

# Fabrication and Optimization of Proton Conductive Polybenzimidazole Electrospun Nanofiber Membranes

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## Abstract

Phosphoric acid (PA)-doped polybenzimidazole (PBI) proton exchange membranes (PEM) have received attention due to their good mechanical properties, moderate gas permeability and superior proton conductivity under high temperature operation. Among PBI based film membranes, nanofibrous membranes withstand to higher strain due to strongly oriented polymer chains while exhibiting higher specific surface area with increased number of proton conducting sites. In this study, PBI electrospun nanofibers were produced and doped with PA to operate as high temperature PEM, while changes in proton conductivity and morphologies were monitored. Proton conductive PBI nanofiber membranes by using the process parameters of 15 kV and 100 µl/hr, at 15 wt% PBI/dimethylacetamide (DMAc) polymer concentration were prepared by varying PA doping time as 24, 48, 72 and 96 hours (hr). The morphological changes associated with PA doping addressed that acid doping significantly caused swelling and 2-fold increase in mean fiber diameter. Tensile strength of the membranes is found to be increased by doping level, whereas the strain at break (15%) decreased due to the brittle nature of *H*-bond network. 72hr doped PBI membranes demonstrated highest proton conductivity whereas the decrease on conductivity for 96hr doped PBI membranes which could be attributed to the morphological changes due to *H*-bond network and acid leaking, were noted. Overall, the results suggested that of 72hr doped PBI membranes with

proton conductivity of 123 mS/cm, could be a potential candidate for proton exchange membrane fuel cell (PEMFC).

**Keywords:** Polybenzimidazole; nanofiber; proton conductivity; fuel cell; high temperature proton exchange membrane

## Introduction

Poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole], polybenzimidazole (PBI) developed in early 1960s, exhibits excellent mechanical, chemical and thermal properties <sup>[1]</sup>. PBI membranes attract a great deal of attention as means for increasing the temperature tolerance of conventional proton exchange membranes (PEM) materials. PBI (Grotthuss (hopping) conduction mechanism of phosphoric acid doped-polybenzimidazole PA-PBI is depicted in **Figure 1**) is capable of absorbing acids (pKa ~ 5.5), which is essential to be used in fuel cell membranes and other proton-conducting applications <sup>[2]</sup>. To overcome the drawbacks of the low-temperature proton exchange membrane fuel cell (PEMFC) such as CO catalyst poisoning, necessity of humidification, heat management, and low diffusion rates of protons, PBI based membranes were preferred due to their superior proton conductivity particularly both at high temperatures <sup>[3-5]</sup> and at 0% relative humidity <sup>[6]</sup>. PA-PBI membranes were first successfully prepared by Wainright *et al.* <sup>[7-9]</sup>. These membranes were recommended as electrolyte for high temperature proton exchange membrane fuel cell (HT-PEMFC) operating at temperatures of up to 200°C <sup>[8]</sup>. They also exhibited good mechanical properties, and low gas permeability <sup>[10-12]</sup> compared to water containing membranes including Nafion<sup>®</sup> whose proton conductivity decreases with increased temperature due to the evaporation of H<sub>2</sub>O molecules <sup>[13]</sup>. In addition, the results showed that an increase in doping level resulted in better proton conductivity, and so more efficient HT-PEMFC performance <sup>[8,14]</sup>. After blended with PA, PBI films might suffer from deterioration due to the slow elution of water-soluble PA, when the vapor was produced <sup>[15]</sup>. Moreover, it was reported that these film membranes also sacrificed the

