Supporting Information

Fabrication of -SO$_3$H Functionalized Polyphosphazene reinforced Proton Conductive Matrix-Mixed Membrane

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Experimental Section

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 Kα radiation (1.5406 Å) measuring in the 2θ range from 5 to 70º with a $2º•min^{-1}$ scanning speed. N_2 adsorption-desorption isotherms measurements were performed on Micromeritics ASAP 2020 system at 77K. Before the sorption measurements, the samples were degassed for 12 h at 120 ℃ under vacuum. Highly pure (99.999%) gas was used in the measurements. Thermogravimetric analyses (TGA) were carried out by a Mettler Toledo TGA/SDTA851 machine under N_2 atmosphere (99.999%) with a flow rate of $50 mL•min^{-1}$ and the operating temperature ranging from 25 to 800 ºC with the heating rate of $5 ºC•min^{-1}$. 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 was performed on CH Instruments (CHI760E) using the quasi-four-probe method and impedance/gain-phase analyzer in 1-10 MHz frequency range and 200mV AC amplitude.

Proton conductivity of the pure sample. AC impedance data and electrical properties of materials were measured in a wide range of temperatures (303-353K) and humid conditions (75%RH-98%RH). For electrical measurements, the powder samples were firstly grinded homogeneously in mortars for 10 minutes, and then cash-like discs with a diameter of 6 mm and thickness ranging from 2 to 4.5 mm were prepared by compressing the materials under a pressure of 7 MPa for 30 s by a tablet press. Copper-based electrodes and a homemade 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 a temperature and humidity-controlled chamber. Before measurements, the sample discs with electrodes were placed in the chamber with a specific temperature and relative humidity for 48 h to balance the sample discs with the set conditions. Further, to improve and get 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 $1\text{-}10^6$ Hz, 100 mV amplitude, and parallel electrode assembly is used to get the Nyquist plot. The equivalent circuit is designed, by which the resistance was acquired, and the 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 (S1):

$$\sigma = \frac{l}{RS} \tag{S1}$$

where l and S represent the disc's thickness (cm) and cross-sectional area (cm^2), 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 (S2):

$$\ln(\sigma T) = \ln A - E_a/k \times 1/T \tag{S2}$$

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 equation (S3) was used to calculate IEC values. [S1-S4]

$$IEC\ (mmol/g) = \frac{C_{NaOH} \cdot V_{NaOH}}{W_{dry}} \tag{S3}$$

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 were dried at 80 °C for 6 h and their weight was measured. The membranes were then

immersed in distilled H_2O at 30 and 80 °C overnight, removed from the H_2O, and rapidly dried using clean paper to determine the weight of the membranes once more. The following equation (S4) was used to calculate the water uptake (%) of matrix-mixed membranes. [S1,S2,S5,S6]

$$WU(\%) = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100 \qquad (S4)$$

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

To study the swelling property, the membranes were dried at 80 °C for 6 h and their diameters was measured. The membranes were then immersed in distilled H_2O at 30 °C and 80 °C overnight, removed from the H_2O, and rapidly dried using clean paper to determine the diameters of the membranes once more. [S1,S2,S5] The equation (S5) was used to calculate the swelling ratio (%) of matrix-mixed membranes.

$$\text{Swelling ratio } (\Delta L) \ (\%) = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100 \qquad (S5)$$

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 (S6). [S1, S2, S5, S6]

$$(\Delta L_c) \ (\%) = \frac{L - L_{dry}}{L_{dry}} \times 100 \qquad (S6)$$

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

The change in width (ΔW_c) of the membrane was calculated by using the equation (S7).

$$(\Delta W_c) \ (\%) = \frac{W - W_{dry}}{W_{dry}} \times 100 \qquad (S7)$$

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

Chemical Stability. A small piece of the matrix-mixed membrane PP-(PhSO$_3$H)$_2$-PAN with different ratios was immersed in Fenton reagent (FeSO$_4$ in H$_2$O$_2$ (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 ≥6 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. [S1, S2, S5]

Hydrolytic Stability. To check the hydrolytic stability of the matrix-mixed membranes toward the water, the membranes were immersed in distilled water at 50 °C and measured 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. [S1, S2, S4]

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

It is calculated by using the equation (S8):

$$\sigma = \frac{l}{WRT} \qquad (S8)$$

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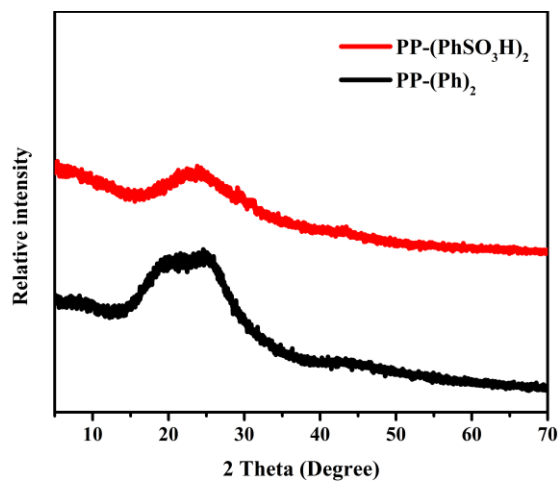
Figures

