



Synthesis and characterization of high molecular weight perfluorocyclobutyl-containing polybenzimidazoles (PFCB–PBI) for high temperature polymer electrolyte membrane fuel cells

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ABSTRACT

High molecular weight perfluorocyclobutyl-containing polybenzimidazoles (PFCB–PBI) were synthesized from 4,4'-((1,2,3,3,4,4-hexafluorocyclobutane-1,2-diyl)bis(oxy))dibenzoic acid (PFCB diacid) and 3,3',4,4'-tetraaminobiphenyl (TAB) in phosphorous pentoxide/methanesulfonic acid (PPMA). PPMA was used as a reaction medium to replace PPA due to the higher monomer solubility. High molecular weight polymer was achieved via optimization of the monomer/solvent ratio, polymerization temperature, and polymerization time. The resulting polymer showed good thermal and chemical stability. Several different phosphoric acid doping membrane preparation processes were investigated. Conventional DMAc solvent casting and direct-casting of the PBI/PPMA solution did not produce sufficiently strong membranes to fabricate into MEAs. A modified PPA process was developed that produced improved membranes. The mechanical properties of these membranes were low compared to other PBI membranes; however, they were sufficiently strong to fabricate into membrane electrode assemblies and tested in single cell fuel cells under various conditions. The polymer dissolved in phosphoric acid at temperatures above 140 °C, which limited the operation of fuel cells below 140 °C. The maximum power densities of fuel cells operated with these membranes were similar to meta-PBI membranes prepared by the conventional casting process and lower than para-PBI membranes prepared by the PPA process.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) operated at temperatures greater than 120 °C offer many benefits including faster electrochemical reaction kinetics at the electrodes, higher fuel impurity tolerance, and reduced heat/water management issues. Extensive work has been dedicated to develop high temperature polymer electrolyte membrane fuel cell membranes [1]. Phosphoric acid doped polybenzimidazoles were reported as promising candidates for high temperature and high performance polymer electrolyte membrane fuel cells [2–17]. These polymer electrolyte membranes exhibited high proton conductivity at temperatures up to 200 °C without humidification, low reactant permeability, high fuel impurity tolerance, excellent oxidative and thermal stability, and nearly zero water drag coefficient. However, the preparation of phosphoric acid doped PBI membranes was costly, time-consuming, required multiple steps and not suitable for industrial scale production.

A novel one-step process to prepare phosphoric doped PBI membranes, named the PPA process, was developed by Benicewicz et al. [18–21]. In the PPA process, the polymerization of high molecular weight PBI from tetraamines and diacids was conducted in polyphosphoric acid (PPA), and then the polymer solution was cast directly from the polymerization mixture. As water was absorbed from the atmosphere, PPA hydrolyzed into phosphoric acid and induced a sol-to-gel transition. The PPA process represents a much simpler, lower cost, time-effective process which solved many problems associated with the conventional phosphoric acid doped PBI membrane preparation process.

In this work, the synthesis of high molecular weight perfluorocyclobutyl-containing polybenzimidazoles (PFCB–PBI) from 4,4'-((1,2,3,3,4,4-hexafluorocyclobutane-1,2-diyl)bis(oxy))dibenzoic acid (PFCB diacid) and 3,3',4,4'-tetraaminobiphenyl (TAB) in phosphorous pentoxide/methanesulfonic acid (PPMA) is described (Fig. 1). The introduction of the PFCB ring into the polymer backbone imparts solubility and flexibility without sacrificing thermal stability and chemical resistance [22–25]. The polymer was characterized by inherent viscosity (I.V.) measurements as a relative determination of polymer molecular weight, thermal and chemical

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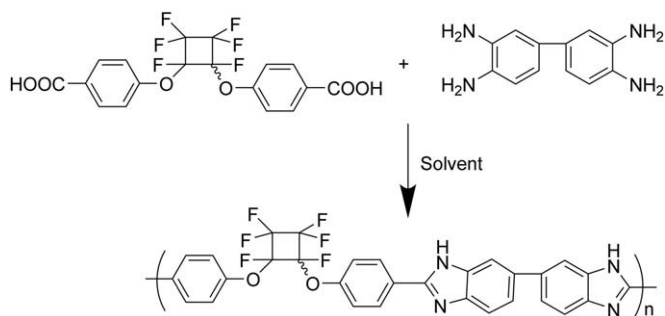


Fig. 1. Synthesis of PFCB-PBI.

stability assessment via thermogravimetric analysis and Fenton's test, respectively. The preparation of phosphoric acid doped PFCB-PBI membranes via a modified PPA process was developed and described herein. The phosphoric acid doping level, mechanical properties, and proton conductivity of the phosphoric acid doped PFCB-PBI membranes were also evaluated. The membranes were fabricated into membrane electrode assemblies and tested in single cell fuel cells under various conditions to explore their high temperature performance.

