Supporting Information

A novel Polysulfone-Polyvinylpyrrolidone membrane with superior proton-to-vanadium ion selectivity for vanadium redox flow battery

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Experimental Section

Sample preparation: The Polysulfone (PSF, MW≈480000, Changchun Jida New Material Co., China) and Polyvinylpyrrolidone (PVP, K90, Guoyao Co., China) homogenous membranes were prepared via a one-step method. The PSF-PVP-x preparing process is as follows: PSF and PVP polymers were mixed at a certain ratio then dissolved in N, N-dimethylformamide (DMF) and stirred at room temperature until the resulting solution was transparent and homogeneous. Finally, the solution was casted onto the casting equipment. After cooling down to room temperature, the hybrid membrane was easily peeled off from the polyethylene terephthalate plate while the thickness of the membrane was controlled in a range between 35±2 μm. The prepared membranes were named as PSF-PVP-x, where x stands for the weight percentage of PVP in the membrane.

Membrane morphology: The morphology of the membrane surface and cross-section were recorded by scanning electron microscope (JEOL JSM-5800). The cross section of the membrane was obtained by breaking the membrane in liquid nitrogen with forceps. All the samples were sputtered with gold and measured at an acceleration voltage of 5 kV. Morphology of the hydrophilic PVP in the hybrid membrane was recorded by transmission electron microscope. The solutions were dropped on a Cu grid to form an ultra-thin film and then loaded with Iodine vapor for about 10 seconds to mark PVP in the membrane.

Membrane resistance: The area resistance of the membranes was measured by a separated cell that with 3M H_2SO_4 solution, detecting according to impedance spectroscopy using an IVIUMSTAT electrochemistry work station. Before test, the samples were immersed in 3M H_2SO_4 at room temperature for 24 h. The proton conductivity was calculated by the following equation:

$$\sigma(mS/cm) = \frac{L}{R \times S}$$

where L is the distance between the two electrodes, S is the cross sectional area of the membrane, and R is the resistance of the membrane.

For each reported, at least four samples were measured and results were averaged.

Vanadium ion permeability: The VO^{2+} permeability was examined on a membrane separated diffusion cell by filling 1M VO^{2+}/ 3M H_2SO_4 solution in left compartment and 1M $MgSO_4$/ 3M H_2SO_4 blank solution in right compartment, according to our previous publication.[1] For each resistance reported, at least three samples were measured and results were averaged.

Water uptake and swelling ratio: Water uptake and swelling ratio of membranes were measured by the following procedures. The sample membranes were immersed in deionized water at room temperature for 24 h. Then the membranes were wiped off the excess water quickly using filter papers and weighed immediately. Afterwards, the membranes were dried at 100 °C for 24 h in vacuum. The water uptake and swelling ratio of membranes were calculated by the following equations:

$$\text{Water uptake (\%)} = \frac{W_{wet} - W_{dry}}{W_{dry}} * 100\%$$

$$\text{Swelling ratio (\%)} = \frac{S_{wet} - S_{dry}}{S_{dry}} * 100\%$$

where W_{wet} and W_{dry} are the weights of membrane in the wet and dry state, respectively; S_{wet} and S_{dry} are the area of the wet and dry membranes, respectively.

Water contact angle measurement: The static water contact angles were measured at 25 °C and 50% relative humidity. For each angle reported, at least three samples were measured and results were averaged.

Yield strength: Mechanical properties of the membranes (dried at 100°C overnight) were measured with a tension tester GMT 4503 instrument (SANS, AUTO graph) at room temperature by using a programmed elongation rate of 10 mm min^{-1}.

Battery performance: In the system, VO^{2+}/ VO_2^+/ H_2SO_4 and V^{2+}/ V^{3+}/ H_2SO_4 solutions serving as electrolytes were designated at the positive and negative sides, respectively. The electrolyte was cyclically pumped through the corresponding electrode via a magnetic drive pump. The cut-off voltage for the charge and discharge process was set between 0.8 V-1.7 V. The coulombic efficiency (CE), voltage efficiency (VE) and energy transfer efficiency (EE) were calculated as following equations,

$$\text{CE} = \frac{\int I_d dt}{\int I_c dt} * 100\%$$

$$\mathrm{EE} = \frac{\int V_d I_d dt}{\int V_c I_c dt} * 100\%$$

$$\mathrm{VE} = \frac{\mathrm{EE}}{\mathrm{CE}} * 100\%$$

Where I_d and I_c were discharging and charging current, V_d and V_c were discharging and charging voltage, respectively.

