

Electronic Supplementary Information

Facile Construction of a Highly Proton Conductive Matrix-Mixed Membrane Based on a -SO₃H Functionalized Polyamide

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Experimental Section

Materials

All the chemicals, reagents and solvents used for the materials syntheses were available commercially and were used as received unless specifically mentioned.

Characterization

Fourier-transform infrared spectroscopy (FTIR) spectra were carried out on a Bruker Optics instrument (Tensor II) with KBr pellets. Powder X-ray diffraction (PXRD) analyses were performed and PXRD patterns were recorded on an X-ray diffractometer (Rigaku Smart lab 9KW) using monochromatic Cu K α radiation (1.5406 Å) measuring in the 2 θ range from 5 to 70° with a 2°•min⁻¹ scanning speed. Thermogravimetric analyses (TGA) were carried out by a Mettler Toledo TGA/SDTA851 machine under N₂ atmosphere (99.999%) with a flow rate of 50 mL•min⁻¹ and the operating temperature ranging from 25 to 800 °C with the heating rate of 5 °C•min⁻¹. Scanning electron microscopy (SEM) images were performed on a JSM-7001F scanning electron microscope, which operated at 3.0 KV accelerating voltage. Transmission electron microscopy (TEM) images were performed on a JEOL JEM-1011 transmission electron microscope, operated at 200 KV. The data for proton conductivities of materials were performed on a CH Instruments (CHI760E) using quasi-four-probe method and impedance/gain-phase analyzer in 1-10 MHz frequency range and 200mV AC amplitude.

Proton conductivity of pure sample. AC impedance data and electrical properties of materials were measured in a wide range of temperature (303-353K) and humid conditions (75%-98%). For electrical measurements, the powder samples were firstly grinded homogeneously in mortars for 10 minutes and then cash-like discs a diameter of 6 mm and thickness ranging from 2 to 4.5 mm were prepared by compressed the materials under a pressure of 7 MPa for 30 s by a tablet press. Copper based electrodes and home-made sample holder were utilized, in which the prepared sample discs were placed for the measurement of resistivity and proton conductivity. The sample discs with electrodes were then placed in temperature and humidity-controlled chambers. Before measurements, the sample discs with electrodes were placed in the chamber with specific temperature and relative humidity for 48 h to balance the sample discs with the setting conditions. Further, to improve and get the accurate results, the impedance measurements were repeatedly

collected until convergent and uniform results are obtained and Nyquist Plot is evaluated. Proton conductivity measurements were carried out in the frequency range of 1-10⁶ Hz, 100 mV amplitude, and parallel electrode assembly is used to get the Nyquist plot. Equivalent circuit is designed, by which the resistance was acquired, and impedance plot was fitted. To analyze this, Z view software was used. Capacitance and resistance were placed parallel to each other in designing the equivalent circuit and measuring resistance.

Their proton conductivity of sample discs was calculated through the formula:

$$\sigma = \frac{l}{RS}$$

where *l* and *S* represent the disc's thickness (cm) and cross-sectional area (cm²), respectively. In a Nyquist plot utilizing Z view software, *R* is the disc's bulk resistance, which is fitted by the equivalent circuit of the semicircle.

Their activation energies during proton conduction processes were calculated by the formula

$$\ln(\sigma T) = \ln A - E_a/k \times 1/T$$

where *T* is the absolute temperature in kelvin, *E_a* is the activation energy, and *k* is the Boltzmann constant.

Physicochemical Investigations of matrix-mixed Membranes

Ion exchange capacity (IEC). The ion exchange capacity (IEC) of matrix-mixed membranes was measured using a titration method. For one day, dried pre-weighted membranes were immersed in a 2 M NaCl solution to replace proton via sodium ions, which were then followed by the liberated positive ions. To determine the endpoint, phenolphthalein was used as an indicator, and the solution was titrated with 0.01 M NaOH solution. The given equation was used to calculate IEC values.^{S1,S2}

$$IEC (mmol/g) = \frac{C_{NaOH} \cdot V_{NaOH}}{W_{dry}} \quad (1)$$

where, *C_{NaOH}* is the concentration of NaOH solution (mol/g) and *V_{NaOH}* is the volume of consumed NaOH solution (mL), respectively.

