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Polyphenylquinoxaline-based proton exchange membranes synthesized via the PPA Process for high temperature fuel cell systems

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ABSTRACT

A novel method for the successful, high temperature (125 °C) polymerization of high inherent viscosity polyphenylquinoxaline (PPQ) homopolymer and copolymers with polybenzimidazole (PBI) was investigated. PPQ homopolymer and PPQ/PBI copolymer membranes were prepared via the Polyphosphoric Acid (PPA) Process for use in high temperature (>120 °C) fuel cell systems. PPQ homopolymer membrane with a polymer content of 8.00 wt% was shown to have a phosphoric acid loading of 36.2 mol phosphoric acid per mol of polymer repeat unit (PA/r.u.) and a Young's modulus of 21 MPa, indicating a rigid gel membrane. PPQ homopolymer membranes with high PA loadings were, however, found to be dimensionally unstable at temperatures greater than 120 °C and reverted to a sol state. To increase the dimensional stability of a PPQ-based proton exchange membrane (PEM), a series of copolymer films containing PPQ and the highly dimensionally stable *p*-PBI polymer were studied. The series of PPQ/PBI copolymer membranes ranged in PPQ content from 10 to 95 mol% and were found to possess phosphoric acid doping levels between 19 and 39 mol PA/r.u. and proton conductivities up to 0.26 S cm^{-1}. Several of the copolymer membranes were also shown to have enhanced rigidity over numerous other membranes developed by the PPA Process as exhibited by Young's moduli between 1.9 and 31.1 MPa. An advantageous balance of properties was found for a PPQ/*p*-PBI copolymer membrane composition of 58 mol% PPQ and 42 mol% *p*-PBI, denoted as PPQ-58. This membrane was found to have a phosphoric acid doping level of 39.2 mol PA/r.u. and a proton conductivity of 0.24 S cm^{-1} at 180 °C. PPQ-58 membranes also showed excellent long-term stability in a fuel cell operating under non-humidified conditions at 160 °C utilizing hydrogen and air (1.2:2.0 stoich.) at a current density of 0.2 A cm^{-2}. Under these conditions, PPQ-58 exhibited a voltage degradation rate of 30 μV h^{-1} during a 2900 h lifetime performance test.

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1. Introduction

Recently, a heightened global environmental awareness has sparked a widespread interest in the development of clean and efficient energy systems. As a result, proton exchange membrane (PEM) – also known as polymer electrolyte membrane – fuel cells have been identified as environmentally beneficial energy systems due to their simple, clean, and efficient operation [1]. The main focus of fuel cell polymer membrane research over the last several decades has been aimed at perfluorosulfonic acid (PFSA)-based membranes such as DuPont's Nafion®, or similar membrane chemistries. These materials are currently considered expensive and are limited by their reliance on water for proton conduction, necessitating humidification of reactant gases and fuel cell operation temperatures less than 100 °C. At these temperatures, catalyst poisoning by reactant gas impurities such as carbon monoxide is also a major concern. To overcome the limitations of PFSA-type systems, development of alternative membranes for fuel cell operation over 100 °C is appealing. High temperature operation may provide multiple system advantages, including faster electrode kinetics, a higher tolerance to reactant gas impurities, no humidification requirements, and an overall simplified system design.

Polyphenylquinoxalines (PPQs) are a well-known class of π-electron deficient, aromatic heterocyclic, high performance thermoplastics that exhibit high glass transition temperatures, excellent tensile properties, good thermal oxidative stability [2–5], and proton conductivity when appropriately doped [6,7]. Furthermore, PPQs are a historical example of a phenyl-functionalized thermally resistant polymer whose bulky phenyl group leads to the increased solubility and higher processability compared to the parent polyquinoxaline polymer [8]. The high processability and physicochemical properties inherent to PPQs make this class of polymers ideal for investigation as proton exchange membranes in high temperature fuel cell systems.

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A classical method for the synthesis of polyphenylquinoxalines was first reported by Hergenrother et al. in 1967 and involves the cyclopolycondensation of aromatic bis(*o*-diamines) with aromatic tetraketones in *m*-cresol [4]. Films were produced by solvent-casting PPQ solutions in *m*-cresol onto glass plates, followed by drying under vacuum at 160 °C for several days. This method results in high molecular weight polymer film with good processability and mechanical integrity. More recent work reported by Baek and Harris describes a method for the formation of hyperbranched PPQs in polyphosphoric acid (PPA) via an aromatic nucleophilic substitution polymerization using a preformed polyphenylquinoxaline-containing AB_2 monomer [9]. One of the foremost drawbacks of PPQ polymerizations is crosslinking of the polymer when polymerization temperatures are exceeded. This crosslinking has been shown to often result in the formation of insoluble PPQ gels and non-processable materials [10,11]. Such problems have previously been circumvented by using monomers with preformed phenylquinoxaline rings and by relying on alternate polymerization mechanisms such as aromatic nucleophilic substitution or electrophilic substitution reactions for the polymerization of both phenylquinoxaline and non-phenylquinoxaline monomers [9,10,12].

In efforts to improve the fuel cell performance of the most widely used perfluorosulfonic acid (PFSA) PEMs, such as Nafion®, several methods have previously been developed to produce polyphenylquinoxaline-based proton exchange membranes suitable for use in low temperature (<100 °C), water-based fuel cell systems [6,13–15]. Kopitzke and coworkers reported a "soak-and-bake" method for the development of a sulfonated PPQ (sPPQ) film suitable for low temperature fuel cell applications [6,15]. The characteristics of water-imbibed sPPQ membranes developed by Kopitzke are summarized in Table 1 and are compared to the performance of Nafion 117 [6]. Conductivity tests were performed in a water-filled, sealed pressure reactor that was submerged in a temperature controlled water bath [6]. Further analyses of sPPQ membranes including fuel cell operating conditions were not reported.

Looking to develop a lower-cost alternative to PFSA-based membranes, Ballard Advanced Materials also attempted to produce sulfonated PPQ membranes for use as low temperature, direct methanol PEM fuel cells. The first series of polymers investigated were based on sulfonated PPQs prepared via the self-polymerization of 4-(6-fluoro-3-phenylquinoxalin-2-yl)phenol in *m*-cresol, followed by soaking the resulting membranes in chlorosulfonic acid. This first generation of Ballard PPQ membranes, termed "BAM-1G", were evaluated as single cells with an active area of 50 cm^2 operating on hydrogen and air (H_2:Air = 42:24 psig) at 70 °C [7]. The BAM-1G membrane was shown to have good mechanical properties and promising initial fuel cell performance, similar to that of Nafion® 117 [16]. Furthermore, BAM-1G was shown to have good polarization curve performance. The major disadvantage of this membrane, however, was extremely short lifetime, averaging approximately 350 h [7]. Due to the extremely unfavorable lifetimes exhibited by BAM-1G, Ballard Advanced Materials deemed PPQ chemistry unsuitable for further investigation as a proton conducting membrane in low temperature systems and their attention was focused elsewhere.

Phosphoric acid (PA) doped proton exchange membranes are among the most promising candidates for high temperature fuel cells [17]. Several high molecular weight PA doped polybenzimidazole-based membranes have been developed for use in high temperature fuel cell systems, utilizing a novel method termed the "PPA Process" [18–24]. This method utilizes polyphosphoric acid (PPA) as a solvent and polycondensation agent for the polymerization between a dicarboxylic acid and a tetraamine, and as the polymer solution casting solvent that aids in formation of a sol–gel membrane as PPA is hydrolyzed into phosphoric acid. The resulting membrane is a low-solids content, phosphoric acid-imbibed membrane with good mechanical properties [18].

