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Supplementary material

A highly proton/vanadium selective perfluorosulfonic acid membrane for vanadium redox flow battery

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Materials characterization

SEM (SUPRA 55 SAPPHIRE, Germany) images along with EDS mapping were collected to investigate the morphologies and element distribution. All of the cross-sections were obtained by immersing the membrane samples in liquid nitrogen, followed by the sputtering of gold onto the samples. Fourier transform infrared spectrometer (FT-IR) characterization was performed using a Nicolet iS5 Spectrum Instrument (resolution 4 cm$^{-1)}$ in the range of 4000-400 cm^{-1}. The samples were characterized by total reflection with the scanning number of 32 times. Ultraviolet-visible (UV-vis) spectroscopy study was carried out in a Lambda XLS spectrophotometer (Perkin Elmer, USA). Thermogravimetric analysis (Q50, AT, USA) was performed from 50 ℃ to 800 ℃ at a heating rate of 10 ℃/min in nitrogen atmosphere. Tensile strength of the composite membranes was evaluated by a tensile test instrument (CMT8102), the test was carried out at a strain rate of 10 mm/min at room temperature (RT).

Water uptake and swelling degree of the membranes were obtained by comparison of weight and dimensions of dry and wet samples according to equation (S1) and (S2) [1]. Membranes were thoroughly dried at 80 ℃ and finally immersed in DI water (24 h) at RT.

$$Water\ \ uptake\ \ (\%) = \frac{W_{wet} - W_{dry}}{w_{dry}} \times 100 \tag{S1}$$

$$Swelling\ \ degree\ \ (\%) = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100 \tag{S2}$$

where W_{wet} is the wet weight of the membrane, and W_{dry} is the dry weight. Similarly, L_{wet} is the membrane length in the wet state and L_{dry} is the length in the dry state.

Ion exchange capacity (IEC) was obtained by neutralization titration, and phenolphthalein was used as an indicator. The membrane was fully dried in the vacuum oven at 80 ℃ and then dipped in 1 M NaCl solution for 24 h to exchange H$^+$ of the membrane with Na$^+$. Finally, titrated using 0.01 M NaOH. The IEC value was determined according to equation (S3) [2].

$$IEC = \frac{V_{NaOH} \times C_{NaOH}}{W_{dry}} \quad \text{(S3)}$$

where V_{NaOH} was the NaOH volume used at the neutralized point, C_{NaOH} was the NaOH concentration (0.01 M in this experiment) and W_{dry} was the dry membrane weight.

The proton conductivity of the composite membranes was determined by means of electrochemical impedance spectroscopy technique (EIS) using a CHI 660E electrochemistry workstation. The membranes were sandwiched between two Teflon plates with platinum wires as electrodes. The measurements were carried out in an atmosphere of 100% humidity at RT, using a frequency ranging from 100 kHz to 0.01 Hz at an oscillating voltage of 10 mV. The proton conductivity was calculated using equation (S4) [3].

$$\sigma = L/(Rdw) \quad \text{(S4)}$$

where L is the distance between the electrodes, while d and w are the thickness and width of the membrane, respectively, and then R is the measured resistance.

For the oxidative stability test, a small part of the membrane was immersed in Fenton's reagent (3 wt% H_2O_2 containing 2 ppm $FeSO_4$) at 80 ℃. The oxidative stability was investigated using the remaining weight of the membrane after 1 h treatment with Fenton's reagent [4].

Measurements of VO^{2+} permeability and ion selectivity

The VO^{2+} permeation rate of the membrane at room temperature (RT) was measured by a diffusion cell (the physical diagram is given in Fig. S1). The membrane with an effective area of 3.14 cm^2 was placed in the middle of the two containers to prevent direct contact of the solution. Both left and right containers were filled with 40 mL of 1.5 mol L^{-1} $VOSO_4$ in 3 mol L^{-1} H_2SO_4 and 40 mL of 1.5 mol L^{-1} $MgSO_4$ in 3 mol L^{-1} H_2SO_4 solution to counteract the effects of osmotic pressure. The solutions in both containers were stirred employing a magnetic stirrer in the process of testing to avoid concentration polarization. The sample was taken from the right container every 12 h and the concentration of VO^{2+} was evaluated by the ultraviolet-visible (UV-vis) spectrometer. The permeability of VO^{2+} was determined by equation (S5) [5].

$$V_R \frac{dC_R(t)}{d(t)} = A\frac{P}{L}[C_L\text{-}C_R(\mathrm{t})] \qquad \text{(S5)}$$

where $C_R(t)$ and C_L are the concentrations of VO^{2+} in the right and left containers, respectively. A is the effective area of the membrane while L is the thickness of the membrane. P indicates the VO^{2+} permeability while V_R means the solution volume in the right container.

