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Polybenzimidazoles containing bulky substituents and ether linkages for high-temperature proton exchange membrane fuel cell applications

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ABSTRACT

Novel solution-processable polybenzimidazoles **P1–P3** were prepared from three new tetraamines and 4,4'-oxybis(benzoic acid) in Eaton's reagent at 145 °C. These tetraamines were 4,4',5,5'-tetraaminodiphenyldiphenyl ether containing bromide, phenyl and trifluoromethyl-substituted phenyl substituents at 2 and 2' positions, respectively. **P1–P3** exhibited good thermal stability, oxidative stability and mechanical properties. Phosphoric acid-doped **P1–P3** membranes also exhibited high proton conductivity in the range of 5.30×10^{-2} – 8.80×10^{-2} S cm⁻¹. They also demonstrated high performance on single cell test, with open circuit voltages of 0.84–0.98 V and peak power density of 478–636 mW cm⁻² at 160 °C with acid uptakes of 199–241%. Especially, the fuel cell based on **P3** with an open circuit voltage of 0.95 V and peak power density of 636 mW cm⁻² exhibited better performance than the one based on *m*-PBI. These membranes provided new options as proton exchange membranes for high-temperature PEMFC applications.

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1. Introduction

In last several decades, in the search of alternative energy sources for the environment sustainability and the reduction in the undesired consequences by using fossil fuels, intensive research efforts from academics and industries as well have been dedicated to improve fuel cell technology. Fuel cells, converting chemical energy directly to electrical energy, are considered as green energy sources with water as the only emission product. If fuel cells can be widely deployed, they might be able to alleviate the greenhouse effect caused by carbon dioxide emission when burning fossil fuels. Among various types of fuel cells, proton exchange membrane fuel cells (PEMFCs), using solid polymer membranes as electrolytes, have received great attention because of their potential applications in vehicles and portable electronic devices. Proton exchange membranes (PEMs) play a crucial role in the performance of PEMFCs. One of the most investigated PEMs is a perfluorosulfonic acid ionomer, Nafion, which serves as the benchmark for membrane performance. In spite of its excellent chemical stability and high proton conductivity in hydrated states, Nafion still has some disadvantages such as high methanol

permeability, low proton conductivity at low water content and low operating temperatures below 80 °C due to the conduction of protons by water [1,2]. Thus, PEMFCs based on Nafion require complicated water and heat management systems [3,4].

Many studies indicated that there are numerous benefits such as faster electrode kinetics, simple water management [3] and more tolerance to fuel impurities (e.g. CO, H₂S) when PEMFCs are operated at higher temperature (100–200 °C) [5–7]. Currently, commercially available poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (*m*-PBI) membranes after phosphoric acid (PA) doping are widely studied as the polymer electrolytes for high-temperature PEMFCs after Wainright et al. first demonstrated the feasibility in 1995 [8,9]. PA-doped *m*-PBI can reach high proton conductivities above 120 °C at low relative humidity [9–12].

In order to prepare mechanically strong PA-doped membranes for membrane electrode assembly (MEA) fabrication, polybenzimidazoles (PBIs) with high molecular weights are necessary. However, *m*-PBI exhibits poor solubility in polar aprotic solvents such as dimethylacetamide (DMAc), dimethylformamide (DMF), dimethylsulfoxide (DMSO) and N-methyl-2-pyrrolidone (NMP) when its inherent viscosity is higher than 1.42 dL g⁻¹ [13]. This is attributed to its structure rigidity and strong hydrogen bonding. Some reports even pointed out that high temperature, high pressure and addition of LiCl were required to obtain a homogeneous

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m-PBI solution for membrane casting [14,15]. Thus, easily solution-processable and high-molecular weight PBIs are still desirable.