The exceptional mechanical properties, thermal stability, and proton-conducting ability of polyphenylquinoxalines make this class of polymer an excellent candidate for investigation as proton exchange membranes for high temperature fuel cells. The success of polybenzimidazole membranes synthesized by the PPA Process [19–24] and the evidence presented by Baek et al. supporting the use of polyphosphoric acid as a condensation agent for the polymerization of preformed phenylquinoxaline monomers [10] provided motivation to devise an efficient method for the formation of high molecular weight PPQ sol–gel membranes via the PPA Process for use in high temperature PEMFCs. The work in this paper focuses on the development and characterization of PPQ homopolymer membranes and a series of PPQ/PBI copolymer membranes prepared via the PPA Process.

2. Experimental

2.1. Materials

3,3′,4,4′-Tetraaminobiphenyl (TAB, 97%) was supplied by Celanese Ventures, GmBH. Terephthalic acid (TA, 99 + %) was purchased from Amoco. 1,4-Bisbenzil (BB, 95+%) was purchased from TCI America. Each monomer was used as received without further purification. Polyphosphoric acid (PPA, 115–118%) was used as supplied from FMC Corporation or Aldrich Chemical Company.

2.2. Polymer synthesis

Several polyphenylquinoxaline (PPQ) homopolymers were synthesized in varying concentrations and at different temperatures according to the PPA Process (Table 2). PPQ homopolymer was synthesized using the following general procedure (Scheme 1): TAB (6.03 g, 28.1 mmol) and BB (9.63 g, 28.1 mmol) were charged in a 100 mL reactor in a nitrogen glove box. PPA (100.63 g, 115%) was added to the reactor to give a solution having an initial monomer concentration of 13.47 wt%. The mixture was stirred by an overhead mechanical stirrer under a slow nitrogen purge. The reaction temperature was controlled by a programmable temperature controller with ramp/soak capabilities. The typical final polymerization temperature for the PPQ homopolymer system was 125 °C for 4.5 h. As the reaction proceeded, the viscosity of the solution increased and the color changed from brown to deep red. At the end of polymerization, 33 mL of phosphoric acid was added to adjust the viscosity of the solution for film casting, and then stirred for an additional 30 min. The polymer solution was then cast onto glass plates at a thickness of 20 mils and placed into a controlled humidity chamber for 24 h to produce a gel film. Residual polymer solution in the reactor was hydrolyzed with distilled water. After complete hydrolysis of the solution, the polymer was pulverized in a blender containing approximately 500 mL of water and the mixture was then heated and neutralized with ammonium hydroxide. The polymer was isolated and dried under vacuum to provide the polymer powder. The I.V. of the polymer was measured to be 1.17 $dL\,g^{-1}$ at a concentration of 0.5 $g\,dL^{-1}$ in concentrated sulfuric acid at 30 °C.

The general synthetic scheme for polybenzimidazole (PBI) homopolymer was as follows (Scheme 2): TAB (2.039 g, 9.52 mmol) and TA (1.581 g, 9.52 mmol) were charged in a 100 mL reactor in a nitrogen glove box. PPA (100.12 g, 115%) was added to the reactor to give a solution having an initial monomer concentration of 3.49 wt%. The mixture was stirred by an overhead mechanical stirrer under a slow nitrogen purge. The reaction temperature

Table 1
Conductivity performance of sulfonated PPQ membrane compared to Nafion® 117 [6].

Polymer	λ (number of H_2O/SO_3H)	σ at 20 °C (S cm^{-1}), 100% RH	σ_{max} at T_{max} (S cm^{-1})	T_{max} [a] (°C)
sPPQ	8.0	9.8×10^{-3}	0.130	180
Nafion® 117	11.5	9.2×10^{-2}	0.250	169

[a] Temperature at maximum conductivity.

Table 2
Summary of PPQ homopolymer syntheses and polymer I.V.s.

Sample no.	[M][a] (wt%)	Casting concentration (wt%)	PZN[b] temp (°C)	Time at PZN temp (h)	I.V.[c] (dL g^{-1})
I	3.51	2.96	130	15	0.98
II	5.01	4.24	130	15	1.10
III	13.51	10.41	130	4	*x*-Linked[d]
IV	16.86	15.00	130	15	*x*-Linked[d]
V	23.48	20.00	130	14	*x*-Linked[d]
VI	13.47	8.00	125	4.5	1.17

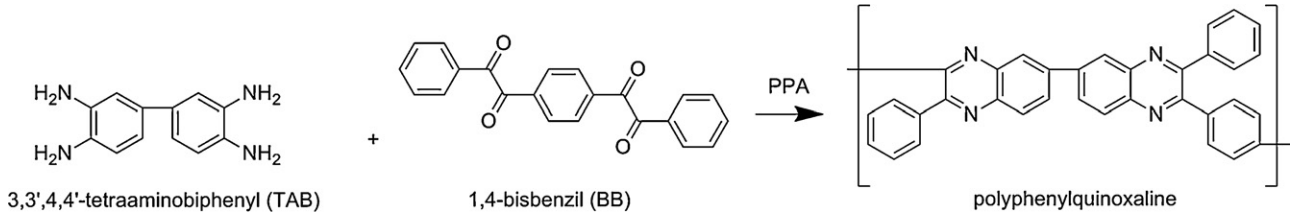
[a] Initial monomer concentration.
[b] Polymerization.
[c] I.V. was determined at a concentration of 0.5 g/dL in conc. H_2SO_4 at 30 °C.
[d] Insoluble gel formation, polymer not suitable for I.V. testing.

was controlled by a programmable temperature controller with ramp/soak capabilities. The typical final polymerization temperature for PBI homopolymer was 195 °C for 13 h. At the end of polymerization, the system temperature was raised to 220 °C and phosphoric acid (9 mL, 15.3 g) was added to the reactor to adjust solution viscosity for film casting. The mixture was then stirred for an additional 30 min. Afterwards, the polymer solution was cast onto glass plates at a thickness of 20 mils and placed into a controlled humidity chamber for 24 h to produce a gel film. Residual polymer solution in the reactor was hydrolyzed with distilled water. After complete hydrolysis of the solution, the polymer was pulverized in a blender containing approximately 500 mL of water and the mixture was then heated and neutralized with ammonium hydroxide. The polymer was then isolated and dried under vacuum to provide the polymer powder. The I.V. of the polymer was measured to be 3.15 dL g^{-1} at a concentration of 0.2 g dL^{-1} in concentrated sulfuric acid at 30 °C.

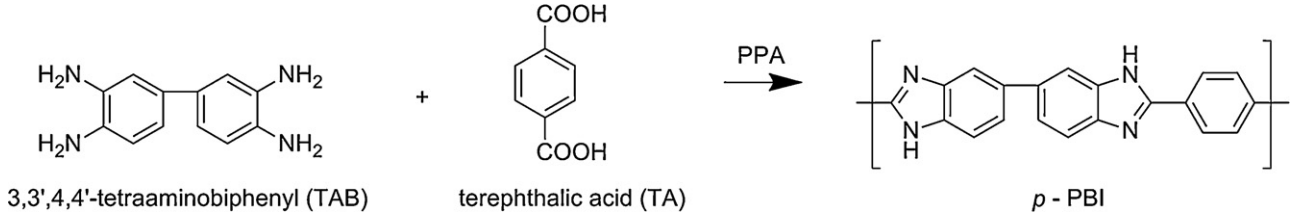
2.3. Comparative polymerizations of PPQ and PBI at 123 °C

To understand the propagation of PPQ/PBI copolymers, polyphenylquinoxaline and polybenzimidazole were synthesized in parallel under identical conditions. Two sets of monomers were weighed as follows: in the first reactor, TAB (1.643 g, 7.67 mmol), and TA (1.274 g, 7.67 mmol), were added along with 100.0 g of PPA. In the second reactor, TAB (1.643 g, 7.67 mmol), 1,4-bisbenzil (2.626 g, 7.67 mmol), and 100.0 g PPA were added. The two reaction mixtures were stirred by overhead mechanical stirrers under a slow nitrogen purge. The reaction temperature was controlled by a programmable temperature controller with ramp/soak capabilities. Each solution was then slowly ramped to a polymerization temperature of 123 °C, and stirred for 8 h. At the end of reaction, the reactor containing TAB, TA, and PPA was extremely fluid with a large amount of undissolved terephthalic acid in the mixture. The reactor containing TAB and 1,4-bisbenzil, however, contained high viscosity polyphenylquinoxaline homopolymer.

