenylene)5,5'-bibenzimidazole), and poly(2,2'-(1,4-phenylene)5,5'-bibenzoxazole). The H_3PO_4 doped PBI-co-PBO membranes were cast *in-situ* from the polymer solution in polyphosphoric acid. In the PBI backbone, the introduction of benzoxazole units (BO units) lowered the doping level, resulting in high mechanical strength. This is due to the BO unit's lower basic property as compared to a benzimidazole units (BI units) (Figure 1). The resultant proton conducting membranes were characterized using a homemade conductivity measurement apparatus, universal testing machine (UTM), and thermogravimetric analyzer (TGA) for evaluating single cell performance.

Experimental

3,3'-Diaminobenzidine (99%), 3,3'-dihydroxybenzidine (99%, TCI), and 4,6-diaminoresorcinol dihydrochloride (> 99%) were purchased from TCI (Tokyo Chemical Industry). Terephthalic acid (> 99%) and isophthalic acid (> 99%) were purchased from Acros. Phosphoric acid (85%) and polyphosphoric acid (PPA) (115% phosphoric acid equivalent) were purchased from Aldrich. All chemicals were used as received. 46.1 wt % Pt/C catalyst (Tanaka), gas diffusion cloth (with microporous layer, HT1410-W from E-Tek), and 60 wt % PTFE dispersion in water (Aldrich) were used for the MEA fabrication.

General Procedure for Synthesis and Membrane Fabrication of PBI-co-PBO. 3,3'-Diaminobenzidine (3.47 g, 16.2 mmol), 3,3'-dihydroxybenzidine (0.39 g, 1.8 mmol) and terephthalic acid (3.00 g, 18 mmol) were placed in a three-necked flask with condenser and mechanical stirrer. Polyphosphoric acid (PPA) was introduced to the reaction flask

under Ar atmosphere. The reaction temperature was kept at 150 °C for 5 h and at 220 °C for 15 h. The viscous polymer solution was poured onto a glass plate and flattened by a Doctor blade to obtain a uniform thickness (300 μm). The membrane was maintained at an ambient condition (25 °C, 45% relative humidity) and the PPA was hydrolyzed to phosphoric acid. The PBI-co-PBO copolymer membrane was used without a further phosphoric acid-doping process.

PBI homopolymer (poly[2,2'-(*p*-phenylene)-5,5'-bibenzimidazole]) and other PBI-co-PBO copolymers with different molar ratios of comonomers were synthesized by the same method as described above.

Characterization of PBI-co-PBO Membranes. The acid-doped membrane was dried in an oven for 12 h to remove residual water. Then phosphoric acid in the membrane was removed with treatment by ammonium hydroxide, and the acid-free (de-doped) membrane was dried in a vacuum oven at 80 °C for 24 h. The doping level was calculated by the difference in weight of the membrane with and without phosphoric acid. The acid-doping level indicates moles of phosphoric acid per mole of PBI repeat unit.

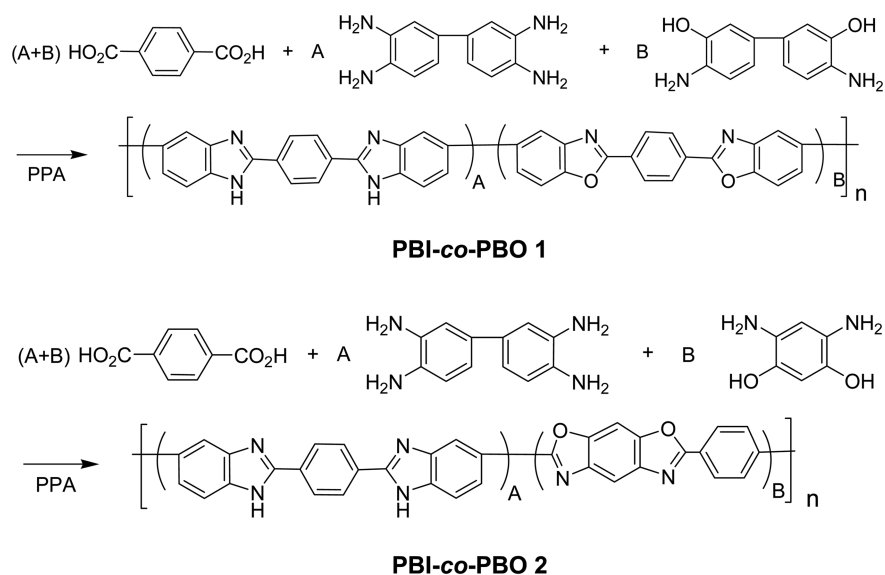
Viscosity was measured at 30 °C using Ubbelode viscometer and concentration of the solution was 0.2 g/dL in 96% sulfuric acid.

