

## Supplementary information

### A Venus-flytrap-inspired pH-responsive porous membrane with internal crosslinking networks

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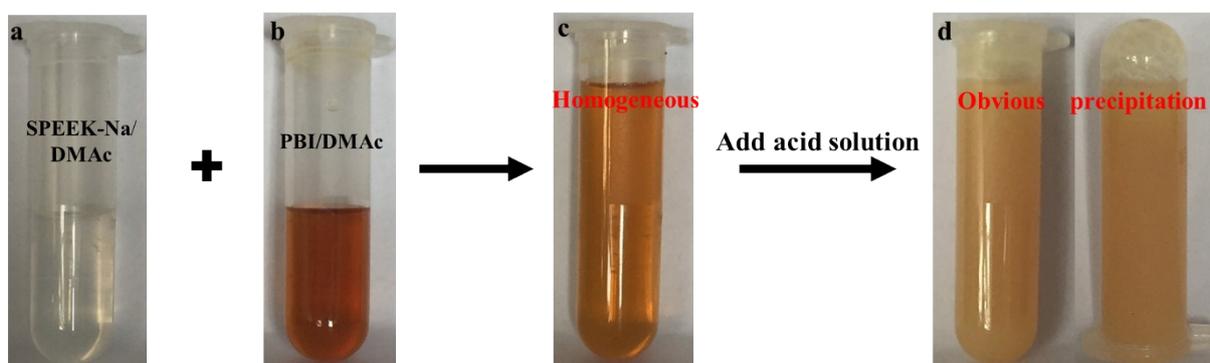
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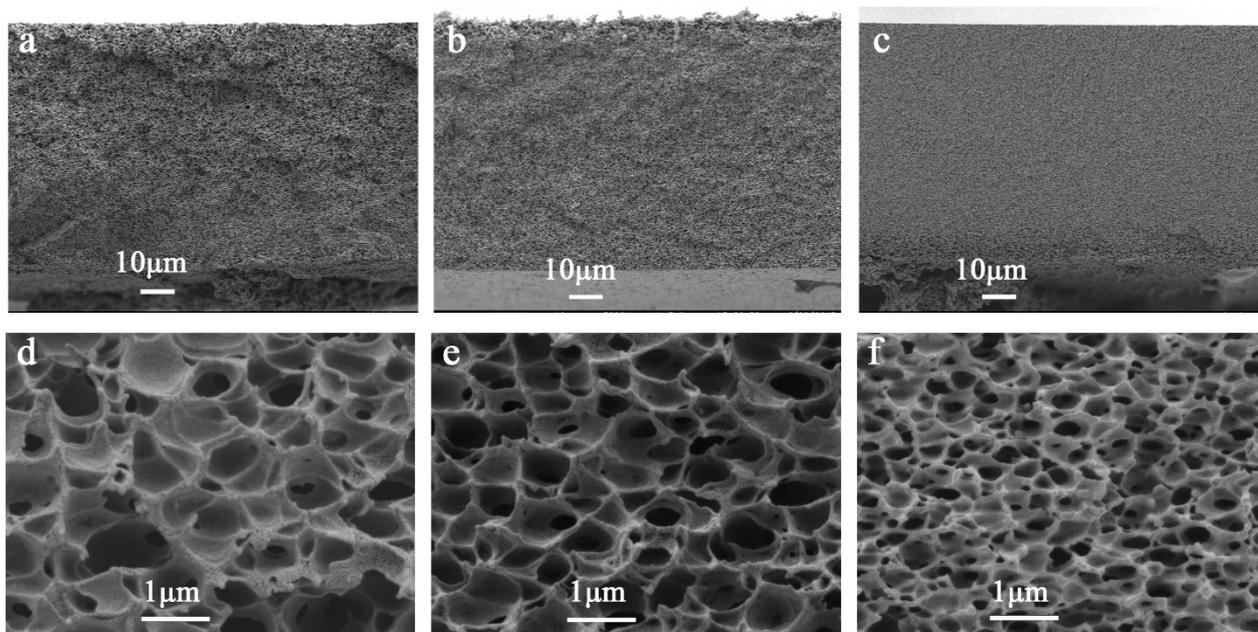
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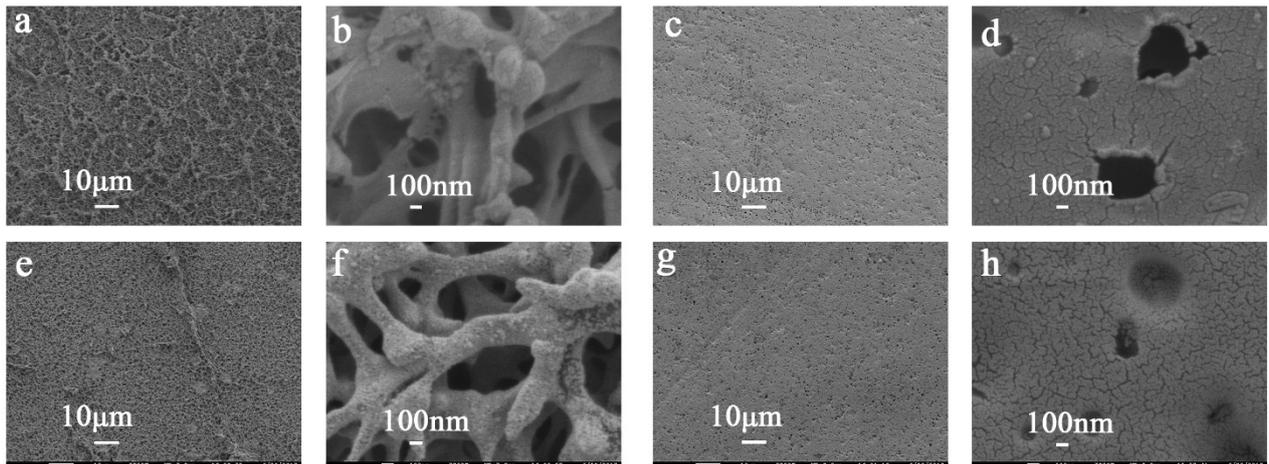
**Fig. S1.** The pictures of SPEEK-H/PBI (left) and SPEEK-Na/PBI (right) solutions in DMAc.