Water Uptake property and Swelling characteristics. To study the water uptake property, the membranes was dried at 80 °C for 6 h and its weight was measured. The membranes were then immersed in distilled H₂O at 30 and 80 °C overnight, removed from the H₂O, and rapidly dried using clean paper to determine the weight of the membranes once more. The following equation (2) was used to calculate the water uptake (%) of matrix-mixed membranes.^{S3,S4}

$$WU(\%) = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100 \quad (2)$$

where M_{wet} and M_{dry} are the weights of wet and dry sample respectively.

To study the swelling property, the membranes was dried at 80 °C for 6 h and its weight was measured. The membranes were then immersed in distilled H₂O at 30 °C and 80 °C overnight, removed from the H₂O, and rapidly dried using clean paper to determine the weight of the membranes once more.^{S3} The equation (3) was used to calculate the swelling ratio (%) of matrix-mixed membranes.

$$Swelling\ ratio\ (\Delta L)\ (\%) = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100 \quad (3)$$

where L_{wet} and L_{dry} are the diameters of wet and dry membranes respectively in round form.

Dimensional Stability. To investigate the dimensional stability of the matrix-mixed membrane, the membranes were submerged in distilled water for 5 h at 30 °C and 80 °C respectively. The membranes' length and width were measured with a vernier caliper. The membrane was then dried and the change in length and width was measured at room temperature. The change in length (ΔL_c) of the membrane was calculated by using the equation (4).^{S3,S4}

$$(\Delta L_c)\ (\%) = \frac{L - L_{dry}}{L_{dry}} \times 100 \quad (4)$$

where L and L_{dry} are the length of wet and dry membranes respectively.

The change in weight (ΔW_c) of the membrane was calculated by using the equation (5).

$$(\Delta W_c) (\%) = \frac{W - W_{dry}}{W_{dry}} \times 100 \quad (5)$$

where W and W_{dry} are the width of wet and dry membranes respectively.

Chemical Stability. A small piece of the matrix-mixed membrane with different ratios (**PA(PhSO₃H)₂-PAN(n:m)**) was immersed in Fenton reagent (FeSO₄ in H₂O₂ (3%), 3.0 ppm) at 30 °C and 80 °C to investigate its chemical stability. The oxidative stability was determined by the elapsed time (t) it took for the membrane to dissolve completely. The results show that at 80 °C, all the membranes have an elapsed time (t) value of ≥ 12 h. This is the standard test to measure the chemical stability of matrix-mixed membranes and the results indicate that these membranes have good chemical stability due to the aromatic structure of sulfonated polyamides.^{S3}

Hydrolytic Stability. To check the hydrolytic stability of the matrix-mixed membranes towards water, the membranes were immersed in distilled water at 50 °C and measuring the elapsed time until the hydrated membranes lost their mechanical properties. When the membranes were slightly bent, they broke, which was the criterion for loss of mechanical property.^{S2}

Proton conductivity of matrix-mixed membrane. The fabricated membranes were cut to a rectangle for the proton conduction measurements.

It is calculated by using the following equation:

$$\sigma = \frac{l}{WRT}$$

Where L is the length, R is the measured resistance, T is the thickness of the membrane and W is the width of the membrane.

Table

Table S1. The temperature-dependent proton conductivities (S cm⁻¹) of **PA(PhSO₃H)₂** under different humidity conditions.

