Supplementary Information

High-performance porous uncharged membranes created by tuning cohesive and swelling force for vanadium flow battery application

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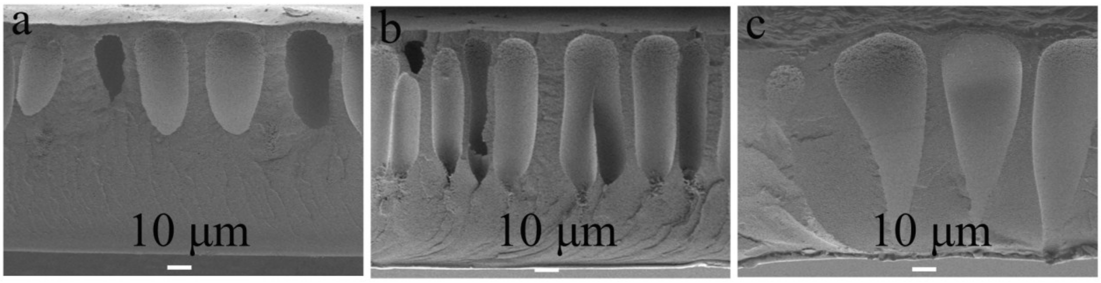
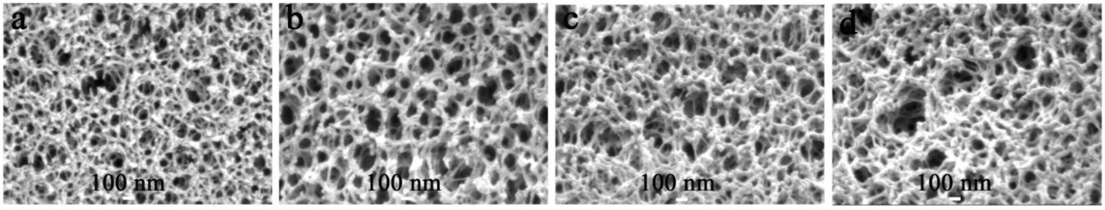
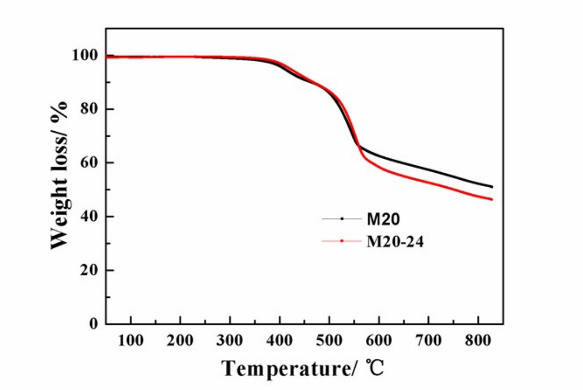


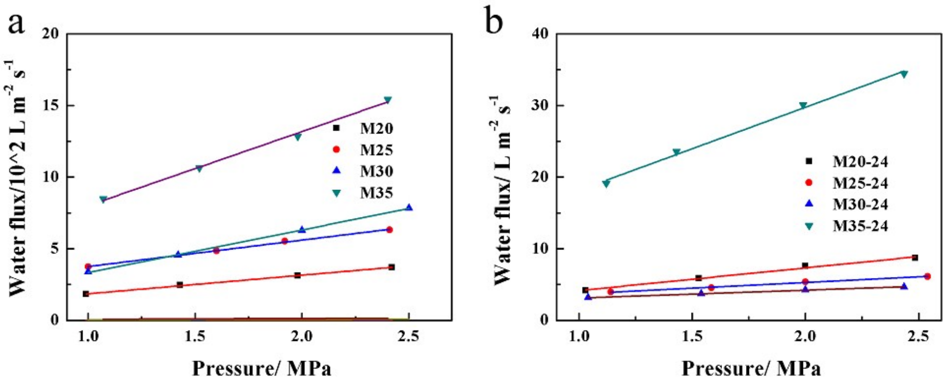
Supplementary Fig. S1 The cross-section morphology of the untreated PES membranes with different PVP content (a) M25, (b) M30, (c) M35.



Supplementary Fig. S2 The cross-section morphology of the skin-layer of the untreated PES membranes with different PVP content (a) M20, (b) M25, (c) M30, (d) M35.