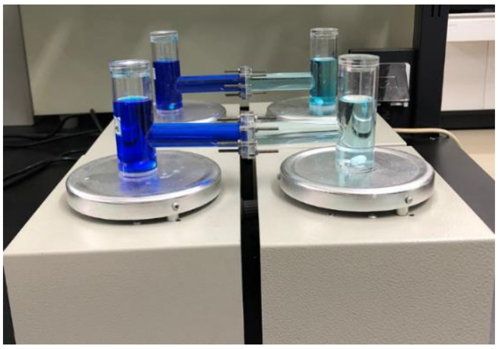

Fig. S1 Physical diagram of the cell used for the measurement of vanadium ion permeability.

The proton/vanadium selectivity (S) of the sample was calculated from the proton conductivity (σ) and VO^{2+} permeability (P) by equation (S6) [6].

$$S = \sigma/P \qquad \text{(S6)}$$

Measurements of vanadium redox flow battery performance

A VRB single cell was constructed by sandwiching the membrane (active area: 14 cm^2) between two carbon felt electrodes with a thickness of 5 mm. The membrane-electrode assembly was then compressed between two graphite plates which acted as the current collectors. Vanadium ion solution composed of 1.7 M V (±3%), V^{3+}/V^{4+} 1:1 (±3%), and 4.5 M SO_4^{2-} (±5%) was used as cathode and anode electrolyte. The solution volume in each positive and negative vessel is 50 ml.

A magnetic drive circulation pump (MP-10RN) was employed to circulate the electrolytes at a flow rate of 30 mL min^{-1}. The VRB charge-discharge test was conducted for membranes with 40, 60, 80, and 100 mA cm^{-2} current density at RT. In order to minimize the corrosion of the carbon felts and graphite plates, the cut-off voltages for the measurement in the process of the VRB operation were set as 1.65 and 0.8 V, respectively. For the self-discharge of VRB, the battery was charged to 75% state of charge (SOC) at the current density of 60 mA cm^{-2}, and then it was shelved until the single cell open circuit voltage (OCV) dropped below 0.8 V. For the cycle performance, discharge capacity and cycle efficiency over 100 cycles were recorded at the constant current of 80 mA cm^{-2}. The coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) of the VRB constructed with various membranes were evaluated according to the following equations [7].

$$CE = \frac{\int I_d dt}{\int I_c dt} \times 100\% \tag{S7}$$

$$EE = \frac{\int V_d I_d dt}{\int V_c I_c dt} \times 100\% \tag{S8}$$

$$VE = \frac{EE}{CE} \times 100\% \tag{S9}$$

where I_c and I_d represent the charge current and discharge current, respectively, while V_c and V_d mean the charge voltage and discharge voltage, respectively.

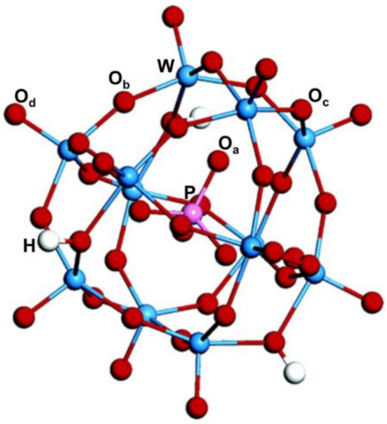

Fig. S2 The structural formula of phosphotungstic acid.

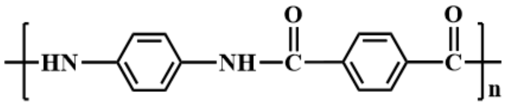

Fig. S3 The structural formula of Nano Kevlar fibers.

