

Supplementary Materials

Robust adamantane-based membranes with enhanced conductivity for vanadium flow battery application

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Materials

Vanadyl sulfate (VOSO₄, purity 99%, Shanghai Luyuan Fine Chemical Plant), benzimidazole (98.0%, Shanghai Aladdin Biochemical Technology Co., Ltd.), 1-Methyl-2-pyrrolidinone (NMP), and other reagents were used as received. All other reagents were analytically pure, and they were obtained commercially and used as received.

Nafion 212 membrane was pre-treated by immersing in hot deionized water (80 °C) for 1 h, and the membrane was immersed in 3 wt. % H₂O₂ solution at 80 °C for 1 h. After that, the membrane was soaked in 1 M H₂SO₄ at 80 °C for 1 h, then washed with deionized water and stored in deionized water.

Synthesis of CAPEK

Chloromethylated adamantane containing poly(aryl ether ketone) (CAPEK) was provided as follows [1]. Adamantane containing poly(aryl ether ketone) (10.0 g) had been dissolved in nitrobenzene (500 mL), then chloromethyl ethyl ether (CMEE) (6 mL) and 2 mL SnCl₄ were added to the polymer solution. The temperature of the polymer solution was maintained at 25 °C for 8 h. After this, the solution was poured into ethanol (500 mL) to precipitate the polymer. To remove all the nitrobenzene, the resulting CAPEK was repeatedly reflux extracted for 12 h using a Soxhlet extractor with ethanol as the solvent and then dried under vacuum at 60 °C for 48 h. The degree of chloromethylation (DC) was then determined using ¹H NMR[2], and CAPEK with DC= 0.5 was prepared.

Characterization Methods

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^1H NMR spectra of the CAPEK polymer were obtained using a Bruker Avance 500 M and CDCl_3 as the test solvent.

FTIR spectra of the membranes were obtained using a Varian 6400 FT-IR spectrometer (32 scans, 4 cm^{-1} resolution, wavenumber range $4000\text{--}500\text{ cm}^{-1}$).

Acid doping level (ADL) and swelling ratio of membranes were tested according to method[3]. ADL is defined as the molar ratio of acid to PAPEK repeat unit in each doped membrane. PAPEK membranes were immersed in H_3PO_4 (85%) for 4 h at different temperatures (60°C , 90°C , and 130°C). Then, the membrane was wiped with filter papers and dried at 80°C until constant weight, and the ADL was determined with equation (1):

$$\text{ADL} = \frac{W_{\text{acid}} - W_{\text{dry}}}{W_{\text{dry}}} \times \frac{M_{\text{polymer}}}{M_{\text{acid}}} \quad (1)$$

where W_{dry} and W_{acid} are the weights of the PAPEK membrane before and after the doping experiment, respectively. M_{acid} and M_{polymer} are the molecular weights of H_3PO_4 and repeat units of PAPEK, respectively.

The ion exchange capacity (IEC) test of membrane. PAPEK-90 membrane samples were soaked in 1M HCl (200mL) for 24 h to exchange the HSO_4^- form into the Cl^- form, then the membrane samples were washed with deionized water and soaked in 1000 mL of deionized water for 24 h to remove residual HCl. Then the Cl-type membrane samples were dried in a vacuum oven at 60°C for 24h, and weighed as M . And then, PAPEK membrane samples in Cl-form were measured with titration method using 0.05 M AgNO_3 and a potentiometric titrator (ZD-2, Shanghai INESA & Scientific Instrument Co., Ltd, China).

IEC was determined using the following equation:

$$\text{IEC (mmol g}^{-1}\text{)} = \frac{V_{\text{AgNO}_3} \times 0.05}{M} \times 100\%$$

where M is the mass of the dried membrane sample in chloride form, V_{AgNO_3} is the used volume of AgNO_3 solution.