T (°C)	100%RH SD# = ±0.035	98%RH SD = ±0.026	85%RH SD = ±0.003	75%RH SD = ±0.001	63%RH SD = ±0.0021	53%RH SD = ±0.00197
100	8.78×10 ⁻²	7.25×10 ⁻²	8.19×10 ⁻³	3.30×10 ⁻³	6.85×10 ⁻⁵	6.12×10 ⁻⁶
90	8.01×10 ⁻²	6.18×10 ⁻²	6.33×10 ⁻³	1.02×10 ⁻³	5.42×10 ⁻⁵	4.31×10 ⁻⁶
80	7.60×10 ⁻²	5.54×10 ⁻²	5.60×10 ⁻³	8.05×10 ⁻⁴	4.17×10 ⁻⁵	1.69×10 ⁻⁶
70	3.98×10 ⁻²	4.27×10 ⁻²	2.70×10 ⁻³	7.73×10 ⁻⁴	3.30×10 ⁻⁵	1.22×10 ⁻⁶
60	1.96×10 ⁻²	1.15×10 ⁻²	2.10×10 ⁻³	5.52×10 ⁻⁴	2.75×10 ⁻⁵	9.57×10 ⁻⁷
50	5.97×10 ⁻²	1.12×10 ⁻²	1.44×10 ⁻³	5.03×10 ⁻⁴	1.70×10 ⁻⁵	7.01×10 ⁻⁷

#SD represents the standard deviation for respective proton conductivities at a different relative humidity.

Figures

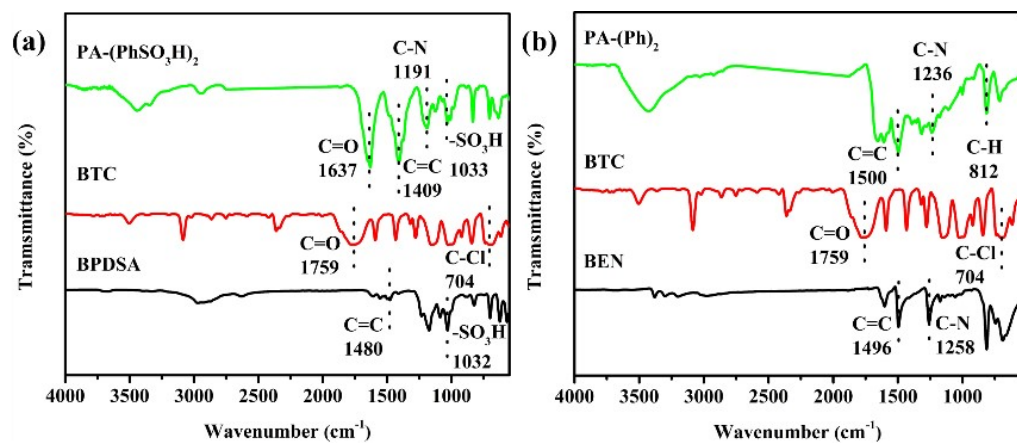


Fig. S1. FTIR spectra of (a) PA(PhSO₃H)₂ and (b) PA(Ph)₂ and the related reactants.

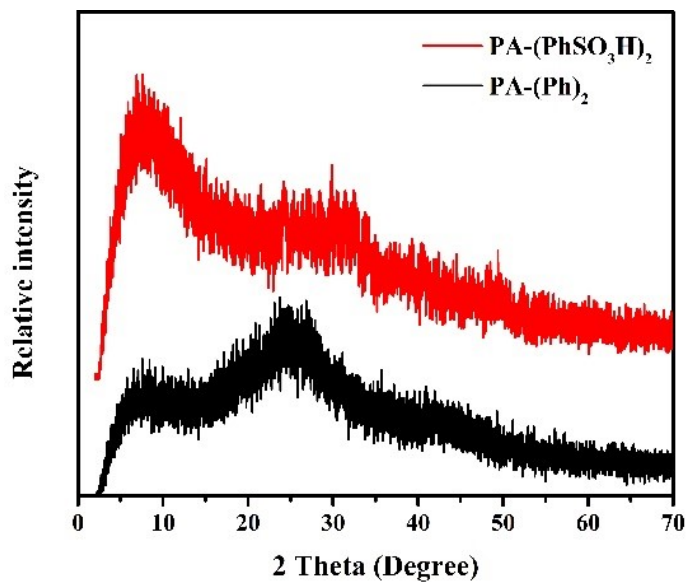


Fig. S2. PXRD patterns of PA(PhSO₃H)₂ and PA(Ph)₂.