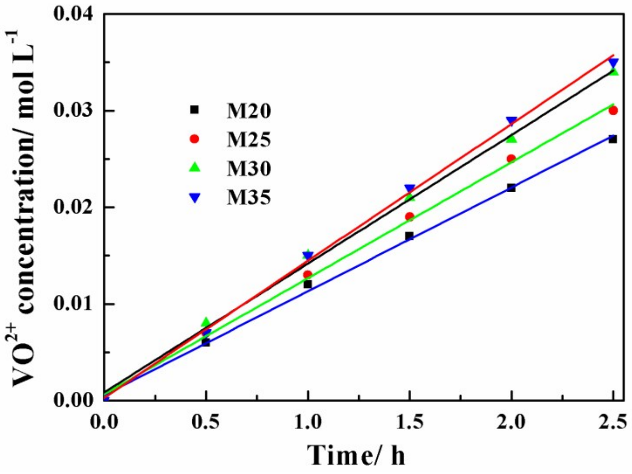
Supplementary Fig. S3 The TGA curves of the untreated PES membrane and the treated PES membrane with complete solvent evaporation.



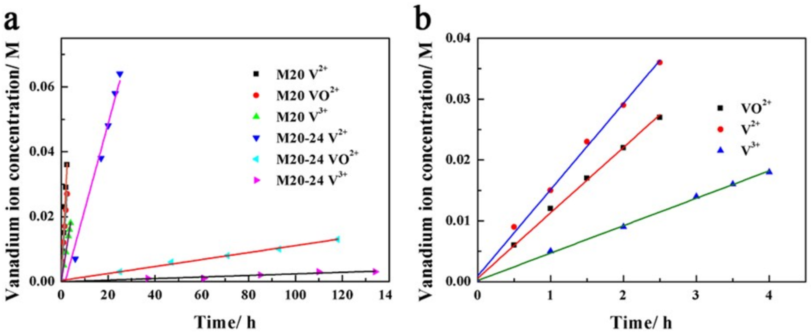
Supplementary Fig. S4 Water fluxes at different pressures (a) the untreated PES membranes, (b) the treated PES membranes (MX-24).

Supplementary Table S1 The physicochemical properties of MX and MX-24 (X=20, 25, 30 or 35) (t=24)

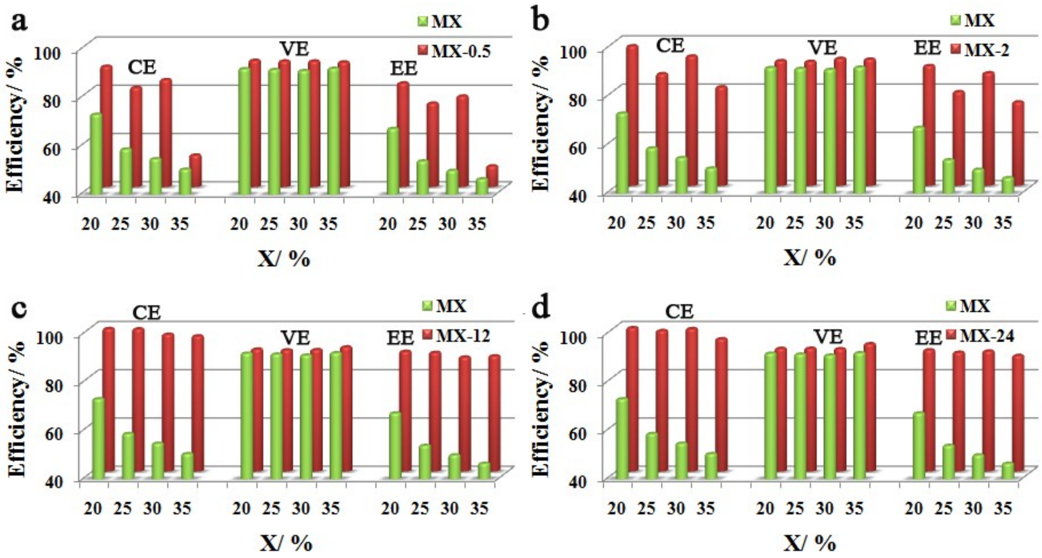
Code	Thickness (μm)	Area resistance (Ω cm^2)	Porosity (%)	Average Pore size (nm)	Swelling ratio in IPA (%)
M20	115±5	0.12	79.45	12.80	5.56
M25	115±5	0.12	81.87	15.77	--
M30	115±5	0.12	89.38	18.63	6.56
M35	115±5	0.12	95.77	22.79	--
M20-24	102±5	0.12	72.24	2.21	--
M25-24	102±5	0.13	72.27	1.57	--
M30-24	102±5	0.13	72.52	1.30	--
M35-24	102±5	0.14	76.20	3.99	--



