

## Supplementary Information

### Advanced porous membranes with ultra-high selectivity and stability for Vanadium flow battery

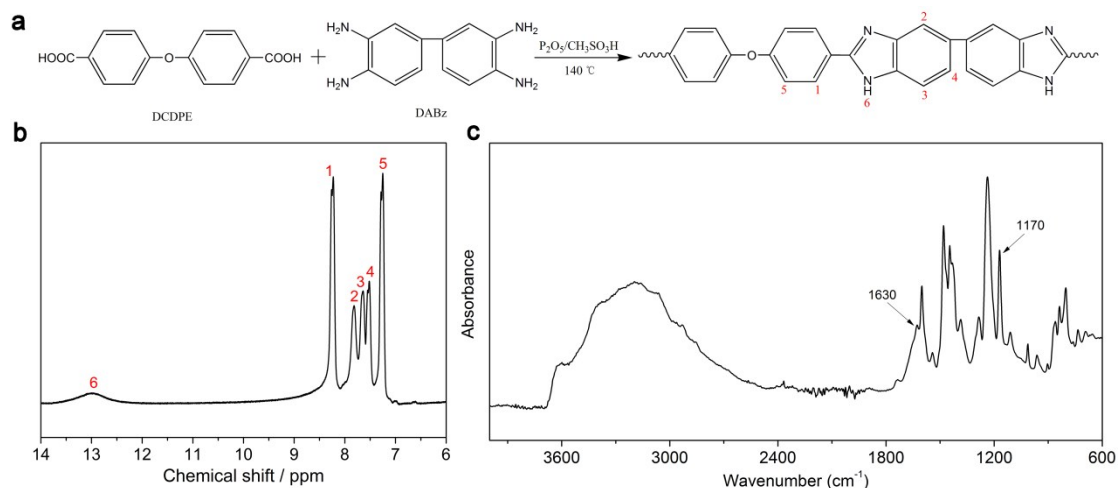
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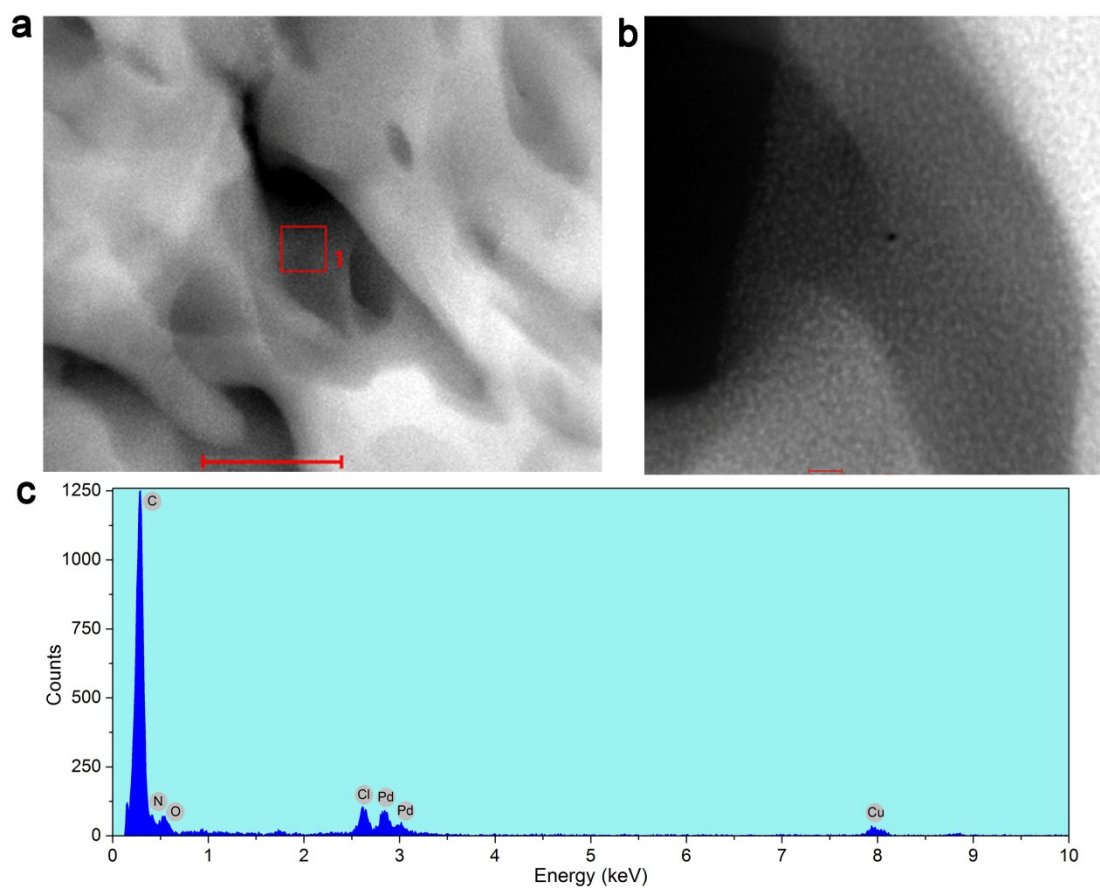
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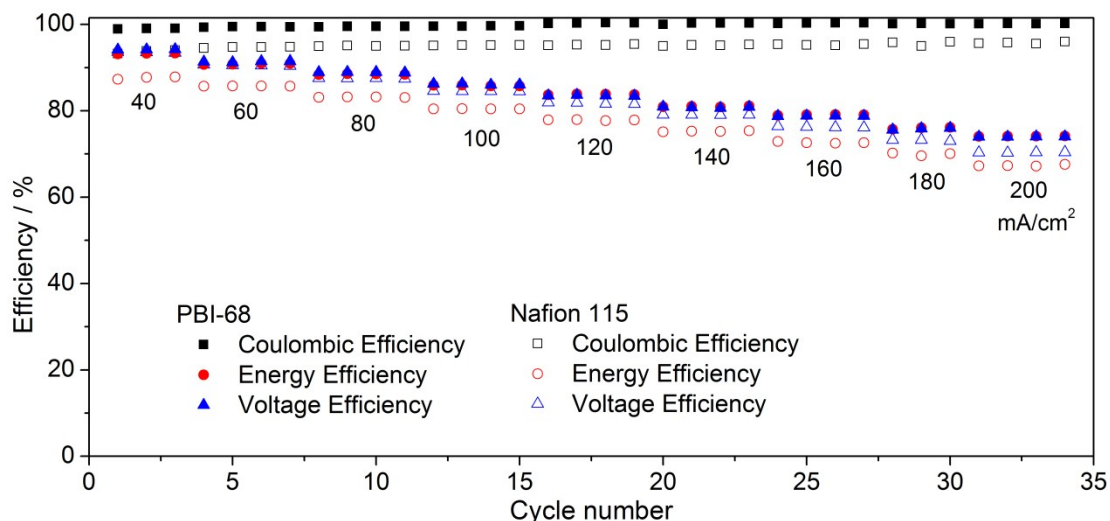
