

Electronic Supplementary Information (ESI) for Chemical Communications

High-Performance Blend Membranes Composed of An Amphoteric Copolymer Containing Supramolecular Nanosieves for Direct Methanol Fuel Cells

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Experimental

1. Materials

Nafion 112 membrane was purchased from Fuel Cell Hub. Sodium p-styrenesulfonate, 4-vinylbenzyl chloride, azobisisobutyronitrile (AIBN), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and dimethylacetamide (DMAc), were purchased from Sigma–Aldrich. Carbon-supported Pt-Ru catalyst (60 wt. %, Pt : Ru = 1 : 1) was bought from E-TEK and carbon-supported Pt catalyst (40 wt.%) was bought from Alfa Aesar. 4-vinylbenzyl chloride was purified by reduced pressure distillation and the initiator AIBN was recrystallized in methanol before polymerization.

2. Sulfonation of PEEK

Typically, 10 g of PEEK was dissolved in 200 mL of concentrated (95-98 %) sulfuric acid under vigorously stirring at room temperature for 48 h. Then, the SPEEK solution was slowly and carefully poured into a large amount of ice water under mechanical stirring. The obtained SPEEK was immersed into deionized water and washed several times to totally remove the residual sulfuric acid. Finally, the wire-like SPEEK was dried in a vacuum oven for about 48 h.

3. Synthesis of amphoteric copolymer

First, sodium p-styrenesulfonate (2.9 g) and redistilled 4-vinylbenzyl chloride

(0.9 g) were dissolved in 20 mL of DMF/H₂O (1 : 1) mixed system, and the reaction was initiated by AIBN under nitrogen atmosphere. The solution gradually turned white after the addition of the initiator. Then, the reaction was kept under vigorous stirring at 70 °C for 24 h under nitrogen protection. After the reaction, the **copolymer 1** was precipitated into 50 mL of methanol. The precipitate was dissolved in dimethyl sulfoxide (DMSO) and reprecipitated in methanol for 3 times to wash out the low weight molecules. The **copolymer 1** thus obtained was dried in a vacuum oven. Finally, the amphoteric copolymer was obtained by the amination reaction of the copolymer 1 with 1-aza-18-crown-6 in the presence of dried K₂CO₃ in DMSO. The as-prepared amphoteric copolymer was precipitated into methanol, washed three times, and dried in a vacuum oven.

4. Preparation of blend membranes

The SPEEK (1.5 g) and certain amount of amphoteric copolymer (dissolved in 2 mL of water) were well dissolved in DMSO under stirring for 4 h. The polymer solution was then cast in a petri dish with a diameter of 15 cm, and dried in a vacuum oven at 80 °C for about 24 h. The blend membranes for DMFC tests were all about 80 μm in thickness.

5. Characterization of the membranes

IEC measurement:

The IEC values of these membranes were determined by suspending 200 mg of samples in 2.0 M NaCl solution (30 mL) for 24 h to liberate the H⁺ ions and then titrating with standardized 0.1 M NaOH solution using phenolphthalein as an indicator. The IEC of copolymer 2 is 2.50 meq.g⁻¹ as calculated from the ¹H-NMR spectrum.

Proton conductivity measurement:

Proton conductivity values of the membranes were obtained from the impedance data, which were collected with an impedance analyzer in the frequency range of 1 Hz to 1 MHz with an applied ac voltage of 10 mV. The impedance measurement was carried out using a home-made two-electrode setup and two platinum foils were used as the blocking electrodes. The proton conductivity (σ) was calculated as

$$\sigma = \frac{d}{Rls}$$

where d is the distance between the two electrodes, R is the resistance of the membrane, l is the width of the membrane, and s is the thickness of the membrane. The thickness of all these membranes is about 85 μm .

Water Uptake and Swelling ratio:

With the aim to determine the water uptake and swelling behavior, the membranes were first dried at 80 °C for 24 h, and their weights and lengths were recorded. After that, the samples were immersed in deionized water and methanol solution (1M) at a specific temperature for about 24 h. Then, the water on the membranes was wiped off with blotting paper, and the membranes were quickly weighed and their lengths were measured. The water uptake of the membranes was calculated as

$$\text{water uptake} = \left(\frac{W_{\text{wet}}}{W_{\text{dry}}} - 1 \right) \times 100$$

where W_{wet} and W_{dry} represent the weights of the wet and dry membranes, respectively.

The swelling was obtained as

$$\text{swelling} = \left(\frac{L_{\text{wet}}}{L_{\text{dry}}} - 1 \right) \times 100$$

where L_{wet} and L_{dry} are the lengths of the wet and dry membranes, respectively.

6. Preparation of membrane-electrode assemblies (MEAs)

The electrodes for single-cell testing in DMFCs contain gas-diffusion layers (carbon paper) and catalyst layers in both the anode and cathode. The anode catalyst was a commercial carbon-supported Pt-Ru catalyst (60 wt. %, Pt : Ru = 1 : 1) (E-TEK) and the cathode catalyst was a commercial carbon-supported Pt catalyst (40 wt.%) (Alfa Aesar). The catalyst dispersion in ethanol with 10 wt. % of Nafion (DuPont) was sprayed onto the carbon paper and dried at 90 °C. The catalyst metal loadings for

the cathode and anode were both 2.0 mg cm^{-2} . The active area of electrodes for single cell testing was 5 cm^2 . The MEAs were fabricated by uniaxially hot-pressing the anode and cathode onto the membrane at $140 \text{ }^\circ\text{C}$ for 3 min. The MEAs with copolymer contents higher than 6.67 % were not assembled due to the poor thermal stability at $60 \text{ }^\circ\text{C}$ caused by the too high IEC. The flow rate of methanol solution is 2.0 mL min^{-1} with a peristaltic pump without back pressurization and the humidified cathode oxygen is 200 mL min^{-1} with a back pressure of 20 psi.

