Supporting information for

Toward enhanced conductivity of high-temperature proton exchange membranes: Development of novel PIM-1 reinforced PBI alloy membranes

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1. Experimental

Materials

3,3'-Diaminobenzidine (DAB, Aladdin Reagent), 4,4'-oxybis (benzoic acid) (OBA, Alfa Aesar Reagent), 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobiindane (TTSBI, TCI Reagent) and 1, 4-dicyanotetrafluorobenzene (DCTB, Energy Chemical Co.) were used without further purification. Phosphorus pentoxide-methanesulfonic acid (PPMA) solution was prepared by dissolving phosphorus pentoxide (Beijing Chemical Reagent, China) in methane sulfonic acid (Aladdin Reagent) in the mass ratio of 1:10. N,N-dimethylformamide (DMF) and N, N-dimethylacetamine (DMAC) were purchased from Tianjin Tiantai Fine Chemicals Co. Ltd., China. Orthophosphoric acid, potassium carbonate (K_2CO_3), acetone and toluene were obtained from Beijing Chemical Reagent, China.

Synthesis of the aryether-type PBI (Scheme S1)

The synthesis procedure of poly(4,4'-diphenylether-5,5'-bibenzimidazole) (OPBI) is as follows: DAB (10.7135 g) and OBA (12.9115 g) were taken into a three-neck round-bottom flask along with 35 ml of PPMA. The mixture was kept at 100 °C for 2 h, and 140 °C for 2 h in nitrogen atmosphere under mechanical stirring. Then the temperature of the system was raised to 180 °C, and stirred for 5~6 h. After the completion of polymerization, the polymer was isolated in deionized water. The solid was neutralized with 10 wt% $NaHCO_3$ solution at 40 °C for 48 h, and then rinsed with deionized water several times to eliminate the remaining sodium bicarbonate. Finally, the OPBI polymer powder was dried at 120 °C for 24 h under vacuum. Mn=70.6 KDa, and polydispersity (Mw/Mn)= 1.44.

FT-IR ν (cm^{-1}): 1616 (C=N), 1483 (C-N), 1285 (C-C), 1014 (Ar-O-Ar). ^{1}H NMR (400 MHz; DMSO-d_6) δ (ppm): 13.01 (s, 2H, NH), 8.30 (d, 4H, CH, J=8.0 Hz), 7.86 (s, 2H, CH), 7.68 (s, 2H, CH), 7.58 (d, 2H, CH, J=8.0 Hz), and 7.28 (d, 4H, CH, J=8.0 Hz).

Synthesis of the low-molecular-weight PIM-1 (Scheme S2)

TTSBI (1.7021 g) and DCTB (1.0005 g) were dissolved into a mixture of DMAc (9 ml) and methylbenzene (5 ml). The obtained solution along with anhydrous K_2CO_3 (1.3821 g) were put into a three neck flask equipped with a Dean-Stark trap and mechanical agitation under nitrogen atmosphere. Then the reaction system was heated to reflux and removed water by Dean-Stark trap. The mixture was vigorously stirred at 140 °C for polymerization. After 0.5 h, a part of the mixture was taken out, and poured into a large excess of deionized water with stirring water. The obtained product was washed several times with deionized water to remove excrescent K_2CO_3, and the crude product was collected by filtration. It was dissolved into chloroform and then precipitated from methanol. A low-molecular-weight polymer was finally obtained after this purification procedure. Mn=8.3 KDa, Mw/Mn=2.81.

FT-IR ν (cm^{-1}): 2239 (C≡N), 1452 (C-H), 1267 (C-O), 1014 (Ar-O-Ar). ^{1}H NMR：(400 MHz; CDCl$_3$) δ (ppm): 1.34 (d, 12H, CH$_3$, J=22.8 Hz), 2.24 (dd, 4H, CH$_2$, J_1=12 Hz, J_2=70 Hz), 6.42 (s, 2H, CH), 6.8 (s, 2H, CH).

Fabrication of the OPBI pristine and OPBI/PIM alloy membranes

The alloy membranes were fabricated from above soluble PIM-1 and OPBI polymers. A detailed procedure is as follows: After stirring at room temperature and then at 120 °C for several hours, OPBI and PIM-1 were completely dissolved in DMAc, respectively. Various amounts of PIM-1/DMAc solution (2% w/v) was added into the OPBI/DMAc (20% w/v), and the weight ratios of PIM-1: OPBI in the mixed solutions were 5%，10% and 15%, respectively. The resulting homogeneous solution was poured onto clean glass plates (11 cm X 11 cm) in an oven and maintained at 80 °C/12h, 100 °C/12h and 120 °C/12h, respectively. The resulting membranes were peeled off after drying in a vacuum oven at 120 °C for 24 h to evaporate the residual solvent. The transparent and flexible OPBI/PIM-1 alloy membranes were obtained and they were named as OPBI/PIM-1 (5%), OPBI/PIM-1 (10%) and OPBI/PIM-1 (15%), respectively.