mechanical properties after PA doping. Other macroscopic forms of PBI such as nanofibers <sup>[16]</sup>, PBI fiber incorporated films <sup>[17,18]</sup> and reinforced films <sup>[19-23]</sup> could overcome these challenges while improving mechanical properties. Among nanofiber production methods, electrospinning approach has received wide attention due to its simple implementation. Randomly oriented electrospun nanofibers benefiting from highly oriented chains along fiber axis have much better tearing and tensile strength than casted films <sup>[24-26]</sup>. The production of PBI nanofibers via electrospinning was first studied by Kim *et.al.* <sup>[16]</sup> and it is pointed out that sulfonic acid treatment increased the mechanical properties of these nanofibers. Dong *et al.* <sup>[27]</sup> fabricated high purity Nafion® electrospun nanofibers and reported one order of magnitude higher proton conductivity compared to bulk Nafion films. This increase was associated to the alignment of the ionic aggregates along fiber axis and also augmented by decreasing fibers diameter. Later, Yu *et. al.* <sup>[28]</sup> produced PBI electrospun mats and immersed them into Nafion® to produce composite membranes for HT-PEMFC. The effect of temperature on PA-PBI membrane conductivity was investigated by Lobato *et al.*, and they reported that dramatically increased proton conductivity with temperature due to promoted proton transportation <sup>[29]</sup>. Recently, Lai *et al.* prepared ultra-thin cross-linked PBI membranes by electron beam irradiation method and noted that these cross-linked membranes had better mechanical performance than pristine PBI membranes as expected <sup>[30]</sup>.

Recent efforts have focused on the preparation of membranes using constructed ion-conductive nanofibrous networks rather than films <sup>[31,32]</sup>. These nanofibers have a very high specific surface to volume ratio, better mechanical performance than films and good pore interconnectivity, which are highly demanding properties in PEMFC. Hwang *et al.* <sup>[33]</sup> reported moderate proton conductivity of PA-PBI based nanofiber membranes as 0.081 S/cm and higher water uptake around 40%, whereas commercial Nafion® exhibited 0.09 S/cm. Later, Kawakami *et al.* fabricated PA doped

sulfonated polyimide (SPI)/PBI composites and investigated ultra-fast proton conduction mechanism which was presumably derived from the aggregation of sulfonic acid groups and acid base interactions at the nanofiber surface [34]. To date, many studies have been focused on creating ion conductive networks, while the effect of doping on the morphology of PBI films and gels [6,35], mechanical and thermal properties were revealed. However, nanofibrous PBI membranes exhibited higher degree of crystallinity and higher porosity with surface roughness compared to casted membranes. All these structural parameters have influence on proton conduction mechanism which strongly depends on the distribution of accumulated doped acid molecules and acid uptake, thus the role of nanofiber morphology should be explored in detail.

In this study, we present the structural design of PEMs with PBI nanofiber membranes at different PA doping levels. Our present experimental procedure began with exploring the effect of electrospinning parameters such as feeding rate, applied voltage and polymer concentration on neat PBI fiber morphology. Hence, a factorial design of experiments (DOE) was performed to determine optimal set of parameters for effective electrospun fibrous membranes. The PBI nanofibers as determined by this DOE were characterized primarily to achieve reproducible PBI nanofiber mats and then PA doped nanofiber membranes were obtained by soaking into PA solution by varying doping time as 24 hour (hr), 48hr, 72hr and 96hr. The morphologies of undoped and doped PBI membranes were systemically evaluated by scanning electron microscope (SEM). To explore the doping mechanism and effective doping time, Fourier transform infrared spectroscopy (FT-IR) was used. The mechanical response and thermal stability were also investigated both for undoped PBI and PA doped proton conductive PBI membranes. The proton conductivity of these membranes were studied at room temperature under hydrous conditions to reveal the dominant effect of *H*-bonding nanofibrous network on the prevention of acid leaking.

