Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information

Solvent Treatment: The Formation Mechanism of Advanced Porous Membranes for Flow Batteries

Wenjing Lu,[ab] Lin Qiao,[ab] Qing Dai,[ab] Huamin Zhang,*[ac] Xianfeng Li,*[ac]

[a] Division of energy storage, Dalian National Lab for Clean Energy (DNL), Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, China

[b] University of Chinese Academy of Sciences, Beijing 100049, China

[c] Collaborative Innovation Centre of Chemistry for Energy Materials (iChEM), Dalian 116023, China

***Corresponding author:**
Prof. Dr. Huamin Zhang
Division of energy storage, Dalian National Laboratory for Clean Energy
Dalian Institute of Chemical Physics
Chinese Academy of Sciences, Dalian 116023, P. R. China.
Email: zhanghm@dicp.ac.cn
Tel.: +86-411-84379072
Fax: +86-411-84665057.

Prof. Dr. Xianfeng Li
Division of energy storage, Dalian National Laboratory for Clean Energy
Dalian Institute of Chemical Physics
Chinese Academy of Sciences, Dalian 116023, P. R. China.
Email: lixianfeng@dicp.ac.cn
Tel.: +86-411-84379669
Fax: +86-411-84665057

Experimental section

1. Materials.

PBI was prepared according to our previous report [1]. Isopropanol (IPA) and N,N-dimethylacetamide (DMAc) were purchased from Tianjin Damao Chemical Reagent Factory.

2. Membrane preparation

A certain amount (13 wt%) of PBI was firstly dissolved in DMAc to form a homogeneous polymer solution. Then the solution was cast on a spotless and smooth glass plate using a doctor blade (Elcometer 3545 adjustable Bird Coater, Scraper, Elcometer 3545/8) at room temperature. Worth noting is that the humidity should be less than 60% to avoid the penetration of water vapor into the polymer solution. Otherwise, the film will be solidified before being immersed into the coagulation bath. Afterwards, the glass plate was immediately immersed into water to form the porous membrane. Then the membrane was peeled off and stored in water before being treated. The as-obtained membranes were referred to as M0.

3. Solvent treatment

The treating solvents with different volume ratio of IPA to Water, were confected in the first place. Membranes with fixed size were then immersed into these treating solvents for different time. Afterwards, the membranes were evaporated at various temperature for different time after wiping off the solvent on the surface. Finally, the membranes were stored in water for use. The codes of the as-obtained membranes were listed in Table 1.

4. Membrane morphology

The cross-section morphology of porous membranes was recorded by field emission scanning electron microscope (FE-SEM: JSM-7800F). The samples were broken in liquid nitrogen and then gold coated before SEM analysis.

5. Shrinking ratio

The porous membranes stored in water were cut into 5 × 5 cm^2 pieces and then immersed in different solvents (pure IPA or Water) for a certain time. After which, the swollen porous membranes were dried at different temperature for at least 24 h. The dimensions of the swollen and dried porous membranes were finally measured. The shrinking ratio (SR) of the porous membranes treated by diverse process parameters was calculated by the following equation:

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

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

6. Vanadium ion permeability

The VO^{2+} ion permeability was measured in a diffusion cell assembled with a porous membrane. The left cell was filled with 120 mL 1.5 M $VOSO_4$ in 3 M H_2SO_4 solution. In order to equalize the ionic strength and minimize the osmotic pressure effect, the right compartment was filled with 120 mL 1.5 M $MgSO_4$ in 3 M H_2SO_4 solution. Both cells were vigorously stirred to minimize the concentration polarization. A 3 mL sample from the right compartment was collected at a regular time interval, the same volume of original solution was then added to the right cell. A UV-vis spectrometer (JASCO, FTIR 4100, Japan) was used to detect the concentration of VO^{2+} ions. The VO^{2+} ion permeability was calculated according to the Ficker diffusion law as below:

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

where V_B is the solution volume in the right cell; A and L are the effective area and thickness of the measured membrane, respectively; P is VO^{2+} ion permeability; 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.

7. Area resistance

The area resistance of a membrane was detected by using a conductive cell. Each half-cell was filled with 0.5 mol L^{-1} H_2SO_4 solution, and a membrane with an effective area of 1 cm^2 was utilized to separate the two cells. The area resistance was measured by the electrochemical impedance spectroscopy (EIS) (Solartron Electrochemical System) over a frequency range from 1 kHz to 1 MHz. It is notable that the membrane and the conductivity cell should be immersed into a 0.5 mol L^{-1}

H_2SO_4 solution for at least 24 h before the measurement. The area resistance (r) is calculated by the following equation:

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

where r_1 and r_2 are the electronic resistances of a conductive cell with and without a membrane, respectively. S is the effective area of a membrane.

8. Battery performance

A VFB single cell assembled with a membrane owning an effective area of 6 × 8 cm^2, was sandwiched between two carbon felt electrodes clamped by two graphite polar plates. All parts were fixed between two stainless plates. 60 ml 1.5 M V^{2+}/V^{3+} in 3.0 M H_2SO_4 solution and 60 ml 1.5 M VO^{2+}/VO_2^+ in 3.0 M H_2SO_4 solution were served as negative and positive electrolytes, respectively. The electrolytes were cyclically pumped into the corresponding electrodes. The charge–discharge cycling test was conducted by an Arbin BT 2000 at a current density range of 40-200 mA cm^{-2}. The limit voltage of the charge-discharge process were set at 1.55 V and 1.00 V respectively to avoid the corrosion of the carbon felt and graphite polar plates. All efficiency datas are based on two parallel experiments.