Also, the pristine OPBI membrane was casted from its DMAc solution and the same drying procedure was adopted. All the obtained membranes were uniform and tough, and their thickness was in the range of 60~70 μm.

Preparation of phosphoric acid doped pristine and alloy membranes

The dried membranes were dipped in 85 wt% phosphoric acid (PA) at 120 °C for 24 h, After treatment, the PA-doped membranes were removed from the PA bath, wiped with filter paper, and dried at 80 °C for 12 h. The obtained PA-doped membranes were stored in the grip bag for further characterization.

Measurements

FT-IR spectra of were measured on a Nicolet Impact 410 Fourier-transform infrared spectrometer, and thin films for polymer samples were used. ^{1}H NMR experiments were carried out on a Bruker Avance III 400 MHz spectrometer by using DMSO-d_6 or CDCl$_3$ as solvents. Gel permeation chromatography (GPC) analyses of PIM-1 were performed on a Waters 1515 instrument equipped with a guard column MIXED 7.5x50 mm PL column and two MIXED-C 7.5X300 columns and a differential refractive index detector using THF (HPLC grade) as the eluent at 35 °C with a flow rate of 1 mL min^{-1}. GPC analyses of OPBI were performed on an Agilent PL-GPC-220 instrument equipped with a guard column 7.5x50 mm PL column and two MIXED-B 7.5X300 columns and a differential refractive index detector using DMF (HPLC grade) as the eluent at 80 °C with a flow rate of 1 mL min^{-1}. Atomic force microscope (AFM) images were taken with a SPA-300HV (Seiko, Japan) under ambient conditions. AFM was operated in the tapping mode with an optical readout using Si cantilevers. Polarized light microscope (PLM) images were measured by LEICA DM 4000/MLED. The thickness of the samples was about 50 μm. Thermogravimetric analysis (TGA) on a Perkin Elmer Pyris 1 thermal analyzer system was employed to assess thermal stability of the membranes. Prior to the analysis, the membranes were dried and kept in the TGA furnace at 120 °C under a nitrogen atmosphere for 30 min to remove residual water. The samples were evaluated in the range of 80~800 °C at a heating rate of 10 °C·min^{-1} under N$_2$ atmosphere. Dynamic mechanical analysis (DMA) measurement was performed with the film specimens (length: 30 mm, width: 10 mm and thickness, 60-80 μm) using a TA instrument DMA Q800 with a load frequency of 1 Hz and a heating rate of 5 °C min^{-1} from room temperature to 400 °C in N$_2$ atmosphere. The mechanical properties of membranes were measured at room temperature on SHIMADZU AG-I 1 KN at a strain rate of 2 mm·min^{-1}. The size of samples was 15 mm×5 mm. Undoped samples were obtained by drying in a vacuum oven at 120 °C for 12 h prior to the measurement. PA-doped samples were obtained by immersing the dry membranes in 85% of PA at 120 °C for 24 h, and then dried in an oven at 80 °C for 12 h. The WAXD patterns of the samples were obtained with Cu Kα radiation (λ = 1.5418 Å) source operated with the angular range (2θ) of 5-40° at a scanning rate of 5 deg min^{-1}.

The density of OPBI and OPBI/PIM blend membranes were measured by an Electronic Densimeter SD-200 L. The membranes were pre-dried in a vacuum oven at 120 °C for 12h. The fractional free volume (FFV) of polymer alloys was calculated from the following correlation:

$$FFV = (V - V_0)/V$$

where V is the specific volume (1/ρ) and V_0 is the impermeable volume occupied by the polymer and is 1.3 times that of its vander Waals volume: $V_0 = 1.3 V_w$. V_w can be obtained by Bondi's group contribution approach. The V_w of OPBI can be obtained from our previous work[1], while the V_w of PIM-1 can be adopted from Thomas et al[2]. The vander Waals volumes of OPBI/PIM-1 blends could be estimated using the equation as following:

$$V_w = n_1 V_{w1} + n_2 V_{w2}$$

where n_1, n_2 and V_{w1}, V_{w2} refer to the mole fractions and vander Waals volumes of PIM-1 and OPBI, respectively. The FFV of OPBI/PIM-1 alloys can be estimated from the following equation.

$$FFV_{12} = \omega_1 FFV_1 + \omega_2 FFV_2$$

FFV$_1$, FFV$_2$, and FFV$_{12}$ are the fractional free volumes of the components 1,2 and the polymer alloys, respectively.