Figure. S1. PXRD patterns of **PP-(PhSO₃H)₂** and **PP-(Ph)₂**.
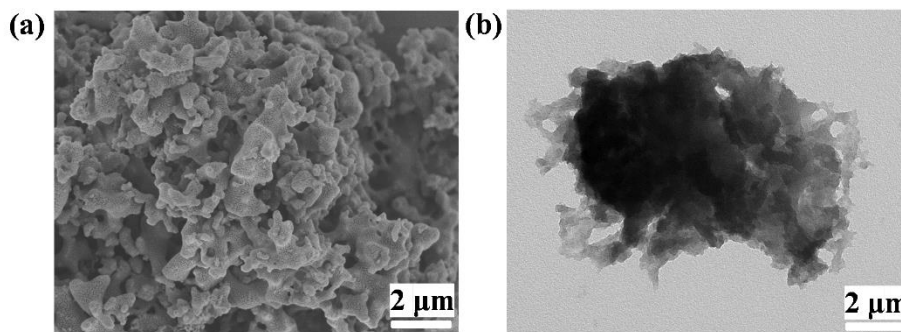
Figure. S2. (a) SEM image and (b) TEM image of **PP-(PhSO₃H)₂**.
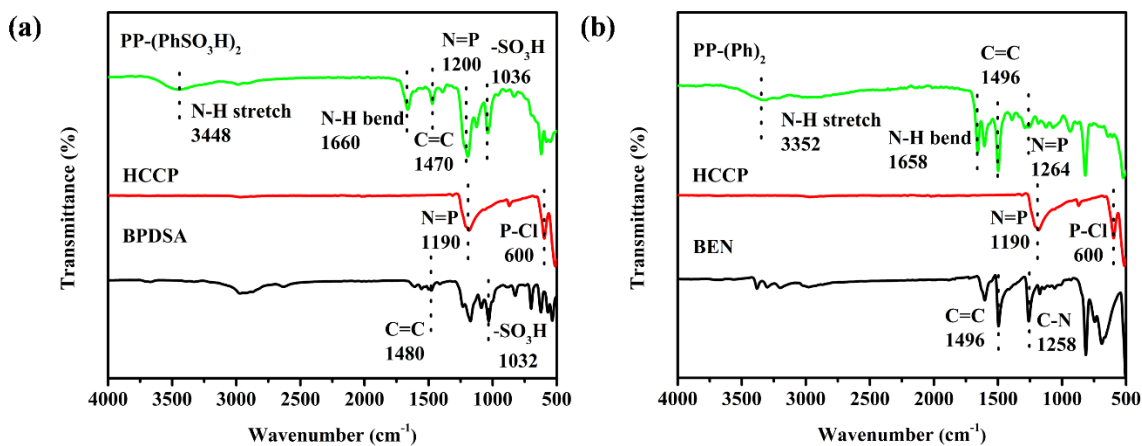
Figure. S3. FTIR spectra of (a) **PP-(PhSO₃H)₂** and (b) **PP-(Ph)₂** and the related reactants.

(a) Sample is grinded well and disperse in DMF according to different ratios

(b) PAN dissolve in DMF and keep at 70 °C overnight

(c) Homogeneous solution of PAN and sample according to different ratios

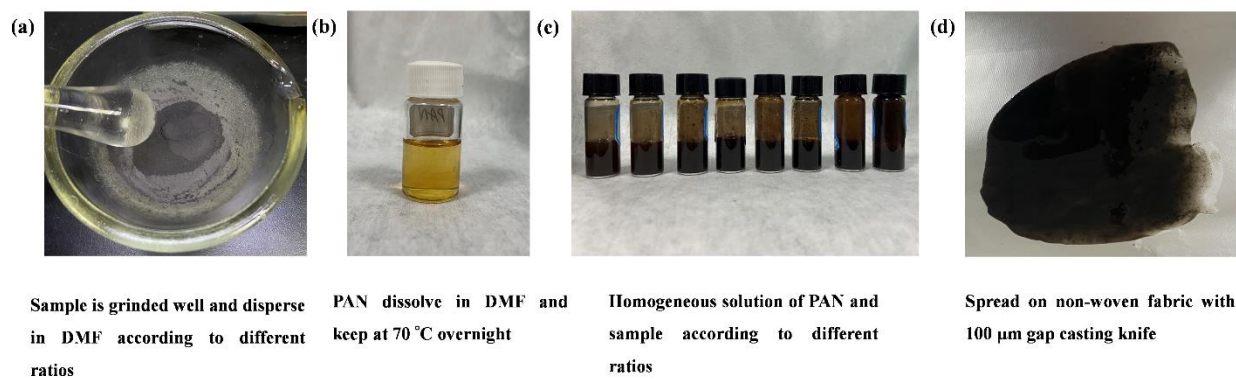(d) Spread on non-woven fabric with 100 μm gap casting knife

Figure. S4. Step-by-step fabrication process for matrix-mixed membranes.

Table S1. List of proton-conductive organic materials and Nafion.

Compounds	RH (%)	T (°C)	Proton Conductivity (S cm⁻¹)
PP-(PhSO$_3$H)$_2$ [this work]	98	80	8.24×10^{-2}
Nafion®117 [S7]	98	80	1.5×10^{-1}
Nafion [S7]	98	30	5×10^{-2}
HOF-GS-11 [S8]	95	30	1.8×10^{-2}
EB-COF:PW$_{12}$ [S9]	97	25	3.32×10^{-3}

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