Supplementary file

Highly selective and high-performance sulfonated poly(ether ether ketone)-based hybrid membrane enabled by complexed UiO-66-NH_2 and sulfonated graphitic carbon nitride for vanadium flow battery

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1. Characterization

1.1 Water uptake (*WU*), swelling ratio (*SR*), Ion exchange capacity (*IEC*) and Degree sulfonation (*DS*)

The membranes were soaked in deionized water at room temperature for 24 h, weighed and subsequently dried until they reached constant weight, and the *WU* and *SR* are calculated using Eq. (1) and (2), respectively.

$$WU(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \quad (1)$$

$$SR(\%) = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\% \quad (2)$$

Where, W_{dry} and W_{wet} are the weight of the membrane in the dry state and wet state; L_{dry} and L_{wet} are the in-plane length in dry and wet states, respectively.

IEC is determined by the classical titration method. The membrane was completely immersed into a saturated NaCl solution for 24 h, and then the H^+ concentration of the solution was titrated with 0.01 M NaOH solution. The *IEC* can be calculated using Eq. (3). According to the *IEC*, the degree sulfonation (*DS*) of the SPEEK is calculated using Eq. (4).

$$IEC = \frac{C_{NaOH} - V_{NaOH}}{W_{dry}} \quad (3)$$

$$DS = \frac{M_{PEEK} \times IEC}{1000 - 80 \times IEC} \times 100\% \quad (4)$$

Where, C_{NaOH} and V_{NaOH} are the concentration and volume of NaOH solution, respectively, and W_{dry} is the weight of the dry membrane. M_{PEEK} is the molar mass (288 g mol^{-1}) of the PEEK repeat unit.

In addition, the sulfonation degree of the SPEEK polymers can also be determined by ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR, Bruker Ascend 400 M). In ^{1}H NMR analysis, the H_E from the benzene ring appears at 7.50 ppm, which is used to estimate the degree sulfonation (n) of each repeating unit. The n is evaluated according to Eq. (5).

$$\frac{n}{(12-2n)} = \frac{AH_E}{\sum AH_{A,A\prime,B,B\prime,C,D}} \quad (5)$$

where n is the number of H_E protons per repeat unit, AH and H_E are the peak area for proton and aromatic protons, respectively.

1.2 Proton conductivity

The proton conductivity (σ) of prepared membrane samples (effective area (S): 2.0096 cm^2) was obtained according to the following method. The conductivity cell is separated into two parts, filled with 2 M H_2SO_4 solution and the electrical resistances of which with the membrane (r_1) and without the membrane (r_2) are measured by electrochemical impedance spectroscopy (EIS) with frequency ranging from 1 MHz to 1 Hz using an electrochemical workstation (CHI604E, China) at room temperature. The area resistance of the membrane is calculated using Eq. (6).

$$R = (r_1 - r_2) \times S \quad (6)$$

The σ is evaluated according to Eq. (7).

$$\sigma = \frac{L}{R} \quad (7)$$

Here, L is the thickness of the membrane (cm), R is the area resistance of the

membrane (Ω cm^2).

The activation energy (Ea) with temperature changing from 303 K to 363 K was calculated from the slope of Arrhenius plots.

$$\sigma = \sigma_0 e^{-\frac{Ea}{RT}} \quad (8)$$

Where, σ and σ_0 are the conductivity and pre-exponential factor values (mS cm^{-1}), respectively, Ea is the activation energy needed to proton transport (kJ mol^{-1}), R is the gas constant (J $mol^{-1}K^{-1}$), and T is the absolute temperature (K).

