

## Hydrolysis of ionic clusters to induce interconnective sieving pores in ion-conductive membranes for vanadium flow batteries

Bo Pang<sup>1</sup>, Zihao Fan<sup>1</sup>, Wanting Chen<sup>1</sup>, Xiaoming Yan<sup>1</sup>, Ruohan Du<sup>1</sup>, Xiaozhou Wang<sup>1</sup>, Xuemei

Wu<sup>1\*</sup>, Fujun Cui<sup>2</sup>, Minggang Guo<sup>2</sup>, Gaohong He<sup>1,2\*</sup>

1 State Key Laboratory of Fine Chemicals, Research and Development Center of Membrane Science and Technology, School of Chemical Engineering, Dalian University of Technology, Dalian, 116024, China.

2 Panjin Institute of Industrial Technology, Liaoning Key Laboratory of Chemical Additive Synthesis and Separation, Dalian University of Technology, Panjin 124221, Liaoning, China

\*Xuemei Wu: xuemeiw@dlut.edu.cn, hgaohong@dlut.edu.cn

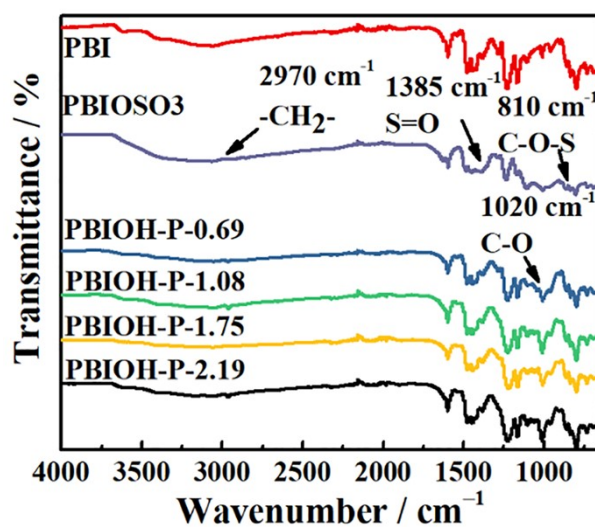
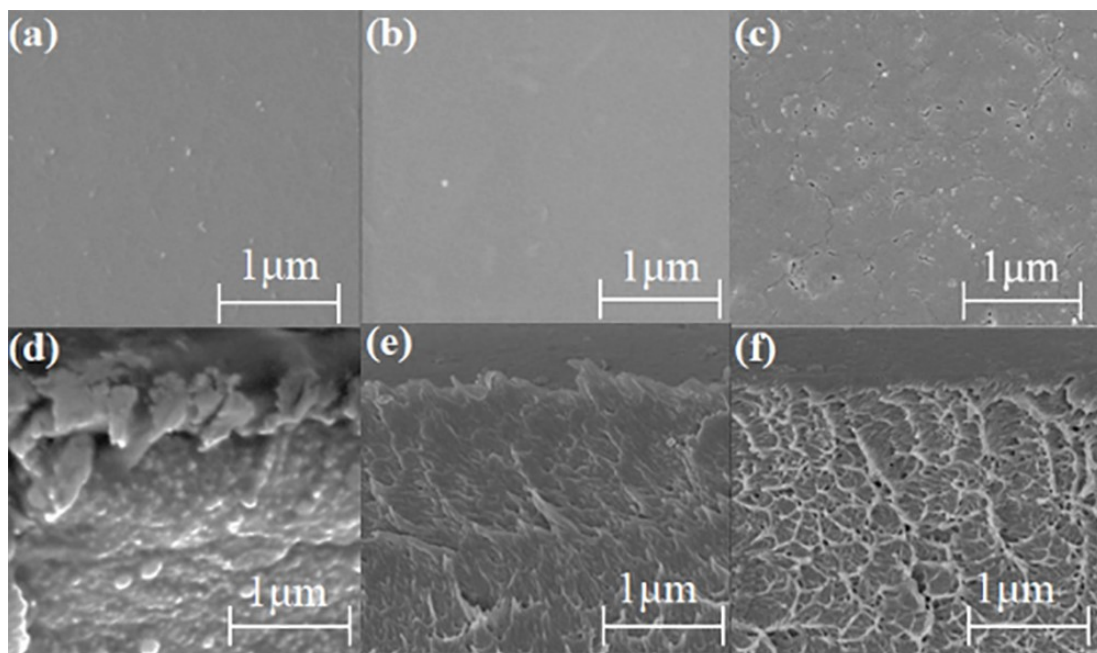
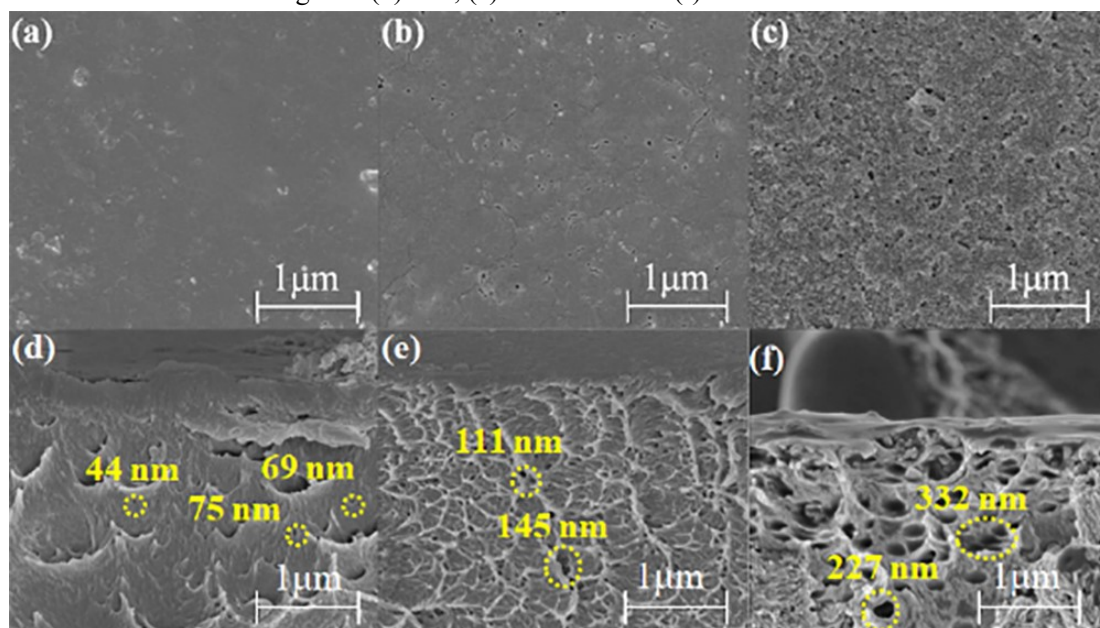