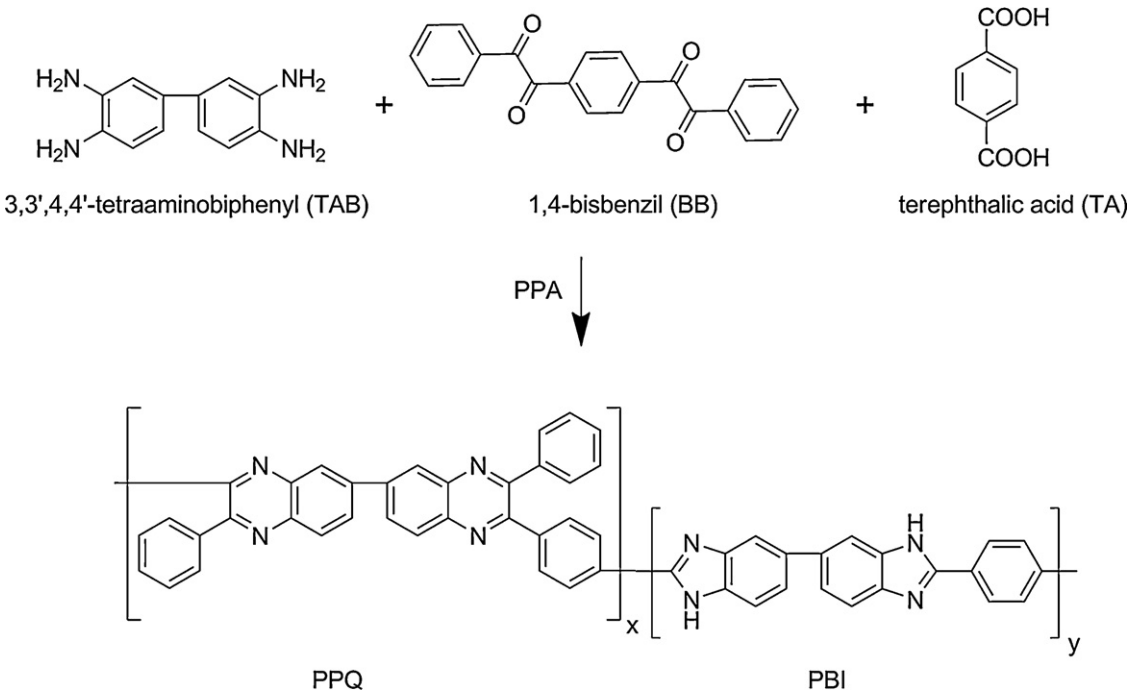
After the polymerization, water was poured into the reactors to quench the reactions and hydrolyze the mixtures therein. The solutions were pulverized in a blender, neutralized with ammonium hydroxide, washed with water, and then dried under vacuum. After workup of the solution containing TAB and terephthalic acid, a liquid solution containing oligomeric *p*-PBI, TAB, and TA starting material was obtained, and I.V. measurement was not possible. The reactor containing TAB, 1,4-bisbenzil, and PPA produced polymer powder with an inherent viscosity of 0.614 dL g^{-1} at a polymer concentration of 0.2 g dL^{-1} in concentrated sulfuric acid at 30 °C.



Scheme 1. Synthetic scheme for polyphenylquinoxaline homopolymer.



Scheme 2. Synthetic scheme for *para*-polybenzimidazole homopolymer.



Scheme 3. PPQ/PBI copolymer synthesis.

2.4. PPQ/PBI copolymer synthesis

Several PPQ/PBI copolymers were prepared across a wide range of PPQ concentrations. An example for the synthesis of high inherent viscosity PPQ/PBI copolymers is given for a 50/50 PPQ/PBI copolymer (Scheme 3): TAB (2.52 g, 11.8 mmol), TA (0.977 g, 5.90 mmol), and BB (2.013 g, 5.90 mmol) were charged in a 100 mL reactor in a nitrogen glove box. PPA (100.39 g, 115%) was added to produce a solution with an initial monomer concentration of 7.31 wt%. The mixture was stirred by an overhead mechanical stirrer under a slow nitrogen purge. The reaction temperature was controlled by a programmable temperature controller with ramp/soak capabilities. The solution temperature was increased stepwise to dissolve the monomers in PPA, and then polymerize the PPQ and PBI portions of the copolymer (Suppl. Fig. 1). For PPQ-50, the polymerization temperature was held at 123 °C for 8 h, followed by an increase in temperature up to 195 °C for an additional 6 h. Note that the time at 195 °C varied based on the composition of the PPQ/PBI copolymer, but the time necessary for low temperature PPQ formation at 123 °C was constant across the PPQ/PBI copolymer series (8 h). At the end of polymerization, phosphoric acid (3 mL, 5.1 g) was added to the reactor to adjust solution viscosity for film casting and then stirred an additional 30 min at 195 °C. For all PPQ/PBI copolymers it was necessary to first obtain a highly viscous final polymer solution, followed by the addition of phosphoric acid to reduce solution viscosity in order to obtain a high inherent viscosity (I.V.) polymer solution with good processability.

2.5. Film formation

Sol–gel films suitable for fuel cell testing were prepared by directly casting the hot polymer solutions onto glass plates using a Gardner blade at a thickness of 20 mils (0.508 mm). The films were then placed into a controlled humidity chamber (55 ± 5% RH) at room temperature for 24 h in order to hydrolyze polyphosphoric to phosphoric acid and excess PA was allowed to drain from the membrane. A sol-to-gel transition was observed during the hydrolysis process which produced a phosphoric acid imbibed gel film. Dimensionally stable PPQ homopolymer membrane was found to be approximately 17 mils in thickness while PPQ/PBI copolymer membranes ranged in thickness from 12 to 22 mils.

2.6. Characterization techniques

To determine the inherent viscosity (I.V.) of each polymer, residual polymer solution was poured into distilled water, pulverized in a blender, and then neutralized with ammonium hydroxide. The polymer powder was isolated via filtration and dried at 120 °C in a vacuum oven overnight. The dried polymer powders were dissolved in concentrated sulfuric acid (96%) at a concentration of 0.5 g dL^{-1} for PPQ homopolymers [2] and 0.2 g dL^{-1} for PPQ/PBI copolymers and PBI homopolymer [19–24]. The I.V. of the polymer solutions in concentrated sulfuric acid were measured at 30 °C using a Canon Ubbelohde viscometer.