Proton conductivity was obtained using a four-platinum wire cell and IM6 (ZAHNER elektrik Inc.) spectrometer. The set condition was the galvanostat mode with a frequency range of 1 Hz - 1 MHz. The membrane was cut into $1 \times 4 \text{ cm}^2$ pieces and put into a temperature controlled chamber (30-170 °C) under N_2 atmosphere to achieve an anhydrous condition. Ion conductivity was calculated by the following equation:

$$\sigma = \frac{L}{A \times R}$$

L is the distance between the electrodes which is fixed as 1 cm. R is the resistance and A is the cross-sectional area of the membrane.

For thermogravimetric analysis (TGA), samples were prepared by wiping the membrane pieces with paper to remove phosphoric acid on their surfaces. Samples were tested under



Scheme 1. Synthetic routes of PBI-co-PBO1 and PBI-co-PBO2 copolymers.

a nitrogen atmosphere with temperatures ranging from room temperature to 1000 °C at a heating rate of 10 °C min⁻¹ (Universal V4.2E TA Instruments, 2050 TGA).

Samples of membranes were prepared following ASTM standard D638. Tensile strength measurements were taken with an H5KT machine (Tinius Olsen; 10 mm min⁻¹ of cross-head speed) at room temperature under ambient humidity.

Preparation of Membrane Electrode Assembly (MEA) and Single Cell Performance Test. The MEAs were prepared using PTFE and PBI binder, and their polarization curves were measured in our previous report.²³

Results and Discussion

Generally, *in-situ*-cast PBI membranes show higher proton conductivity but lower mechanical strength than post-fabricated PBI because of highly doped H₃PO₄.²¹ To improve mechanical strength without sacrificing proton conductivity, we introduced benzoxazole units (BO units) in the PBI backbone. A BO unit is less basic than a benzimidazole unit (BI unit), so copolymers containing BO units have good mechanical strength after the doping process.

As shown in Scheme 1, the copolymer (PBI-co-PBO1) was synthesized with terephthalic acid, 3,3'-diaminobenzidine and 3,3'-dihydroxybenzidine in polyphosphoric acid (PPA), whereas PBI-co-PBO2 was synthesized with 4,6-diaminoresorcinol instead of 3,3'-dihydroxybenzidine. All series of copolymers were synthesized under the same conditions and cast *in-situ* from the polymerization mixture without a further acid-doping procedure.

The inherent viscosities of all series of homo- and copolymers were obtained over 1.5 dL/g and it was sufficient to fabricate flexible and tough membranes (Table 1).

Figure 2 shows the mechanical property of PBI-co-PBO1 copolymers which have two different molar ratios of BO units (10 and 50 mol %) in a polymer backbone. The maximum tensile strength of membrane was determined to be 3.4 MPa

Table 1. Key properties of PBI-co-PBO membranes

Membranes	Acid doping level (mol H ₃ PO ₄ /mol copolymer unit)	Inherent viscosity (dL/g)	Tensile strength (MPa)	Conductivity at 170 °C (S/cm)
PBI	22.6	3.1	2.0	1.29 × 10 ⁻¹
PBI-co-PBO1 (0.9:0.1)	13.8	2.1	3.4	1.09 × 10 ⁻¹
PBI-co-PBO1 (0.5:0.5)	13.3	1.5	2.1	9.56 × 10 ⁻²
PBI-co-PBO2 (0.9:0.1)	13.1	2.3	4.1	8.78 × 10 ⁻²

