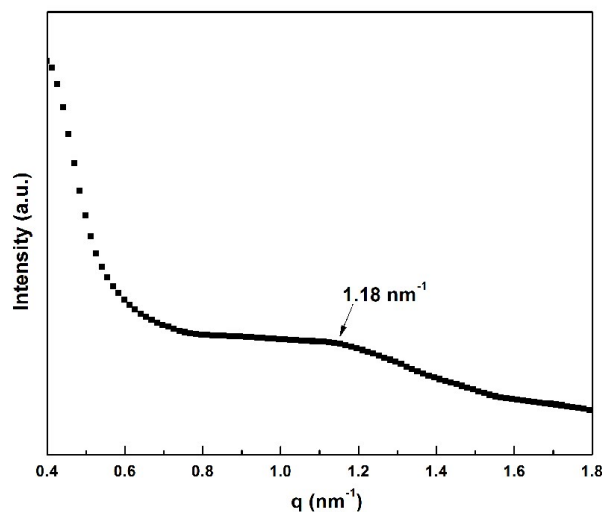


## Supporting Information

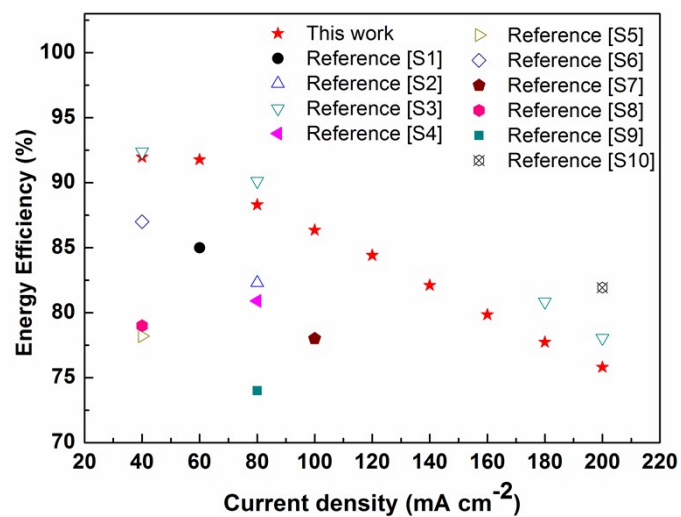
### **Polybenzimidazole membranes with nanophase-separated structure induced by non-ionic hydrophilic side chain for vanadium flow batteries**

Sangshan Peng,<sup>a</sup> Xuemei Wu,<sup>a</sup> Xiaoming Yan,<sup>a,b\*</sup> Li Gao,<sup>a,b</sup> Yangzhi Zhu,<sup>c</sup>  
Daishuang Zhang,<sup>a</sup> Jie Li,<sup>a</sup> Qian Wang,<sup>a</sup> Gaohong He<sup>a,b\*</sup>