The first synthesis of PBI was reported by Vogel et al. at 1961 using melt polycondensation of equimolar 3,3'-diaminebenzidine and diphenyl isophthalate in a two-step process [16]. However, instead of using that process, several groups have synthesized PBIs with various structures by the polycondensation of tetraamines and dicarboxylic acids or their derivatives using polyphosphoric acid (PPA) or Eaton's reagent as the solvent at lower temperature in one step [14,17,18]. Numerous attempts have been reported to increase the solubility and processability of PBIs. The successful approaches involved the introduction of bulky substituents, non-coplanar structures and flexible linkages [19–23]. Among these approaches, the modifications were mainly carried on the chemical structures of diacids. There are mainly four tetraamines reported for the synthesis of PBIs, including 3,3'-diaminebenzidine [14], 1,2,4,5-tetraaminobenzene [24], 3,3',4,4'-tetraamimodiphenyl ether [25] and 3,3',4,4'-tetraamimodiphenyl sulfone [26]. This could be attributed to the complicated synthetic routes for tetraamines preparation and the possible oxidation of the amino groups in ambient conditions as well. Recently, Jana et al. reported the synthesis of soluble PBIs derived from a new pyridine-containing tetraamine (Py-TAB). Unfortunately, neither the fabrication of MEA nor the performance of the fuel cell based on this PBI membrane was reported [27,28].

In this study, we report the synthesis of three novel tetraamines **5**, **8** and **11** with bulky substituents and ether linkages from the monomer which has been reported in our previous study as a starting material [29]. Highly soluble PBIs, **P1–P3**, were prepared from these tetraamines and 4,4'-oxybis(benzoic acid) (OBA). These PBI membranes demonstrate comparable or better fuel cell performance than *m*-PBI in terms of open circuit voltages (OCVs) and peak power density.

2. Experimental

Materials, measurements, membrane preparation, evaluation of oxidative stability, impedance measurements and fabrication of MEAs are included in [Supporting supplement](#).

2.1. Tetraamine synthesis

2.1.1. 4,4'-Diacetamido-2,2'-dibromodiphenyl ether **2**

To a 500-mL, three-necked, round bottomed flask were added compound **1** (10.00 g, 28.00 mmol) and acetic anhydride (400 mL). The reaction mixture was dramatically stirred at room temperature for 24 h. The white precipitate that formed was collected by filtration, washed with water and dried at 80 °C overnight under vacuum to afford 12.05 g of white solid (yield: 97%). The crude product was used for the next step without further purification, mp 243–246 °C. ¹H NMR (600 MHz, DMSO-*d*₆, δ, ppm): 2.04 (s, 6H), 6.86 (d, *J* = 7.4 Hz, 2H), 7.44 (dd, *J*₁ = 7.4 Hz, *J*₂ = 2.1 Hz, 2H), 8.07 (d, *J* = 2.1 Hz, 2H), 10.08 (s, 2H). ¹³C NMR (150 MHz, DMSO-*d*₆, δ, ppm): 24.8, 113.6, 120.4, 120.6, 124.5, 137.3, 149.0, 169.3. EIMS (m/z): calcd for C₁₆H₁₄Br₂N₂O₃, 439.9; found, 439.9 [M]⁺.

2.1.2. 4,4'-Diacetamido-2,2'-dibromo-5,5'-dinitrodiphenyl ether **3**

To a 100-mL, three-necked, round bottomed flask were added compound **2** (7.04 g, 15.92 mmol) and concentrated sulfuric acid (22 mL). After the reaction mixture was stirred at room temperature to form a homogeneous solution, the reaction mixture was cooled by an ice bath (0–5 °C) for 30 min Nitric acid (2 mL, 65%) was then added slowly and the reaction mixture was further stirred for 2 h in an ice bath and then 2 h at room temperature. It was then poured into water. The precipitate was collected, washed

with water and dried at 130 °C overnight in a vacuum oven to afford 8.04 g of yellow solid (yield: 95%). The crude product was used for the next step without further purification, mp 260–265 °C. ¹H NMR (600 MHz, DMSO-*d*₆, δ, ppm): 2.08 (s, 6H), 7.66 (s, 2H), 8.09 (s, 2H), 10.30 (s, 2H). ¹³C NMR (150 MHz, DMSO-*d*₆, δ, ppm): 24.3, 116.5, 119.8, 129.6, 130.8, 142.6, 149.0, 169.6. EIMS (m/z): calcd for C₁₆H₁₂Br₂N₄O₇, 529.9; found, 529.9 [M]⁺.