1.3 VO^{2+} permeability and ion selectivity

The permeability of VO^{2+} was measured by a diffusion cell, the membrane was exposed to a solution of 1 M $VOSO_4$ in 2 M H_2SO_4 (30 mL in the left reservoir) and a solution of 1 M $MgSO_4$ in 2 M H_2SO_4 (30 mL in the right reservoir). The effective area of the membrane was 2.0096 cm^2. About 3 mL $MgSO_4$ solution of the right cell was taken out at a regular time interval, and then the VO^{2+} concentration was measured by a UV-vis spectrometer (UT-1800PC, Beijing Purkinje General Instrument Co. Ltd, China). After that, it was put back into the right cell. The VO^{2+} concentration was calculated by Eq. (9).

$$V_B \frac{dC_B(t)}{d_t} = A\frac{P}{L}(C_A - C_B(t)) \quad (9)$$

Where, V_B is the volume of VO^{2+} solution; C_B is the VO^{2+} concentration in $MgSO_4$ solution; t is time. A and L are the effective area and the thickness of the membrane, respectively. P is the VO^{2+} ion permeability; C_A is the initial concentration of the VO^{2+} in the left cell. And, it is supposed that the change of C_A and C_B is small and negligible. Thus, (C_A- $C_B(t)$) is constant, which equals the initial concentration of the VO^{2+} in the left cell.

Ion selectivity (S) of the membrane was defined as the ratio of proton conductivity

over VO^{2+} permeability, and it was evaluated according to Eq. (10):

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

1.4 Chemical stability

The membrane was soaked by the strong oxidizing electrolyte (1.5 M VO_2^+ in 3 M H_2SO_4 solution) for 20 days and the chemical stability was analyzed by the weight loss (calculated from Eq. (11)), the reduction of VO_2^+ to VO^{2+}(calculated from Eq. (12)), and the decreased tensile strength. The concentration of VO^{2+} ions at 760 nm for the immersed solution is determined using a UV-vis spectrometer (TU-1800PC, Beijing Purkinje General Instrument Co. Ltd China).

$$\text{Weight loss}(\%) = \frac{W_0 - W}{W_0} \times 100\% \tag{11}$$

$$\text{Reduction of } VO_2^+ \text{ to } VO^{2+}(\%) = \frac{C(VO^{2+})}{C(VO_2^+)} \times 100\% \tag{12}$$

Where W_0 and W are the membrane weight before and after immersing into VO_2^+ solution; $C(VO^{2+})$ is the VO^{2+}concentration from the VO_2^+ reduced solution after 20 days, and $C(VO_2^+)$ is the initial concentration of the VO_2^+ solution.

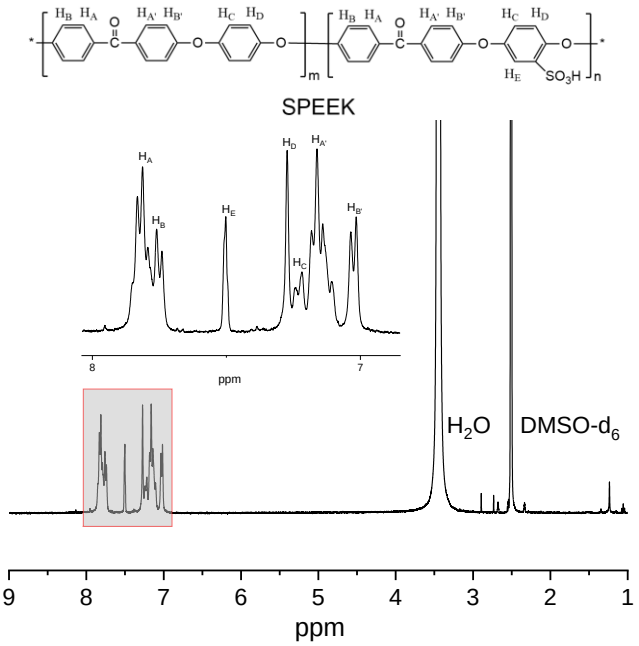

Fig. S1. ^{1}H NMR of SPEEK.

Integrating H_E peak area as 1.00, the sum of other hydrogen proton peak area amounts to 14.91. Through Eq. (5), the sulfonation degree of SPEEK polymer is n=70.96%. From the presented results in Table 1, the IEC of our prepared SPEEK is 2.06 mmol g^{-1}, and then the DS calculated by Eq. (4) is 71.03%. Two DS results from the titration method and ^{1}H NMR are identical, so the degree sulfonation of the SPEEK polymers is about 71%.