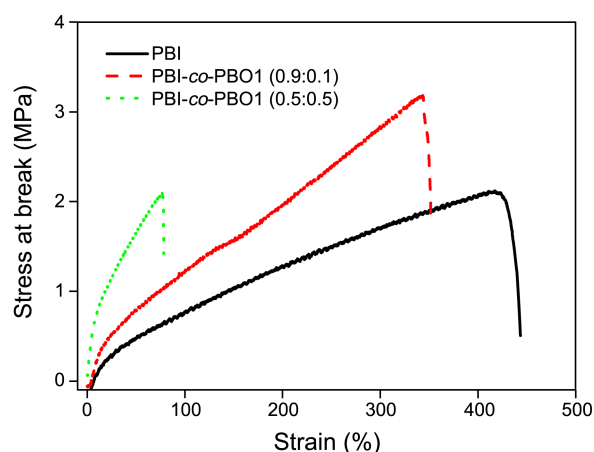


Figure 2. Mechanical strength of PBI-co-PBO1 with different concentrations of PBO.

with a 10% mol ratio of BO units, which was 1.7 times greater than that of a PBI membrane. Elongation property decreased with increasing BO units. At 50% of PBO, tensile strength was similar to PBI; however, elongation at the breaking point was only 76%, which was 20% that of PBI. It is obvious that the addition of BO units increases mechanical property.

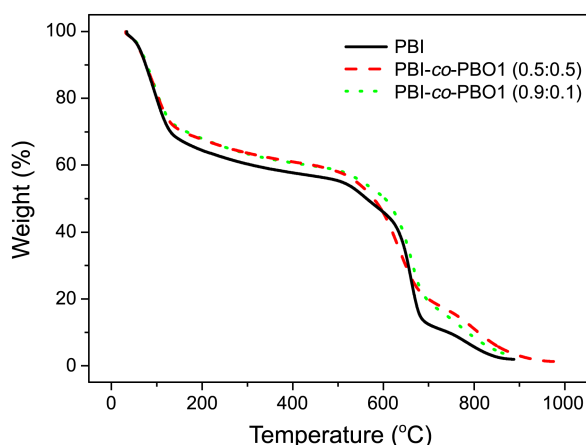


Figure 3. TGA curves of PBI-co-PBO1 with different concentrations of PBO.

Thermal stabilities of the copolymers are presented in Figure 3. This thermogravimetric analysis (TGA) was taken under a nitrogen atmosphere with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ and showed that all PBI-co-PBO1 polymers are stable up to $600\text{ }^{\circ}\text{C}$. The first weight loss registered in the range between room temperature to $130\text{ }^{\circ}\text{C}$ is due to the loss of free water in the membranes. The second weight loss is due to the loss of water produced by phosphoric acid dimerization. In a dry state, phosphoric acid dehydrates to form diposphoric acid. The third weight loss, occurring above $600\text{ }^{\circ}\text{C}$, was caused by polymer main chain decomposition. In the second weight loss region, *m*-PBI lost more weight than the other PBI-co-PBO1 samples, which implies that *m*-PBI contains more phosphoric acid in its membrane than other PBI-co-PBO1 copolymers. The 10% and 50% PBO copolymers show similar weight loss in the second decomposition temperature region, which means the two samples have a similar acid-doping level. This result showed good agreement with the acid-doping level of the membranes (Table 1).