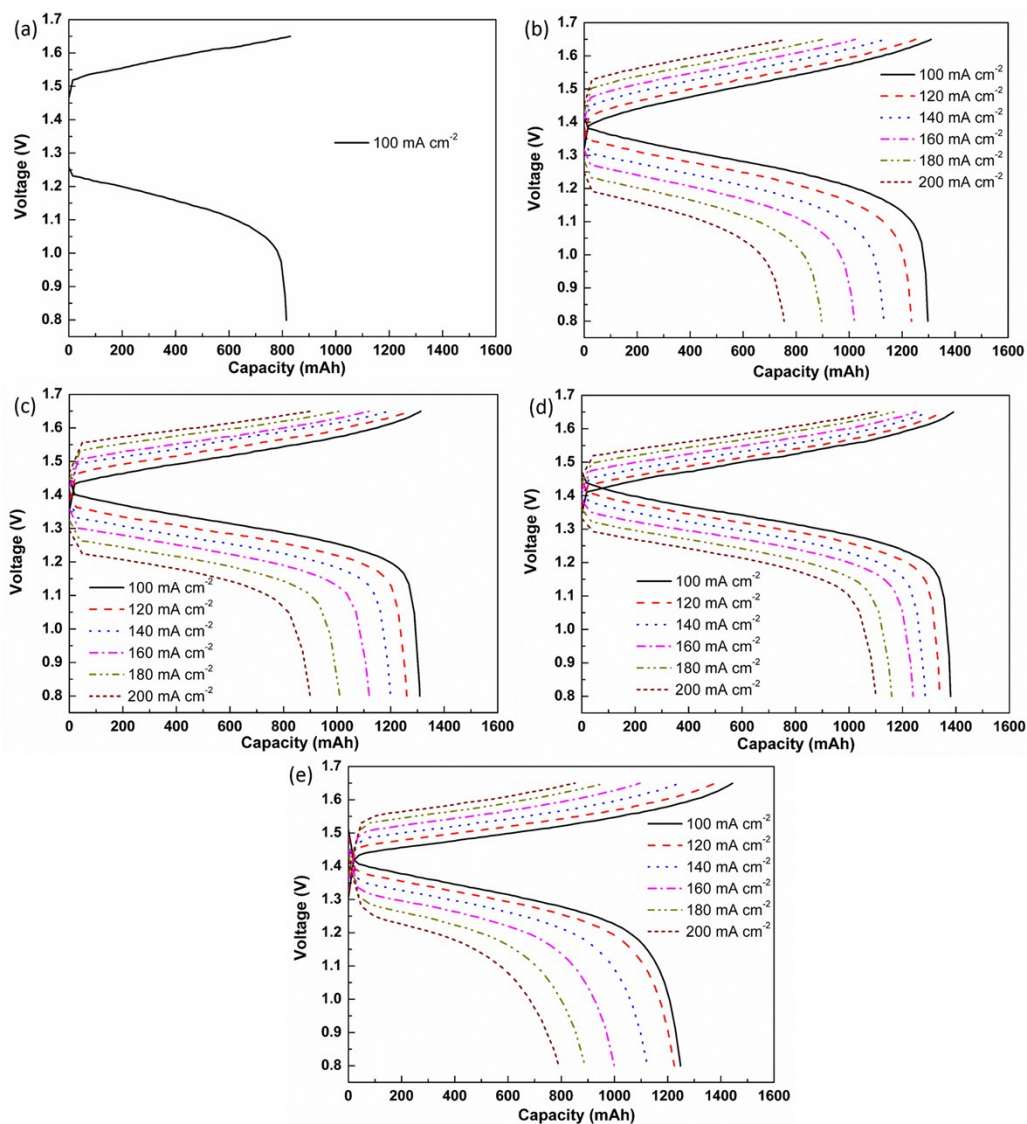
- a. State Key Laboratory of Fine Chemicals, R&D Center of Membrane Science and Technology, School of Chemical Engineering, Dalian University of Technology, Dalian, 116023, China. E-mail: yanxiaoming@dlut.edu.cn; hgaohong@dlut.edu.cn
- b. School of Petroleum and Chemical Engineering, Dalian University of Technology, Panjin, 124221, China
- c. Department of Chemical and Environmental Engineering, and Materials Science Engineering program, Bourns College of Engineering, University of California, Riverside, California 92521, United States



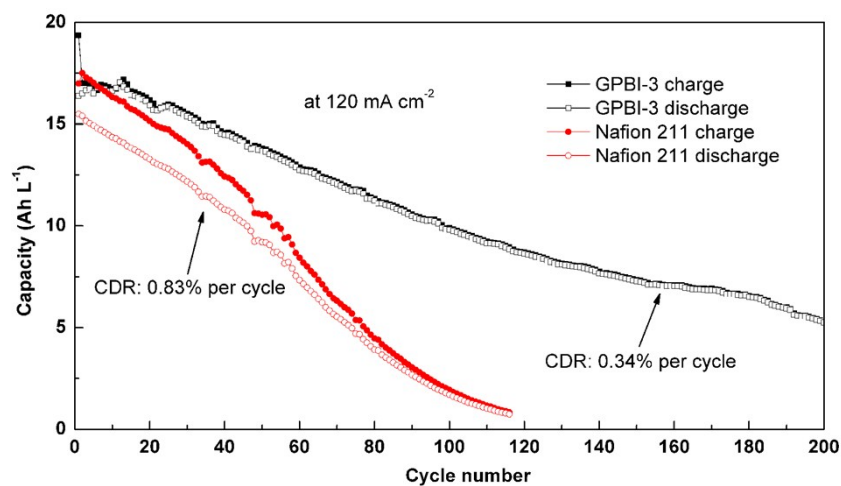
**Fig. S1.** SAXS pattern of Nafion membrane.