## Materials and Methods

PBI S26 Solution with viscosity of  $2100 \pm 200$  poise at  $25^\circ\text{C}$  (containing 26.2 wt% of PBI powder with repeating unit MW of 308g/mole, 18000 chain weight average MW and inherent viscosity of 0.46 dL/g, 72.3 wt% *N, N*-dimethylacetamide (DMAc) and 1.5 wt% LiCl), was purchased from PBI Products Inc. USA. Solvent DMAc, PA and deionized water (DI) were supplied by Sigma Aldrich Chemical Co. All chemicals are used without further purification. Electrospinning solutions were prepared at three different PBI concentrations 10 wt%, 12.5 wt% and 15 wt% by diluting PBI condensed solutions. Each PBI/DMAc solutions was stirred magnetically for 24 hr at room temperature, to ensure homogeneity. With three levels of each variable, the polymer concentration, applied voltage and feeding rate, a total of fifteen different combinations were used to produce nanofiber (**Table 1**). An electrical bias potential was applied to the polymer solutions in electrospinning device (Argeteknolab<sup>®</sup>) which were contained in a 5 mL syringe. An alligator clip attached to the syringe needle (inner diameter 300  $\mu\text{m}$ ) enabled biasing of the solution. The applied voltage was adjusted, while the grounded rounding drum covered with aluminum foil was placed 10 cm away from the syringe needle tip. A syringe pump (NewEra NE 1000 Syringe Pump) was used to maintain a solution flow rate during electrospinning. The experiments for electrospun PBI nanofiber processing are summarized in **Table 1**. In order to gain proton conductivity, PBI electrospun nanofibers were doped with 85% PA at room temperature for 24, 48, 72 and 96 hr consecutively. Then, doped PBI mats were washed with distilled water at least five times, dried in vacuum oven at  $150^\circ\text{C}$  for 2 hr to ensure the removal of existing LiCl and conditioned prior testing

[36].

For characterizing the materials and processes in this work, a variety of techniques and equipment were used. The morphologies of doped and undoped fibrous webs were evaluated by imaging using 2 keV secondary electrons in field-emission gun equipped scanning electron microscope (FE-SEM, LEO 1530VP). The diameter of electrospun nanofibers was estimated by ImageJ software®. The average fiber diameter and distribution were determined from at least 40 measurements on the randomly selected fibers. Thermogravimetric analysis (TGA) were carried out on Netzsch-STA equipment to probe the degradation temperature of mats, as a measure of the thermal stability of membranes under the conditions of N<sub>2</sub> atmosphere, heating rate of 5 K/min, with 75 mL/min gas flow from room temperature to 1200 °C. To verify the effect of PA in the composite nanofiber mats, FT-IR spectroscopy (Perkin Elmer UATR Two) was used to see structural response which was in the range of 4000-400 cm<sup>-1</sup>. Universal Testing Machine (UTM) (Shimadzu AG-X Plus 100kN) was used to determine tensile strength and tensile modulus using the standard ASTM D882-12. The dimensions of testing samples were 60 x 20 mm and the thickness of mats were 30 μm. The extension rate was calculated as in equation (1):

$$V = 0.1 * L \quad (1)$$

where  $V$  is the extension rate (mm/min) and  $L$  is the length of the specimen.

To measure the proton conductivity of the doped PBI membranes Bekktech in-plane conductivity method was used. For this aim, the specimens were cut into 2x2 cm membrane pieces, placed into the conductivity cell and immersed into the DI water bath. The 4-point proton conductivity method was conducted at the standard room temperature and 100% relative humidity (RH). The proton conductivity and specific resistance of the membranes were calculated from the resultant resistance using the equation (2) as:

$$\sigma = \left(\frac{T}{R * A}\right) \quad (2)$$

where  $\sigma$  is the conductivity in S/cm,  $R$  is the resistance offered by the membrane in ohms,  $T$  is the thickness of the membrane in cm,  $A$  is the area of the membrane in cm<sup>2</sup>.

## Results and Discussion

Properties of the electrospun nanofibers, in particular the fiber diameter and morphology, depend on various parameters that can be divided into three groups: polymer solution properties (solution viscosity, solution concentration, polymer molecular weight etc.); processing conditions (applied voltage, volume flow rate etc.); and ambient conditions (temperature, humidity etc. [37]). In this study, ambient conditions were held constant, in order to systematically investigate the effects of processing and solution properties on the mean fiber diameter and bead formation. First, three levels of polymer concentration (10 wt%, 12.5 wt% and 15 wt%) and three levels of feeding rate (70, 85 and 100  $\mu$ L/hr) resulted in nine possible combinations for factor setting at constant 15 kV (**Table 1**). Then the feeding rate was kept constant and the effects of applied voltage and polymer concentration on mean fiber diameter was discovered, in tandem.