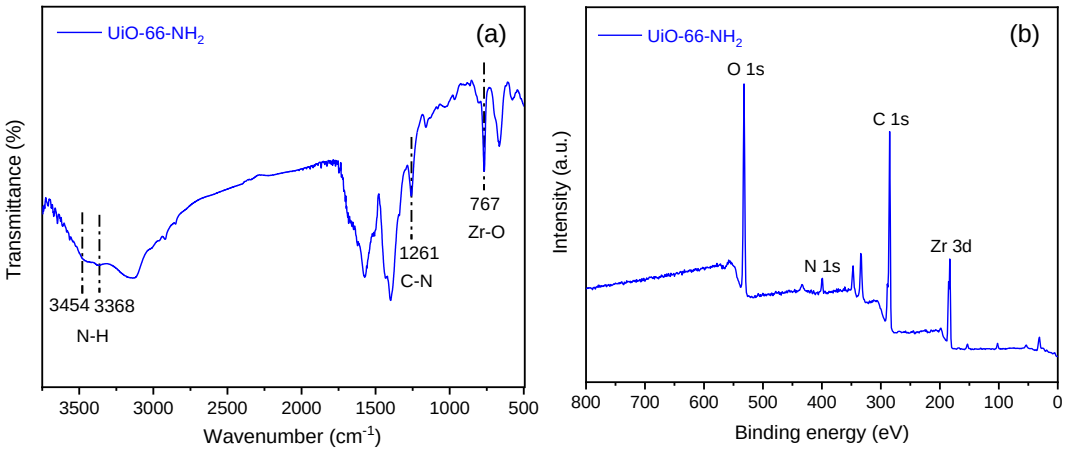

Fig. S2. FT-IR spectra (a) and XPS (b) of UiO-66-NH_2 nanofillers.

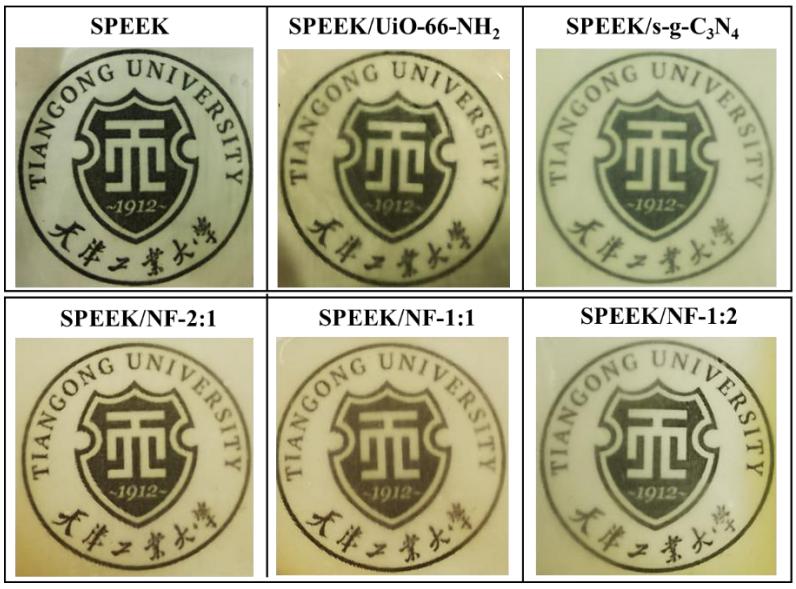

Fig. S3. Digital picture of SPEEK and hybrid membranes.