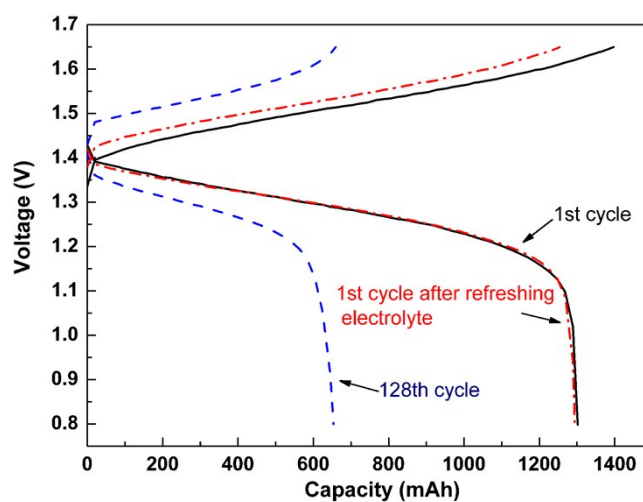
**Fig. S2.** Representative EE of ever reported PBI-based VFBS and this work (solid: dense membranes; hollow: porous membranes).<sup>S1-S10</sup>



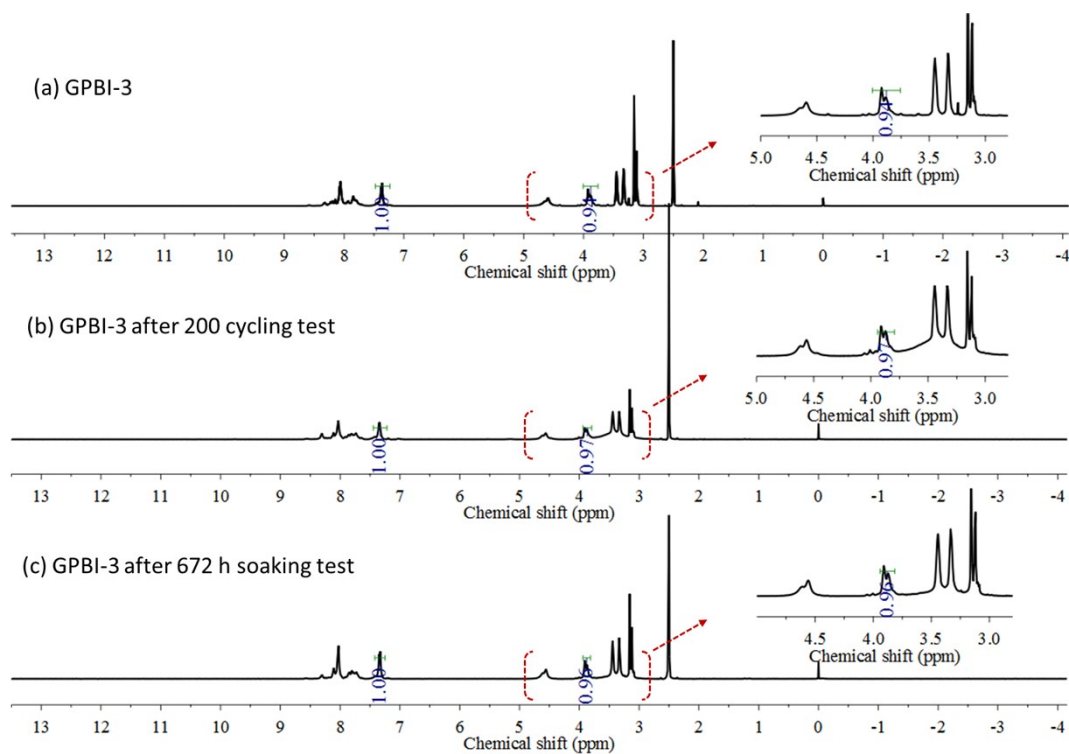
**Fig. S3.** Charge/discharge curves of VFB with (a) PBI, (b) GPBI-1, (c) GPBI-2, (d) GPBI-3 and (e) Nafion 211 under different current densities.