The hydroxyethylpiperazine content of PAPEK membrane. One unit of protonated piperazine group will bind to 2 units of Cl ions. Therefore, the piperazine content of the PAPEK membrane is half the ion exchange capacity (IEC) of the PAPEK membrane (Cl form), which is calculated as $\text{IEC} / 2$.

The swelling ratio of PAPEK membranes. The PAPEK membrane samples were dried in a vacuum oven (60°C , 24 hours) and cut into membrane samples with a length and width of $76\text{mm} \times 26\text{mm}$, and the area (A_{dry}) was calculated. Next, after the H_3PO_4 selective swelling process, filter paper was used to remove residual acid from the membrane samples, then the length and width of the membrane were measured with a Vernier caliper (0.01mm) and the area (A_{acid}) was calculated. The length and width measurement errors were lower than 0.13%

and 0.38%, respectively. The swelling ratio of doped membranes[4] was calculated with equation (2).

$$S_{area} = \frac{A_{acid} - A_{dry}}{A_{dry}} \quad (2)$$

A_{dry} is the area value of the dry membrane before membrane doping. A_{acid} is the area value of the membrane after membrane doping.

Acid doping level (ADL) and swelling ratio of PAPEK membranes after H_3PO_4 pre-swelling process then immersed in 3 M H_2SO_4 were tested. $ADL_{H_2SO_4}$ is defined as the molar ratio of H_2SO_4 to PAPEK repeat unit in each doped membrane. PAPEK membranes after H_3PO_4 pre-swelling process were then immersed in 3M H_2SO_4 for 24 h at room temperature. Then, the membrane was wiped with filter papers and dried at 80 °C until constant weight, and the $ADL_{H_2SO_4}$ was determined with equation (3):

$$ADL_{H_2SO_4} = \frac{W_{H_2SO_4} - W_{dry}}{W_{dry}} \times \frac{M_{polymer}}{M_{H_2SO_4}} \quad (3)$$

where W_{dry} and $W_{H_2SO_4}$ are the weights of the PAPEK membrane before and after the doping experiment, respectively. $M_{H_2SO_4}$ and $M_{polymer}$ are the molecular weights of H_2SO_4 and repeat units of PAPEK, respectively.

The swelling ratio of PAPEK membranes after the H_3PO_4 pre-swelling process then immersed in 3 M H_2SO_4 was calculated with equation (4).

$$S_{H_2SO_4} = \frac{A_{H_2SO_4} - A_{dry}}{A_{dry}} \quad (4)$$

A_{dry} is the area value of the dry membrane before membrane doping in acid. $A_{H_2SO_4}$ is the area value of the membrane after H_3PO_4 pre-swelling process, then immersed in 3 M H_2SO_4 .

Area resistance (R) was determined using AC impedance technique (100 kHz to 20 Hz, AC amplitude 10 mV) (Wayne Kerr 4310, UK). The resistance test cell has two half-cells which were separated with the membrane (effective area, 0.636 cm²) and filled with vanadium electrolyte (1.5 M VO_2SO_4 in 3 M H_2SO_4). Area resistance was calculated using the following equation (5):

$$R (\Omega \text{ cm}^2) = (R_1 - R_0) \times 0.636 \quad (5)$$

where R_1 is the resistance of test cell with membrane, R_0 is the resistance of test cell without membrane. The conductivity (δ) was calculated using the equation:

$$\delta = L/R$$

where L was the thickness of membrane and R was the area resistance of the membrane in 1.5 M VO_2SO_4 in 3 M H_2SO_4 , respectively.

Membrane mechanical strength testing. Membranes were measured using a mechanical testing instrument with a standard test method for tensile properties of thin plastic sheeting ASTM D 882-02. The testing speed was 5 mm/min, and the initial gage length was 50 mm at

atmosphere conditions (room temperature, 50% relative humidity). For each membrane, five membrane samples (10 mm × 100mm, 40-45 um thickness) were tested, and their average value was calculated.