Membrane oxidation stability: The oxidation test was carried out by immersing the sample membranes in 1 M VO_2^+ / 3M H_2SO_4 solution. Then, the solution was determined by UV-visible spectroscopy at certain time internals to detect the concentration of VO^{2+}.

Gel Permeation Chromatography: The molecular weights of the polymers were determined by gel permeation chromatography (GPC). The measurements were performed in a Waters chromatographic instrument equipped with a 1515 Isocratic HPLC Pump, a 410 differential refractometer, and a 486 Tunable absorbance detector. 5 microns hard styrene divinyl benzene particles were used to calibrate the molecular weights. The DMF mobile phase was delivered at 1.0 mL/min.

Table S1. Physicochemical properties of PSF-PVP-x (35 μm) and commercial Nafion212 membranes (51 μm). PSF-PVP-x membranes exhibit adequate mechanical strength, dimensional stability, water uptake and high selectivity.

Membrane	**Permeability (10^{-7} cm^2/min)**	**Area Resistance (mΩ cm^2)**	**Swelling ratio (%)**	**Water uptake (%)**	**Yield strength (MPa)**	**Selectivity (10^7 S min/cm^3)**
PSF-PVP-40	**0.003**	**154.2**	**8.6**	**9.7**	**69.5**	**6.7**
PSF-PVP-50	**0.007**	**97.2**	**8.9**	**12.4**	**66.2**	**4.8**
PSF-PVP-60	**0.03**	**94.6**	**20.1**	**20.6**	**60.3**	**1.5**
PSF-PVP-70	**0.05**	**87.5**	**41.0**	**47.4**	**51.3**	**0.8**
Nafion212	**3.3**	**91.1**	**29.3**	**26.1**	**50.5**	**0.017**

Table S2. VRFB performance with different PSF-PVP-x membranes. The VRFB with PSF-PVP-50 membrane exhibits the highest EE (85%) under charge-discharge current density of 60 mA cm^{-2}.

	Thickness (μm)	CE (%)	EE (%)	VE (%)
PSF-PVP-40	35±2	98	79	81
PSF-PVP-50	35±2	97	85	88
PSF-PVP-60	35±2	93	82	89

Table S3. VRFB performance based on PSF-PVP-50 membrane with different thickness under charge-discharge current density of 60 mA cm^{-2}. The VRFB with 35 μm thickness PSF-PVP-50 membrane exhibits the highest EE.

Membrane	Thickness (μm)	CE (%)	VE (%)	EE (%)
PSF-PVP-50	23	94	90	83
	35	97	88	85
	47	98	82	80
	55	98	81	79
Nafion212	51	90	87	78

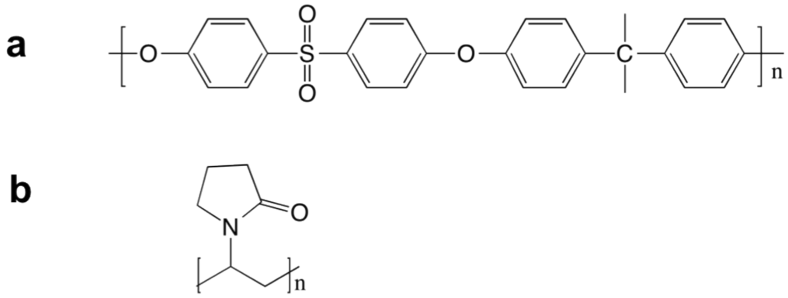

Fig. S1 The molecular structure of the Polysulfone (a) and Polyvinylpyrrolidone (b) molucures.

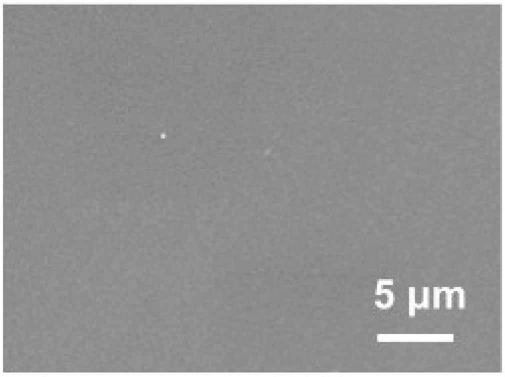

Fig. S2 The SEM surface image of PSF-PVP-x membrane. The membrane is dense without obvious porosity in the surface on micro scale.