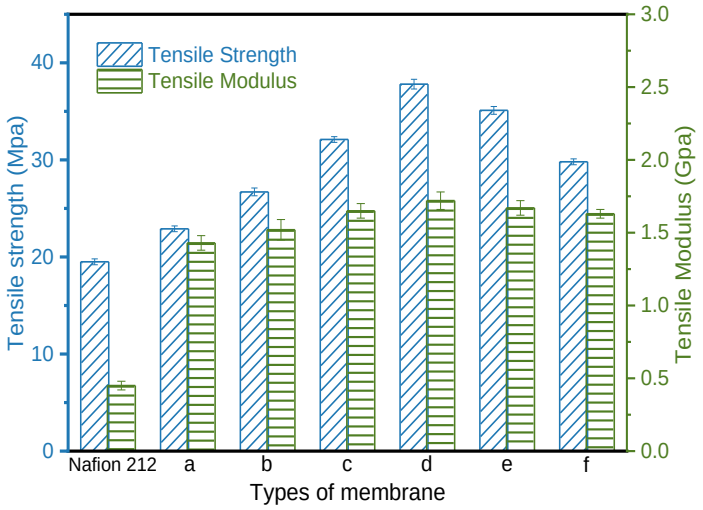

Fig. S4. Mechanical properties of various membranes. Including the Nafion 212, SPEEK (a), SPEEK/UiO-66-NH_2 (b), SPEEK/NF-2:1 (c), SPEEK/NF-1:1 (d), SPEEK/NF-1:2 (e) and SPEEK/s-g-C_3N_4 (f).

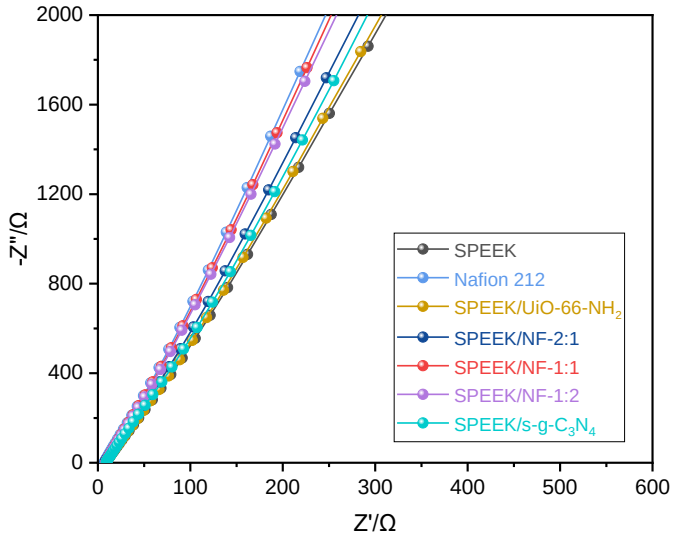

Fig. S5. The AC-impedance spectra of Nafion 212, SPEEK, and SPEEK/NF hybrid membranes.

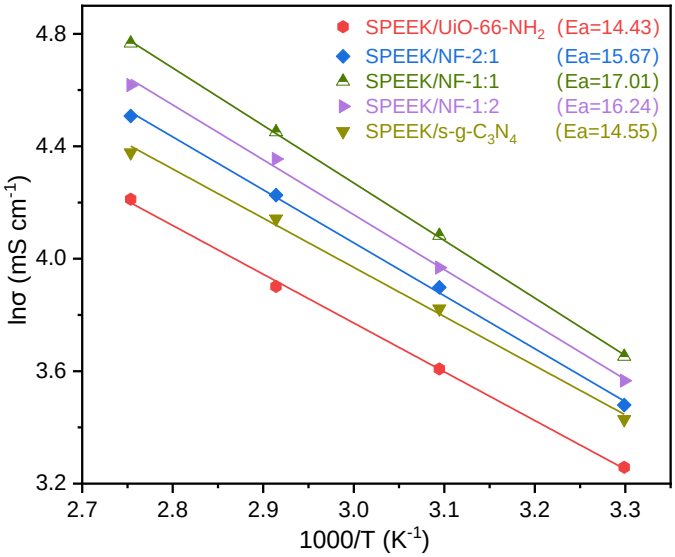

Fig. S6. Proton conductivity of hybrid membranes at different temperatures.