First, electrospun mats were produced by varying polymer concentration such as 10 wt%, 12.5 wt% and 15 wt% at 15 kV constant DC voltage while the feeding rates were differed from 70 to 100  $\mu$ L/hr as shown in **Table 1. Figure 2 (Figure S1** gives fiber diameter distribution of each mat) shows the SEM micrographs of fibers obtained by varying the polymer concentration and feeding rate at 15 kV and a constant nozzle-collector distance of 10 cm. Using a polymer concentration of 10 wt% yielded thinner fibers (50% narrower compared to nanofibers at 15 wt%), but less homogeneous nanowebs due to bead formations. Besides, in PBI-1 systems, we could not obtain stable flow for

electrospinning. To increase flow rate from 70  $\mu\text{L/hr}$  to 85  $\mu\text{L/hr}$  and 100  $\mu\text{L/hr}$  enabled fiber formation but it could not prevent partial electro spraying and electro sprayed beads. Thus, we raised polymer concentration to 12.5wt%. However, the process again resulted in spraying along with spinning, which again prevented the formation of homogenous webs at 12.5 wt% concentrations. It is worthy to note that increasing feeding rate at this concentration also led to the formation of bead-like structures and thicker fibers with high variance in fiber diameter. It was known that increasing the feeding rate decreased the charge density, whereas intense charge density lead to jet bending instabilities, that caused the formation of thinner fibers [38,39]. Besides, when the feeding rate is higher, solvent molecules cannot be fully evaporated and that resulted in bead-like formation [40,41]. **Figure 2** suggests that homogenous webs for PEM can be obtained at polymer concentration of 15 wt%. PBI-9 systems exhibited bead-free mats with mean fiber diameter of  $170 \pm 10$  nm whereas PBI-7 and PBI-8 systems have mean fiber diameter of  $179 \pm 11$  nm and  $184 \pm 13$  nm, respectively. PBI-9 system was chosen due to their narrower fiber diameter distribution and bead-free mat morphologies for further studies. Afterwards, 100  $\mu\text{L/hr}$  feeding rate was kept constant to shed a light on the effects of polymer concentration and applied voltage on the fiber morphology (12, 15 and 18 kV and 10, 12.5 and 15 wt%). It was still not possible to achieve homogenous webs at lower concentrations (10 wt% and 12.5%). Besides, applied voltage has impact on bead formation in which is more obvious at 12.5 wt% polymer concentrations. As seen in **Figure 3 (Figure S2** provides fiber diameter distribution of each mat), PBI-15 (mean fiber diameter  $173 \pm 8$  nm) system resulted in reproducible nanofiber webs with thicker fibers compared to PBI-9 and PBI-14 (mean fiber diameter  $121 \pm 6$  nm) systems. High electrostatic forces as 18 kV caused wider fiber diameter distribution. Overall, PBI-9 system have promised reproducible homogenous nanofiber webs, thus

these process parameters were chosen for the production of PBI mats for proton conducting membranes.

PBI electrospun nanofibers were doped with 85 wt% PA at room temperature for 24, 48, 72 and 96 hr.

First, FT-IR analysis was conducted to examine the protonation degree of PA in PBI polymer structure by monitoring doping time. PA doping in PBI resulted in broad absorption bands at between 2400 and 3000  $\text{cm}^{-1}$ , which were sensitive to the protonation of *N*-sites on the imidazole groups of PBI, and thus was not observed in undoped PBI membranes [42]. This absorption band increases with the degree of protonation [42] where the absorption band of acid anion ( $\text{H}_2\text{PO}_4^-$ ) between 400 and 1300  $\text{cm}^{-1}$  represents the protonation degree of PBI, as displayed in **Figure 4**. In addition, the area under the peaks at 1565  $\text{cm}^{-1}$  and 1630  $\text{cm}^{-1}$  are sensitive to the acid content in the membrane [43]. The area under the peak at 1630  $\text{cm}^{-1}$  increases with the doping level and it reaches a maximum value which corresponds to transfer of two protons (from PA to the two imidazole groups) of the repeating unit PBI [43]. The presence of the absorption band at 942  $\text{cm}^{-1}$  is also attributed to the presence of  $\text{H}_2\text{PO}_4^-$  ions. The absorption band at 998  $\text{cm}^{-1}$  keeps growing when the amount of acid in membrane exceeds the number of imidazole sites and free PA accumulates in the membrane [42]. IR analysis of PA doped PBI membranes revealed that there is excessive amount of PA molecules accumulated, as interpreted from the absorption peak at 998  $\text{cm}^{-1}$ , and it increased with doping time. To reveal the effect of free acid molecules and acid doping on fiber morphologies, we performed SEM analysis, which will be discussed in next section.