2. Experimental

2.1. Materials

4,4'-((1,2,3,3,4,4-Hexafluorocyclobutane-1,2-diyl)bis(oxy))dibenzoic acid (PFCB diacid) was obtained commercially from Tetramer Technologies, LLC (www.tetramertechnologies.com) and distributed through Oakwood Chemicals, Inc. (Columbia, SC), purity: >99%. 3,3',4,4'-Tetraaminobiphenyl (TAB, polymer grade, ~97.5%) was donated by Celanese Ventures, GmbH and used as received. Polyphosphoric acid (115%) was used as supplied from Aldrich Chemical Co. Methanesulfonic acid (Acros, 99%) and phosphorus pentoxide (Acros, 98+%) were used as received. The solution phosphorus pentoxide/methanesulfonic acid (PPMA, w/w: 1/10) was prepared as stated in the literature [26].

2.2. Polymer synthesis

The general procedure for the synthesis of perfluorocyclobutyl-containing polybenzimidazoles (PFCB-PBI) is described as follows: A 100 ml, three-necked, round bottom flask was equipped with an overhead mechanical stirrer, a water-cooled condenser, and nitrogen-purge inlet and outlet. 4,4'-((1,2,3,3,4,4-Hexafluorocyclobutane-1,2-diyl)bis(oxy))dibenzoic acid (PFCB diacid, 2.116 g, 5 mmol) and 3,3',4,4'-tetraaminobiphenyl (TAB, 1.071 g, 5 mmol) were added, followed by 15–50 ml PPMA. The reaction mixture was stirred using a mechanical stirrer at 100 rpm and purged with dry nitrogen, and the reaction temperature was controlled by a programmable temperature controller with ramp and soak features. The final polymerization conditions were approximately 140–150 °C for 24 h. A small amount of the reaction mixture was poured into water and a brown mass was isolated. The mass was pulverized, and then neutralized with ammonium hydroxide, washed thoroughly with water, and dried in a vacuum oven (–30 inch Hg, 110 °C) for 24 h to obtain the dry PFCB-PBI powder for further polymer characterization.

2.3. Membrane preparation

A calculated amount of polyphosphoric acid was added in the reaction flask with PFCB-PBI/PPMA, and then the temperature was raised to 200 °C for 24 h. The resulting viscous solution was cast

onto clear glass plates in air using a film applicator followed by polyphosphoric acid (PPA) hydrolysis under controlled conditions (for example, by placing membranes at 25 °C and relative humidity of 55% for 24 h).

2.4. Characterization

The inherent viscosity (I.V.) of the polymer was measured at a concentration of 0.2 g dry PBI/100 ml solution of the polymer dissolved in concentrated sulfuric acid (96 wt%) at 30 °C with a Cannon Ubbelohde viscometer.

Thermal gravimetric analysis (TGA) thermograms were obtained using a METTLER TOLEDO TGA/SDTA 851 with a nitrogen flow rate at 20 ml/min. The temperature range was from room temperature to 900 °C and the temperature scan speed was 10 °C/min.

Fenton's test was performed on both dry polymer and phosphoric acid doped membrane. Fenton's reagent (20 ppm Fe(II), 3 wt% H₂O₂) is a very effective method to generate hydroxyl and peroxy radicals. The test samples (except the phosphoric acid doped membrane) were dried in a vacuum oven at 110 °C overnight and weighed. The test sample and 10 ml Fenton's reagent solution were placed in a sealed glass bottle, and then heated at 40 °C or 160 °C for 24 h. After that, the test sample was rinsed with water, dried in a vacuum oven at 110 °C overnight, and measured for the final weight. The weight loss was used to characterize the resistance to hydroxyl/peroxy free radicals.

The mechanical properties of the membrane were measured on ASTM D683 Type V specimens cut from the bulk phosphoric acid doped PFCB-PBI membrane using a United Tensile Tester (SSTM-1-PC) with a 22.2 N load cell.