The acid doping level and membrane composition for PPQ homopolymer and PPQ/PBI copolymer membranes were determined via titration of the phosphoric acid doped gel membranes with 0.1 N sodium hydroxide using a Metrohm 716 DMS Titrino autotitrator as reported previously [18]. The acid doping level of a membrane, x, was calculated as expressed in Eq. (1) as a function of the weight of the polymer solid, the molecular weight of the polymer repeat unit, the exact sodium hydroxide titer concentration, and the amount of titer to reach endpoint. Phosphoric acid content of membranes is expressed as the number of moles of phosphoric acid per mole of polymer repeat unit, and abbreviated as mol PA/r.u.

$$\text{acid doping level, } x = \frac{V_{\text{NaOH}} \times C_{\text{NaOH}}}{W_{\text{dry}} \times MW_{\text{r.u.}}} \quad (1)$$

V_{NaOH} (L) is the volume of sodium hydroxide titer; C_{NaOH} (mol/L) is the molar concentration of sodium hydroxide titer; W_{dry} (grams) is the dry weight of membrane sample; $MW_{\text{r.u.}}$ (g/mol) is the molecular weight of polymer repeat unit.

The through-plane proton conductivities of polymer gel membranes were measured with a Zahner IM6e impedance spectrometer. A 3.5 cm × 7.0 cm membrane sample of known thickness (measured by digital micrometer) was placed into a glass

impedance cell with four platinum wire probes. Two outer electrodes, set 6.0 cm apart on opposite sides of the membrane supplied current to the membrane, while two inner electrodes, spaced 2.0 cm apart on opposite sides of the membrane, measured the voltage drop that occurred through the membrane. The assembled impedance cell was placed in a temperature programmable oven to study the temperature dependence on a membrane's proton conductivity. Two conductivity tests were completed in air for each sample.

Since a gel-to-sol transition was observed for PPQ homopolymer membranes at temperatures greater than 120 °C, proton conductivity tests were conducted as a two run sequence with a maximum temperature of 120 °C. The first conductivity run was conducted from room temperature to 120 °C to expel water. Proton conductivities were recorded at 20 °C increments, with a 15 min thermal equilibration at each temperature prior to measurement. Following a 1 h cool down under vacuum, the second conductivity run was performed in the same manner, followed by a period when the temperature was held constant for 6 h at 120 °C. A 15 min thermal equilibration time was performed at 20 °C increments from room temperature and measurements were taken every 20 min during the entire second run.

Because of the generally higher thermal gel stability of PPQ/PBI copolymer membranes, a higher temperature conductivity test was performed during a two run sequence. During the first run, the temperature was increased from room temperature to 180 °C in 20 °C increments to remove water from the membrane. The second run was initiated after a 1 h cool-down period under vacuum. The temperature during the second run was increased to 180 °C in 20 °C increments from room temperature and then held at 180 °C for 5 h. At each temperature interval in the first and second run, a 15 min thermal equilibration period was performed.

The proton conductivity of a membrane, σ, was calculated from Eq. (2), where D is the distance between the two inner electrodes, W is the width of the membrane, T is membrane thickness, and R is the resistance of the membrane that was obtained through model fitting of the impedance data.

$$\sigma = \frac{D}{W \times T \times R} \quad (2)$$

The mechanical properties of membranes were determined using an Instron 5543A dual column table top mechanical test system with a 10 N load cell. Maximum load, tensile strength, strain at maximum load, strain at break, and Young's modulus were measured to characterize the mechanical properties of the membrane chemistry for processing, handling, and fuel cell construction. Type V test specimens were cut according to ASTM D638 specifications.

Thermogravimetric analysis (TGA) of polymer samples was conducted using a TA Instruments TGA Q-5000 IR with a heating rate of 10 °C/min under nitrogen.

2.7. Membrane electrode assembly (MEA) fabrication and fuel cell testing

Membrane electrode assemblies, or MEAs, with an active area of 45.15 cm^2 were prepared by hot pressing polymer membrane between an anode and a cathode catalyst-coated gas diffusion layer at 140 °C. Gas diffusion electrodes were acquired from BASF Fuel Cell, Inc. with a Pt loading of 1.0 mg cm^{-2}. The pressure and time at which the MEA components were hot pressed was dependent upon the chemistry specific to the membrane composition. For example, *p*-PBI MEAs were formed by pressing the membrane between a platinum coated anode and cathode for 40 s at 4500 lb and 140 °C, while PPQ-90, a copolymer containing 90 mol% PPQ and 10 mol% PBI, was hot pressed at 140 °C and a pressure of 9000 lb for 30 s. Determination of the appropriate time, temperature, and pressure necessary was made through experimentation to ensure a strong adhesive bond between the membrane and electrode for each membrane composition. After MEA preparation, a single fuel cell was assembled with graphite flow plates and temperature-controlled stainless steel endplates on either side of the MEA. A Fuel Cell Technologies, Inc. fuel cell testing station equipped with mass flow controllers was used for all testing as current-voltage performance was monitored. Reactant gases at the anode and cathode were fed into the cell at a stoichiometric ratio of 1.2 and 2.0, respectively. Lifetime testing reported herein was conducted using hydrogen and air (H_2:air = 1.2:2.0 stoich.) at 160 °C. All performance data were collected under atmospheric pressure without humidification.

3. Results and discussion

3.1. Synthesis of PPQ homopolymers and membranes

To determine the appropriate conditions for obtaining high I.V. PPQ homopolymer in PPA, several syntheses were conducted. Both the effect of monomer concentration and polymerization temperature were studied. The results of these syntheses are summarized in Table 2.

Due to the known importance of polymerization temperature control in PPQ systems as described earlier in this work, the effect of polymerization temperature on inherent viscosity and membrane formation of the PPQ homopolymer solution was first studied. Syntheses ranging in monomer concentration from approximately 3.5 wt% to 23.5 wt% were carried out at a polymerization temperature of 130 °C. At this temperature, initial experimentation (Table 2, sample I) to determine the PPA Process' applicability toward developing high I.V. PPQ polymer was promising, indicated by an increase in solution viscosity after 15 h and hydrolysis of the cast polymer solution. Membrane formation for Sample I was poor, however, and several subsequent attempts were made to produce a film-forming PPQ homopolymer solution in PPA at a polymerization temperature of 130 °C (sample II–V). Although solution viscosity increased as reactions II–V proceeded, poor or no membrane formation occurred upon cooling and hydrolysis of the cast polymer solution. Further investigation of the polymerization process at different temperatures was therefore necessary.

For PPQ homopolymer polymerizations carried out at 130 °C, an important observation was made for sample III, with an initial monomer concentration of approximately 13.5 wt%. At this monomer concentration, a high solution viscosity was obtained after 4 h at 130 °C. Before solution casting, the temperature of the solution was increased to 220 °C in order to reduce the viscosity of the solution. Due to this increase in temperature, crosslinking of the polymer occurred within several minutes and the polymer could not be cast into a film. Polymerizations subsequent to sample III were cast at their respective polymerization temperatures to avoid crosslinking but poor membrane formation was still observed and the I.V. measurements indicated that crosslinking had begun, even at the polymerization temperature of 130 °C.

A final polymerization at 125 °C (Table 2, sample VI) was then attempted, aiming to produce higher I.V. polymer with reduced crosslinking. At an initial monomer concentration of 13.5 wt%, high viscosity polymer solution formation was observed after 4.5 h at 125 °C. Subsequent casting and hydrolysis of the polymer solution at 55% RH and room temperature yielded a mechanically stable gel membrane. The inherent viscosity of this polymer (fully soluble) was measured to be 1.17 dL g^{-1}, indicating high molecular weight polymer formation [2].

Table 3
Results of PPQ/PBI copolymer syntheses.