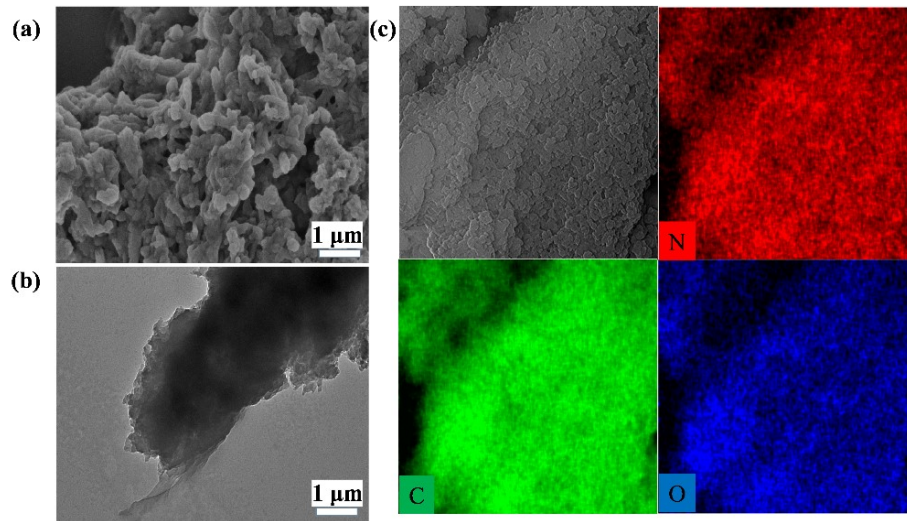


Fig. S3. (a) SEM image, (b) TEM image, and (c) EDX spectroscopy mapping images of PA(Ph)_2 .