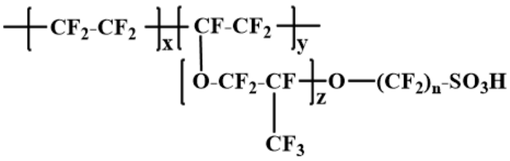

Fig. S4 The structural formula of Nafion.

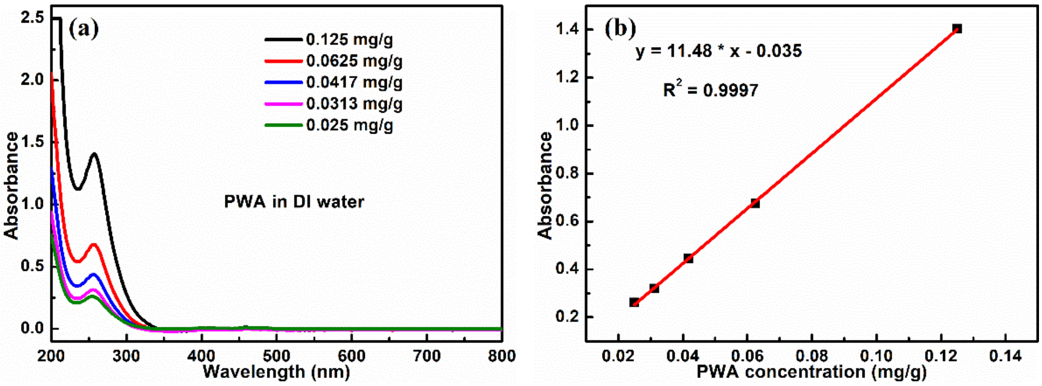

Fig. S5 (a) UV-vis characteristic absorption peaks of PWA at different concentrations and (b) its corresponding standard curves.

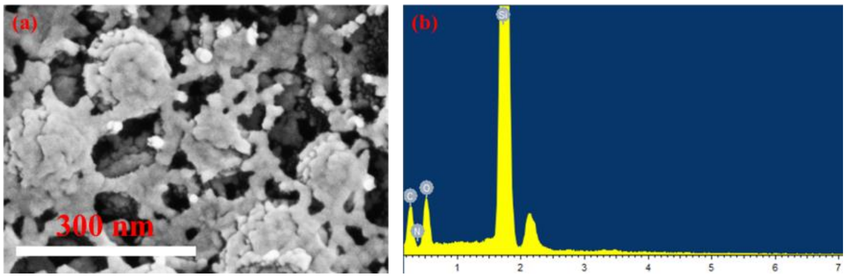

Fig. S6 (a) SEM image of NKFs@NSP. (b) EDS of NKFs@NSP.

Table S1. Element content of NKFs@NSP.

Element	**Wt%**	**At%**
C K	23.17	35.94
N K	3.59	4.85
O K	20.96	24.39
Si K	52.28	34.82
Total	100	100

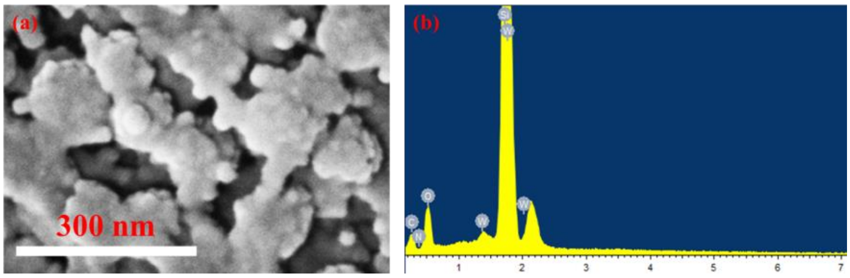

Fig. S7 (a) SEM image of NKFs@NSP/PWA. (b) EDS of NKFs@NSP/PWA.

Table S2. Element content of NKFs@NSP/PWA.