The phosphoric acid doping level of the membrane was determined by titration with 0.1 M sodium hydroxide using a Metrohm 716 DMS Titrino titrator. The first equivalence point was used to determine the volume of sodium hydroxide necessary for neutralization. Acid doping levels, X , moles of phosphoric acid per mole of PBI repeat unit (X H₃PO₄/PBI) were calculated from the equation:

$$X = \frac{(V_{\text{NaOH}} \times C_{\text{NaOH}})}{(W_{\text{dry}}/M_{\text{polymer}})}$$

where V_{NaOH} and C_{NaOH} are the volume and concentration of the sodium hydroxide solution required to neutralize the phosphoric acid to the first equivalence point, W_{dry} is the dry weight of the polymer sample, and M_{polymer} is the molecular weight of the polymer repeat unit.

Proton conductivities were measured by a four-probe electrochemical impedance spectroscopy method using a Zahner IM6e electrochemical workstation over the frequency range from 1 Hz to 100 kHz with amplitude of 5 mV. The conductivities of the membrane were calculated:

$$\sigma = \frac{d}{lwR_m}$$

where d is the distance between the two inner probes, l is the thickness of the membrane, w is the width of the membrane, and R_m is the ohmic resistance from the model fitting.

2.5. Membrane electrode assembly (MEA) preparation and fuel cell testing

The MEA was prepared by hot-pressing a piece of membrane between the two gas diffusion electrodes (GDE, acquired from BASF Fuel Cell, Inc., platinum loading: 1.0 mg/cm²). The MEA was then assembled into a single cell fuel cell testing hardware. A

commercial fuel cell testing station (Fuel Cell Technology, Inc.) was used for fuel cell testing, while gases were fed to the anode and cathode without any humidification. The instrument was controlled by home-programmed Lab View Software (National Instruments, Austin, TX).

3. Results and discussion

3.1. Polymer synthesis

A number of synthetic routes for synthesizing PBI polymers have been developed. The routes widely employed in the synthesis of PBI are represented by melt polymerization of tetraamines with dicarboxylic acid diphenyl esters and by solution polymerization of tetraamines with dicarboxylic acids or their derivatives in polyphosphoric acid (PPA) as a reaction medium. The solution polymerization of PFCB–PBI in PPA was investigated early in this study. During the initial polymerization, the sublimation of PFCB–diacid monomer was observed, and the polymerization only produced low I.V. polymer (0.15 dL/g, measured in 0.2 g/dL, 96% concentrated H₂SO₄ at 30 °C). The reasons for the low molecular weight polymer were attributed to the low solubility of PFCB–diacid monomer in PPA and the unequal stoichiometry of monomers caused by PFCB–diacid monomer sublimation at high polymerization temperatures. Additional intermediate temperature polymerization steps were inserted into the polymerization scheme to promote monomer dissolution and reaction. However, the sublimation of PFCB–diacid monomer still occurred at higher polymerization temperatures. It was concluded that polyphosphoric acid was not a good solvent for PFCB–diacid even at high temperatures (150–170 °C) and the reaction rate to form oligomers was also low.

Various solution media were tested to increase the monomer solubility and reaction rate. The results are summarized in Table 1.

Polyphosphoric acid (115%), polyphosphoric acid with added phosphorus pentoxide, and polyphosphoric acid with NMP were all tested as polymerization solvents and resulted in low I.V. polymers, 0.15, 0.16, 0.20 dL/g, respectively. This study confirmed that polyphosphoric acid was not a good polymerization solvent for PFCB–PBI synthesis, even with the increase of phosphorus pentoxide content in PPA or the addition of NMP to increase the solubility of the monomer in PPA.

Another solution medium was tested – phosphorus pentoxide/methanesulfonic acid (PPMA). Eaton et al. [26] reported that PPMA was a convenient alternative to polyphosphoric acid. The reactive components in phosphorus pentoxide/methanesulfonic acid (P₂O₅–MSA or PPMA) were very similar to those present in PPA [27]. PPMA provided the advantages of a less viscous solution and better solubility of certain organic compounds. The polymerization of PFCB–PBI in PPMA was conducted and resulted in high molecular weight polymer with the polymer I.V.'s as high as 1.5 dL/g.

The investigation of PFCB–PBI polymerization in PPMA to achieve the high molecular weight polymer was conducted by adjusting the monomer/solvent ratio, polymerization temperature, and polymerization time. The details of the experimental design and results are shown in Table 2.