PA uptake is the weight of PA per dry composite membranes, and was calculated using Equation (1). The acid (PA) doping level (ADL) is defined as the number of moles of acid (PA) per mole PBI repeat unit and was calculated using Equation (1).

(1) $$ADL = \left[(W_d - W_u)/M_{PA} \right] / \left[W_u/M_{PBI} \right]$$

Where W_u and W_d are the weight of undoped and the PA-doped membrane respectively and M_{PBI} and M_{PA} are the repeating unit molecular weight of the polymer and molecular weight of the phosphoric acid, respectively. For each sample, three similar size pieces of samples were measured and the reported acid doping level values are the average of these three parallel test value.

The dimensional stability was the swelling ratio of composite membranes including area, thickness and volume swelling. The dimensional swellings were calculated from Equations (2), (3) and (4). And we

introduced a specific value to measure the membrane capability of balancing the PA uptake and the loss of dimensional stability. The specific values were calculated from Equation (5).

(2) $$Area\ Swelling(\%) = \left[(A_d - A_u)/A_u\right] \times 100\%$$

(3) $$Thickness\ swelling(\%) = \left[T_d - T_u/T_u\right] \times 100\%$$

(4) $$Volume\ swelling(\%) = \left[(V_d - V_u)/V_u\right] \times 100\%$$

(5) $$ADL\ /Volume\ swelling(1/\%) = ADL/\Delta V$$

Ad, Au, Td, Tu, Vd and *Vu* are the area, thickness, and volumes of the doped and undoped samples, respectively.

Proton conductivity of PA-PBI membranes (4 cm × 1 cm) were measured by a four-electrode AC impedance method from 0.1 Hz to 100 kHz with 10 mV AC perturbation and 0.0 V DC rest voltage using a Princeton Applied Research Model 273 A potentiostat (Model5210 frequency response detector, EG&GPARC, Princeton, NJ). All the membranes were immersed into 85 wt% PA for 24 h at 120 °C before test. The measurements were carried out with the cells immersed in constant-temperature water, and the proton conductivity was determined by the following formula:

$$\sigma = \frac{L}{RA}$$

where σ (S cm^{-1}) is the proton conductivity, L (cm) is the distance between the electrodes used to measure the potential, R (Ω) is the membrane resistance, and A (cm^2) is the membrane area.

Fuel cell test

The OPBI powder was firstly dissolved in a mixture of formic acid and phosphoric acid at a concentration of 0.5 wt%, and the molar ratio of phosphoric acid to OPBI is 10:1. The catalyst ink was prepared by mixing platinum catalysts and the above solution with a ratio of the platinum loading to the OPBI loading in the final ink was about 13:1. The catalyst ink was sprayed onto the gas diffusion layer to form a gas diffusion electrode. The loading of Pt in the catalyst layer was approximately 0.6 mg Pt cm^{-2}. This solution was used as the solvent to prepare the catalyst inks for spraying electrodes. The acid-doped membranes, which doped in PA at 120 °C for 24h, were sandwiched between two pieces of gas diffusion electrode and hot-pressed under a pressure of about 4 MPa at 135 °C for 3 min. The active electrode area of the MEAs was 9 cm^2. The polarization curves were obtained using a Fuel Cell Test System (Arbin Instrument Corp.) under the operation conditions of 160 °C. Dry hydrogen (0.3 L/min) and oxygen (0.15 L/min) were supplied to the fuel cell under atmospheric pressure without pre-humidification. Polarization curves were obtained by a current step potentiometry with the steady state potential recorded 2 min after each current was set.