Figure 4 illustrates proton conductivity at different temperatures. The conductivity increased as temperature increased. However, a slight decrease of conductivity was observed

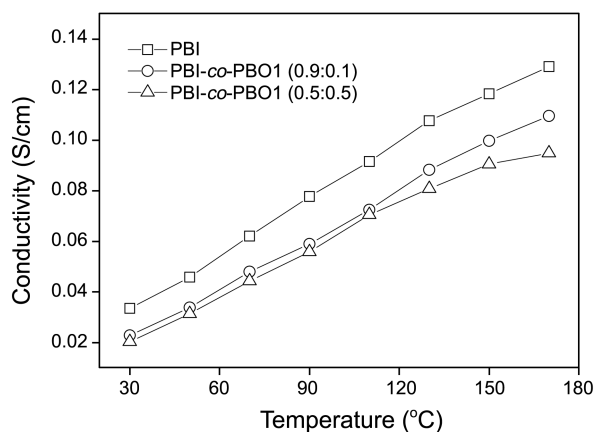


Figure 4. Conductivity of PBI-co-PBO1 with different concentrations of PBO.

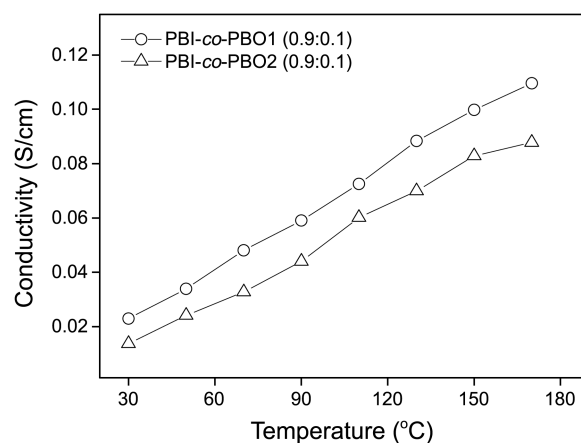


Figure 5. Conductivity of different PBO structure membranes. The acid doping levels of both PBI-co-PBO1 and 2 are 13.8 mmol and 13.7 mmol per mol copolymer unit, respectively.

with increasing BO units. At $30\text{ }^{\circ}\text{C}$, proton conductivity of PBI and the copolymer which contains 10% BO units are 0.033 and 0.023 S cm^{-1} , respectively. We assume that the decrease in conductivity is caused by the decrease of the phosphoric acid doping level. As described in Table 1, increasing BO units in a polymer membrane decreases the phosphoric acid doping level. A PBI-co-PBO1 membrane that has 10% BO units resulted in a 40% decrease of the acid-doping level and a 1.7 times greater mechanical strength, whereas conductivity at $170\text{ }^{\circ}\text{C}$ decreased only by 15% compared with the *m*-PBI membrane. PBI-co-PBO2 that has 10% BO units showed 4.1 MPa of tensile strength, a value which was double that of *m*-PBI. Interestingly, PBI-co-PBO2 showed a low acid-doping level, and consequently, a higher mechanical property compared to PBI-co-PBO1. As the structure of PBO1 has flexible ether linkage with two phenyl groups, it has higher acid doping level than PBO2 which has rigid one phenyl group.²⁴ Figure 5 shows the conductivity with a different type of BO unit. The maximum proton conductivities of each copolymer were 0.088 (PBI-co-PBO2) and 0.11 S cm^{-1} (PBI-co-PBO1). The acid-doping levels of these copolymers were 13.8 (PBI-co-PBO1) and 13.1 (PBI-co-PBO2) mmol , respectively. Despite having the same BO ratio in the copolymer structures, different PBO copolymer structure led to different acid doping levels and resulted in different proton conductivity. Therefore, it is observed that the BO unit structure affects proton conductivity.

Single cell performance of *m*-PBI, PBI-co-PBO1 and 2 are shown in Figure 6. The single cell was operated with non-humidified hydrogen and air at $150\text{ }^{\circ}\text{C}$. The PBI membrane produced the best performance, and PBI-co-PBO1 and 2 showed similar performances. EIS results indicated that the ohmic resistance of all three MEAs was similar and the diameter of semi circles increased as: $\text{PBI} < \text{PBI-co-PBO2} < \text{PBI-co-PBO1}$. Diameter of Semi circle, which is inversely proportional to the amount of oxygen reduction reaction (ORR) site, mainly dependent on the characteristic of cathode catalyst layers, such as Pt loading, ionomer dispersion, and