2.1.3. 4,4'-Diamino-2,2'-dibromo-5,5'-dinitrodiphenyl ether **4**

To a 500-mL, three-necked, round bottomed flask equipped with a condenser were added compound **3** (6.00 g, 11.27 mmol), water (152 mL) and 37% hydrochloric acid (152 mL). The reaction mixture was stirred at 110 °C for 24 h. After cooled to room temperature, the reaction mixture was neutralized by 33% ammonium hydroxide until the pH was 10. The precipitate was collected, washed with water and dried at 80 °C in a vacuum oven overnight to afford 4.85 g of orange solid (yield: 96%) The crude product was used for the next step without further purification. mp 249–253 °C, ¹H NMR (600 MHz, DMSO-*d*₆, δ, ppm): 7.47–7.50(m, 8H). ¹³C NMR (150 MHz, DMSO-*d*₆, δ, ppm): 115.1, 124.2, 124.3, 129.7, 142.5, 144.5. EIMS (m/z): calcd for C₁₂H₈Br₂N₄O₅, 445.9; found, 445.9 [M]⁺.

2.1.4. 4,4',5,5'-Tetraamino-2,2'-dibromodiphenyl ether **5**

To a 100-mL, three-necked, round bottomed flask equipped with a condenser were added compound **4** (2.00 g, 4.46 mmol), ethanol/D. I. water (5:1, v/v) solution (50 mL), saturated NH₄Cl aqueous solution (1 mL) and iron powder (1.50 g). The reaction mixture was stirred at 80 °C for 3 h. After cooled to room temperature, the reaction mixture was filtered through a short Celite pad to remove the insoluble components. The filtrate was evaporated under reduced pressure to remove ethanol and then extracted with ethyl acetate. The organic solution was collected and dried with anhydrous magnesium sulfate. After the solvent was evaporated, the solid was purified by column chromatography using ethyl acetate as the eluent to afford 0.82 g of beige solid (yield: 48%), mp 105–107 °C. ¹H NMR (600 MHz, DMSO-*d*₆, δ, ppm): 4.60(br s, 8H), 6.08(s, 2H), 6.69(s, 2H). ¹³C NMR (150 MHz, DMSO-*d*₆, δ, ppm): 97.8, 105.2, 117.1, 131.9, 136.2, 145.2. EIMS (m/z): calcd for C₁₂H₁₂Br₂N₄O, 385.9; found, 385.9 [M]⁺. Anal. calcd for C₁₂H₁₂Br₂N₄O: C, 37.14; H, 3.12; N, 14.44; found: C, 37.41; H, 3.16; N, 14.30.

2.1.5. 4,4'-Diacetamido-5,5'-dinitro-2,2'-diphenyldiphenyl ether **6**

To a 250-mL, three-necked, round bottomed flask equipped with a condenser and a nitrogen inlet and an outlet were added compound **3** (4.00 g, 7.52 mmol) and toluene (200 mL). The reaction mixture was stirred at 80 °C under nitrogen. A sodium carbonate aqueous solution (3.50 g, in 35 mL of water) and Pd(PPh₃)₄ (0.55 g) were added into the reaction mixture. The solution was vigorously stirred for 60 min at 80 °C under nitrogen. A solution of phenylboronic acid (2.29 g, 18.78 mmol) in 40 mL ethanol was added. The reaction mixture was heated at reflux for 24 h under nitrogen. It was then filtered using a short Celite pad to remove the insoluble components. The filtrate was washed several times with a saturated NaCl aqueous solution and dried with anhydrous magnesium sulfate. After the solvent was evaporated, the crude product was purified by column chromatography using ethyl acetate/dichloromethane (1/24, v/v) as the eluent to afford 2.37 g of yellow solid (yield: 60%), mp 189–191 °C, ¹H NMR (600 MHz, DMSO-*d*₆, δ, ppm): 2.07 (s, 6H), 7.38–7.43 (m, 10H), 7.60 (s, 2H), 7.68 (s, 2H), 10.24 (s, 2H). ¹³C NMR (150 MHz, DMSO-*d*₆, δ, ppm): 23.3, 114.8, 127.5, 127.6, 128.4, 128.6, 128.7, 134.8, 137.6, 141.5, 148.4, 168.5. EIMS (m/z): calcd for C₂₈H₂₂N₄O₇, 526.2; found, 526.1[M]⁺.

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