Sample	[M] (wt%)	Time at Pzn temp (h)	Casting concentration (wt%)	I.V. (dL/g)	PA content (mol PA/r.u.)
PPQ-0	3.5	6.5	2.87	3.15	28.43
PPQ-10	3.2	5	2.5	1.32	28.34
PPQ-25	4.72	7	3.28	1.13	39.34
PPQ-40	6.06	4	3.83	1.07	36.07
PPQ-50	7.32	6	4.94	1.38	25.11
PPQ-58	7.22	5	4.46	1.26	39.24
PPQ-65	8.28	2	5.09	0.73	25.09
PPA-75	8.31	3.5	4.68	1.13	26.93
PPQ-90	9.08	4	4.84	1.61	31.42
PPQ-95	9.82	1.5	5.21	1.55	19.77

Compared to the previously reported mechanical properties of high molecular weight *p*-PBI membranes [18], which include tensile strengths between 3.0–3.5 MPa and 150–390% elongation at break, PPQ homopolymer (VI) showed a similar tensile strength of 2.3 MPa and a considerably lower elongation at break of 114%. More significantly, PPQ homopolymer membrane VI showed a Young's modulus of 21 MPa, which is approximately three times higher than that of *p*-PBI, whose Young's modulus was measured to be approximately 7 MPa. Although the elongation at break of the PPQ homopolymer membranes was lower than that of typical *p*-PBI membranes, the three-fold increase in the Young's modulus of the PPQ homopolymer membrane indicates a much stiffer and sturdier material. Measurement of the proton conductivity of the PPQ homopolymer membrane revealed a significant softening of the membrane at temperatures greater than 120 °C, indicating a relatively low upper temperature limit for fuel cell operation compared to other phosphoric acid doped membranes. The softening observed for the PPQ homopolymer membrane was attributed to the higher solubility of polyphenylquinoxaline in phosphoric acid. As reported previously, *p*-PBI films are extremely stable in phosphoric acid at elevated temperatures (up to 200 °C) [18–24], while PPQ homopolymer membranes prepared by the PPA Process in this work were found to have lower gel stabilities in PA.

3.2. Synthesis of PPQ/PBI copolymers and membranes

Polybenzimidazole has been shown to produce highly dimensionally stable sol–gel membranes when prepared by the PPA Process [18–24]. Since the PPQ homopolymer gel membrane was shown to lack the dimensional stability in PA at high temperatures, copolymers with PBI were investigated. The copolymer samples were denoted as "PPQ-*x*" where *x* denotes the mole percent of polyphenylquinoxaline in the copolymer. The results of PPQ/PBI copolymer syntheses via the PPA Process are summarized in Table 3.

PPQ-50 copolymer was selected for the initial polymerization experiments using time, temperature and initial monomer concentration as the key variables to control final polymer I.V. After several trials ranging in initial monomer concentration between 5.22 and 11.57 wt%, it was determined that an initial monomer concentration of approximately 7.30 wt% resulted in high I.V. polymer solution after 3.5–7 h at the final polymerization temperature of 195 °C. At this monomer concentration, polymerizations longer than 6–7 h at 195 °C produced high I.V. polymers, but low quality membranes due to excessively high solution viscosities that were difficult to cast into membranes. The membranes produced from these solutions exhibited defects that made them unsuitable for conductivity measurements. Polymerization times of less than 6–7 h resulted in high I.V. polymers that also formed high quality membranes. The remainder of the copolymers were prepared using the two-stage polymerization experimental conditions developed for PPQ-50 (see Experimental), and varied only in the time of stirring at 195 °C.

The results of the low temperature PPQ homopolymerizations in PPA strongly suggested that the condensation polymerization for the copolymers occurred nearly exclusively to form PPQ oligomers at low temperature (120–125 °C) and the formation of PBI at these temperatures was negligible. Furthermore, it can be deduced that as temperature is increased, PBI formation becomes the more dominant reaction as both the solubility and reactivity of terephthalic acid increases which results in multi-block copolymer structures. Further evidence of complete oligomeric PPQ formation at temperatures of approximately 123 °C for 8 h is supported by observations that polymer crosslinking did not occur for any of the PPQ/PBI copolymers when the temperature of the reaction was subsequently increased to 195 °C for PBI formation. Earlier reports [9] showed that PPQ polymerization temperatures of 160 °C in PPA with added P_2O_5 resulted in crosslinking of PPQ polymers, whereas the PPQ/PBI copolymers prepared in this work by a one-pot, two-stage method did not result in any observable crosslinking at 195 °C. Thus, the differences in solubility and reactivity between terephthalic acid and 1,4-bisbenzil which make random copolymerizations difficult are useful for multi-block copolymerizations where each block composition can be formed efficiently at two different temperature regimes (120–130 °C for 1,4-bisbenzil and TAB, and 180–200 °C for TA and TAB) as shown in Fig. 1 (see also Supplemental).

3.3. PPQ/PBI copolymer membrane properties

The mechanical properties of the PPQ/PBI copolymer membranes formed by the PPA process are summarized in Table 4. There is an overall trend that shows that membranes composed of higher PPQ content exhibit higher mechanical properties than those of lower PPQ content with significantly higher tensile strengths and Young's moduli. From the previous discussion on multi-block formation, this represents polymers that statistically have longer PPQ blocks and shorter PBI blocks.

The acid doping levels and the weight percentages of phosphoric acid, polymer, and water were determined via titration for the PPQ/PBI copolymer membranes. Fig. 2 shows the membrane compositions of the PPQ/PBI copolymers. Slightly higher polymer content was observed with increasing PPQ content, most likely resulting from the higher monomer solubility and higher monomer concentrations needed to obtain high I.V., mechanically stable membranes. The change in copolymer composition also caused a change in the PA and water composition in the membranes. Copolymers with greater than 20 mol% PPQ showed higher PA and lower water content than the other copolymers or *p*-PBI homopolymer.

The through-plane proton conductivity at 180 °C for the PPQ/PBI copolymers ranged from approximately 0.13–0.28 S cm^{-1}, as shown in Fig. 3a. Lower proton conductivities were observed in