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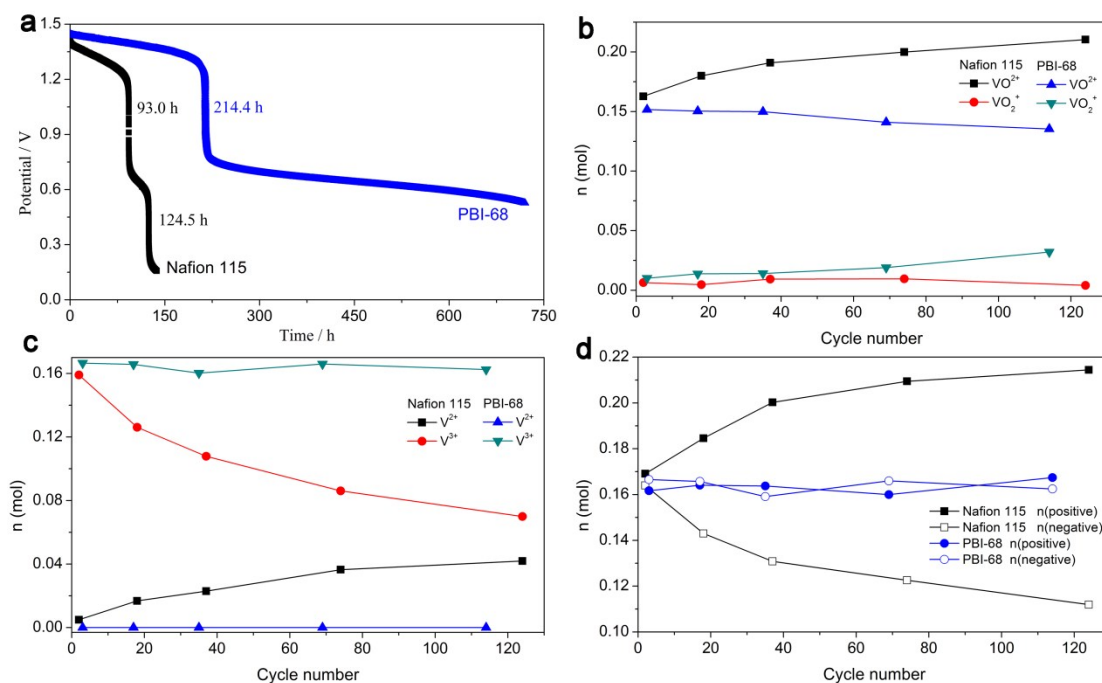
**Supplementary Fig. S1** Polybenzimidazole (PBI) polymer synthesis and characterization. a, the synthesis of PBI. b, the  $^1\text{H}$  NMR spectra of PBI. c, the FTIR spectra of PBI.



