Supplementary Information

Facile One-Step Fabrication of Sulfonated Polyhedral Oligomeric Silsesquioxane Crosslinked Poly(ether ether ketone) for Proton Exchange Membrane

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Membrane Characterization

FT-IR measurements were performed with a Nicolet NEXUS670 FT-IR spectrometer. NMR experiments were carried out on a JEOL EX-400 spectrometer with d_6 -dimethylsulfoxide (d_6 -DMSO) or Chloroform- d (CDCl₃) as a solvent.

The molecular weights (Mw and Mn) of PEEK-20-OCH₃ polymer were performed by gel permeation chromatography on a Waters 1515 instrument equipped with tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min. The column system was calibrated by standard polystyrene.

The ion exchange capacity (IEC, mequiv g⁻¹) and EW (g mol⁻¹) were measured by a classic acid-base titration method. The prepared C-PEEK-sPOSS-x membranes (0.12-0.16 g) were immersed into 2 M NaCl solution for 48 h. Then the resulting solution was titrated with 0.01 M NaOH and phenolphthalein (titration indicator). The titration IEC and EW were expressed as follows 1 and 2:

$$IEC(mequiv/g) = \frac{\Delta V_{NaOH} \times C_{NaOH}}{W}$$
(1)
$$EW(g/mol) = \frac{1000}{IEC}$$
(2)

Where, ΔV_{NaOH} and C_{NaOH} are the consumed volume and the concentration of NaOH solution, the *W* refers to the weight of dried membranes.

The thermal behavior of the C-PEEK-sPOSS-x membrane was evaluated by thermogravimetric analysis (TGA: Diamond TG/DTA-6300, USA). The measurement was performed on under nitrogen atmosphere at a heating rate of 20 °C min⁻¹ from 120 °C to 800 °C. Samples were dried at 120 °C in vacuum overnight before the measurement.

The dynamic mechanical thermal analyses (DMA) was performed on a Metter Toledo DMA/SDTA861e instrument and obtained the fundamental parameters such as storage modulus (E), glass transition temperature (T_g) and loss tangent (tan δ) with a constant frequency of 1 Hz with varying temperature in tension mode and initial static force of 0.1 N under dry air atmosphere. The temperature range was set from 70 to 400 °C at a heating rate of 10 °C min⁻¹ and at a constant strain of 0.1%. The size of dry membranes for DMA measurement was 10 mm long, 3 mm wide and 38-57 µm thick.

The elongation and tensile strength measurement of the hydrated state membranes were performed on Universal Testing Machine (AGS-X 5KN, Shimadzu, Japan) with a stretching speed of 10 mm min⁻¹ at room temperature. Before the measurement in hydrated state, membranes were soaked in deionized water for 48 h at room temperature for fully hydration.

The water uptake of the C-PEEK-sPOSS-x membranes were measured by weighting the membrane before and after the hydration. Samples were dried at 120 °C in vacuum for 13 h until constant weight to obtain the dry membrane. Three sheets of dried films (20-35 mg peer sheet) were immersed in deionized water at 20 °C, 40 °C, 60 °C and 80 °C for 4 h, respectively. Then the films were taken out, wiped with tissue paper, and finally, weighted on a microbalance. The water uptake (WU) was expressed as follows 3:

$$WU(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100$$
(3)

The number of water molecules per sulfonic acid (λ) was expressed as follows 4:

$$\lambda = \frac{(W_{wet} \ W_{dry})EW}{W_{dry}M_{H_2O}} + 1$$
(4)

Where W_{wet} and W_{dry} are the weighted of the wetted membranes and the weighted of the dried membranes, respectively.

Water swelling ratios of the C-PEEK-sPOSS-x membranes was measured by the $1.5 \text{ cm} \times 1 \text{ cm}$ membrane into deionized water at 20 °C, 40 °C, 60 °C and 80 °C for 3 h, the change length change of each membrane, respectively. The swelling ratios (L) was expressed as follows 5:

$$\Delta L(\%) = \frac{L_W - L_D}{L_D} \times 100 \tag{5}$$

Where, L_W and L_D are the lengths of wetted membranes and dried membranes, respectively.

The gel fraction of the membranes was measured using Soxhlet method. 0.1 g-0.3 g sample was soxhletly extracted by DMF until no further soluble polymer was found. The residue was then dried until constant mass. The gel fraction of the membrane was calculated as follows 6:

Gel fraction =
$$W_1/W_0$$
 (6)

where W_0 is the original mass of the cross-linked membrane, and W_1 is the mass of the dried membrane after complete solution extraction.