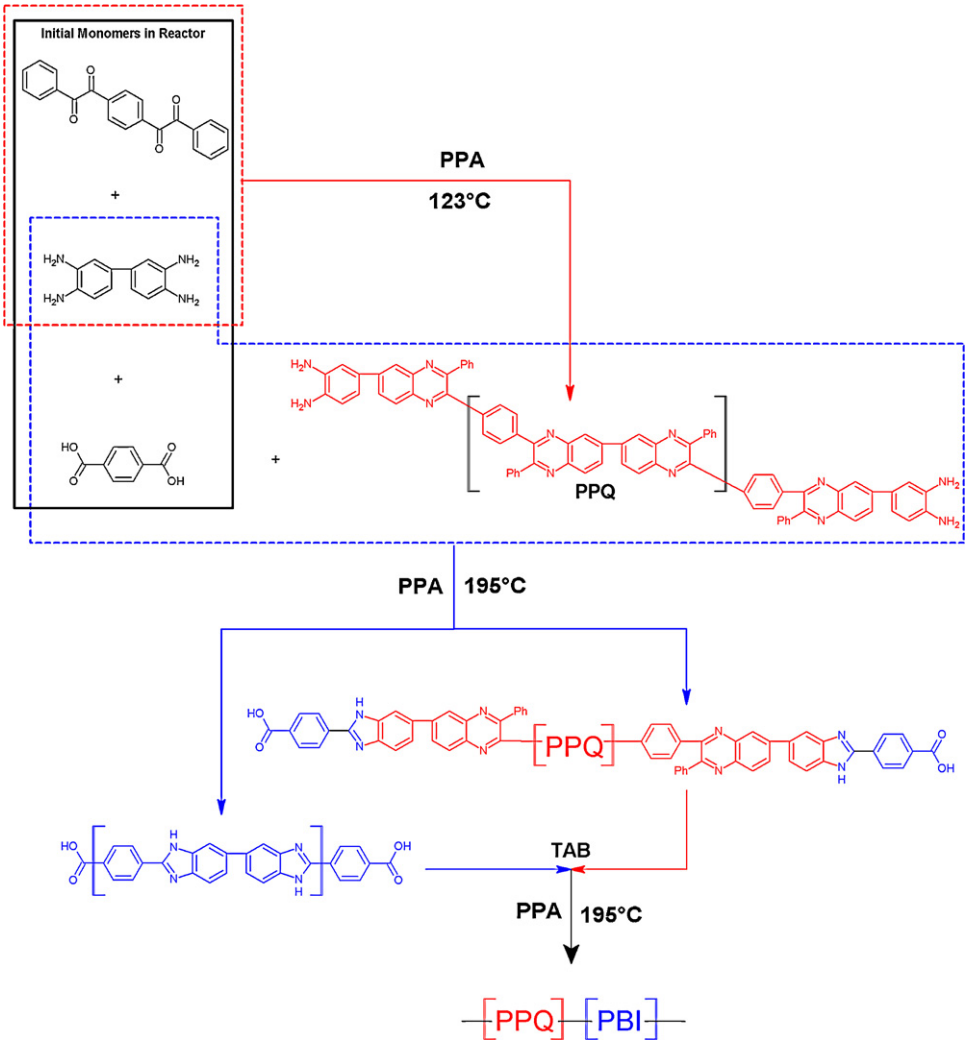


Fig. 1. Mode of multi-block formation of PPQ/PBI copolymers.

copolymer membranes with greater than approximately 60 mol% PPQ even though the polymer solids content and PA content were fairly constant throughout this range. The proton conductivity of *p*-PBI (0.27 S cm^{-1} at 180 °C) was determined to be greater than any PPQ/PBI copolymer membranes prepared in this work.

For comparison, the conductivity curves for Nafion^{TM} 117 [25], PPQ/PBI copolymer membranes and *m*-PBI cast from dimethylacetamide (DMAc) or trifluoroacetic acid (TFA) [26] and later imbibed with phosphoric acid, are shown in Fig. 3b. At temperatures greater than 100 °C, phosphoric acid doped PPQ/PBI membranes exhibited higher proton conductivities than the other membranes. This is expected for water based membranes and can be attributed to the loss of water from the membranes.

The PPQ/PBI membranes produced by the PPA process were shown to have higher phosphoric acid contents than membranes prepared conventionally by casting from either DMAc or TFA and then imbibing with PA. This is likely the cause for the higher conductivities shown in Fig. 3b. However, the mechanical properties of membranes containing greater than approximately 60 mol% PPQ decreased with increasing PPQ content. During conductivity testing of these membranes, flow of polymer out of the conductivity test cell was observed and it was concluded that the more soluble PPQ

Table 4
Mechanical test data for the PPQ/PBI copolymer membranes.

Sample I.D.	Max load (N)	Tensile strength (MPa)	Tensile strain at break (mm/mm)	Young's modulus (MPa)
PPQ-100	2.22	2.32	1.15	20.37
PPQ-95	1.99	1.13	0.80	22.80
PPQ-90	2.77	2.91	1.64	19.58
PPQ-75	1.60	1.67	0.41	19.16
PPQ-65	1.71	1.15	0.17	31.10
PPQ-58	0.90	0.94	0.35	7.65
PPQ-50	1.49	1.71	0.66	10.87
PPQ-40	0.64	0.68	0.43	4.20
PPQ-25	0.55	0.57	0.52	2.86
PPQ-10	0.53	0.56	0.83	1.87
PPQ-0	1.30	1.36	3.84	1.91

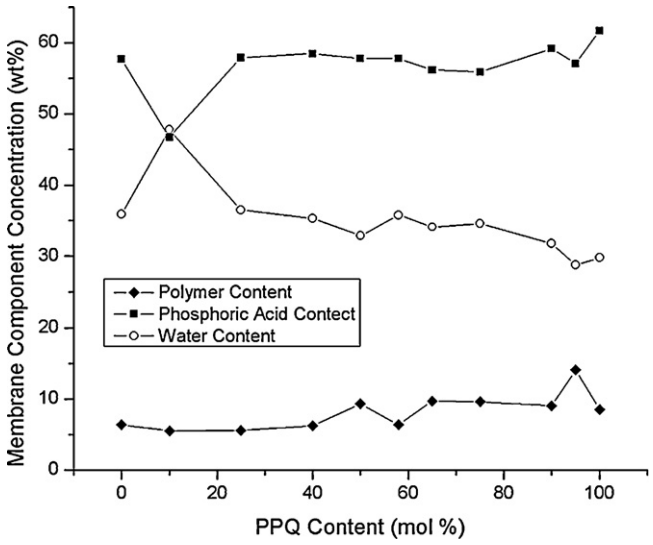


Fig. 2. Membrane compositions for the PPQ/PBI copolymers.

component was decreasing the gel stability at higher PPQ compositions. Fig. 4 shows the Young's modulus and proton conductivity data for the PPQ/PBI copolymers. The area shaded in gray indicates the compositions that exhibited high mechanical properties while still maintaining high proton conductivities and did not suffer from poor gel stability at high temperatures. From this data, PPQ-58 was selected for more extensive evaluations.

3.4. Fuel cell testing

Hydrogen/air, hydrogen/oxygen, and reformate/air polarization curve testing was performed for *p*-PBI, PPQ-25, and PPQ-58. In all cases the reformate was a mixture of 70% hydrogen, 28% carbon dioxide, and 2% carbon monoxide. Fuel cell testing of PPQ-90 failed due to the instability of the gel phase at higher temperatures. Fuel cell testing was performed for PPQ-25 and was demonstrated for over 1000 h. The lower mechanical properties of PPQ-25 membranes, however, caused creep of the membrane into the gas diffusion layer and resulted in high mass transport losses in the

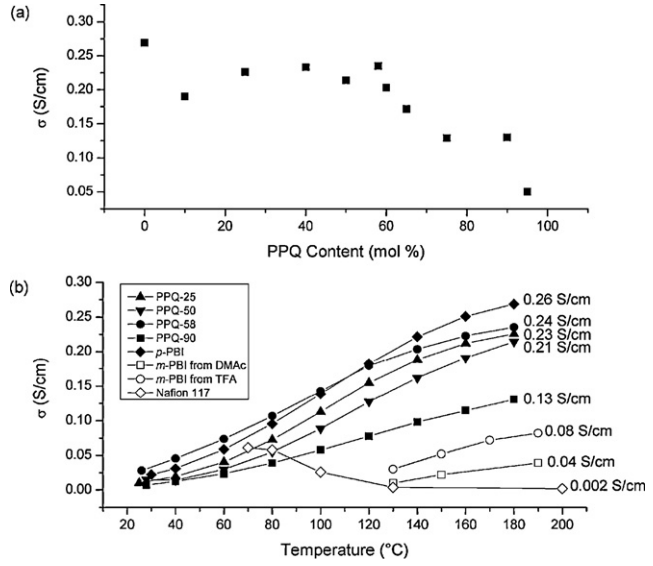


Fig. 3. (a) Proton conductivity at 180 °C for the PPQ/PBI copolymers, and (b) Proton conductivity-temperature curves for selected PPQ/PBI copolymer membranes, Nafion™ 117 [25], and *m*-PBI cast from DMAc [26] and TFA [26].