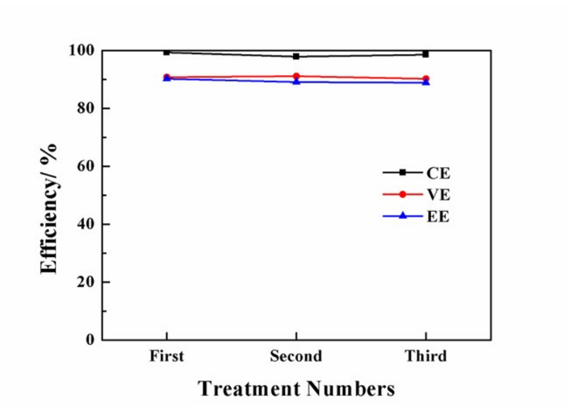
Supplementary Fig. S5 Vanadium ion permeability of the untreated PES membranes with different PVP content.



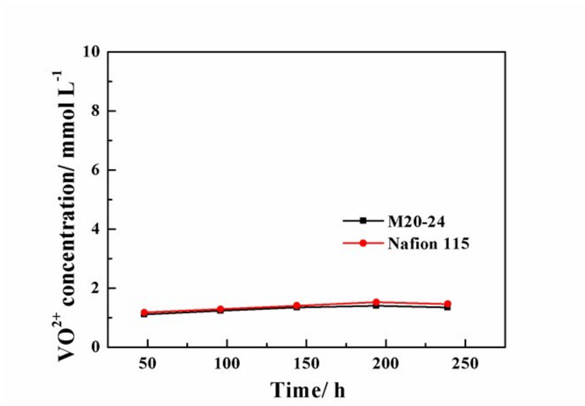
Supplementary Fig. S6 Vanadium ions permeability of (a) M20 *vs*. M20-24, (b) M20.



Supplementary Fig. S7 VFB performance of the untreated and treated PES membranes with different solvent evaporation times at 80 mA cm^{-2} (a) 0.5 h, (b) 2 h, (c) 12 h, (d) 24 h.



Supplementary Fig. S8 VFB performance of M20-24 with different solvent immersion/evaporation cycles at 80 mA cm^{-2}.



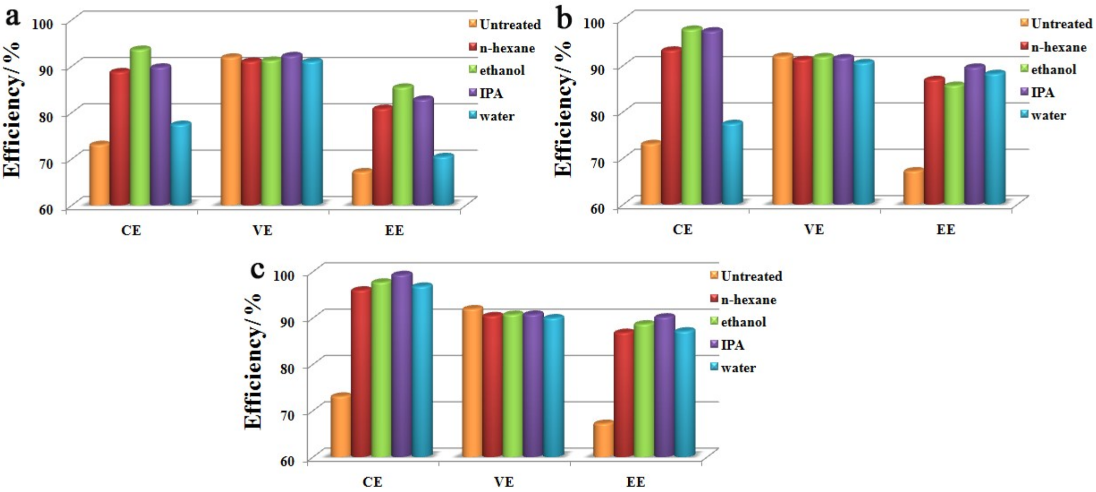
Supplementary Fig. S9 VO^{2+} concentration change containing a M20-24 *vs* a Nafion 115 in 0.15 M VO_2^+ + 3 M H_2SO_4 at 40 °C as a function of time.

Supplementary Table S2 The vapor pressure and PES swelling ratio for different solvents.

Solvent	Vapor pressure [a] (mm Hg)	Swelling ratio [b] (%)
n-hexane	151.44	10.23
ethanol	59.77	6.39
IPA	45.16	5.56
water	23.76	11.14

[a] The vapor pressures were calculated according to LANGE'SHANDBOOK OFCHEMISTRY (James G. Speight, Ph. D. CD&W Inc., Laramie, Wyoming).