2. Figures and table
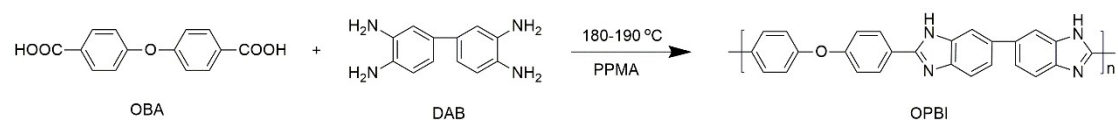
Scheme S1 Synthesis of poly (4, 4'-diphenylether-5, 5'-bibenzimidazole).
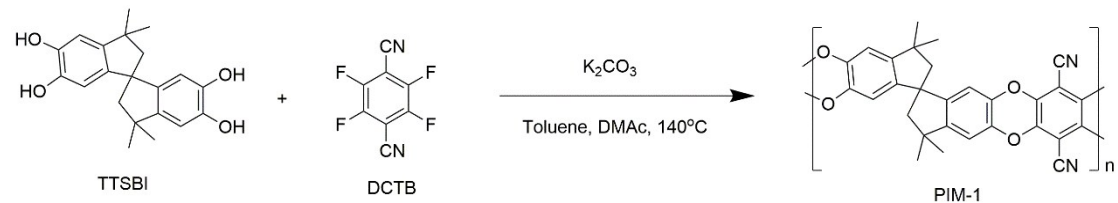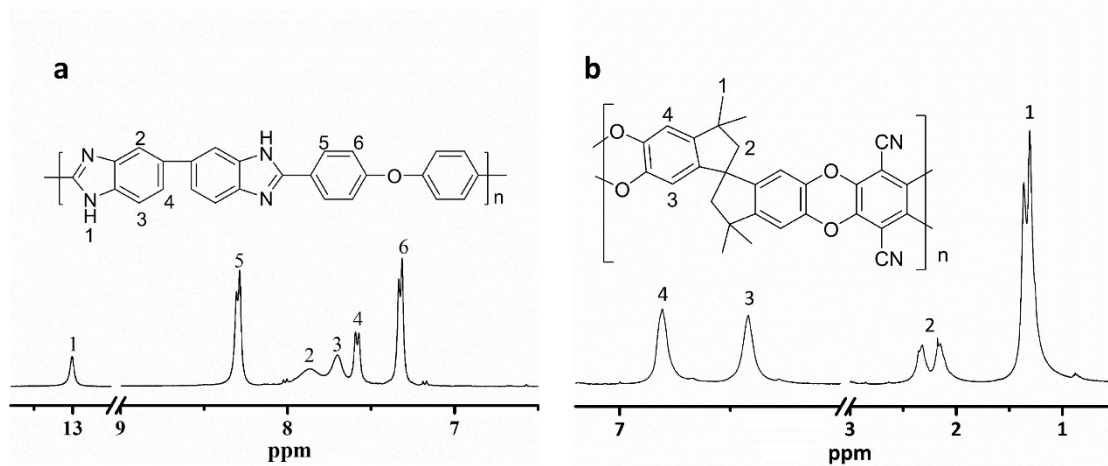

Scheme S2 Synthesis of PIM-1.

Fig. S1 ^{1}H NMR spectra of (a) OPBI and (b) PIM-1.
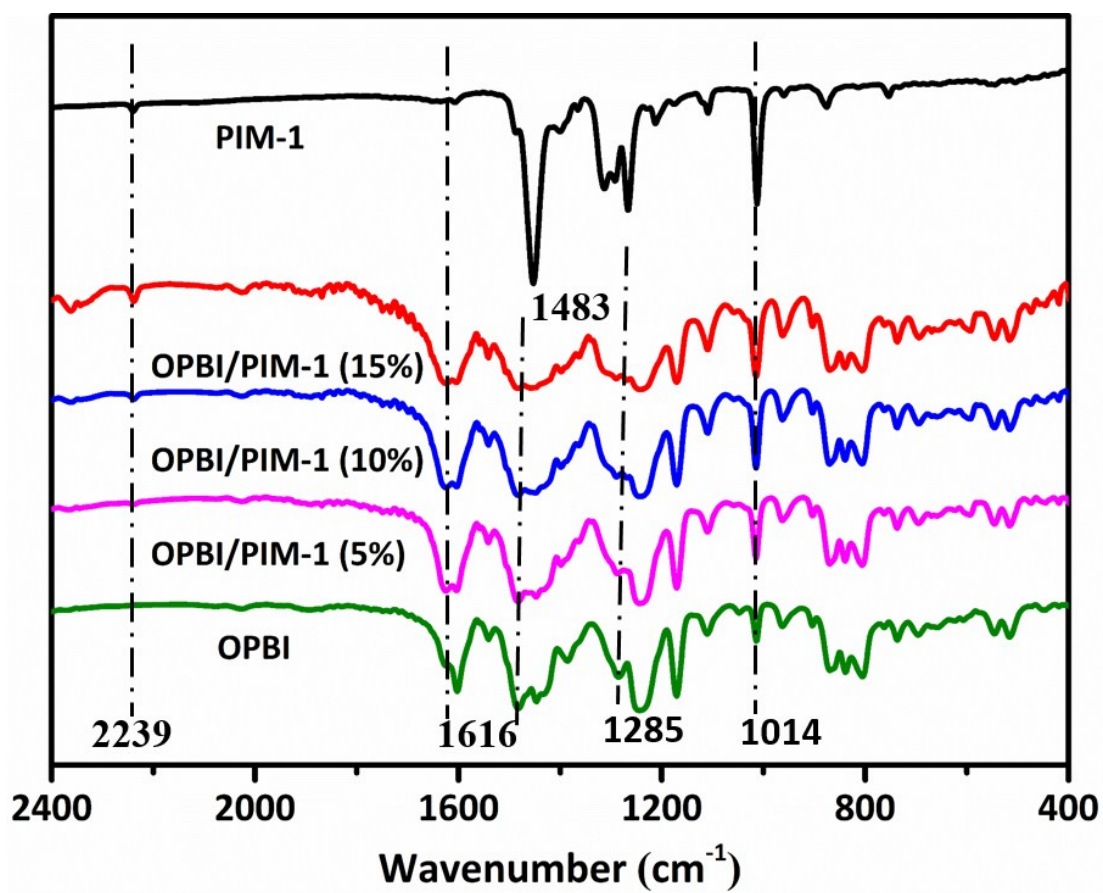
Fig. S2 FTIR spectra of OPBI, PIM-1 and OPBI/PIM-1 alloy membranes.