The conductivity measurements would provide complimentary information to optimize required doping time. **Table 2** displays the proton conductivity measurements of PA doped PBI nanofiber membranes at room temperature and 100% RH. Undoped PBI membranes are not proton

conducting materials but, a PA molecule can be immobilized via protonating a benzimidazole ring, when it is accumulated in PBI membranes, as depicted in **Figure 1** [44]. It also enables proton conductivity at higher temperatures up to 200°C without any requirement of any diffusion ease media such as water. But herein, we preferred to test in hydrous medium to see the effectiveness of nanofibrous network on the prevention of acid leaking. Proton conductivity strongly depends on the amount of acid present in the membrane. So, the conductivities of PBI nanofiber membranes after immersion into PA bath for 24hr, 48hr, 72hr and 96hr time intervals at room temperature are reported in **Table 2**. The results suggested that PA immersion for 72hr leads to highest proton conductivity. Even though, the time of immersion in the acid bath is an important factor for proton conductivity, we observed that best conductivity value, cannot be achieved for the samples immersed during 96hr. This can be attributed to the morphological changes due to the formed *H*-bonding network [45,46] and free PA molecules accumulated into the membrane which caused acid leaking [47,48]. Thus, we studied the morphological changes depending on immersion time by SEM, as given in **Figure 5**.

The mean fiber diameters of undoped and 24hr, 48hr, 72hr and 96hr doped PBI membranes were 170±10, 574±55, 915±74, 327±23 and 418±37 nm respectively. Investigation on the mean fiber diameter showed that 72hr doped PBI fibers have minimum fiber diameter deviation and more homogenous fibers. As displayed in **Figure 5** (**Figure S3** provides fiber diameter distribution of each mat), acid immersion caused significant changes in fiber morphology which could be related to the swelling effect of physisorbed PA molecules and coalesced neighboring fibers due to *H*-bond network. In these membranes, free acid can be easily eluted by washing [49]. On one hand, FTIR analysis pointed out that there were excess acid molecules in the membrane that increases proton conductivity. On the other hand, the decrease in proton conductivity for 96hr doped PBI membranes

was observed related to acid leaking in membrane due to over saturation (**Table 2**). These merged and swelled fibers (as seen in **Figure 5d**) may augment the effect of PA dehydration. As reported by Litt *et al.* PA separation from the more crystalline PBI phase, produces more concentrated acid domains <sup>[48]</sup>. This phenomenon might cause uneven distribution of PA molecules and changes in resistivity. As a consequence, 96hr PA doped PBI membranes exhibited higher resistivity than 72hr PA doped PBI membranes <sup>[48]</sup>. Among the well-known factors directly affecting conductivity such as nature of the acid, temperature, relative humidity, we noted that for fibrous membranes fiber morphology has influence on proton conduction mechanism due to the variations of accumulated PA molecules.