Table 1
Polymerization solvent study.

Solvent	Polymerization condition	Polymer I.V.(dL/g)
Polyphosphoric acid (PA: 115 wt%)	220 °C, 48 h	0.15
Polyphosphoric acid + P ₂ O ₅ ^a	220 °C, 48 h	0.16
Polyphosphoric acid + NMP ^b	220 °C, 48 h	0.20
Methanesulfonic acid + P ₂ O ₅ (PPMA)	140 °C, 24 h	up to 1.55

^a The amount of added P₂O₅ was calculated for a PPA concentration of 128 wt%.

^b NMP: *N*-methyl-2-pyrrolidinone, the added amount was equal to 5 wt% of PPA.

As shown in Table 2, the monomer/solvent ratio ranged from 1 mmol monomer:3 ml solvent to 1 mmol monomer:10 ml solvent. Among these monomer/solvent ratios, 1 mmol monomer:5 ml solvent was found to be most suitable for the PFCB–PBI polymerization in PPMA for producing high molecular weight polymers. For the lower monomer/solvent ratios such as 1 mmol monomer:3 ml solvent, the solution became very viscous, difficult to stir, and the monomer was not completely dissolved in PPMA. For the higher ratios such as 1 mmol monomer:8 ml solvent and 1 mmol monomer:10 ml solvent, the polymerization was very slow, even at the higher polymerization temperature (150 °C) and long polymerization time (48 h).

The effect of polymerization temperature on the polymer molecular weight was examined at 120 °C, 140 °C and 150 °C. At the lowest polymerization temperature (120 °C), the solution was very viscous and the reaction rate was low. A polymer I.V. of 0.16 dL/g was achieved after polymerization at 120 °C for 24 h. Thus, the polymerization only achieved low molecular weight polymer. At the highest polymerization temperature (150 °C), the polymerization rate was much higher. After 24 h, the solution became jelly-like, which was difficult to cast into a membrane. The polymer isolated from the jelly-like solution did not totally dissolve in concentrated sulfuric acid (96 wt%) at a concentration ~0.2 g/dL. The polymerization conducted at 140 °C gave polymer with I.V.'s as high as 1.55 dL/g.

The effect of polymerization time on the polymer inherent viscosity was examined for the polymerization solvent mixture of 1 mmol monomer:5 ml solvent and at 140 °C. Small volumes of the polymer solution were sampled from the polymerization system at 3, 6, 9, 12, 24, 36, 48, 60, and 72 h, respectively. The effect of polymerization time on the resulting polymer I.V. is shown in Fig. 2.

The I.V. of PFCB–PBI increased quickly with the polymerization time in the initial 24 h and increased only slightly after 24 h. Subsequent attempts to increase polymer I.V. by adding PPA and extending the polymerization time were conducted. After 72 h, PPA was added and the temperature was raised to 200 °C. However, the addition of PPA into the reaction system, and heating at 200 °C for 80 h did not result in any further increase in polymer I.V.

3.2. Polymer characterization

TGA was used to test the thermal stability of the PFCB–PBI polymers (Fig. 3). The TGA thermogram of PFCB–PBI was measured in flowing nitrogen (20 ml/min) at 10 °C/min heating rate from room temperature up to 900 °C. The polymer was stable at temperatures as high as approximately 358 °C (0.02 wt% loss), and the decomposition temperatures TD₅ and TD₁₀ (where 5 wt% and 10 wt% of the original weight was lost, respectively) under nitrogen were 466 °C and 493 °C, respectively. The residue weight at 900 °C was approximately 57.4 wt% of the original weight. The TGA data showed that the introduction of perfluorocyclobutyl (PFCB) group into the polymer main chain decreased the thermal stability of PBI polymer only slightly as compared to the previously reported high thermal stability of meta-PBI (the polymer was stable up to approximately 450 °C) [28]. Approximately 4% weight loss from room temperature to 120 °C was attributed to the loss of water in the PFCB–PBI. This moisture loss was lower than for meta-PBI (15–18 wt%) [29]. The introduction of the hydrophobic perfluorocyclobutyl functional group into the polymer main chain decreased the hydrophilicity of the PBI polymer.