**Fig. S2.** Pictures to show the function of the added acid solution.



**Fig. S3.** The cross-sectional SEM images of a,d) M-5-Shut, b,e) M-10-Shut and c,f) M-15-Shut.



**Fig. S4.** The surface SEM images of a-d) M-5-Open and e-h) M-5-Shut. a,e) surface and b, f) magnified surface images upon vapor side of M-5-Open and M-5-Shut; c,g) surface and d,h) magnified surface images upon glass side of M-5-Open and M-5-Shut.

**Table S1.** The physicochemical properties of M-X-Shut (X=5, 10, 15) membranes.

Code	SPEEK-Na/ (SPEEK-Na+ PBI) (%)	Thickness ( $\mu\text{m}$ )	Porosity (%)	Water uptake (%)
M-5-Shut	5	75 $\pm$ 5	60.16	151.09
M-10-Shut	10	75 $\pm$ 5	60.19	171.59
M-15-Shut	15	75 $\pm$ 5	64.96	182.15

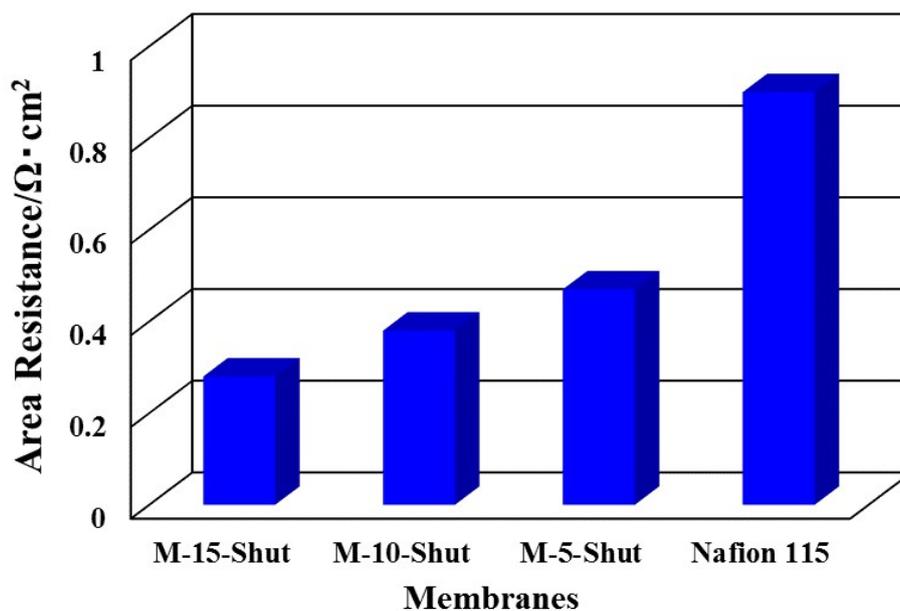


Fig. S5. Area resistance of the prepared M-X-Shut (X=5, 10, 15) and Nafion 115.

