Electronic Supplementary Material

Design and development of nucleobase modified sulfonated poly(ether ether ketone) membranes for high-performance direct methanol fuel cell

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Experimental Section

Characterization

^1H nuclear magnetic resonance spectroscopy (^1H NMR) was measured on a Varian INOVA spectrometer (600 MHz, USA) at room temperature using DMSO-d_6 as the solvent. Fourier transform infrared spectroscopy (FTIR) was recorded on a Nicolet iS50 spectrometer (Thermo fisher, USA) from 4000 cm^{-1} to 400 cm^{-1} using polymer thin films. Thermogravimetric analysis of the membrane samples was tested by a TGA-1 thermogravimetric analyzer (Mettler Toledo., Switzerland) scanning from 50 to 800 °C with a scanning rate 10 °C/min under N_2 atmosphere. The tensile test of membrane samples with a size of 1 cm × 4 cm was performed at room temperature at a tensile rate of 0.50 N/min by an XLW(EC)-A (Jinan Languang electromechanical technology Co. LTD, China) mechanical testing instrument.

Water uptake, swelling ratio, and ion exchange capacity

Dried membrane samples with a size of 1 cm × 3 cm were soaked in deionized water at room temperature for at least 24 h. The samples were weighted on an analytical balance until constant masses obtained. And their length and width were also measured to calculate the area of the membrane. The water uptake (WU) and swelling ratio (SR) of membranes were calculated by the following equations:

$$WU = \frac{W_w - W_d}{W_d} \times 100\%$$

$$SR = \frac{S_w - S_d}{S_d} \times 100\%$$

Where W_d and W_w are the masses of the membranes in dry and wet states, S_d and S_w represent the area of the dried membrane and wet membrane, respectively.

Ion exchange capacity (IEC) of membranes was determined by acid-base titration. Before IEC measurements, dried membranes with a size of 1 cm × 3 cm were immersed in deionized water for 24 h to release free phosphoric acid molecules. Followed by soaking in 1 M NaCl aqueous solution for 24 h to exchange H^+ in membrane to solution. The H^+ in the eluent was titrated with a standard NaOH solution of 0.01 M, using phenolphthalein as indicator. The IEC was calculated using the following equation:

$$IEC = \frac{C_{NaOH} * V_{NaOH}}{m_{dry}} \times 100\%$$

Where m_{dry} is the mass of the dried membrane, C_{NaOH} and V_{NaOH} are the concentration and volume of the standard NaOH solution, respectively.

The hydration coefficient (λ) was defined as the average number of water molecules adsorbed by each cationic group, the λ value is obtained as follows:

$$\lambda = \frac{W_u \times 10}{IEC \times 18}$$

Where W_u represents the water absorption (%) and IEC is the ion exchange capacity measured above.

Proton conductivity

The proton conductivity (σ) of membranes was measured on an Autolab PGSTAT302N electrochemical workstation (Netherlands) using AC impedance technique. Polymer membranes with a size of 1 cm × 3 cm were immersed into deionized water at room temperature for 24 h, followed by assembling in a custom built open-frame two-electrode clamp for measurements at different temperatures

with frequencies ranged from 1 Hz to 1.0 MHz. The proton conductivity (σ) was calculated as follows:

$$\sigma = \frac{L}{R \times A}$$

Where L is the distance between the two electrodes, which is taken as 2.06 cm in this work, R and A are the impedance and effective cross-sectional area of the membrane, respectively.

Methanol permeability

Methanol permeability through the membrane was measured by a diffusion method: The membrane was sandwiched between two chambers diffusion cell, in which one was filled with a certain volume of methanol solution and the other was filled with the same volume of deionized water. The change of methanol concentration with time was measured by gas chromatograph equipped with a flame ionization detector (Trace 1300, Thermo, USA). The methanol permeability can be calculated as follows:

$$P = \frac{V \times L \times \Delta C}{A \times C_0 \times \Delta t}$$

where P (cm^2 s^{-1}) is the methanol permeation rate; L (cm) and A (cm^2) are the thickness and effective area of the test membrane sample, respectively; V (cm^3) and C_0 (mol L^{-1}) are the volume and initial concentration of the methanol solution, respectively; ΔC (mol L^{-1}) is the change of methanol concentration and Δt (s) is the time difference of methanol penetration. $\Delta C/\Delta t$ is the slope of the methanol concentration in the water compartment with time.

Preparation of membrane electrode assemblies

A slurry of mixture consisted of carbon and 20 wt% of PTFE emulsion (HCP120, Hesen, China) was deposited on carbon paper with gas diffusion layer (HCP120,

HESEN, China) to form the microporous layer (MPL). The catalysts for the anode and cathode were 4.0 mg cm^{-2} of Pt-Ru/C and 2.0 mg cm^{-2} of Pt/C, respectively. Then the catalyst inks comprising of catalyst powders, 5 wt% Nafion ionomer solution and isopropanol-water mixture (volume ratio 1:1) were well dispersed by ultrasonic treatment and homogeneously coated onto MPL to form the catalyst layers. The membrane was clamped between the anode and the cathode and hot pressed for 3 min at 130 °C and 1.0 MPa to form a membrane electrode assembly (MEA) with an effective area of 4 cm^2.