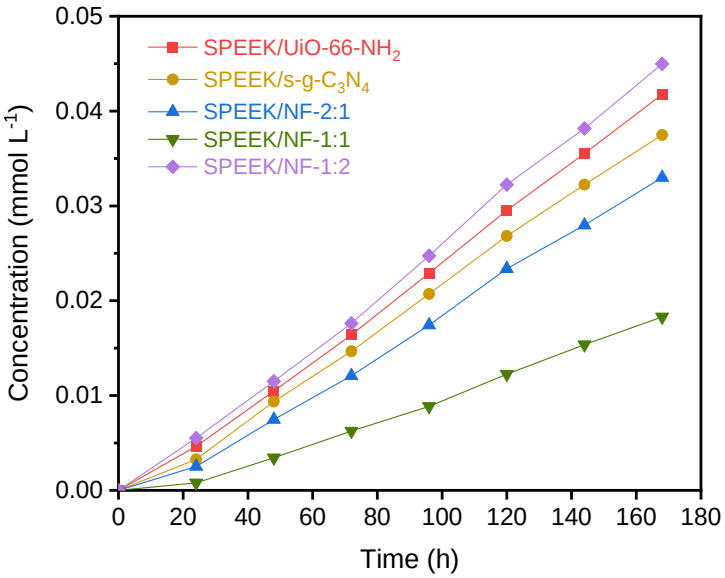

Fig. S7. The change of VO^{2+} concentration in the hybrid membranes for 7 days

Table S1. Comparison of VFB efficiencies of the reported membranes.

Membrane	Fillers' Type	CE (%)	VE (%)	EE (%)	Current density (mA cm^{-2})	Ref
SPEEK	Organic	94.5	69.0	65.2	160	[1]
SPEEK/SPPS-15	Organic	98.9	75.0	74.2	150	[2]
SPEEK/SPPTA-20	Organic	97.5	77.5	75.6	150	[3]
SPEEK/SPAES-15	Organic	98.0	76.0	74.5	160	[4]
SPEEK-IM	Organic	97.2	81.5	79.2	100	[5]
SPEEK-IM/CSPF-10	Organic	97.2	87.1	84.6	100	[5]
SPEEK/PAN-20	Organic	97.0	73.0	70.8	160	[6]
SPI-50	Organic	96.5	75.5	72.9	160	[7]
dbSPI-50	Organic	97.0	75.5	73.2	160	[8]
BPFSPI-10-50	Organic	93.0	76.0	70.7	160	[9]
S/P@f	Organic	98.0	74.0	72.5	160	[10]
S/SP@f-10	Organic	97.9	78.0	76.4	160	[10]
S/SMA-SN-0.5	Organic	98.1	76.6	75.1	160	[11]
Nafion 117	Nafion	94.0	69.0	64.9	160	[12]
Nafion 212	Nafion	98.0	73.5	72.0	160	[13]
SPEEK/G	Inorganic	97.0	72.0	69.9	160	[14]
SPEEK/GO-2	Inorganic	97.1	73.0	70.1	160	[1]
SPEEK/ZC-GO-2	Inorganic	96.8	82.0	79.4	100	[15]
SPEEK/NH_2-GO-2	Inorganic	97.1	86.9	84.9	50	[16]
SPEEK/EDA-GO-1	Inorganic	96.6	91.6	88.5	50	[16]
SPEEK/HMD-GO-2	Inorganic	98.1	89.4	87.7	50	[16]
S/MWCNTs@PDA-1	Inorganic	98.0	77.5	76.0	100	[17]
SPEEK-GO-BDSA-1	Inorganic	98.7	80.0	79.0	100	[18]
S/DCNTs-HPW-1	Inorganic	99.0	70.5	70.0	150	[19]
SPEEK/S-TiO_2-3	Inorganic	98.7	67.5	66.6	160	[20]
S/GO-VIPS-5	Inorganic	99.0	74.0	72.7	160	[21]
S/GO-DA-1	Inorganic	98.4	75.0	73.8	160	[22]
SPEEK/NF-1:1	Inorganic	98.1	81.6	80.0	160	This work

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