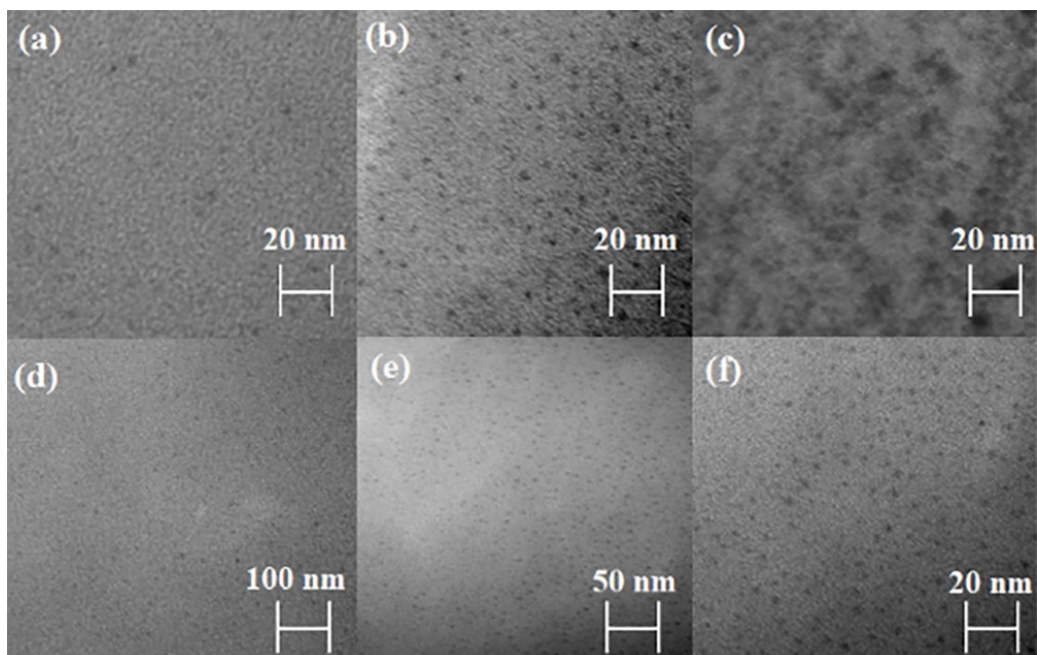
Fig. S1. The FTIR patterns of PBI, PBIOSO3 and PBIOSH-P membranes.



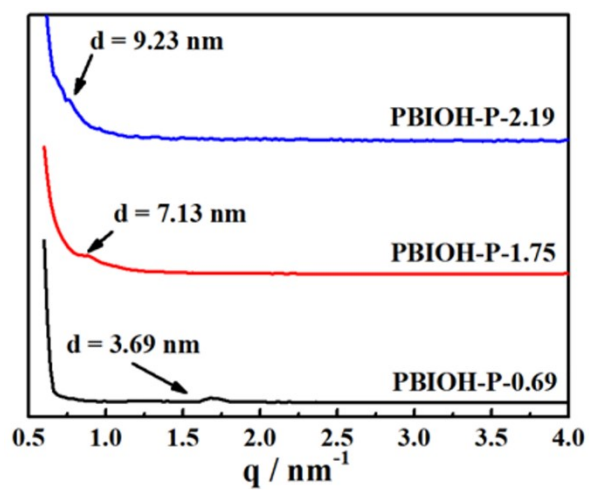
**Fig. S2.** The SEM surface images of (a) PBI, (b) PBIOSO3 and (c) PBIOH-P-1.75 membranes; cross-section images of (d) PBI, (e) PBIOSO3 and (f) PBIOH-P-1.75 membranes.



**Fig. S3.** The SEM surface images of (a) PBIOH-P-0.69, (b) PBIOH-P-1.75 and (c) PBIOH-P-2.19 membranes; cross-section images of (d) PBIOH-P-0.69, (e) PBIOH-P-1.75 and (f) PBIOH-P-2.19 membranes



**Fig. S4.** The TEM ions clusters images of (a) OPBIO3-0.69, (b) OPBIO3-1.75 and (c) OPBIO3-2.19 membranes; TEM ions clusters images of OPBIO3-1.75 membrane with 100 nm, 50 nm and 20 nm.