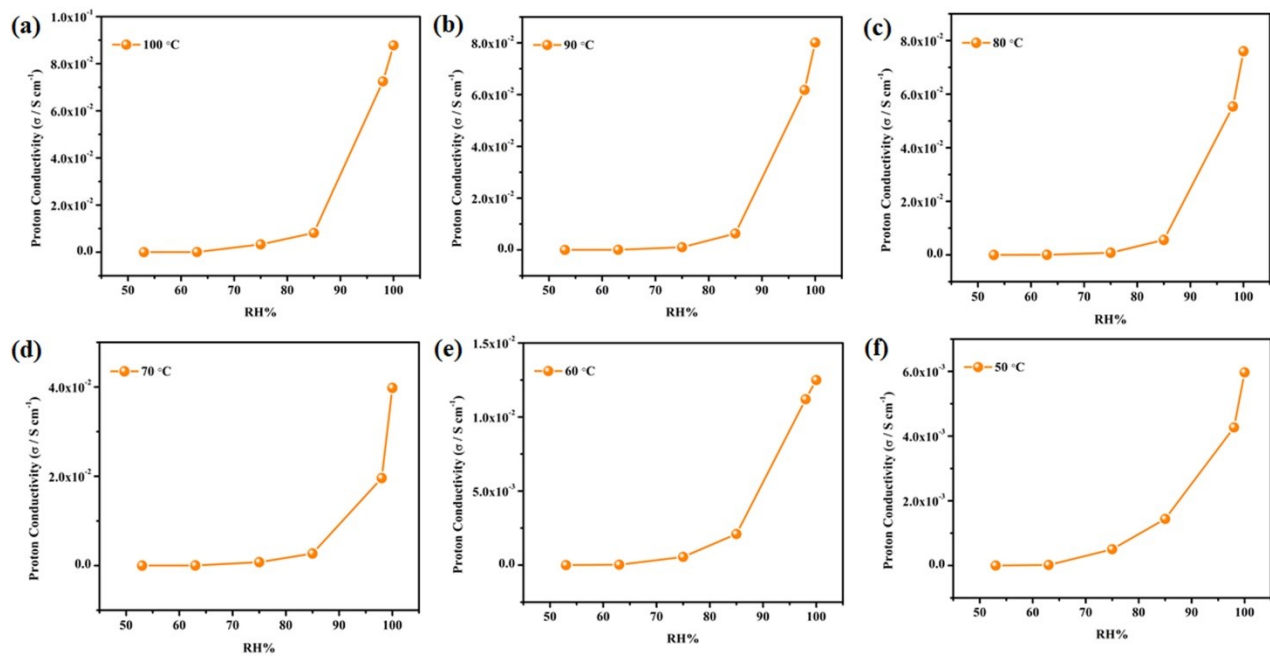


Fig. S4. Proton Conductivity (S cm^{-1}) of $\text{PA(PhSO}_3\text{H)}_2$ versus relative humidity at different temperatures: (a) 100 °C (b) 90 °C (c) 80 °C (d) 70 °C (e) 60 °C and (f) 50 °C.

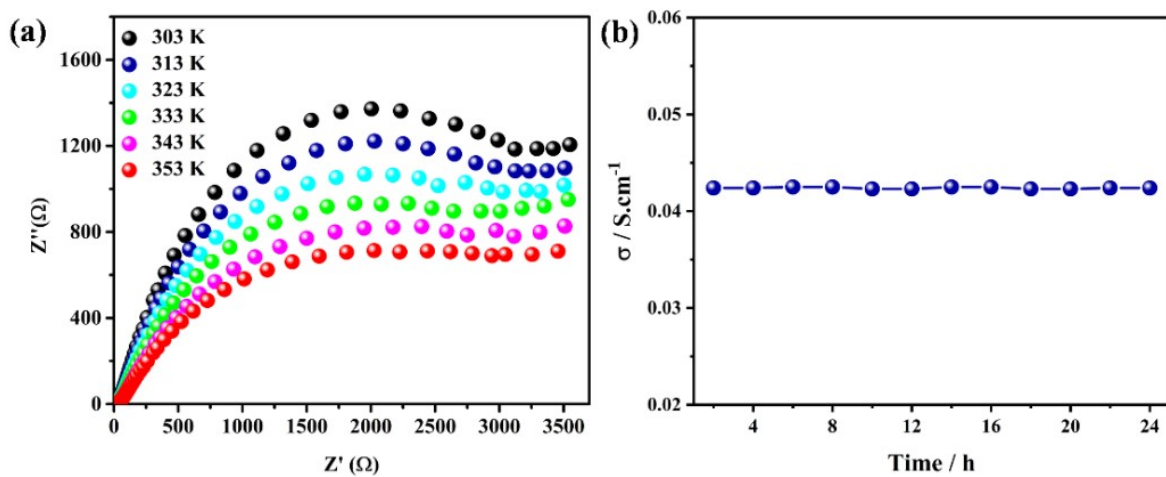


Fig. S5. (a) Nyquist plot at 98%RH and different temperatures. (b) Long-life reusability test at 80°C and 98%RH of $\text{PA}(\text{PhSO}_3\text{H})_2\text{-PAN}(1:1)$.