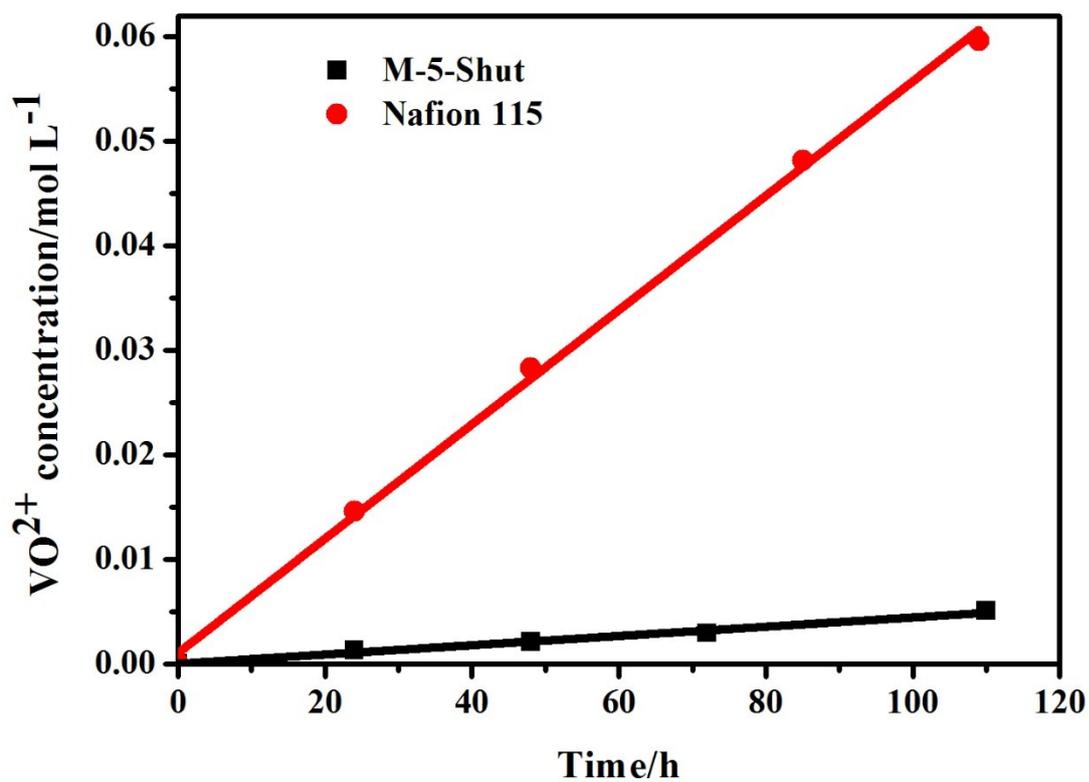
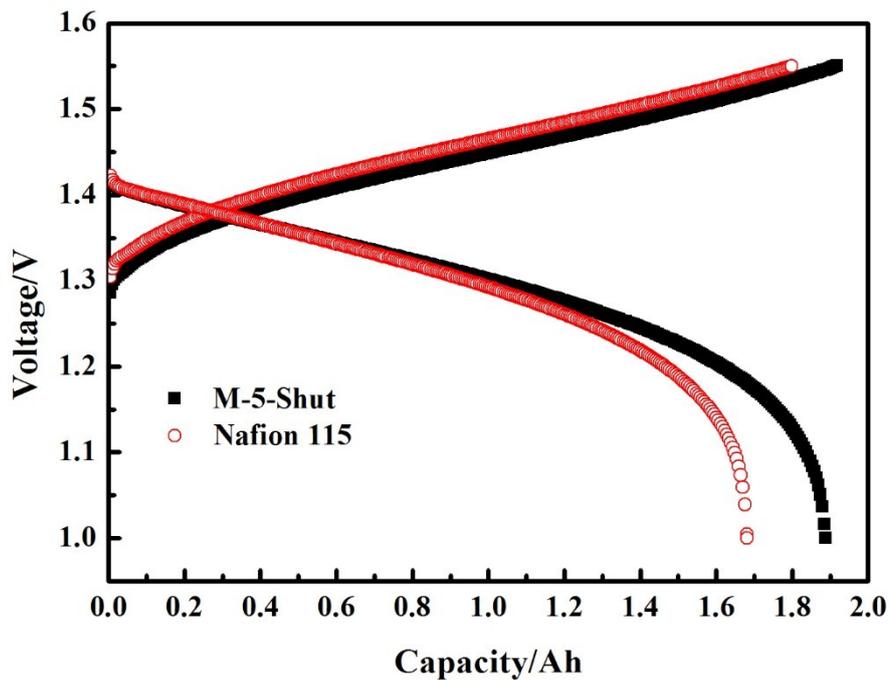
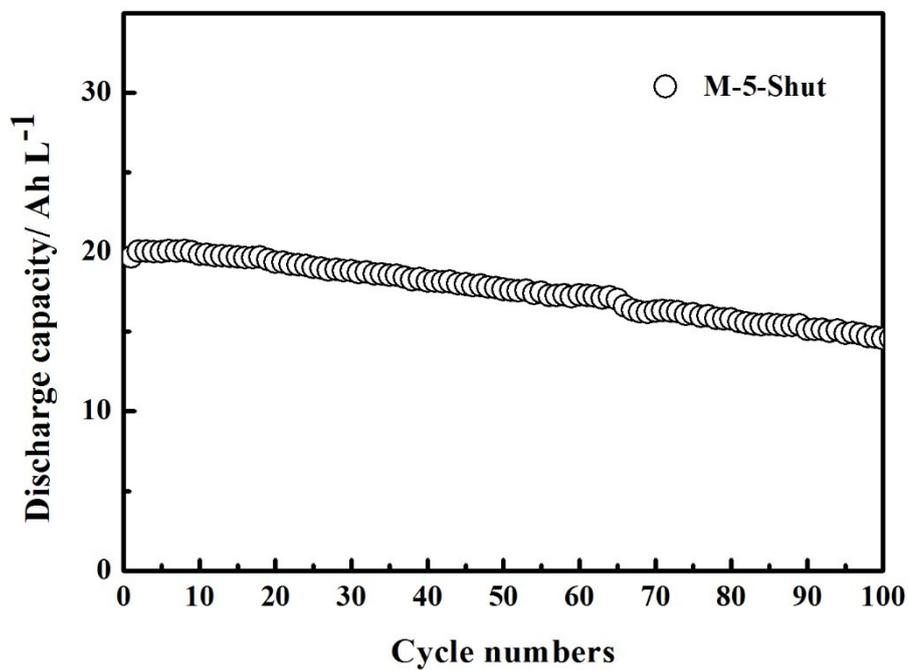