**Fig. S5.** SAXS curves of the PBIOH-P membranes.

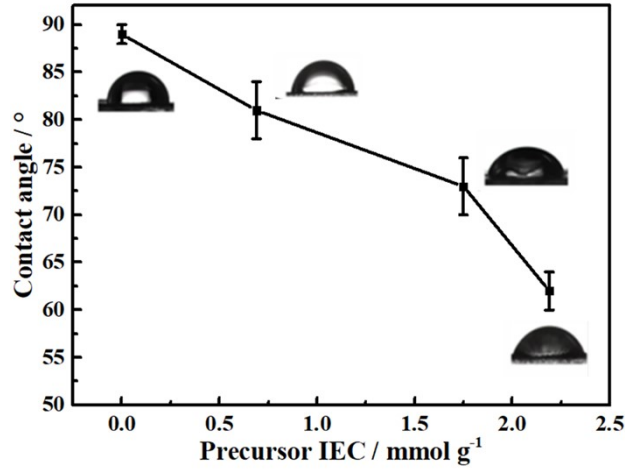


Fig. S6. The contact angle of the PBI and PBIOH-P membranes.

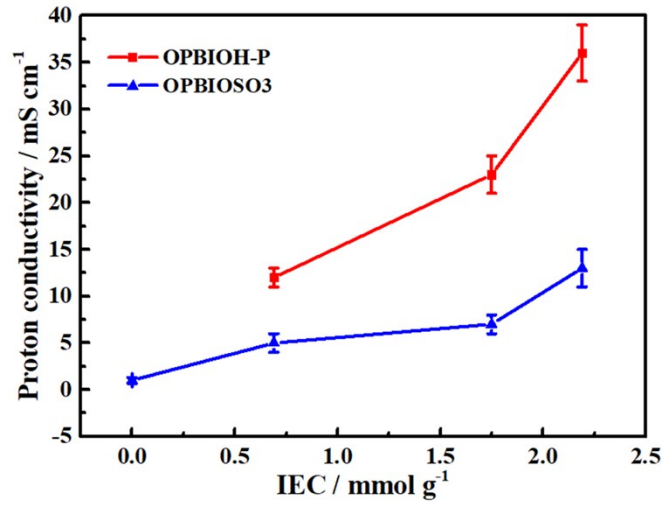


Fig. S7. The proton conductivity of the PBIOH-P and PBIO3 membranes.

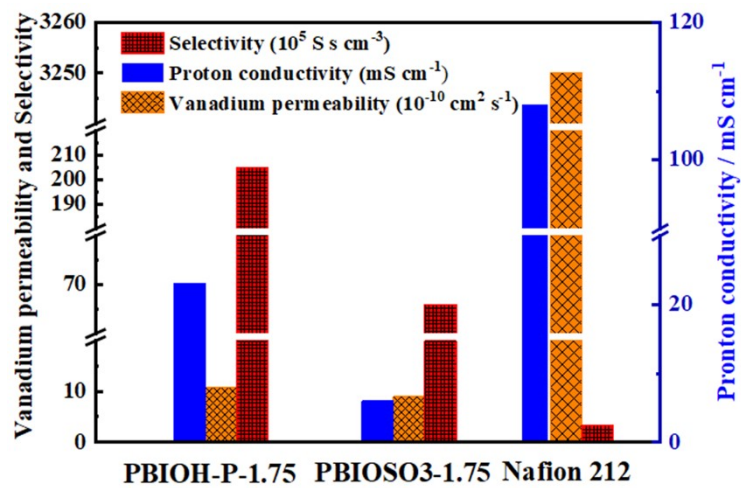


Fig. S8. The Selectivity, proton conductivity and vanadium permeability of the PBIOH-P, PBIO3-1.75 and Nafion 212 membranes. (Selectivity is denoted as proton conductivity divided by vanadium permeability)