Table S1 The surface roughness of the OPBI and OPBI/PIM-1 alloy membranes.

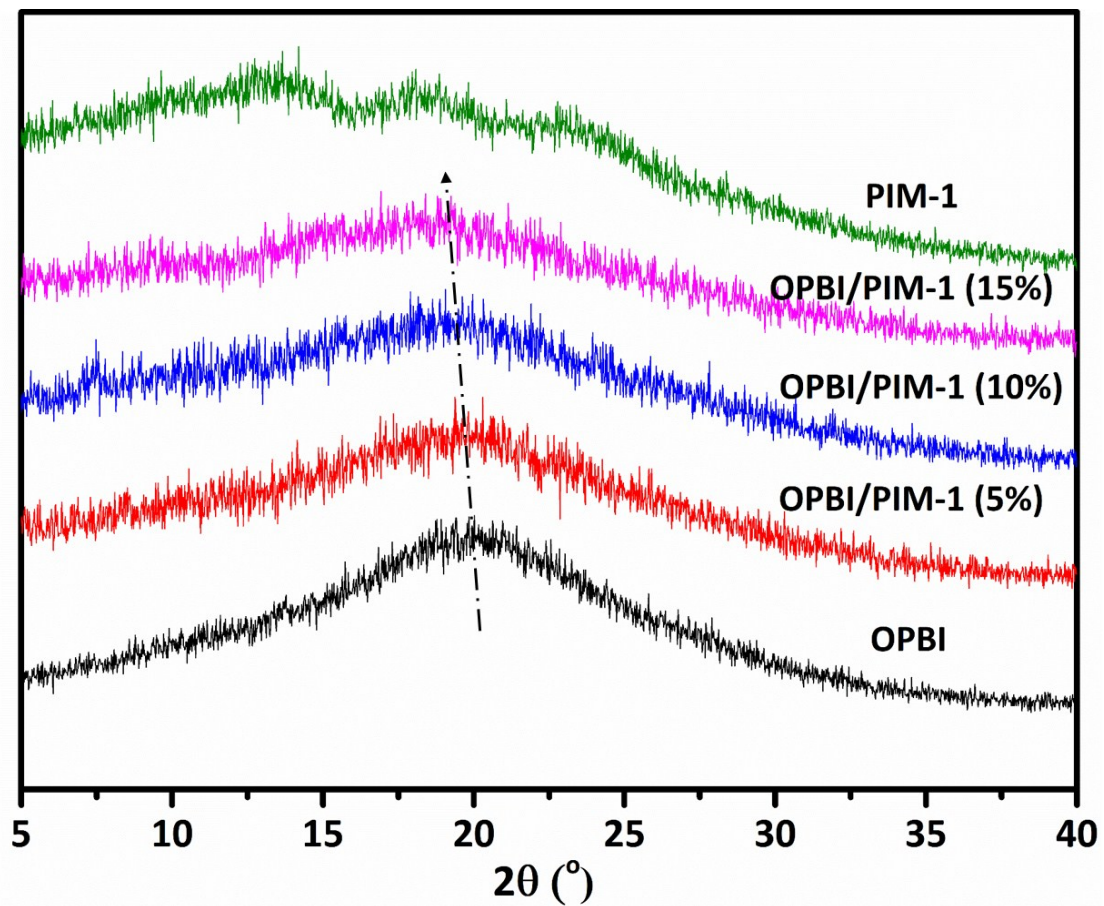| Samples	Surface roughness	
	Rq/nm	Ra/nm
OPBI	3.72	3.08
OPBI/PIM-1 (5%)	23.1	17.7
OPBI/PIM-1 (10%)	26.3	21.5
OPBI/PIM-1 (15%)	36.5	28.4