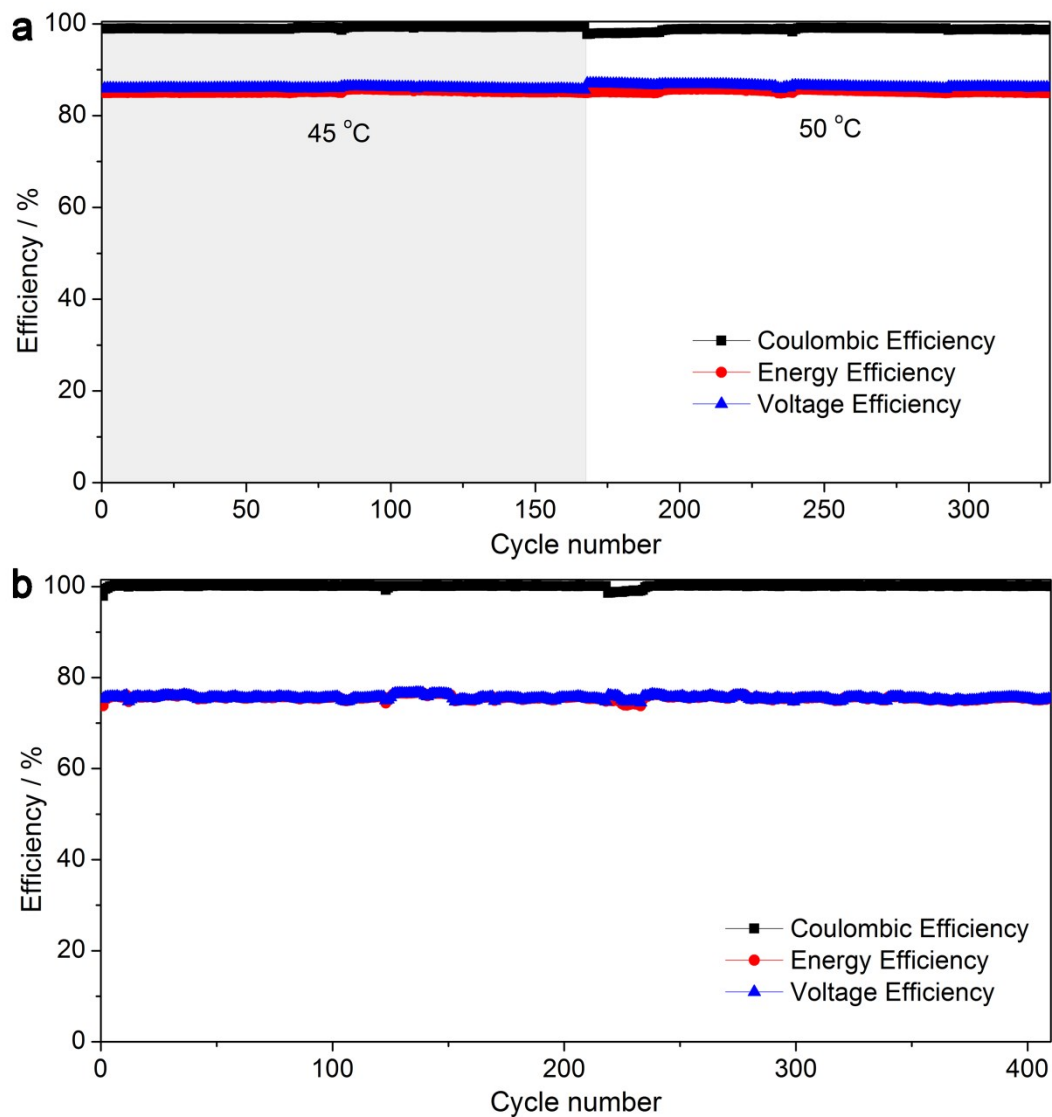
**Supplementary Fig. S2** The morphology of PBI-68 and the distribution of positively charged nitrogen in it. a, HR-STEM image of PBI-68; scale bar, 200 nm. b, magnified HR-STEM image of PBI-68; scale bar, 10 nm. c, Corresponding EDS spectra of the marked area in panel a.



**Supplementary Fig. S3** The cycling performance of a vanadium flow battery using PBI-68 and Nafion 115 with current densities ranging from 40 to 200 mA/cm<sup>2</sup>.



**Supplementary Fig. S4** Vanadium transfer behavior of prepared PBI porous membranes and Nafion 115 membrane. a, Open circuit voltage of the VFB assembled with PBI-68 and Nafion 115 membranes. b, Change of VO<sup>2+</sup> and VO<sub>2</sub><sup>+</sup> in the positive half cells when employing PBI-68 or Nafion 115 as a membrane during the cycling test. c, Change of V<sup>2+</sup> and V<sup>3+</sup> in the negative half cells when employing PBI-68 or Nafion 115 as a membrane during the cycling test. d, Molar quantity of total vanadium ions in the positive and negative half cells when employing PBI-68 or Nafion 115 as a membrane during the cycling test.



**Supplementary Fig. S5** Electrochemical stability of PBI-68 porous membrane. a, outstanding cycling stability of PBI-68 at high temperatures (45 °C and 50 °C; current density, 120 mA/cm<sup>2</sup>). b, cycling performance of PBI-68 at high current density (180 mA/cm<sup>2</sup>).