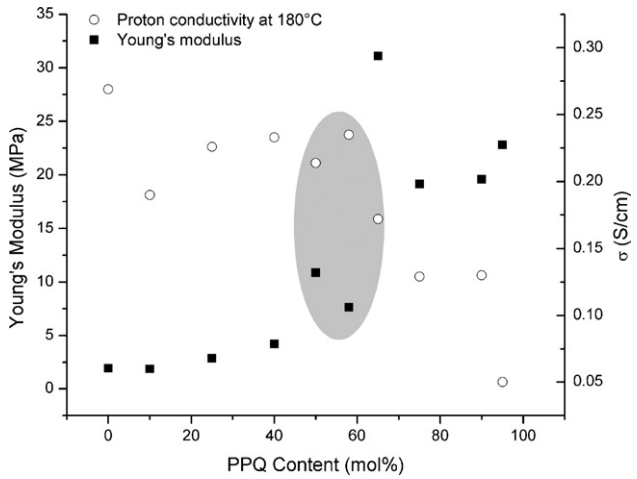


Fig. 4. Dependence of Young's modulus and proton conductivity for PPQ/PBI copolymer membranes.

fuel cell performance curves. For reasons discussed earlier, PPQ-58 was evaluated more thoroughly.

The fuel cell performance and lifetime plots for PPQ-58 are shown in Fig. 5. The polarization curves for PPQ-58 obtained with hydrogen/air and hydrogen/oxygen gases were comparable but slightly lower than previously reported for *p*-PBI membranes [19–22]. PPQ-58 showed increasingly poor performance with decreasing temperature while operating on reformate/air and the membrane was only able to produce voltages greater than 0.2 V at a current densities up to 0.5 A cm^{-2} and 180 °C indicating that the increased PPQ content made the PEM more susceptible to fuel impurities (CO) and hydrogen dilution effects. PPQ-58 was subjected to lifetime testing as shown in Fig. 5b. The cell was operated for approximately 2900 h using non-humidified hydrogen/air gases and maintained relatively constant voltage despite several uncontrolled station shutdowns and facility outages.

Fig. 6 shows the fuel cell performance curves for PPQ-58 and *p*-PBI membranes synthesized via the PPA Process at 160 °C operating under hydrogen/air and hydrogen/oxygen at a fuel and oxidant stoichiometric ratios of 1.2/2.0. As can be seen from the figure, the performance of PPQ-58 was lower than *p*-PBI membrane under both H_2/air and H_2/O_2 gases. Although the membrane proton conductivities were comparable for the two membranes, MEA pressing conditions, interface resistances, or other properties inherent to each membrane chemistry may affect cell performance. Some of these variables, e.g., MEA pressing conditions, have been studied for many years and optimized for p-PBI membranes, but not for newer experimental membranes such as PPQ-58. Obviously, further experimentation is warranted for newer membranes that show improvements in other properties such as mechanical properties that may lead to more creep resistance membranes.

After 2900 h, end-of-life polarization curves were measured for PPQ-58. To compare the beginning-of-life (BOL) operation at 600 h to the end-of-life (EOL) performance for PPQ-58 (2900 h) operating under non-humidified hydrogen and air at 160 °C, the change in voltage at several current densities was calculated by subtracting the BOL voltage from the EOL voltage. Fig. 7 shows the voltage difference between BOL and EOL operation for PPQ-58 membranes, where a ΔV of 0 mV represents no change in operation between beginning and end of life. A drop in open circuit voltage (OCV) performance from BOL to EOL operation of nearly 100 mV was observed for all temperatures, and is most likely the result of crossover of reactant gases across the membrane. Comparison of BOL to EOL polarization curve measurements showed that operation at current densities of 0.1 and 0.2 A cm^{-2}, the MEA showed

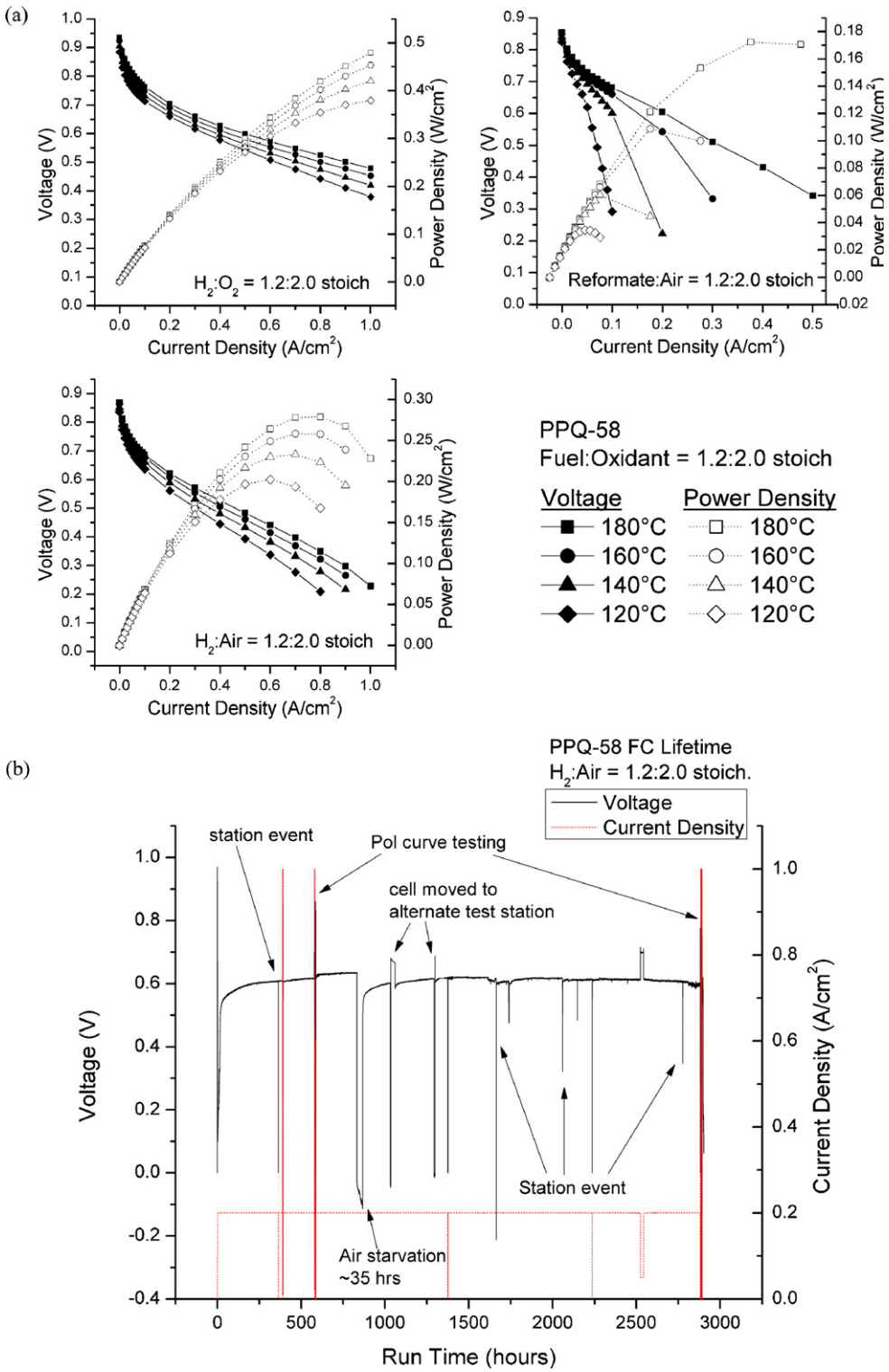


Fig. 5. (a) Beginning of life fuel cell performance curves (at 600 h), and (b) lifetime plot for PPQ-58 operating at 160 °C under hydrogen and air (fuel:oxidant = 1.2:2.0 gas stoichiometry).

almost no deviation in performance over 2300 h for PPQ-58. This result is significant in the fact that long-term operation is generally performed at or between these current densities and, for PPQ-58, approximately equivalent performance at 0.2 A cm^{-2} between beginning and end of life signifies a robust and reliable membrane. Higher current densities, approaching 1.0 A cm^{-2}, showed significant improvements in voltage after 2300 h, especially for lower temperature operation. Performance improvements as high as approximately 250 mV were observed at 120, 140, and 160 °C, while 180 °C testing showed voltage improvements up to approximately 65 mV when comparing BOL to EOL operation.