The chemical stability of PFCB–PBI, or specifically the resistance to hydroxyl/peroxyl free radicals, was tested via Fenton's test. Fenton's test was performed by placing the dried test sample in 10 ml Fenton's reagent solution (20 ppm Fe(II), 3 wt% H₂O₂) in a sealed bottle at 40 °C or 160 °C for 24 h. The weight loss was used

Table 2
Investigation of PFCB–PBI polymerization in PPMA.

Monomer:PPMA	Temperature	Time	Observation	Polymer I.V. ^a (dL/g)
1 mmol:3 ml	140 °C	24 h	Solution: very viscous Monomer: not completely dissolved	0.16
1 mmol:3 ml	150 °C	24 h	Solution: very viscous Monomer: not completely dissolved	0.18
1 mmol:5 ml	120 °C	24 h	Solution: very viscous Monomer: not completely dissolved	0.16
1 mmol:5 ml	140 °C	24 h	Solution: less viscous, easy to stir Monomer: completely dissolved	up to 1.55
1 mmol:5 ml	150 °C	24 h	Solution: less viscous, easy to stir Monomer: completely dissolved	^b
1 mmol:8 ml	140 °C	48 h	Solution: less viscous, easy to stir Monomer: completely dissolved	0.40
1 mmol:10 ml	150 °C	48 h	Solution: less viscous, easy to stir Monomer: completely dissolved	0.28

^a I.V.s were measured at a concentration of 0.2 g/dL in concentrated H₂SO₄ at 30 °C with a Cannon Ubbelohde viscometer.

^b I.V.s were not measured due to the incomplete dissolution of the polymer in concentrated sulfuric acid.

to characterize the resistance to hydroxyl/peroxyl free radicals. The weight losses and various testing conditions are summarized in Table 3.

The weight loss of PFCB–PBIs were low, all less than 0.5 wt%. Under the same harsh conditions, Nafion and Kapton had higher weight loss. The weight loss data for Fenton's test on Nafion in this work are similar to Fenton's test data widely reported for Nafion polymer in the literature [30,31]. The low weight loss of PFCB–PBI indicated excellent hydroxyl/peroxyl radical resistance of PFCB–PBI regardless if the sample was in polymer or membrane form, with or without phosphoric acid, and at low or high temperatures. It also demonstrated that the perfluorocyclobutyl group in the polymer was stable from the free radical attack in the harsh conditions of this common test.

3.3. Phosphoric acid doped membrane preparation

Several different membrane preparation processes were investigated as part of this work. The PFCB–PBI dry polymer readily dissolved in DMAc. Concentrated polymer solutions (10 wt%) were prepared without the need for high pressures or high temperatures, and the solution did not require lithium chloride for polymer dissolution. However, the resulting films were brittle and easy to break. The conventional DMAc process did not produce strong

films, even with the highest I.V. PFCB–PBI. The phosphoric acid doped PFCB–PBI membranes were also prepared by directly casting the PFCB–PBI/PPMA solution on to glass plates with a film applicator, then hydrolyzed under controlled conditions (25 °C, relative humidity, 55%). A sol-to-gel transition was observed as water was absorbed from the atmosphere. The resulting gel membranes were washed in water several times, and then soaked in a 70% phosphoric acid bath. This process required multiple steps of soaking in liquid baths, and generated a large volume of hazardous waste. The resulting membranes were weak and difficult to handle. To resolve the problems mentioned above, a modified PPA process was developed. The PFCB–PBI was polymerized in PPMA at 140 °C, and at the end of polymerization, a calculated amount of polyphosphoric acid was added to control the ultimate polymer concentration, followed by an increase in the temperature to 200 °C for 24 h. The methanesulfonic acid is thermally unstable at these temperatures and the gaseous decomposition products were removed from the solution [26]. The complete removal of methanesulfonic acid was verified by elemental analysis of the phosphoric acid doped PFCB–PBI membrane. No sulfur was detected in the cast membranes. The PFCB–PBI/PPA solution was cast onto glass plates with a film applicator. The membranes were formed during the hydrolysis of polyphosphoric acid to phosphoric acid under controlled conditions (25 °C and relative humidity of 55% for 24 h). Among these membrane preparation processes, only the modified