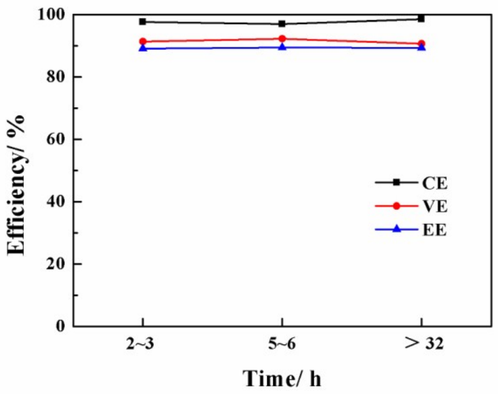
[b] Swelling ratio of M20 in different solvents.



Supplementary Fig. S10 VFB performance of different solvent treated membranes with different solvent evaporation times (a) 0.5 h, (b) 2 h, (c) 24 h, when PVP/(PES+PVP) mass ratio is 20% at 80 mA cm^{-2}.

Supplementary Table S3 VFB performance of different kinds of membranes when IPA was used as the solvent at 80 mA cm^{-2}

Membranes	Solvent evaporation time (h)	CE (%)	VE (%)	EE (%)
PES	Untreated	73.11	91.96	67.23
	0.5	89.82	92.28	82.89
PVDF	Untreated	72.38	92.60	67.03
	0.5	84.62	89.18	75.47



Supplementary Fig. S11 VFB performance of M30-24 after immersion in water for different times.

Experimental Section

Porous PES membrane preparation. The porous PES membranes were prepared *via* the phase inversion method. A certain mass ratio of PES and PVP was first dissolved in *N,N*-dimethylacetamide (DMAc, Tianjin Damao Chemical Reagent Factory) to form a homogeneous polymer solution. The polymer solution was then cast on a dry, dust-free and smooth glass plate using a doctor blade (Elcometer 3545 adjustable Bird Coater, Scraper, Elcometer 3545/8) at room temperature with humidity less than 50% to avoid the penetration of water vapor into the polymer solution. Afterward, the glass plate was immersed into water to solidify the porous membrane. The membrane was peeled off and soaked in water before solvent treatment. The prepared PES membranes with different PVP/(PVP+PES) mass ratio in the casting solution were referred to as MX, where X is this mass ratio. The detailed composition of the as-prepared membranes is shown in Table S1.

Solvent treatment. Membrane pieces of 11.4×9.0 cm^2 were immersed in the solvent for a certain time. The membranes were then evaporated at room temperature for different times after wiping off the solvent from the surface with filter paper. Finally, the membranes were stored in water for use. Immersing the treated PES membranes in water for different times did not influence their performance in VFB operating environment (Fig. S11). The PES membranes with different solvent evaporation times were referred to as MX-t, where t is the solvent evaporation time. The detailed composition of the treated PES membranes is shown in Table S1.

Membrane morphology. The cross-section morphology of membranes was recorded by using a field emission scanning electron microscope (FE-SEM: JSM-7800F and Philips FEI QUANTA 200FEG). In order to avoid the shrinkage and collapse of pores in the untreated membranes, the membranes were frozen in a freeze dryer (FD-1A-5, Shanghai Bi Lang instrument manufacturing Co., Ltd). The freeze-dried samples were broken in liquid nitrogen and then gold coated before SEM analysis.

Vanadium ion permeability. The permeability of vanadium ions with different valences was detected in a diffusion cell assembled with the membranes. The left cell was filled with 120 mL solution containing vanadium ions with different valence states ($V^{2+}/V^{3+}/VO^{2+}$, 1.5 M in 3 M H_2SO_4 solution), while the right one was filled with 120 mL 1.5 M $MgSO_4$ in 3 M H_2SO_4 solution to equalize the ionic strength and minimize the osmotic pressure effect. The solutions in both cells were vigorously stirred to minimize concentration polarization. A 3 mL sample from the right cell was collected at regular time intervals. The same volume of original solution was then added to the right compartment. A UV-vis spectrometer (JASCO, FT-IR 4100, Japan) was utilized to measure the concentration of vanadium ions. The vanadium ions permeability was calculated according to Fick's diffusion law as below:

$$V_B \frac{dC_B(t)}{dt} = A \frac{p}{L}(C_A - C_B(t))$$

where V_B is the solution volume in the right cell; A and L are the effective area and thickness of the membrane, respectively; P is the permeability of vanadium ions; C_A is the ion concentration in the left cell while $C_B(t)$ is the ion concentration in the right compartment as a function of time. For comparison, the vanadium ion permeability of Nafion 115 was also measured.