There may be several possible changes related to the improvement in the performance of PPQ-58 over 2900 h at current densities near 1.0 A cm^{-2}. First, the pressing conditions used to form the MEA may not have been optimal (as mentioned earlier) and thus resulted in a longer break-in time for the MEA to reach

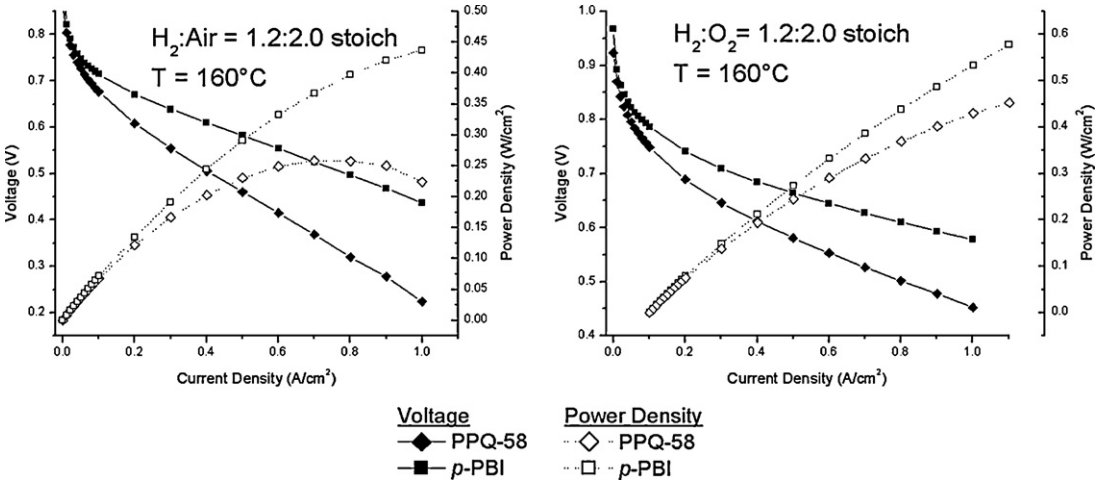


Fig. 6. PPQ-58 fuel cell performance comparison to *p*-PBI under H_2/air and H_2/O_2 operation (fuel:oxidant = 1.2:2.0 stoich.).

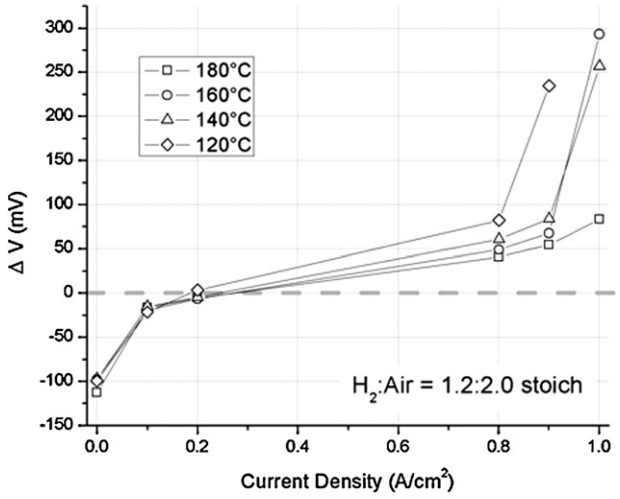


Fig. 7. Voltage differences from beginning-of-life to end-of-life operation for PPQ-58 over 2300 h at 160 °C under hydrogen and air (H_2:air = 1.2:2.0 stoich.).

steady-state voltage. This possibility is likely and can be supported by the increase in voltage during the initial 800 h of testing as illustrated on the lifetime plot of PPQ-58 (Fig. 5b). Additionally, the overall performance increase would be attributed to wetting of the electrodes and improvement of the interface between the membrane and the electrode gas diffusion layer.

Compared to the sulfonated PPQ membranes developed by Ballard (BAM-1G) for water-based PEM systems, phosphoric acid doped PPQ/PBI copolymer membranes prepared by the PPA Process were shown to have improved lifetime performance and durability. BAM-1G membranes showed lifetimes of approximately 350 h before MEA failure occurred. This indicates that the PPQ backbone chemistry is not inherently unstable in fuel cell operating conditions and should be further investigated as a candidate for polymer electrolyte membranes.

4. Conclusions

A novel, high temperature (>100 °C), method for the preparation of non-crosslinked polyphenylquinoxaline in polyphosphoric acid and a novel one-pot, two-stage polymerization method to prepare multi-block PPQ/PBI copolymers in PPA were developed. Careful control of the polymerization temperature was used to selectively polymerize each block in a stepwise manner.

It was determined that a polymerization temperature of ~125 °C and an initial monomer concentration of approximately 13.5 wt% in PPA produced a high I.V. PPQ homopolymer solution and mechanically stable membrane upon hydrolysis of the cast polymer solution. PPQ homopolymer membrane was determined to have high room temperature mechanical properties with a Young's modulus of 21 MPa, and a high phosphoric acid doping level of approximately 36 mol PA/r.u. However, the gel membrane stability of the polyphenylquinoxaline homopolymer was found to be unstable in phosphoric acid at temperatures higher than approximately 120 °C. Thus, highly phosphoric acid-doped PPQ homopolymer membranes were found to be unsuitable as PEMs and attention was turned to more dimensionally stable PPQ/PBI copolymers.

The synthesis and membrane formation of a series of PPQ/PBI copolymers made by the PPA Process was investigated to study the effects of composition on the gel stability of PPQ/PBI copolymers. The much lower solubility of PBI in phosphoric acid at elevated temperatures contributed to an increase in the gel stability of PPQ/PBI multiblock copolymer membranes made by the PPA Process. PPQ/PBI copolymer membranes containing up to approximately 70 mol% PPQ were found to be thermally stable up to 180 °C. Higher PPQ content membranes showed polymer dissolution in phosphoric acid at elevated temperatures, similar to the behavior observed for PPQ homopolymer membranes.

The mode of propagation of PPQ/PBI copolymer systems was shown to be characteristic of a multiblock copolymer through a study of the inherent viscosity of the two polymer systems when each was polymerized separately according to different time-temperature profiles. It was determined from these studies that an excess of TAB was beneficial in the formation of PPQ oligomeric species and resulted in end-functionalization of oligomeric species by 1,2-phenylenediamine moieties. Crosslinking was thus avoided when the system temperature was raised to 195 °C for the formation and addition of PBI into the system. The results of the I.V. study suggested that PPQ oligomers end-functionalized by phenyl-1,2-diketone moieties in the synthesis of PPQ homopolymers participated in a crosslinking reaction observed previously when higher temperature polymerizations were conducted.

The measurement of the acid content, proton conductivity, and mechanical properties of a series of PPQ/PBI copolymers showed a tradeoff of desired properties for a proton exchange membrane. A PPQ/PBI copolymer membrane consisting of 58 mol% PPQ with high proton conductivity and good room temperature mechanical properties was selected for fuel cell evaluation. Fuel cell testing of PPQ-58 membranes showed excellent polarization curve performance with hydrogen/air and hydrogen/oxygen gases over the

temperature range 120–180 °C and a 2900 h lifetime performance with minimal voltage degradation over this time period.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.memsci.2012.02.044.

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