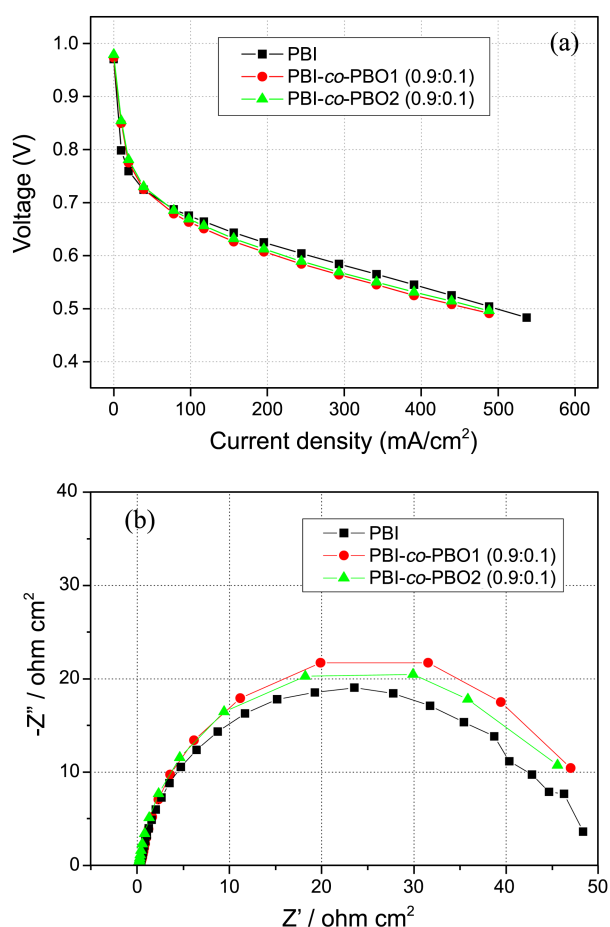


Figure 6. The polarization curves (a) and impedance spectroscopy (EIS) (b) of PBI and PBI-co-PBO1 and 2. Test conditions: 150 °C; non-humidified; ambient pressure; flow rate of H₂ 100 sccm and air 300 sccm.

Table 2. Single cell performance of PBI, PBI-co-PBO1 and 2 membranes

Membranes	OCV (V)	@ 0.6 V (mA cm ⁻²)	@0.5 V (mA cm ⁻²)
PBI	0.970	253	498
PBI-co-PBO1 (0.9:0.1)	0.973	210	463
PBI-co-PBO2 (0.9:0.1)	0.979	220	478

porous structures.²⁵ In this study, even though catalyst layers for each membrane were fabricated from a single batch, it seems that the amounts of impregnated phosphoric acid in catalyst layer were varied according to membrane properties, influencing the cell performances. Therefore, higher cell performances were obtained for MEAs with lower polarization resistances: PBI < PBI-co-PBO2 < PBI-co-PBO1, while the ohmic loss was similar for each MEA and the mass transport effect was negligible. As reflected in Table 2, the OCV values were similar for all samples (PBI: 0.97 V, PBI-co-PBO1: 0.973 V, PBI-co-PBO2: 0.979 V). Current densities at 0.6 V were 253 (PBI), 210 (PBI-co-

PBO1) and 220 (PBI-co-PBO2) mA cm⁻². Although PBO copolymers demonstrated inferior performance as compared to PBI homopolymer, we concluded that PBO copolymer is a more suitable candidate for high-temperature polymer electrolyte membranes because of its stronger mechanical property.

Conclusions

We developed phosphoric acid doped PBI-based copolymer membranes for high-temperature PEMFCs. PBI-co-PBOs were prepared by polycondensation reaction with polyphosphoric acid, and membranes were obtained by the *in-situ* fabrication method. The proton conductivity and cell performance of phosphoric acid doped PBI-co-PBO copolymer membranes decreased as PBO amounts were added. However, the PBO copolymer exhibited higher mechanical strength compared to *m*-PBI. Based on the obtained results, our conclusion is that PBO copolymer membranes could be utilized as alternative proton exchange membranes for high-temperature PEMFC applications.

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