Permeability measurements were performed with diffusion cells. The diffusion cell had two half-cells, and the membrane was sandwiched between two half-cells (effective membrane area, 7.068 cm²), one half-cell filled with 30 mL vanadium solution (1.5 M VOSO₄ in 3 M H₂SO₄), and the other half-cell filled with 30 mL MgSO₄ solution (1.5 M MgSO₄ in 3 M H₂SO₄). The absorbance value of VO²⁺ in MgSO₄ solution was determined periodically with a UV-VIS spectrophotometer at 764 nm. Permeability was calculated with the equation (6):

$$V_B \frac{dC_B(t)}{dt} = S \frac{P}{L} (C_A - C_B(t)) \quad (6)$$

where V_B is the volume of MgSO₄ solution; t is the test time, S is the effective membrane area; L is the thickness of membrane; P is the permeability of VO²⁺; C_A is the concentration of VO²⁺ in vanadium solution; C_B was the concentration of VO²⁺ in MgSO₄ solution.

Small angle X-ray scattering (SAXS) testing of membranes. Membrane samples were soaked in water for 24h before the SAXS test. SAXS patterns of the membranes were conducted on a Bruker D8 Advance high resolution diffractometer between 0.05° and 10°. The scattering vector was calculated according to equation (7):

$$q = \frac{4\pi \sin \theta}{\lambda} \quad (7)$$

where 2θ is the scattering angle and λ is the scattering wavelength, 0.1541 nm.

The Bragg spacing was calculated as following equation (8):

$$d = \frac{2\pi}{q} \quad (8)$$

VRFB cell test

VRFB performance measurements were performed using previously reported method[5]. The experimental membranes were sandwiched between two carbon felt electrodes (effective area 5 cm², pre-treated in a muffle furnace at 500 °C in the air for four h before use), and this sandwich was clamped between two graphite plates to form a VRFB. The electrolytes for the experimental VRFBs were 20 mL 1.5 M V²⁺/V³⁺ in 3.0 M H₂SO₄ and 20 mL 1.5 M VO²⁺/VO₂⁺ in 3.0 M H₂SO₄. The negative electrolyte and positive electrolyte were pumped through VRFB. Battery tests were conducted at 25°C using a Neware 5V/3A battery test system. The charge cut-off voltage and discharge cut-off voltage were 1.65 V and 0.8 V, respectively. Cycling tests of VRFB were obtained at a constant current density of 160 mA cm⁻² and 200 mA cm⁻². Due to the vanadium ion imbalance between the positive and negative electrolytes after extended VRFB cycling, the electrolyte in the cell was replaced with a new electrolyte after each 100 cycle sequence.

The DS of CAPEK was defined as the number of chloromethyl groups per polymer repeating unit. ¹H NMR analysis was used to calculate the degree of substitution (DS) of CAPEK. In the ¹H NMR spectrum of CAPEK, the methylene proton in the chloromethyl group appeared at a new peak (4.64 ppm). Therefore, DS is estimated from the integral ratio of 4.64 ppm of -CH₂Cl (H5) to the intact protons (H4, 7.79 ppm) that do not react during the chloromethylation reaction [1,6,7]. The DS of CAPEK was calculated according to the equation: [DS=2A₅ / A₄],

where A_5 is the intensity value of the H-5 protons (4.64 ppm), and A_4 is the intensity value of the H-4 protons (7.79 ppm) (Figure S1).

^1H NMR for CAPEK, Figure S1. (500 MHz, CDCl_3), δ = ppm: 7.90-7.60 (4H, ortho $\text{C}_6\text{H}_2\text{COC}_6\text{H}_2$), 7.5-7.3 (4H, $\text{C}_6\text{H}_2(\text{C}_{10}\text{H}_{14})\text{C}_6\text{H}_2$), 7.10-6.85 (8H, $2\text{C}_6\text{H}_2\text{OC}_6\text{H}_2$), 4.64 (CH_2Cl), 3.45-1.55 (14H, $\text{C}_{10}\text{H}_{14}$).