Acidic direct methanol fuel cell performance

The DMFC stack use in this work is shown in Fig. S1. The DMFC performance of the polymer membranes was recorded on an electrochemical workstation (Autolab PGSTAT 302N, Switzerland) to obtain the current density (I) and potential (V) curves. The membrane was sandwiched between the anode with P_t-R_u loading of 4.0 mg cm^{-2} and cathode with P_t loading of 2.0 mg cm^{-2} to form a membrane electrode assembly (MEA). During the test, oxygen was supplied to the cathode side (flow rate of 50 mL min^{-1}) and the methanol fuel (1 M, 2 M or 5 M) was feeding to the anode side (1 mL min^{-1}). The operation was carried out at temperature of 80 °C and relative humidity of 100%.

After the DMFC cell polarization, the long-term durability test for the MEA comprising SPEEK-C$_{50}$/PA membrane in the cell was also performed by chronopotentiometry under a constant current density of 300 mA cm^{-2} for 100 h with 2 M MeOH at 80 °C.
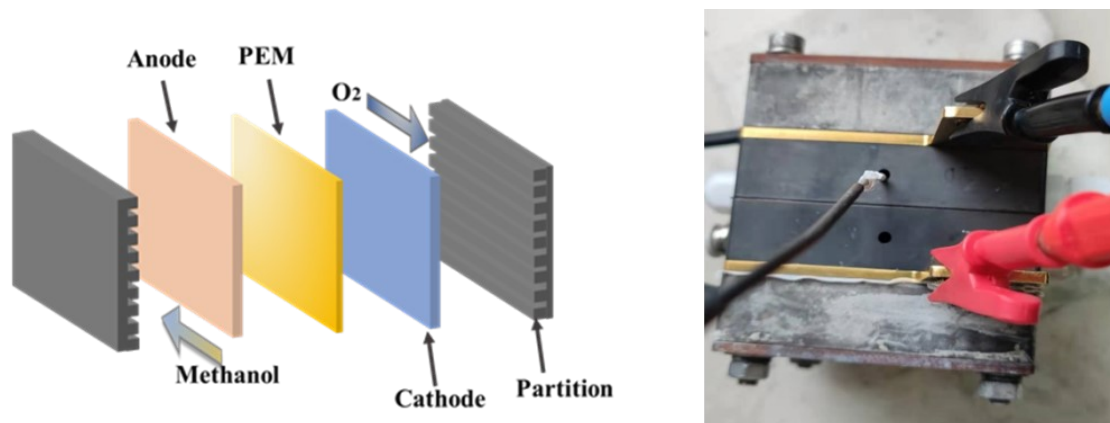
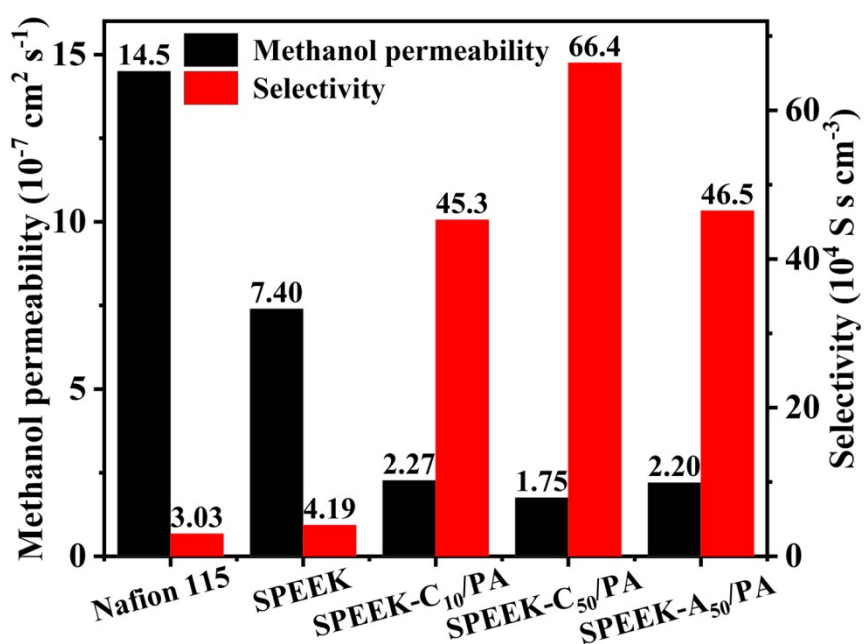**Fig. S1** The stack for DMFC performance test

Fig. S2 Methanol permeability of typical PA-doped SPEEK-A_x/C_x membranes

compared with SPEEK and commercial Nafion 115.