Thermogravimetric analysis was conducted to find the decomposition temperature of undoped and PA doped PBI nanofibers. As seen in **Figure 6a**, decomposition temperature of optimized undoped PBI nanofibers were at around 700°C whereas first mass change interpreted from DTG (%/min) took place at around 80°C due to the decomposed LiCl stabilizer <sup>[36]</sup>. To remove the inevitable entrapped DMAc solvent molecules and LiCl stabilizer, prior proton conductivity measurements, each membrane were dried in vacuum oven at 150°C for 2 hr and conditioned. The effect of doping time on decomposition temperature was studied at time intervals of 24hr, 48hr, 72hr and 96hr (see **Figure 6b-e**). **Figure 6b** suggests that PA doping for 24hr altered decomposition temperature to 820°C due to formed *H*-bond network where PA doping for 48hr shifted this temperature to 840°C (**Figure 6c**). Besides, another peak was observed at the range of 160-200°C in **Figure 6c**, which pointed out the excess amount of PA molecules. **Figure 6d** revealed that PA doping during 72hr increased decomposition temperature to 860°C. However, when the doping time was altered to 96hr, two more distinctive peaks (at around 650°C and 800°C) were observed as displayed in **Figure 6e**. Broader peak at around 650-700°C pointed out the undoped PBI structures which can

be seen due to the accumulation of PA molecules. This uneven distribution of PA molecules caused decreased in proton conductivity, was also noted in the morphological changes.

Mechanical properties of undoped and PA doped PBI membranes were investigated so that an associated reinforcement due to the doping could be evaluated. Hydrogen bonding between *N* and *-NH-* groups in PBI, are the dominant molecular forces, resulting in close chain packing, so as good mechanical performance of these membranes [9,50,51]. However, the results showed that PA doping sacrificed mechanical properties of PBI films [15], so several approaches including crosslinked [52] and reinforced membranes [21,23] were investigated to improve tensile properties. **Figure 7** and **Table 3**, emphasized on the effect of doping time, and reported the Young's modulus, ultimate strength and elongation at break (%) of the doped and undoped membranes. The results suggested that due to *H*-bond network, ultimate tensile strength increased by doping time while plastic deformation was observed in all cases. At the same time, these inter-molecular forces contributed to brittleness of membranes due to formed restrictions on plasticization. Thus, PA doped membranes showed lower ductility than neat specimens. **Table 3** pointed out that 96hr PA doped PBI electrospun membranes had lower ultimate tensile strength and Young's modulus than 72hr PA doped PBI electrospun membranes. This decrease in Young's modulus and ultimate tensile strength could be related to differences in accumulation of PA molecules which caused doped and undoped sites. Thus, even though the synergetic effect of interconnected network increased stiffness and strength, undoped regions promoted lower stiffness and strength. Previous studies reported that in high doping levels due to the separation of inter-chains, mechanical properties were decreased contrary to the effect of crosslinking or interconnected network [53,54].

**Table 3** also exhibits the dimensional changes (%) and mass change (%) upon acid doping for undoped and 24hr, 48hr, 72hr and 96hr doped PBI-9 mats with 30  $\mu\text{m}$  thickness. Results suggest

that PA rich domains in the membrane resulted in higher proton conductivity due to the interaction of water and excess acid molecules in hydrous medium. At the same time, these PA concentrated domains caused to adsorb more water molecules [45]. We immersed commercial PBI film, undoped PBI and doped PBI nanofibrous membranes into dye colored DI water bath to visually monitor the water diffusion and then to calculate water uptake (%), as given in **Figure S4**. It is clear that compared to PBI proton exchange film, much more water molecules were accumulated into the nanofibrous PBI membranes, thus revealing higher difference in water uptake (%). When PBI membrane was doped, the active sites of the imidazole ring were preferably occupied by the acid molecules, thus the water uptake becomes consequently lower, as seen in **Figure S4**. Once the system reached saturation at higher acid doping levels, the water uptake was also influenced by the excess of hygroscopic acid and so water uptake (%) slightly increased as the doping level rises, as in 72hr and 96hr doped PBI-9 membranes. The swelling related to PA doping also could be interpreted from the mass change % as predicted. Randomness of nanofibers do not create any anisotropic behavior in the membranes. When the membranes were doped, depending on the distribution of PA molecules and new formed short-range linkages, physical properties may differ and exhibit directionality. Each doped specimen showed contraction (%) both in  $x$  and  $z$  direction. We should note that along  $x$ -direction, due to the use of rotating drum during electrospinning, nanofibers were slightly better oriented compared to  $z$ -direction. Hence, oriented chains preferably in  $x$ -directions showed lower contraction value (%) as seen in **Table 3**. Moreover, local undoped and doped sites in 96hr doped PBI-9 membranes can lead to higher contraction (%) in  $z$  axis than in  $x$ -axis, finally caused anisotropy in doped membrane.