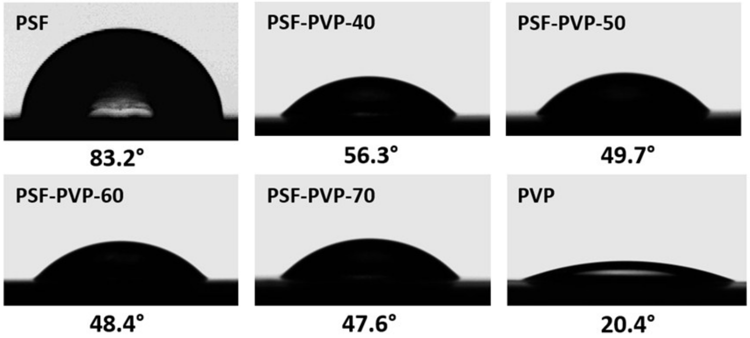

Fig. S3 Contact angle of PSF-PVP-x with various PVP content. Due to the hydrophilicity of PVP, contact angles are substantially improved from 83.2° to 20.4° with increasing content of PVP, which confirms the hydrophilicity of PVP.

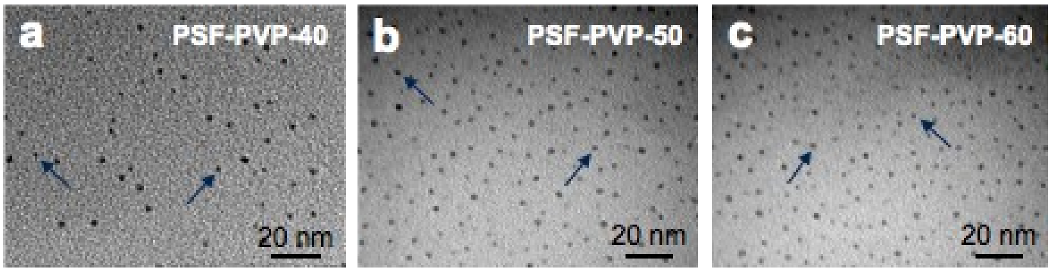

Fig. S4 Transmission electron microscope (TEM) images of PSF-PVP-x membranes. TEM images of PSF-PVP-x membranes after staining with iodine vapour and the dark zones (I_2 nanoparticles) indicating the size of hydrophilic channel of around 2 nm.

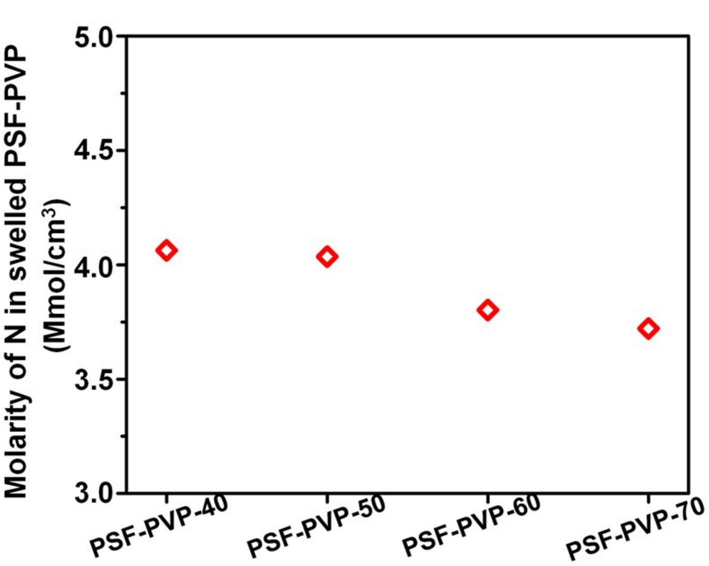

Fig. S5 The molarities of N-heterocylic groups in the fully swollen membrane with different PVP contents.

