Supporting Information

Thermally Crosslinked Multiblock Sulfonated Poly(arylene ether ketone nitrile) Copolymer with 1,2,3-Triazole Pendant for Proton Conducting Membrane

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Characterizations

¹H NMR spectra were recorded on a Bruker AVANCE III spectrometer (500 MHz) using DMSO- d_6 as the solvent. Fourier transform infrared (FTIR) spectra were obtained from a Nicolet IS-10 Fourier transform spectrophotometer equipped DTGS detector. Thermogravimetric analysis (TGA) was measured on a SDT Q600 in N₂ from 120 to 800 °C with a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) curves of polymers were recorded in N2 on DSC-823 (Swiss-Mettler Toledo), and the temperature was set in the range of 30-300 °C. Number- and weight-average molecular weights (M_n and M_w) were measured by gel permeation chromatography (GPC) on a Waters 1515 HPLC system equipped with polystyrene gel columns eluted with N,Ndimethylformamide (DMF) containing 0.05 M LiBr at a flow rate of 1.0 mL min⁻¹ calibrated by standard polystyrene samples. Mechanical properties were analyzed on a Shimazu AGS-100NX with membrane thin films (length, 40 mm; width, 5 mm) under a stretching rate of 2 mm/s. For transmission electron microscopy (TEM) observations, the membrane samples were immersed in 0.5 M lead acetate aqueous for ion exchange of sulfonic acid groups. Then the membranes were washed with deionized water for several times and dried in vacuum oven for 24 h. The stained membranes were embedded in epoxy resin, sectioned to 70 nm thicknesses with Power-Tome-XL, and placed on copper grids. Images were taken on a Hitachi H-7650 with an accelerating voltage of 80 kV.

Water Uptake (WU) measurements. WU was measured by keeping the membranes in thermo-controlled humid equipment under various relative humidity conditions at 80 °C for 2 h. The initial weight (W_0) was recorded by drying the membrane in a vacuum oven at 120 °C for 2 h. The samples were then removed from the chamber and quickly weighed. WU was calculated using Eq. (1).

$$WU = (W_1 - W_0) / W_0 \times 100\%$$
(1)

where W_l refers to weight of the membrane samples at the wet condition.

Dimensional Change (DC). The dimensional change was measured by putting the membranes in a thermo-controlled humid equipment for at least 2 h at 80 °C under

different relative humidity conditions. The dimensional change in membrane thickness direction (Δt_c) and the plane direction (Δl_c) were calculated using Eqs. (2) and (3).

$$\Delta t_c = (t - t_s)/t_s \tag{2}$$
$$\Delta l_c = (l - l_s)/l_s \tag{3}$$

where t_s and l_s refer to the thickness and length of the membranes measured at 30 °C/30% RH, respectively. *t* and *l* are the same parameters of the membranes under different RH conditions.

Ion Exchange Capacity (IEC). IEC was measured using the acid–base back-titration method. The acidified membranes were immersed in a 20 wt% sodium chloride solutions for ion exchange of H⁺ at 50 °C for 3 days. Sodium hydroxide standard solutions were then used to neutralize the acid solutions by adding phenolphthalein as an indicator. The ion exchange capacity was calculated using Eq. (4).

$$IEC = C_{NaOH} \times V_{NaOH} / W_0 \tag{4}$$

where C_{NaOH} and V_{NaOH} refer to the concentration and consumed volume of NaOH solution, respectively.

Proton Conductivity (σ). The proton conductivity was estimated by means of an Hioki IM 3533-01 impedance analyzer at a frequency ranging from 1 to 10⁶ Hz. The membranes were placed in a two-point probe conductivity cell equipped with two Pt plate electrodes. The cell was then kept in a thermo-controlled humidity equipment at different testing conditions for 1 h before each measurement. σ was calculated using Eq. (5).

$$\sigma = d/(t_{\rm s} w_{\rm s} R) \tag{5}$$

where *d* is the distance between the two Pt plates, t_s and w_s are the thickness and width of the membrane film, and *R* is the measured resistance.

Gel Fraction. The gel fraction (GF) measurement was carried out by immersing the initially-dried M10N5-CR membrane (~100 mg) into DMSO (50 mL), and stirred at 50 °C for 24 h. After that, the membrane was taken out, thoroughly washed with DI water many times, and dried again under vacuum at 120 °C for 2 h. The gel fraction was then calculated using Eq.(6).

$$GF = (W_0 - W_2)/W_0$$

S-3

where W_2 refers to weight of the membrane sample after the extraction test.

Evaluation of Fuel Cell Performance. The membrane electrolyte assembly (MEA) was performed according to our previous method.^{1,2} Briefly, commercial Pt/C (30.6 mg, 60 wt.%) (Hispec4000, Johnson and Matthey) was firstly soaked in 0.6 mL deionized water under sonication for 10 min. The suspension was then mixed with 257.3 mg Nafion isopropyl alcohol solution (5 wt%). Excess isopropyl alcohol was added to control the total solid content to 1 wt%. After 30 min of further sonication at 5 °C, the well-dispersed catalyst ink was sprayed on the membrane surface as conventional catalyst materials using an electrostatic spraying equipment with a platform heating temperature of 80 °C (SP 201, Kunshan Sunlaite New Energy Co. Ltd.). The active surface area of the MEA was measured as 9.0 cm² (3.0 cm \times 3.0 cm) and the loading amounts of Pt on each side were 0.5 mg cm⁻².

The single-cell performance was investigated using an in-house fuel cell station (HTS-125, Shanghai Hephas Energy Co. Ltd.) under ambient pressure. At medium temperature testing, the cell temperature was set to 80 °C, and the gas humidifying temperatures were both controlled at 78.5, 71.5 and 52.5 °C for the anode and cathode, which corresponded 95%, 70% and 30% RH, respectively. During the tests, the H₂ gas and O₂ flow rates were fixed to 200 and 100 mL min⁻¹, respectively, with back pressure at 0.1 MPa.



Scheme S1. Synthetic route of O1 and O2.



Scheme S2. Self-crosslinkable sites on the chemical structure of O2.



Scheme S3. Chemical structure of M10N5 used in this work.³



Figure S1. ¹H NMR spectra of a) O2, b) O1 and c) P1.



Figure S2. FTIR spectra of P3 and P4.



Figure S3. Tensile-strain test of the three membrane samples.



Figure S4 Cross-sectional TEM images for a) M10N5-Br and b) M10N5-CR.

Code	DMSO	DMAc	NMP	CH_2Cl_2	CHCl ₂ CHCl ₂	MeOH
01	+	+	+	-	-	-
02	+	+	+	-	-	-
P1	+	+	+	-	-	-
P2	+	+	+	+	+	-
P3	±	+	+	-	-	-
P4	+	+	+	±	+	-
P5	+	+	+	-	-	-
P6	+	+	+	-	-	-
P7	+	+	+	-	-	-
P8	-	-	-	-	-	-

Table S1 The solubility of oligomers and polymers in common organic solvents.

All the polymer solutions were prepared at 5% (w/v) and heated at 50 °C. "+"refers to soluble, " \pm "refers to partially soluble and "-"refers to insoluble, respectively.

References

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