## **Conclusion**

Produced PBI electrospun nanofiber mats were optimized systematically, based on the fiber diameter and morphology of fibers, and among 15 different systems, the best results were obtained at PBI-9 system with mean fiber diameter of  $170\pm 10$  nm. Immersion in PA for 72hr led to highest proton conductivity whereas the conductivity of 96hr doped PBI mats was decreased. On the other hand, PA doping significantly caused swelling and 2-fold increase in mean fiber diameter and led to anisotropy in fibrous membranes. FT-IR analysis demonstrated that the amount of accumulated PA increased by doping time but still there were excessive PA molecules seen. So, the results revealed that the morphological changes due to *H*-bond network and free PA molecules accumulated into the membrane caused acid leaking. Thermogravimetric analysis also pointed out the two degradation peaks around 650°C and 800°C for 96hr PA doped membranes due to uneven distribution of PA molecules which induced doped and undoped regions. Tensile strength of the membranes was found to be increased by doping level, whereas the strain at break (%) decreased due to the brittle nature of formed network.

**Supporting information is available.**

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**Table 1.** Electrospun PBI nanofibers and their assigned electrospinning parameters

Specimen Name	Polymer concentration (wt %)	Applied Voltage (kV)	Feeding Rate ( $\mu\text{L/hr}$ )
PBI-1	10	15	70
PBI-2	10	15	85
PBI-3	10	15	100
PBI-4	12.5	15	70
PBI-5	12.5	15	85
PBI-6	12.5	15	100
PBI-7	15	15	70
PBI-8	15	15	85
PBI-9	15	15	100
PBI-10	10	12	100
PBI-11	10	18	100
PBI-12	12.5	12	100
PBI-13	12.5	18	100
PBI-14	15	12	100
PBI-15	15	18	100

**Table 2.** Proton conductivity and resistivity of produced doped PBI-9 membranes in 100% RH at room temperature.

<b>Membrane</b>	<b>Resistance (Ohms)</b>	<b>Resistivity (ohm. cm)</b>	<b>Conductivity (mS/cm)</b>
PBI-9-24 hr	2.14	14.445	69
PBI-9-48 hr	1.4	9.45	106
PBI-9-72 hr	1.2	8.1	123
PBI-9-96 hr	1.4	9.45	106

**Table 3.** Dimensional changes (%) and mass change (%) upon acid doping for undoped and 24hr, 48hr, 72hr and 96hr doped PBI-9 membranes with 30  $\mu\text{m}$  thickness are reported. Tensile properties such as Young's modulus, strain at break (%) and ultimate strength are given for all doped and undoped membranes. ( $x$  and  $z$  stand for the length and width of membranes, respectively)

Membrane	Young's modulus (MPa)	Ultimate strength (MPa)	Strain at break (%)	Mass change after doping (%)	Dimensional changes upon acid doping (%)	
					$x$	$z$
Undoped PBI-9	0.65 $\pm$ 0.05	4.19 $\pm$ 0.65	24.0 $\pm$ 4.8			
PBI-9-24 hr	0.39 $\pm$ 0.01	4.40 $\pm$ 1.28	23.95 $\pm$ 6.68	26.3 $\pm$ 4.6	-21.2	-25
PBI-9-48 hr	0.32 $\pm$ 0.29	3.80 $\pm$ 0.08	25.19 $\pm$ 15.23	21.1 $\pm$ 0.7	-20	-25
PBI-9-72 hr	2.55 $\pm$ 0.44	10.24 $\pm$ 1.98	15.03 $\pm$ 0.154	27.3 $\pm$ 3.2	-21.8	-25
PBI-9-96 hr	1.08 $\pm$ 0.08	15.00 $\pm$ 1.41	10.51 $\pm$ 14.49	26.4 $\pm$ 2.7	-15.6	-25