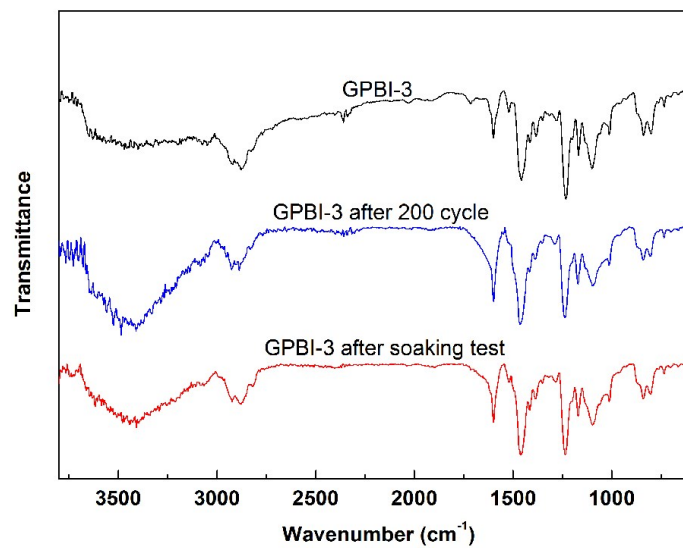
**Fig. S4.** Capacity decay in cycling test (CDR refers to capacity decay rate of discharge capacity).



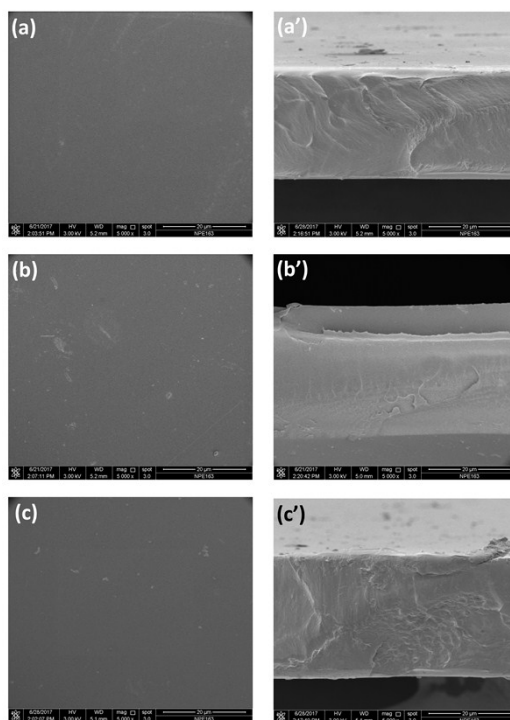
**Fig. S5.** Charge/discharge curves of VFB assembled with GPBI-3 in cycling test with refreshing electrolyte.



**Fig. S6.**  $^1\text{H}$  NMR spectra of GPBI-3 membranes.



**Fig. S7.** FTIR spectra of GPBI-3 membranes.



**Fig. S8.** SEM images of GPBI-3 membranes: pristine (a: surface, a': cross section), after 200 cycling test (b: surface, b': cross section), and after 672 h soaking test (c: surface, c': cross section).

#### References for the SI:

- S1. Z. Xia, L. Ying, J. Fang, Y.-Y. Du, W.-M. Zhang, X. Guo and J. Yin, *J Membr. Sci.*, 2017, **525**, 229-239.
- S2. S. Peng, X. Yan, X. Wu, D. Zhang, Y. Luo, L. Su and G. He, *RSC Adv.*, 2017, **7**, 1852-1862.
- S3. Z. Yuan, Y. Duan, H. Zhang, X. Li, H. Zhang and I. Vankelecom, *Energy Environ. Sci.*, 2016, **9**, 441-447.
- S4. S. Peng, X. Yan, D. Zhang, X. Wu, Y. Luo and G. He, *RSC Adv.*, 2016, **6**, 23479-23488.
- S5. S. Maurya, S.-H. Shin, J.-Y. Lee, Y. Kim and S.-H. Moon, *RSC Adv.*, 2016, **6**, 5198-5204.
- S6. T. Luo, O. David, Y. Gendel and M. Wessling, *J. Power Sources*, 2016, **312**, 45-54.
- S7. J.-K. Jang, T.-H. Kim, S. J. Yoon, J. Y. Lee, J.-C. Lee and Y. T. Hong, *J. Mater. Chem. A*, 2016, **4**, 14342-14355.
- S8. X. L. Zhou, T. S. Zhao, L. An, L. Wei and C. Zhang, *Electrochim. Acta*, 2015, **153**, 492-498.
- S9. G. Liu, Z. Xia, S. Jin, X. Guo and J. Fang, *High Perform. Polym.*, 2017, DOI: 10.1177/0954008317711235, 095400831771123.
- S10. W. Lu, Z. Yuan, Y. Zhao, L. Qiao, H. Zhang and X. Li, *Energy Storage Materials*, 2018, **10**, 40-47.