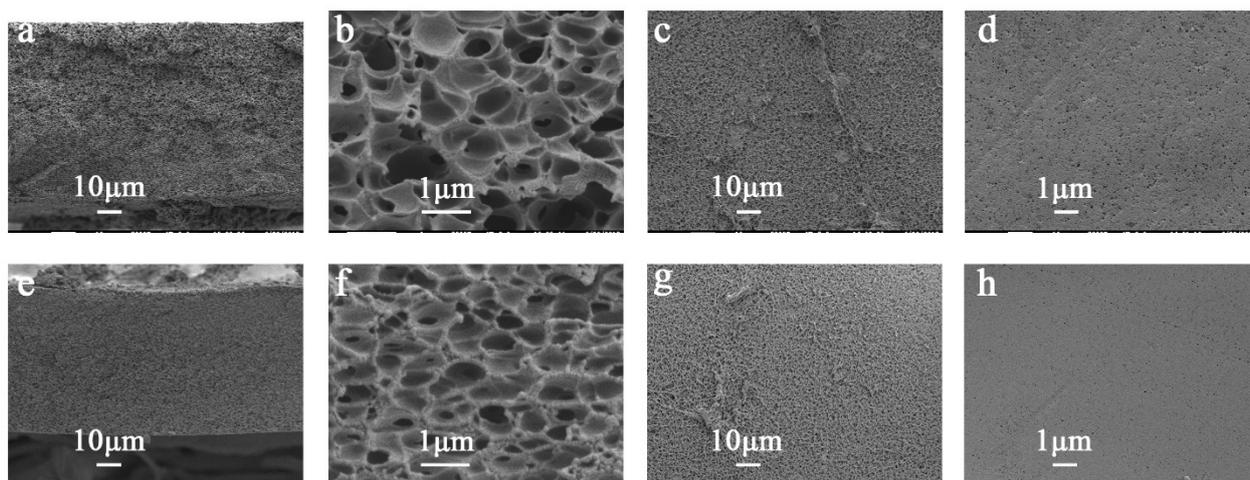
Fig. S6. Vanadium ion permeability of M-5-Shut and Nafion 115.