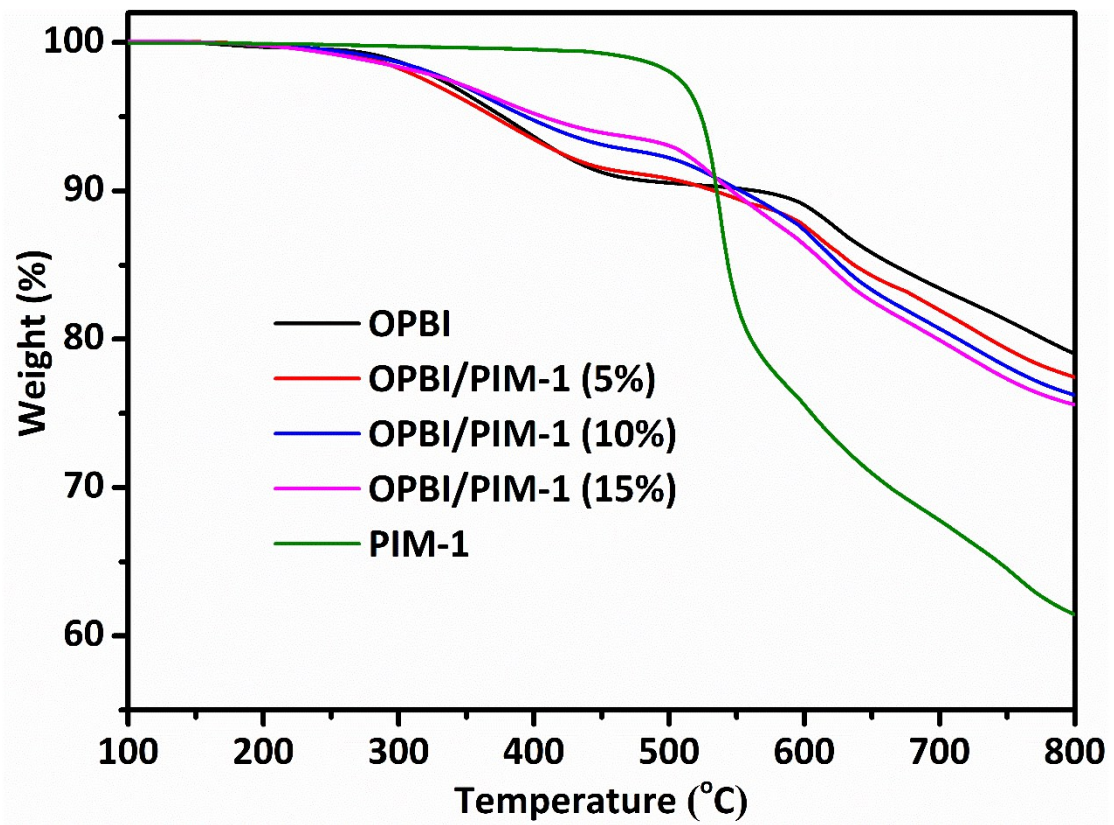Fig. S3 XRD patterns of OPBI, PIM-1 and OPBI/PIM-1 alloy membranes.

Fig. S4 TGA curves of OPBI, PIM-1 and OPBI/PIM-1 alloys in N$_2$.

References

1   X. Li, H. Ma, Y. Shen, W. Hu, Z. Jiang, B. Liu and M. D. Guiver, *J Power Sources*, 2016, **336**, 391-400.
2   S. Thomas, I. Pinnau, N. Y. Du and M. D. Guiver, *J Membrane Sci*, 2009, **333**, 125-131.