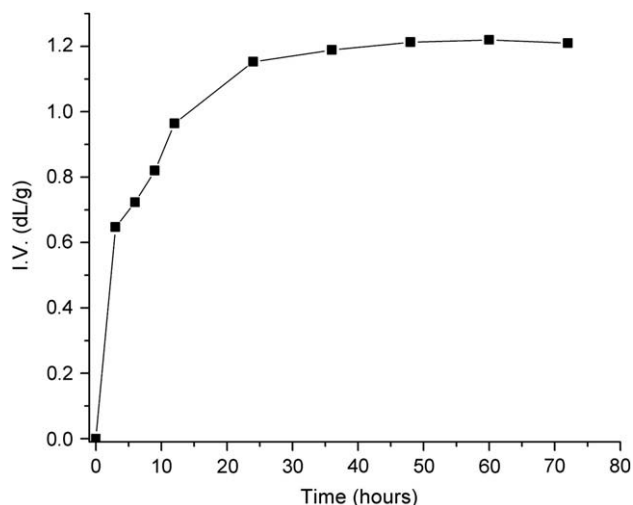


Fig. 2. I.V. of PFCB–PBI with polymerization time in PPMA. Polymerization conditions: 1 mmol monomer: 5 ml PPMA, 140 °C.

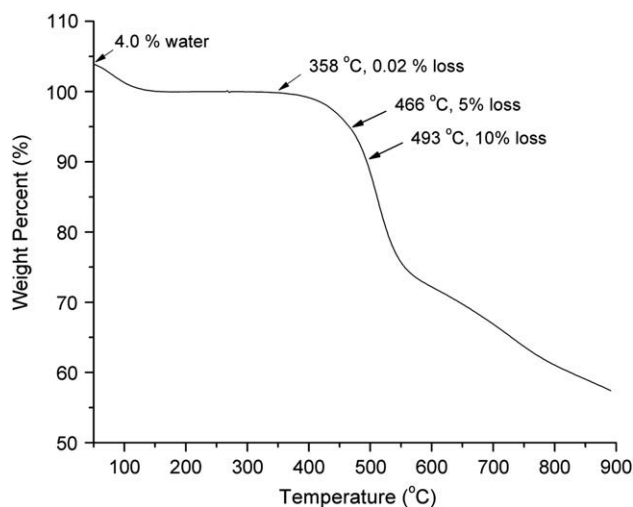


Fig. 3. TGA thermogram of PFCB–PBI.

Table 3
Fenton's test of PFCB–PBI.

Test sample	Weight loss (%)	
	40 °C	160 °C
Nafion 115	1.8	4.8
Kapton	<0.5	0.8
PFCB–PBI ^a	<0.5	<0.5
Dry membrane (a) ^b	<0.5	<0.5
Dry membrane (b) ^b	<0.5	<0.5
Phosphoric acid doped membrane ^c	<0.5	<0.5

^a PFCB–PBI was dried polymer powder, I.V. = 1.5 dL/g.

^b Dry membrane was prepared via neutralizing phosphoric acid doped membrane with ammonium hydroxide, washing with water, then drying in a vacuum oven at 110 °C. (a) No phosphoric acid was used in Fenton's test, (b) 1 ml 85% phosphoric acid was added into Fenton's reagent.

^c Initial phosphoric acid doped membrane was a disk-shaped sample cut from bulk membrane with 2 cm diameter. The initial weight of polymer in phosphoric acid doped membrane was calculated from the polymer weight percentage of bulk membrane and initial weight of disk-shaped membrane sample.

PPA process produced the phosphoric acid doped PFCB–PBI membranes sufficiently strong to fabricate into a membrane electrode assembly. The membrane properties such as phosphoric acid doping level, proton conductivity, and mechanical properties were tested with the membranes prepared by the modified PPA process.

3.4. Membrane characterization

The phosphoric acid doping levels of PFCB–PBI membranes prepared by direct-casting of PFCB–PBI/PPMA solutions and the modified PPA process are shown in Table 4. The phosphoric acid doping levels for PFCB–PBI membranes produced by both processes were considerably higher than other phosphoric acid doped PBI (meta-PBI, para-PBI, 6F-PBI etc.) membranes prepared by the PPA process (30–40 PA/PBI repeat unit) [18,19]. This was somewhat surprising since it was anticipated that the increased hydrophobicity of the partially fluorinated polymer would lead to lower phosphoric acid doping levels.