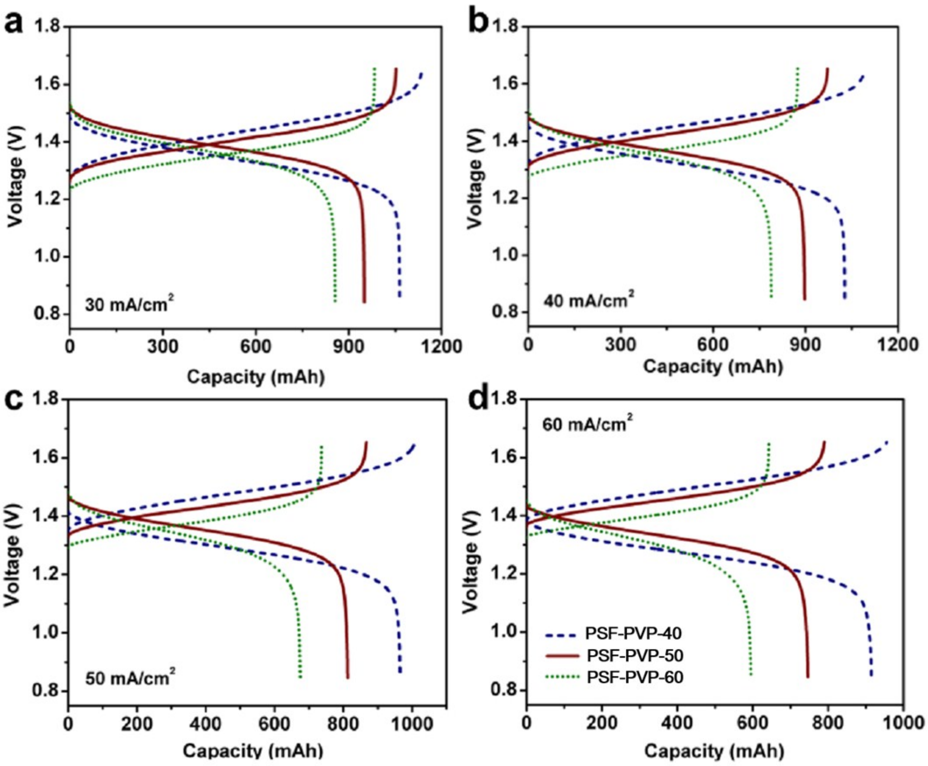

Fig. S6 Charge-discharge curves VRFB based on PSF-PVP with varied PVP content under different current densities. VRFBs with PSF-PVP membranes show different voltage platforms and charge-discharge capacities under 30~60 mA cm^{-2} current densities, indicating the battery with PSF-PVP-50 membrane exhibits optimal performance.

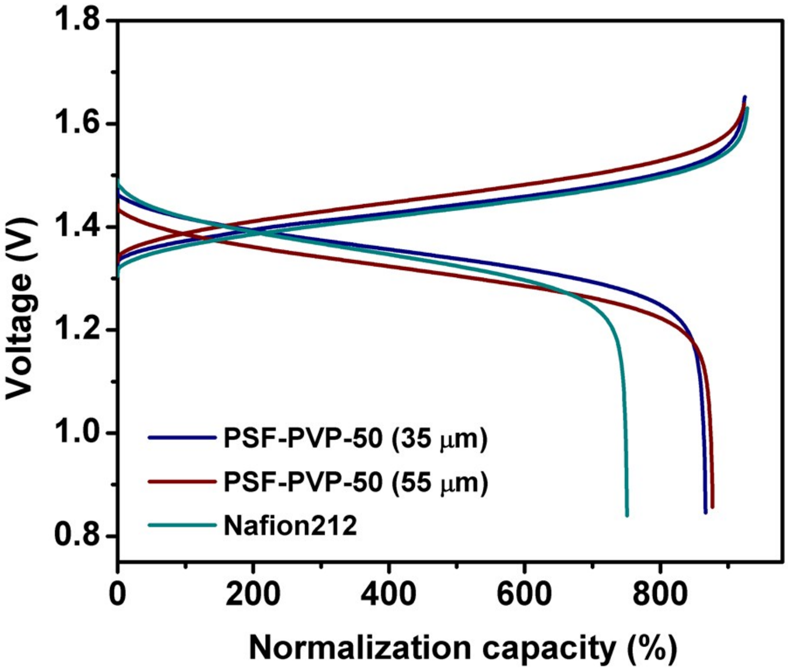

Fig. S7 Charge-discharge curves of VRFB based on PSF-PVP-50 with the thickness of 35 μm or 55 μm and Nafion212 membranes respectively under the charge-discharge current density of 60 mA cm^{-2}.