Element	Wt%	At%
C K	14.33	31.18
N K	2.34	4.37
O K	15.03	24.54
Si K	38.32	35.65
W M	29.98	4.26
Total	100	100

Table S3 Charge-discharge voltage, charge-discharge capacity, and CE for VRB with recast Nafion (A) and Nafion-(NKFs@NSP/PWA)-15 wt% (B) at 40-100 mA cm^{-2}.

Current density (mA cm^{-2})	**40**	**60**	**80**	**100**
Charge voltage (V)	A: 1.24 B: 1.22	A: 1.31 B: 1.28	A: 1.36 B: 1.32	A: 1.43 B: 1.41
Discharge voltage (V)	A: 1.49 B: 1.52	A: 1.46 B: 1.50	A: 1.42 B: 1.45	A: 1.39 B: 1.43
Charge capacity (mAh)	A: 2048 B: 2190	A: 1785 B: 1936	A: 1629 B: 1721	A: 1343 B: 1422
Discharge capacity (mAh)	A: 1707 B: 1894	A: 1552 B: 1733	A: 1436 B: 1553	A: 1201 B: 1302
CE (%)	A: 83.2 B: 86.5	A: 86.9 B: 89.7	A: 88.1 B: 90.3	A: 89.4 B: 91.6

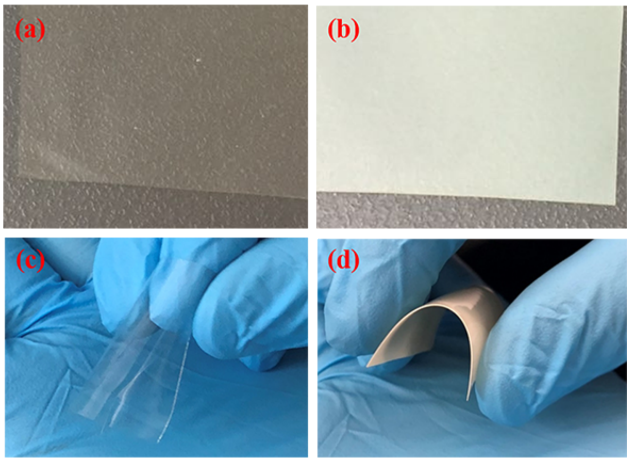

Fig. S8 Digital images of the recast Nafion (a, c) and Nafion-(NKFs@NSP/PWA)-15 wt% composite membrane (b, d).

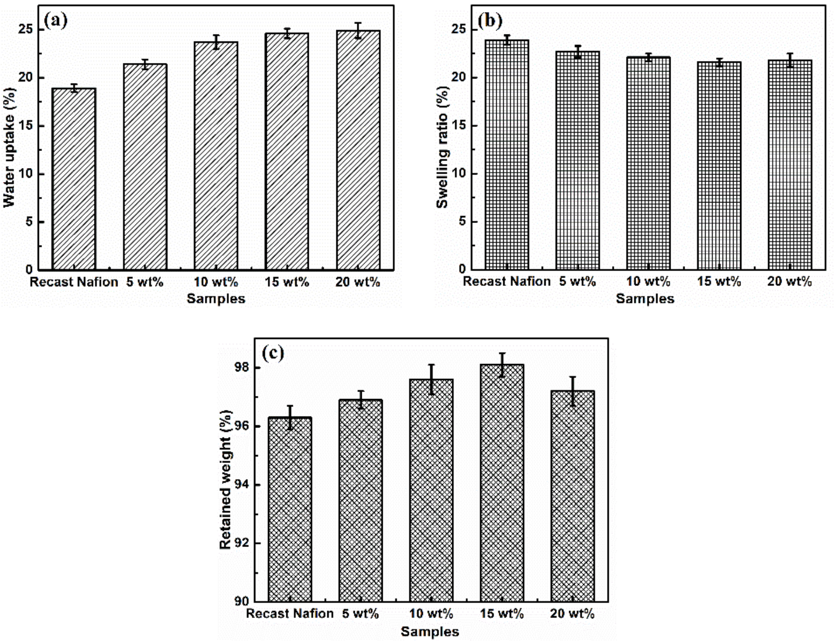

Fig. S9 (a) Water uptake, (b) swelling ratio and (c) oxidative stability of recast Nafion and Nafion-(NKFs@NSP/PWA) membrane.

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