^1H NMR for APEK, Figure S2. (500 MHz, CDCl_3), δ = ppm: 7.90-7.60 (4H, ortho $\text{C}_6\text{H}_2\text{COC}_6\text{H}_2$), 7.5-7.3 (4H, $\text{C}_6\text{H}_2(\text{C}_{10}\text{H}_{14})\text{C}_6\text{H}_2$), 7.10-6.85 (8H, $2\text{C}_6\text{H}_2\text{OC}_6\text{H}_2$), 3.45-1.55 (14H, $\text{C}_{10}\text{H}_{14}$).

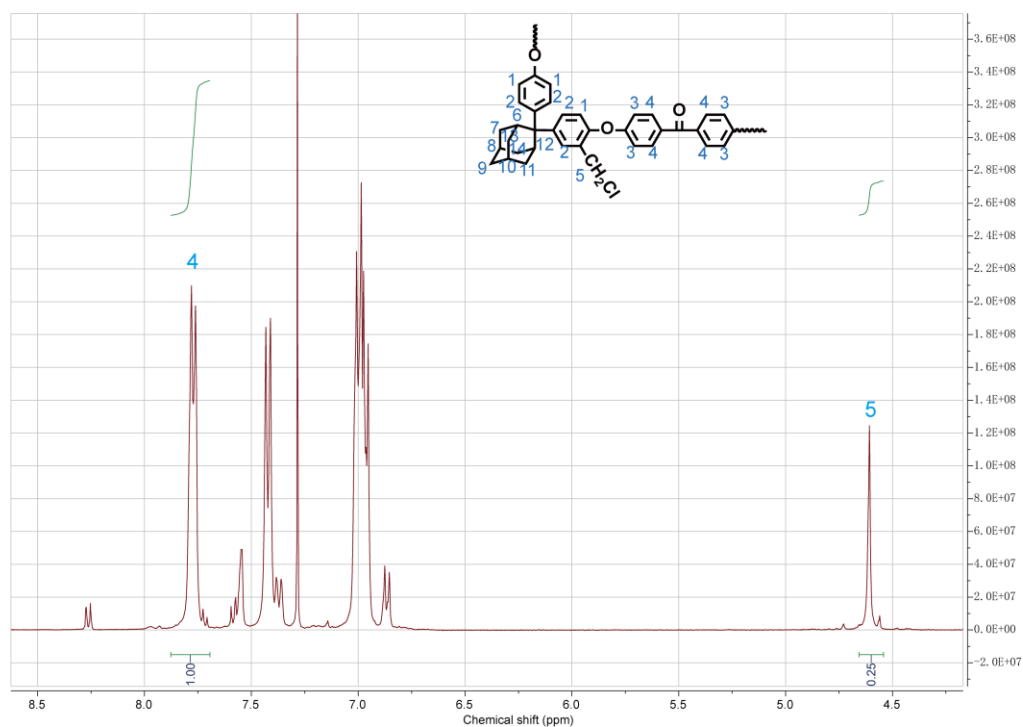


Figure S1. ^1H NMR of CAPEK

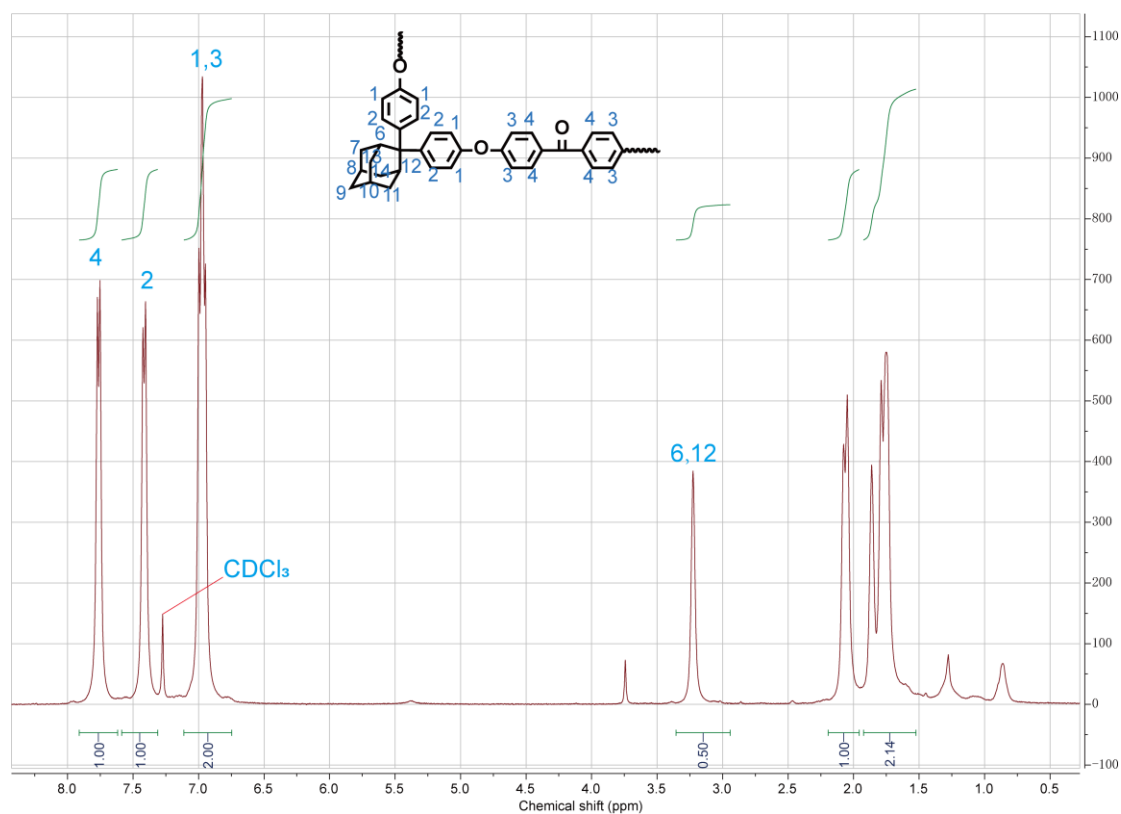


Figure S2. ^1H NMR of APEK

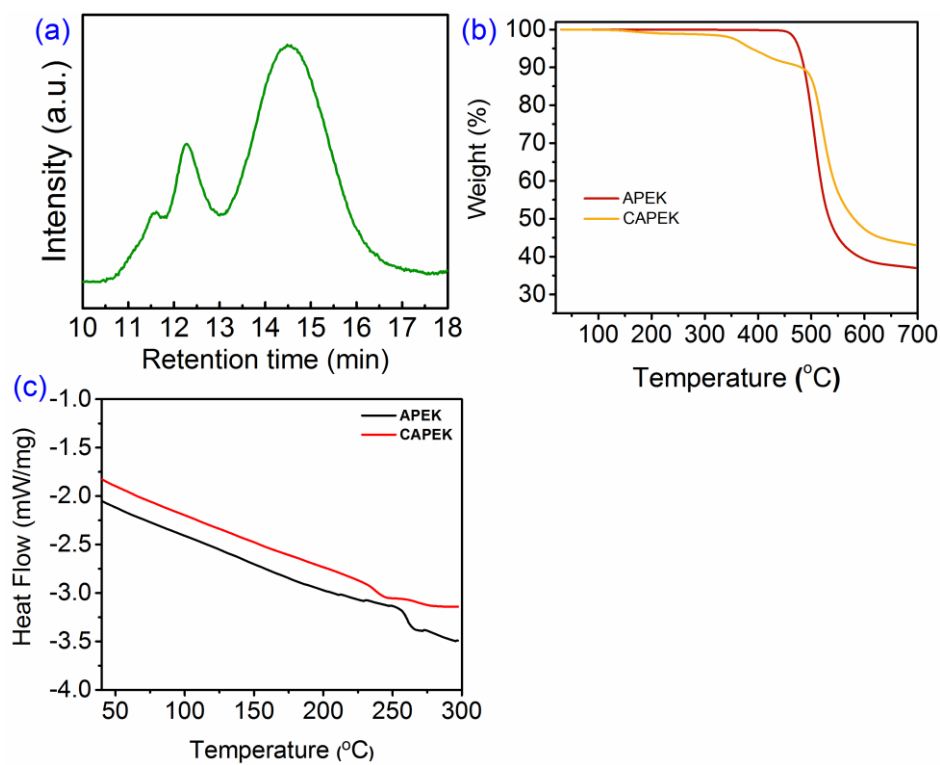


Figure S3 (a) GPC of APEK [8]; (b) TGA of APEK and CAPEK [1]; (c) DSC of APEK and CAPEK [1]