Area resistance. The area resistance of membranes was detected using a conductive cell. Each half-cell was filled with 0.5 mol L^{-1} H_2SO_4 solution, which was separated by a membrane with an effective area of 1 cm^2. The area resistance was measured by using electrochemical impedance spectroscopy (EIS) (Solartron Electrochemical System) over a frequency range from 1 kHz to 1 MHz. The membrane was immersed in a 0.5 mol L^{-1} H_2SO_4 solution for 24 h before the measurement. The area resistance (r) is calculated by the formula below:

$$r = (r_1 - r_2) \times S$$

where r_1 and r_2 are the electronic resistance of a conductive cell with and without a membrane, respectively. S is the effective area of a membrane. The area resistance of Nafion 115 was also measured for comparison.

Porosity. A membrane was immersed in water for 24 h. The membrane was then weighed after wiping off the water on the surface with filter paper. The membrane was subsequently fully dried and weighed. The porosity of the resulting membrane was calculated by the formula below:

$$\varepsilon = \frac{M_\mathrm{w} - M_\mathrm{d}}{\rho \times S \times l}$$

where M_w and M_d are the mass of the wet and dried membrane, respectively; ρ is the density of water at room temperature; S is the surface area of the dried membrane; l is the thickness of the dried membrane.

Pure water flux. In order to obtain the average pore size of the porous PES membranes, pure water flux was measured in a stainless steel dead-end pressure cell with an effective membrane area of 19.6 cm^2. The device was pressurized with nitrogen to a pressure of X MPa (X=1, 1.5, 2 and 2.5). Permeate samples were collected in cooled flasks as a function of time, then weighed and analyzed. The permeation was stopped when the water flux reached to a constant value. All measurements were based on at least three samples and average values were used. The water permeation flux is calculated by the formula below:

$$J = \frac{m}{\rho \times S \times t}$$

where J is pure water flux; m is the water mass of each sample; ρ is the water density at room temperature; S is the effective area of measured membrane and t is the water permeation time of each sample.

The average pore size (diameter) of membranes was calculated by the Hagen-Poiseuille equation below:

$$\mathrm{D} = \sqrt{\frac{32 J \eta L \tau}{\varepsilon \Delta \mathrm{P}}}$$

where D is the average pore size; J is the water flux; η is the water viscosity at room temperature; L is the average thickness of the measured membrane; τ is the tortuosity; ε is the porosity and ΔP is the pressure difference across the membrane.

Swelling ratio. The swelling ratio (SR) of the membranes in the solvent was determined by cutting membranes into 5× 5 cm^2 pieces and drying them at room temperature for at least 24 h. The dried membranes were immersed in the solvent for a certain time and their dimensions were then measured. The swelling ratio was calculated by the formula below:

$$\mathrm{SR} = \frac{L_\mathrm{s} - L_\mathrm{d}}{L_\mathrm{d}} \times 100$$

where L_s and L_d are the length of the swollen and dried PES membrane, respectively.

Battery performance. The VRB single cell was assembled by sandwiching a membrane between two carbon felt electrodes whose effective area is 48 cm^2, clamped by two graphite polar plates. All these components were fixed between two stainless plates. 60 ml 1.5 M V^{2+}/V^{3+} in 3.0 M H_2SO_4 and 60 ml 1.5 M VO^{2+}/VO_2^+ in 3.0 M H_2SO_4 solution were used as the negative and positive electrolytes, respectively. The electrolytes were cyclically pumped into the corresponding electrodes. The flow rate of electrolyte was kept at 50~60 mL min^{-1}.The charge–discharge cycling tests were conducted by an Arbin BT 2000 at a constant current density of 80 mA cm^{-2}. The charge-discharge limit voltages were set at 1.55 V and 1.0 V respectively to avoid the corrosion of carbon felt and graphite polar plates. All efficiency data are based on two parallel experiments.

Stability test. PES membrane pieces of 5×5 cm^2 were soaked in 60 mL electrolytes (0.15 M VO_2^+ in 3 M H_2SO_4) in sealed glass bottles at 40 $^\circ$C. A 3 mL sample was collected from the bottles at regular time intervals. A UV-vis spectrometer (JASCO, FT-IR 4100, Japan) was utilized to detect the concentration of VO^{2+} in the testing samples, which is regarded as an indicator of membrane oxidation degradation. To further investigate the chemical stability of a membrane, the charge-discharge cycling life test was carried out at a constant current density of 80 mA cm^{-2}.