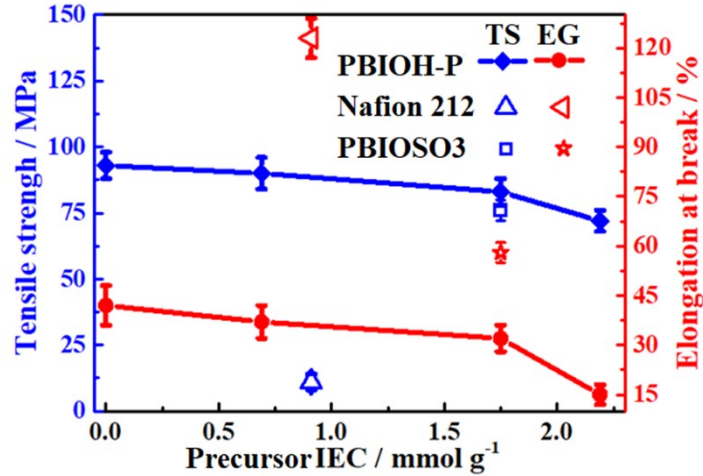


Fig. S9. Tensile strength and elongation at break of the PBIOH-P and PBIOSO3 membranes with precursor IEC of 1.75, and Nafion 212 membrane.

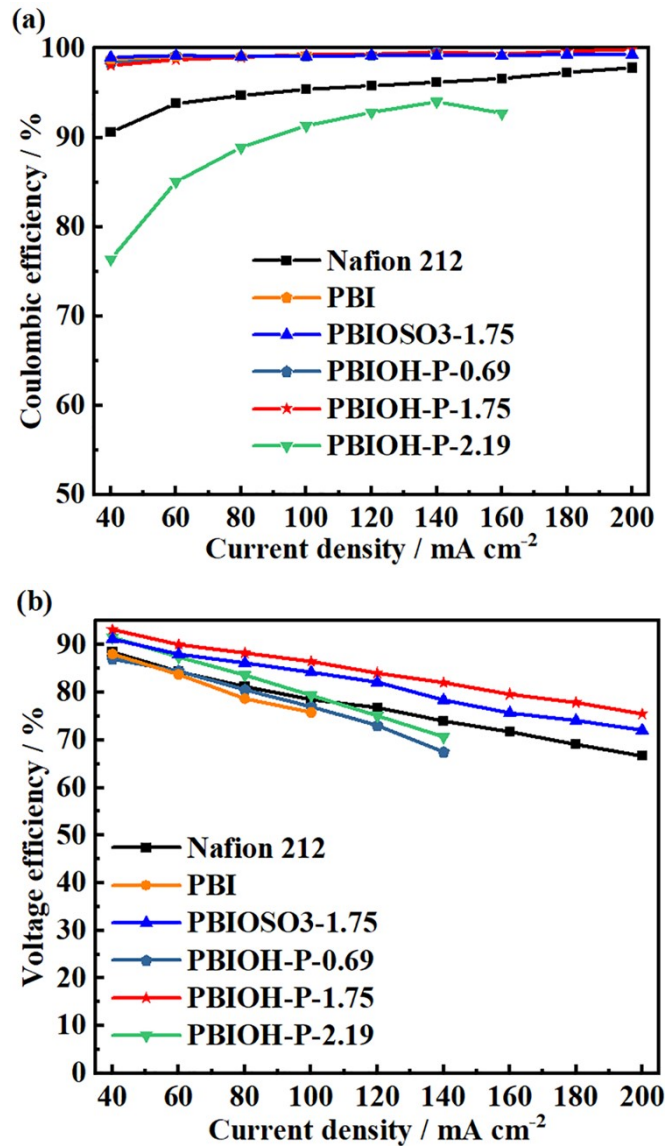
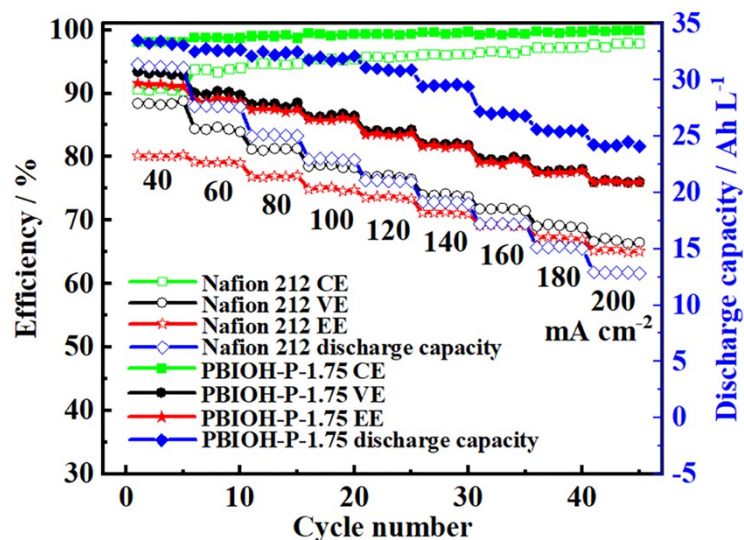
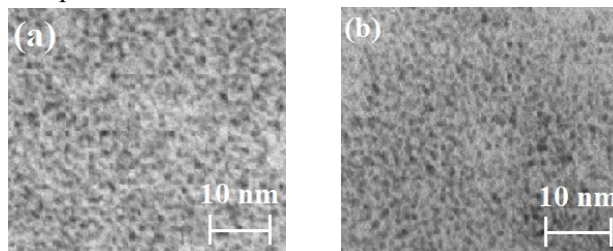