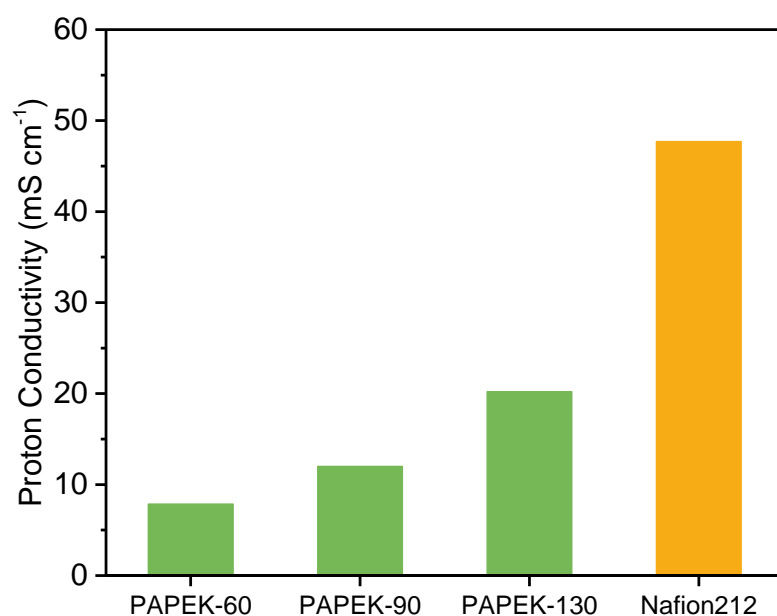


Figure S4 Conductivity of PAPEK and Nafion212 membranes in 1.5M VO²⁺ in 3M H₂SO₄

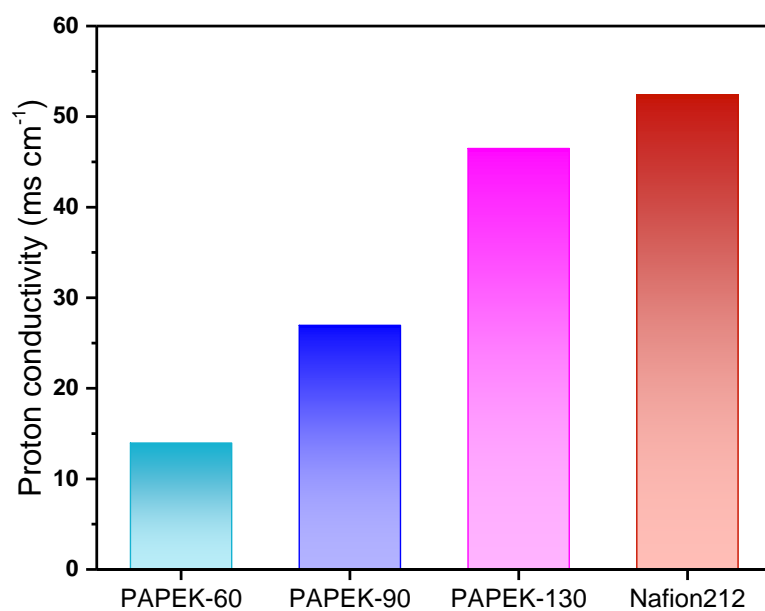


Figure S5 Proton conductivity of PAPEK and Nafion212 membranes in 3M H₂SO₄