The proton conductivity (σ , S cm⁻¹) in plane of membrane was measured on an Hioki-3532-50 electrochemical workstation by an electrochemical impedance spectroscopy technique with two platinum-plate electrodes over the frequency range from 50 Hz to 100 kHz, and a temperature range from 20 °C to 80 °C. Each

membrane (4 cm \times 1 cm) was placed tightly in PTFE clamps and immersed in deionized water. The proton conductivity (σ) was expressed as follows 7:

$$\sigma = \frac{l}{R \times A} \tag{7}$$

Where, l is the distance between reference electrodes, R was measured by two-point probe AC impedance method and A represents the cross-sectional area of the measured membrane.

The activation energy for ion conduction, E_a , was calculated from temperature dependence upon the proton conductivity of the C-PEEK-sPOSS-x membranes immersed in deionized water .The Arrhenius activation energy (E_a) was expressed as follows 8:

$$\sigma = A e^{\frac{E_a}{RT}}$$
(8)

Where, E_a is the activation energy (kJ mol⁻¹), σ is the proton conductivity (S cm⁻¹), *R* is the pre-exponential factor (8.314 J mol⁻¹ K⁻¹), and *T* is the absolute temperature (K).

Methanol permeability was determined using a diffusion cell. The diffusion cell consists of two half-cells, which were separated by the prepared membrane. Before the measurement, one cell was filled with deionized water and another with 5 M methanol. Then the cell was placed in a biochemical incubator (SPX-250B-Z, Shanghai) and maintained at 30 °C. Samples were taken from the deionized-water-cell every 30 min and the methanol fluxes were analysed by using a gas chromatograph. The methanol permeability was expressed as follows 9:

$$P = \frac{1}{A} \frac{C_B(t)}{C_A(t-t_0)} \cdot V_B L$$
(9)

Where *A*, *L* are the area and a thickness of the tested membranes, respectively. C_A is the initial methanol concentration of the methanol-cell, C_B is the methanol concentration of the deionized- water-cell and α is the slope of C_B -*t* curve. *P* represents the methanol permeability.

Selectivity (S_P) was expressed as follows 10:

$$S_P = \frac{\sigma}{P} \tag{10}$$

The oxidative stability of C-PEEK-sPOSS-x membrane was investigated by immersing the membranes in Fenton's reagent of the 3 wt% H₂O₂ solution containing 2 ppm FeSO₄. The stability was obtained by recording the weight remained after treating in Fenton's reagent at 80 °C for 1 h.

For the Transmission electron microscopy (TEM) observation, the C-PEEK-sPOSS-x membrane were stained with lead ions (Pb²⁺) by immersion in a 0.5 M lead acetate solution, rinsed repeatedly with deionized water, and then dried in vacuum overnight. The morphology of the pattern was studied by TEM (JEM-1200 EX/S, JEOL, Tokyo, Japan).

The membrane electrode assembly (MEA) was prepared by spraying catalyst ink onto the carbon paper. The catalyst ink was prepared as follows. First, PEEK-20-OH, epoxy-POSS and 4-phenolsulfonic acid sodium salt were mixed with dimethyl sulfoxide with stirring for 12 h to form precursor sol. Then Pt-C (40wt% P/C, Johnson Matthey Co., UK) was mixed with precursor sol under ultrasonic vibration to fabricate catalyst ink. And then the catalyst solution was coated onto a carbon paper (2050-A, Ballard, USA) using an ultrasonic spray. The catalyst was Pt/C with a Pt loading of 0.2 mg cm⁻² for both anode and cathode. Two sheets of carbon paper

coated with a layer of the catalyst were placed on both sides of a membrane and pressed at 130 °C with a pressure of 50 kg cm⁻² for 5 min to obtain an MEA. The unit cell performance of each MEA was tested under 25 and 80 °C at 100% relative humidity condition using a G50 Fuel Cell Test Station (Green Light, Canada). The active area was 5 cm \times 5 cm. H₂ and O₂ were supplied to the anode and the cathode at flow rates of 300 mL min⁻¹ and 400 mL min⁻¹, respectively.



Figure S1. a) ¹H NMR spectra and b) ²⁹Si NMR of epoxy-POSS monomer.



Figure S2. Comparative ¹H NMR spectra of a) PEEK-20-OCH₃ and b) PEEK-20-OH.



Figure S3. ¹⁹F NMR spectra of PEEK-20- CH₃



Figure S4. FT-IR spectra of copolymer PEEK-20-OCH₃ and PEEK-20-OH.