The mechanical properties of phosphoric acid doped PFCB–PBI membranes with high phosphoric acid doping level prepared by the modified PPA process were tested and exhibited a tensile strength and elongation at break of 0.35 MPa and 130%, respectively. For the phosphoric acid doped PBI membranes prepared by the conventional DMAc process, there was a tradeoff between the desired properties of the membrane, such as high phosphoric acid doping levels and proton conductivity, with high mechanical properties. Li et al. [14] reported one of the highest phosphoric acid doping levels (13–16 PA/PBI repeat unit, using the commercially available meta-PBI with an I.V. of 1.0 dL/g) attained using the conventional membrane fabrication process. These membranes with “high” phosphoric acid loading levels resulted in poor mechanical properties and were too weak to fabricate into membrane electrode assemblies. In contrast, phosphoric acid doped PFCB–PBI membranes were sufficiently strong to fabricate into membrane electrode assemblies with very high phosphoric acid doping level (more than 50 PA/PBI repeat unit).

Table 4
Composition of phosphoric acid doped PFCB–PBI membranes.

Sample	Phosphoric acid (wt%)	Polymer (wt%)	Water (wt%)	PA/PBI repeat unit
A	49.3	4.1	46.7	71
B	47.2	5.3	47.5	53

Sample A: prepared from direct-casting of PFCB–PBI/PPMA solution.

Sample B: prepared from the modified PPA process.

The proton conductivity of the phosphoric acid doped PFCB–PBI membranes prepared by the modified PPA process is shown in Fig. 4. The proton conductivity was approximately 0.01 S/cm at room temperature and reached as high as 0.12 S/cm at 140 °C without humidification. The proton conductivity of the membrane at 160 °C or above could not be measured on the as-produced films since it appeared that the PFCB–PBI dissolved at the higher temperatures for the membranes with these high levels of phosphoric acid. We conclude that the physical gel formed in the PPA process simply underwent a reversible gel-to-sol transition at this temperature range. The proton conductivity of the resulting phosphoric acid doped PFCB–PBI membrane was lower compared to the other PBI membranes (for example, para-PBI, ~0.20 S/cm at 140 °C) prepared by the PPA process although the phosphoric acid doping levels of PFCB–PBI membrane (~50 PA/PBI repeat unit) were higher than those PBI membranes (~40 PA/PBI repeat unit) [19]. It was previously proposed that high phosphoric acid doping levels led to high proton conductivity [14]. The current work suggests a more complicated relationship between the proton conductivity and membrane gel structure than a simple relationship of phosphoric acid doping level in the membrane with the proton conductivity [18].

3.5. MEA and fuel cell testing

The high temperature fuel cell performance of phosphoric acid doped PFCB–PBI membranes prepared by the modified PPA process was investigated in a 50 cm² single cell fuel cell and the polarization curves are shown in Fig. 5. The fuel cell was operated at 140 °C, atmospheric pressure and dry gases without external humidification. Fuel cells with phosphoric acid doped PFCB–PBI membrane could not be operated above 140 °C since the re-dissolution (gel-to-sol) of the PFCB–PBI in phosphoric acid occurs at those temperatures and high phosphoric acid doping levels.

At a current density of 0.2 A/cm², a voltage of approximately 0.51 V was obtained when operated on hydrogen (1.2 stoichiometric flows) and air (2.0 stoichiometric flows). When the oxidant gas changed from air to oxygen, oxygen partial pressure increased from 0.21 atm to 1 atm and the cell voltage at 0.2 A/cm² increased from 0.51 V to 0.59 V. The maximum power densities of fuel cells with phosphoric acid doped PFCB–PBI membranes were 0.21 W/cm² (hydrogen/oxygen) and 0.15 W/cm² (hydrogen/air) at 140 °C, atmospheric pressure, stoichiometric flows –1.2:2.0. The performance of phosphoric acid doped PFCB–PBI membranes was similar to the previous results on meta-PBI membranes prepared by the

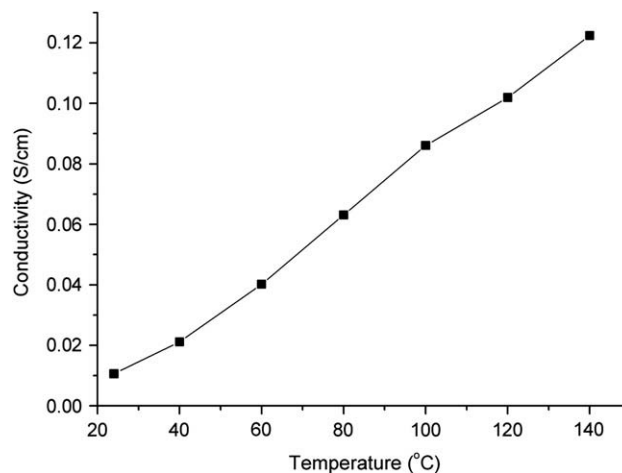


Fig. 4. Proton conductivity of phosphoric acid doped PFCB–PBI membrane prepared by the modified PPA process.