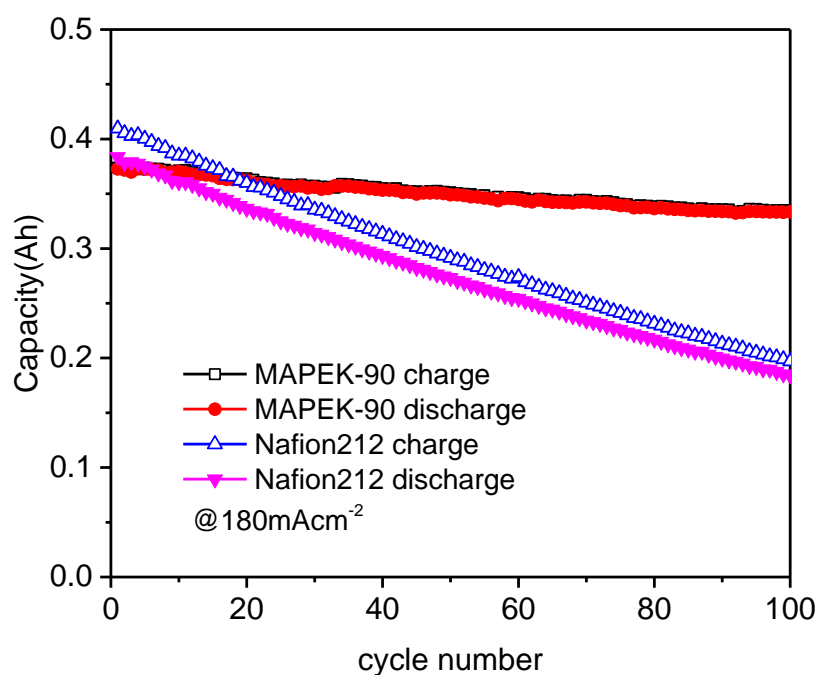


Figure S6 Charge-discharge capacities of VFB with PAPEK-90 and Nafion212 membranes

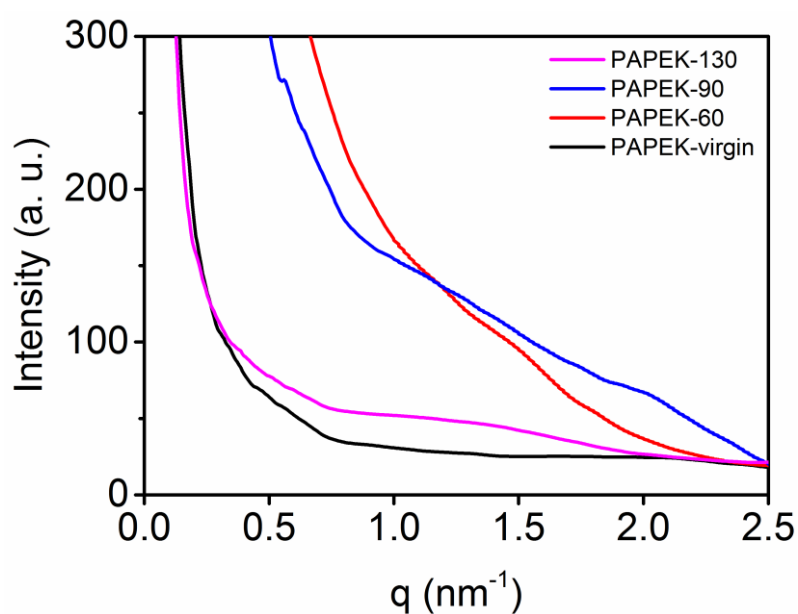


Figure S7 SAXS of PAPEK membranes

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