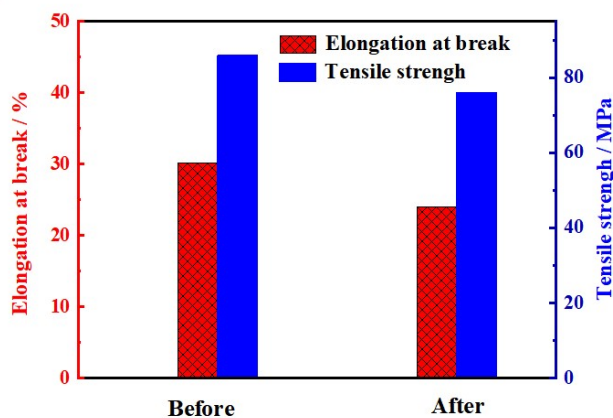
Fig. S10. Coulombic efficiency and voltage efficiency of the PBIOH-P, Nafion 212, PBI and PBIOSO3-1.75 based cells.



**Fig. S11.** The rate performance of the PBI0H-P-1.75 and Nafion 212 based VFBS.



**Fig. S12.** The TEM images of pore morphology (a) before and (b) after VFB cycling test



**Fig. S13.** The mechanical properties before and after VFB cycling test

*Table S1* The comparison of  $H^+/V^{n+}$  ion selectivity with recently reported porous membranes, composite membranes, and anion exchange membranes

Membranes	Category	$H^+/V^{n+}$ Selectivity	Conductivity	Reference
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		$\times 10^5 S \text{ min cm}^{-3}$	$mS \text{ cm}^{-1}$	
<i>This work</i>	<i>Porous membranes</i>	3.42	70	
<i>SPEEK/SPAES-15</i>	<i>Composite membrane</i>	0.29	29.3	1
<i>SPI/2% PMPP</i>	<i>Composite membrane</i>	1.42	116	2
<i>SPEEK/Hi m-pS-3</i>	<i>Composite membrane</i>	0.40	31.54	3
<i>S/801&amp;808-4</i>	<i>Composite membrane</i>	2.2	78	4
<i>SPEEK/SP PTA-25</i>	<i>Composite membrane</i>	0.23	29.08	5
<i>QCPPAE</i>	<i>Anion exchange membrane</i>	0.96	21	6
<i>CAPSU</i>	<i>Anion exchange membrane</i>	2.08	15	7
<i>PyPPSU</i>	<i>Anion exchange membrane</i>	2.44	8.8	8
<i>PVDF/SiO<sub>2</sub>-SO<sub>3</sub>H-42</i>	<i>Porous membranes</i>	1.25	14	9
<i>2# ABPBI</i>	<i>Porous</i>	0.79	30	10

Reference:

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