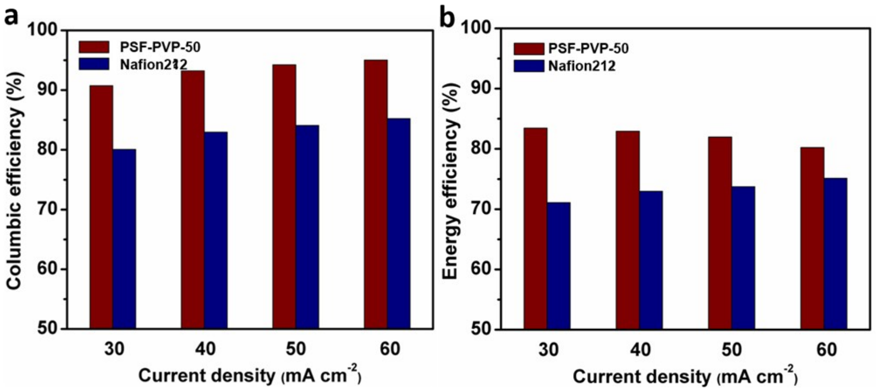

Fig. S8 (a) Columbic efficiency and (b) energy efficiency of the VRFB with PSF-PVP-50 compared to that of Nafion212 under different current densities. Compared to VRFB with Nafion212, the one with PSF-PVP-50 shows a higher columbic efficiency of 97% and energy efficiency 85%.

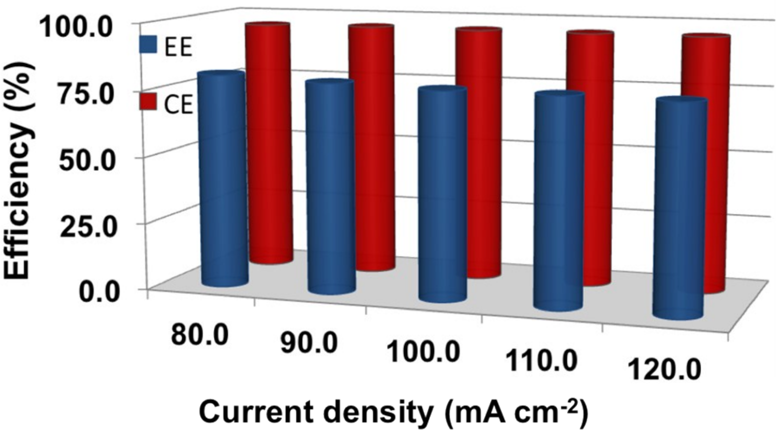

Fig. S9 Columbic efficiency (CE) and energy efficiency (EE) of the VRFB with PSF-PVP-50 under large current density from 80 to 120 mA cm^{-2}. The VRFB with PSF-PVP-50 obtains a CE up to 95% and EE up to 80% even under a large current density range.

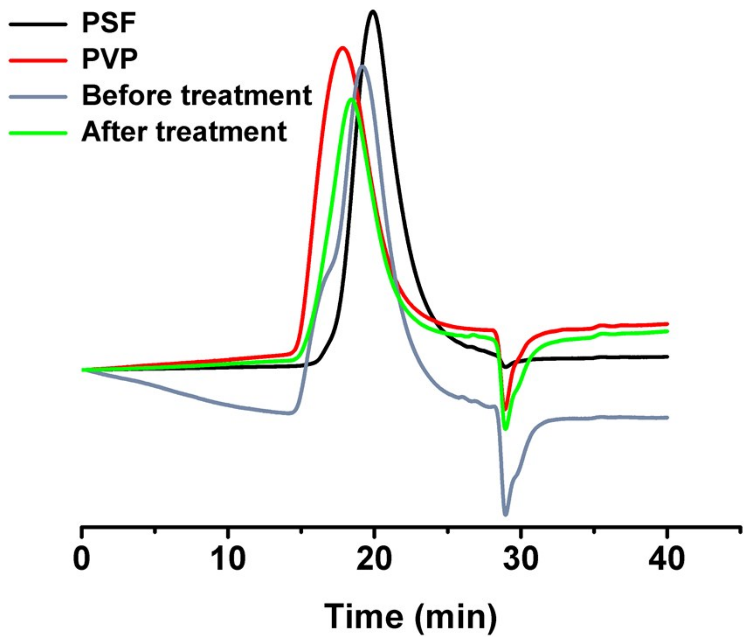

Fig. S10 Gel Permeation Chromatography (GPC) of the PSF and PVP polymers, as well as the membrane before and after exposure to the VO_2^+ solution for about 400 days.