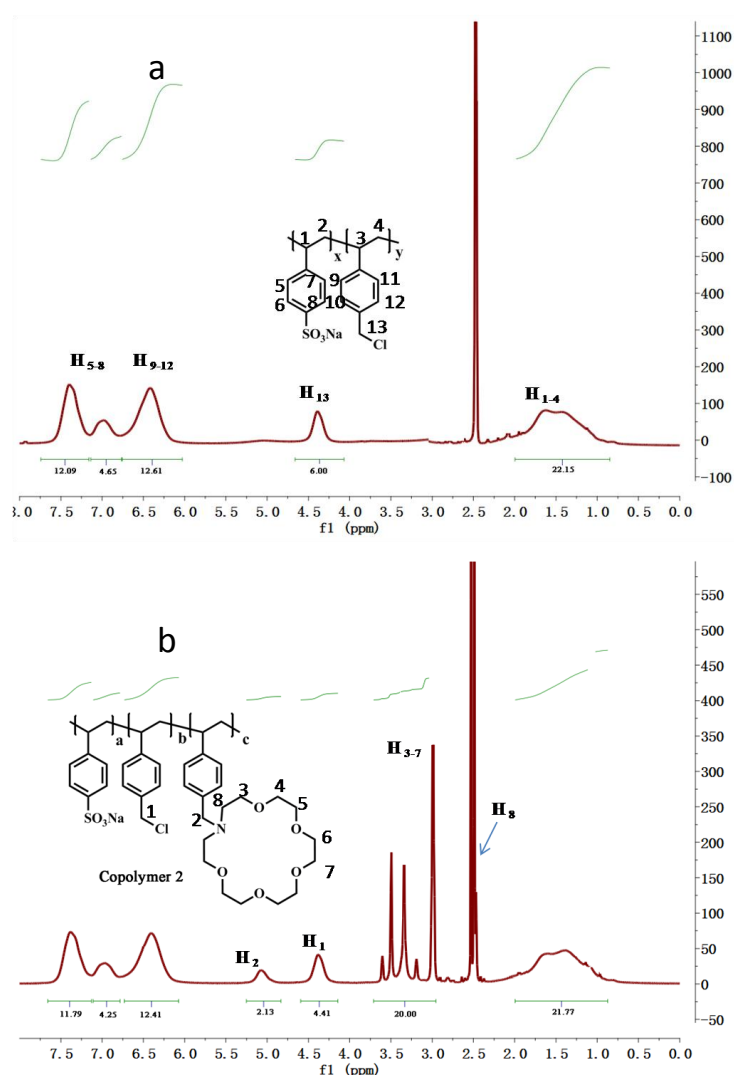


Figure S1. $^1\text{H-NMR}$ spectrum of (a) copolymer 1 and (b) copolymer 2.

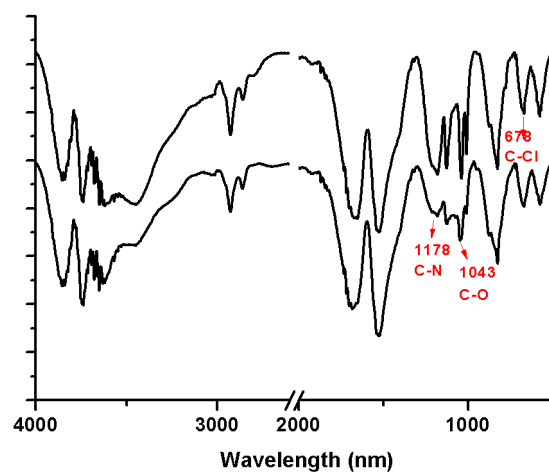


Figure S2. FT-IR spectrum of copolymer 1 and copolymer 2.

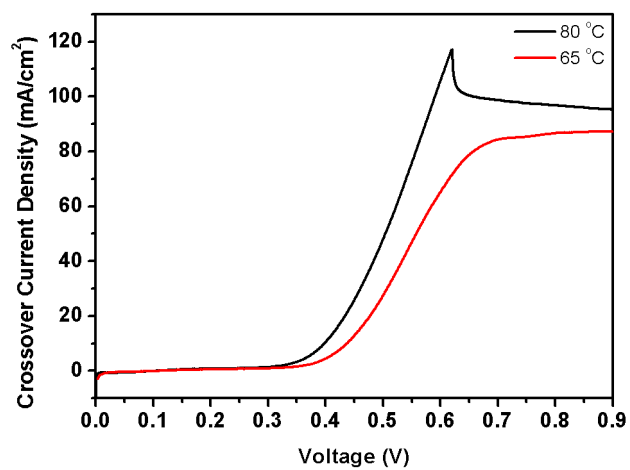


Figure S3. Methanol crossover current density at 80 °C for the membrane with 6.67 wt. % Amph in 1 M methanol solution.