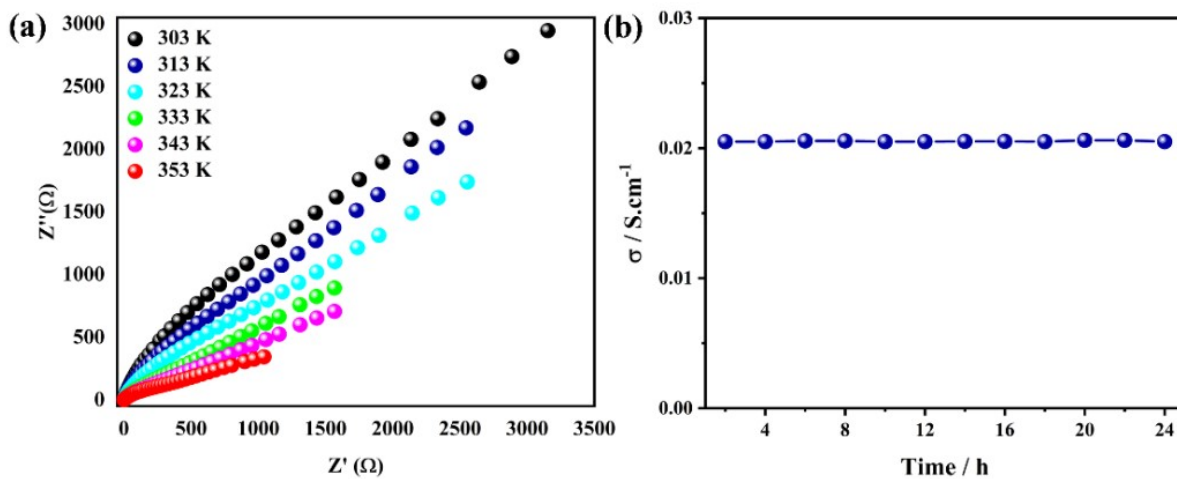


Fig. S6. (a) Nyquist plot at 98%RH and different temperatures. (b) Long-life reusability test at 80°C and 98%RH of $\text{PA}(\text{PhSO}_3\text{H})_2\text{-PAN}(0.4:1)$.

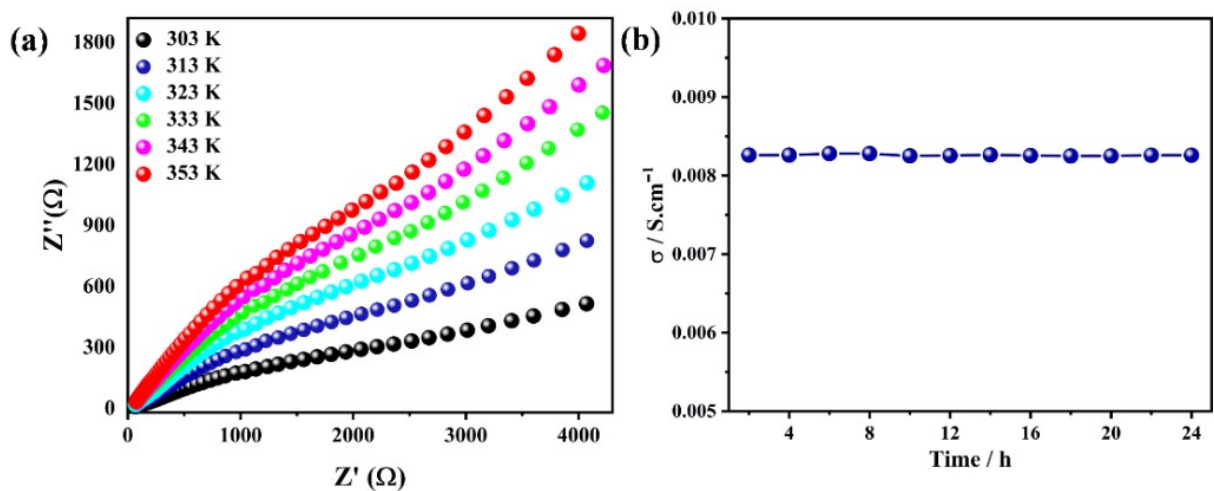


Fig. S7. (a) Nyquist plot at 98%RH and different temperatures. (b) Long-life reusability test at 80°C and 98%RH of **PA(PhSO₃H)₂-PAN(0.1:1)**.

References

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- S2. F. Ali, S. Saeed, S. S. Shah, F. Rahim, L. Duclaux, J.-M. Levêque and L. Reinert, *Recent Patents on Nanotechnology* 2016, **10**, 221-230.
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