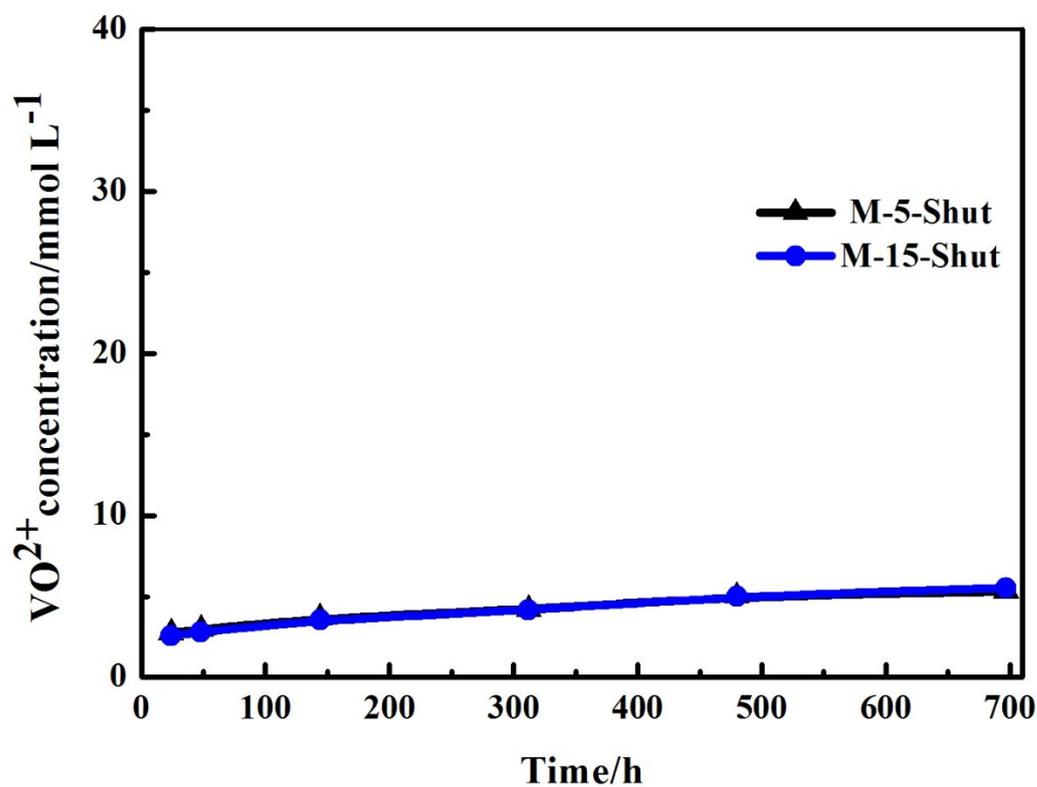
**Fig. S7.** The charge-discharge curves (the first cycle) of VFB with M-5-Shut and Nafion 115 membrane at  $80 \text{ mA cm}^{-2}$ .



**Fig. S8.** Discharge capacity retention of M-5-Shut at  $140 \text{ mA cm}^{-2}$  in a VFB.



**Fig. S9.** The cross-sectional and surface SEM images of M-5-Shut a-d) before and e-h) after 10000 cycles. a,e) Cross-section and b,f) magnified cross-section images of before and after 10000 cycles; c,g) surface images upon vapor side of before and after 10000 cycles; d,h) surface images upon glass side of before and after 10000 cycles.



**Fig. S10.** The change of  $\text{VO}_2^+$  concentration containing M-5-Shut and M-15-Shut membranes in 0.15 M  $\text{VO}_2^+$  3 M  $\text{H}_2\text{SO}_4$  at 40°C versus time.