Table S1 The SRs of porous membranes treated at various E_T with complete solvent evaporation

Solvent	IPA				Water			
E_T (°C)	Rt	50	80	120	Rt	50	80	120
SR (%)	19.91	20.54	20.02	19.53	24.21	26.60	28.64	32.45

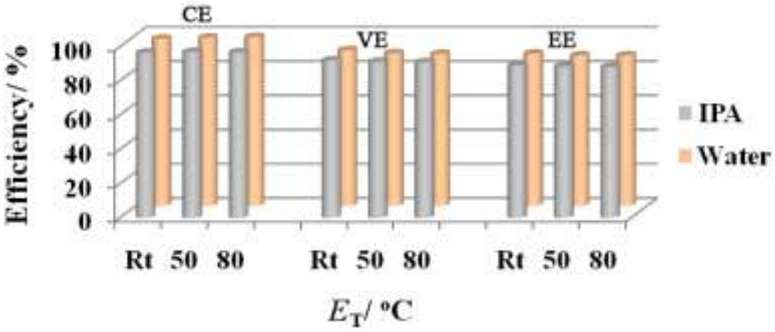


Fig. S1 The VFB performance at 80 mA cm^{-2} of IPA and Water treated membranes at different E_T when evaporating the solvent entirely.

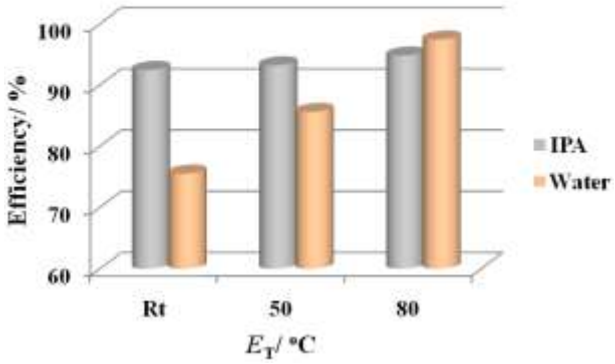
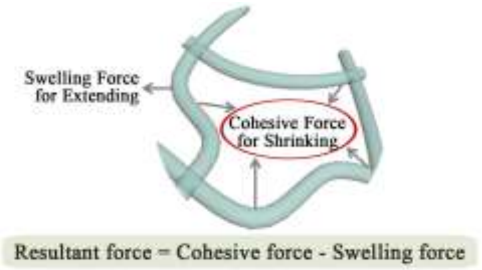


Fig. S2 The comparison of CEs of VFBs assembled with membranes treated by IPA and Water at 80 mA cm^{-2} when at different E_T (E_t = 0.5 h).



Scheme S1 The schematic diagram of the resultant force between the cohesive force and the swelling force.

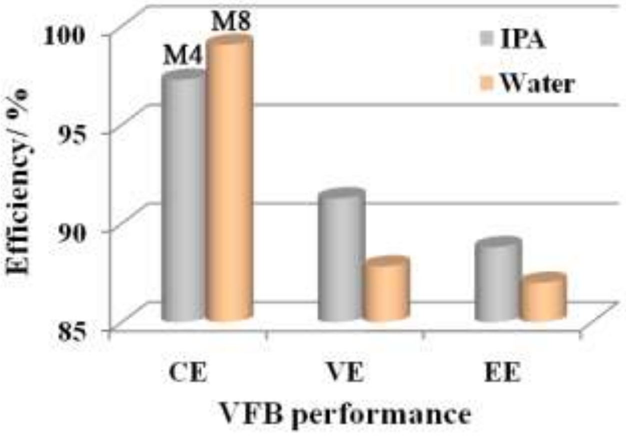


Fig. S3 The comparison of the VFB performance of membranes treated by IPA and Water with entire solvent evaporation at 80 mA cm^{-2} when at E_T = 120 °C.

Table S2 The area resistances of porous membranes before and after solvent treatment with different process parameters

Code	M0	M1	M2	M4	M5	M6	M8	M9	M10
Area resistance (Ω cm^2)	0.320	0.327	0.332	0.335	0.332	0.354	0.936	0.355	0.332

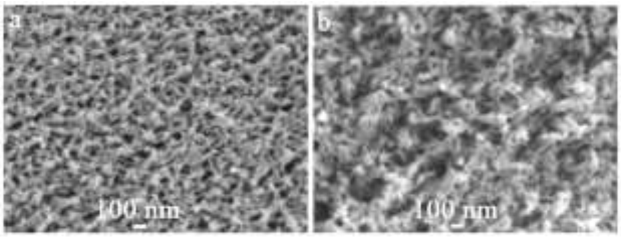


Fig. S4 The cross-section morphology of porous membranes after being treated (a) M9; (b) M10.

[1] Z. Yuan, Y. Duan, H. Zhang, X. Li, H. Zhang, I. Vankelecom, *Energy & Environmental Science*, 2016, **9**, 441.