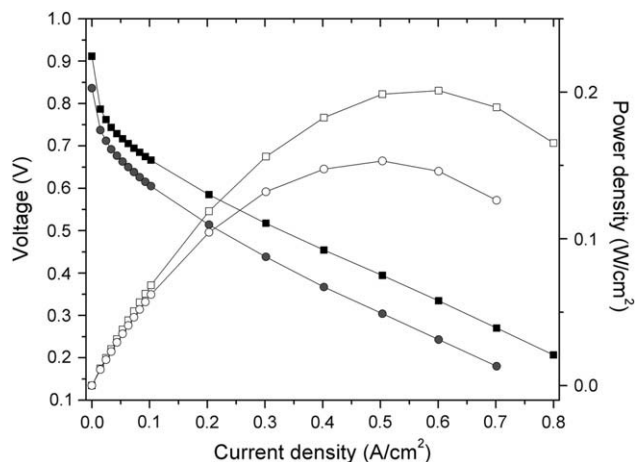


Fig. 5. Typical polarization curves (filled symbols) and power density curves (unfilled symbols) of fuel cells with phosphoric acid doped PFCB-PBI membranes prepared by the modified PPA process. Fuel cell operation conditions: atmospheric pressure, H₂/air (square) or H₂/O₂ (circle), stoichiometric flows –1.2 and 2.0, respectively.

conventional DMAc process [32], which showed a maximum power density of 0.25 W/cm² at 150 °C. However, the fuel cell performance of the phosphoric acid doped PFCB-PBI membranes was lower compared to para-PBI membranes prepared by the PPA process (maximum power density can reach 0.9 W/cm² at approximately 2.0 A/cm², 160 °C, atmospheric pressure, hydrogen/oxygen) [19], which can be attributed to the low proton conductivity of the PFCB-PBI membranes compared to the para-PBI and the limited fuel cell operational temperature (140 °C).

4. Conclusions

A high molecular weight PFCB-PBI was synthesized from 3,3'-diaminobenzidine and 4,4'-((1,2,3,3,4,4-hexafluorocyclobutane-1,2-diyl)bis(oxy))dibenzoic acid in phosphorous pentoxide/methanesulfonic acid (PPMA). Exploration of different reaction solvent mixtures led to the identification of a solvent mixture, phosphorous pentoxide/methanesulfonic acid (PPMA) that successfully produced high I.V. polymer. High molecular weight polymer (I.V. = 1.5 dL/g) was achieved with the optimized polymerization conditions: 1 mmol monomer in 5 ml PPMA, 140 °C polymerization temperature and long polymerization time (more than 24 h). The resulting PFCB-PBI polymer showed high thermal stability which was similar to wholly aromatic PBIs that did not contain PFCB rings. Excellent hydroxyl/peroxyl free radical resistance of the polymers and membranes was established in Fenton reagent testing experiments. A modified PPA process was developed to prepare phosphoric acid doped PFCB-PBI membranes. The mechanical properties of these membranes (tensile strength > 0.35 MPa and elongation at break ~130%) were low compared to other PBI membranes; however, they were sufficiently strong to fabricate into membrane electrode assemblies. The proton conductivity was 0.01 S/cm at room temperature and reached as high as 0.12 S/cm at 140 °C without external humidification. The polymer underwent a gel-to-sol transition and re-dissolved the membrane in phosphoric acid at

temperatures above 140 °C, which limited the operation of fuel cells based on phosphoric acid doped PFCB-PBI membranes containing high levels of phosphoric acid. The maximum power densities of fuel cells with phosphoric acid doped PFCB-PBI membranes was 0.21 W/cm² (hydrogen/oxygen) and 0.15 W/cm² (hydrogen/air) at 140 °C, atmospheric pressure, stoichiometric flows –1.2:2.0, which are similar values to meta-PBI membranes prepared by the conventional process and lower than para-PBI membranes prepared by the PPA process.

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