

Electronic Supplementary Information

Single-ion dominantly conducting polyborates towards high performance electrolytes in lithium batteries

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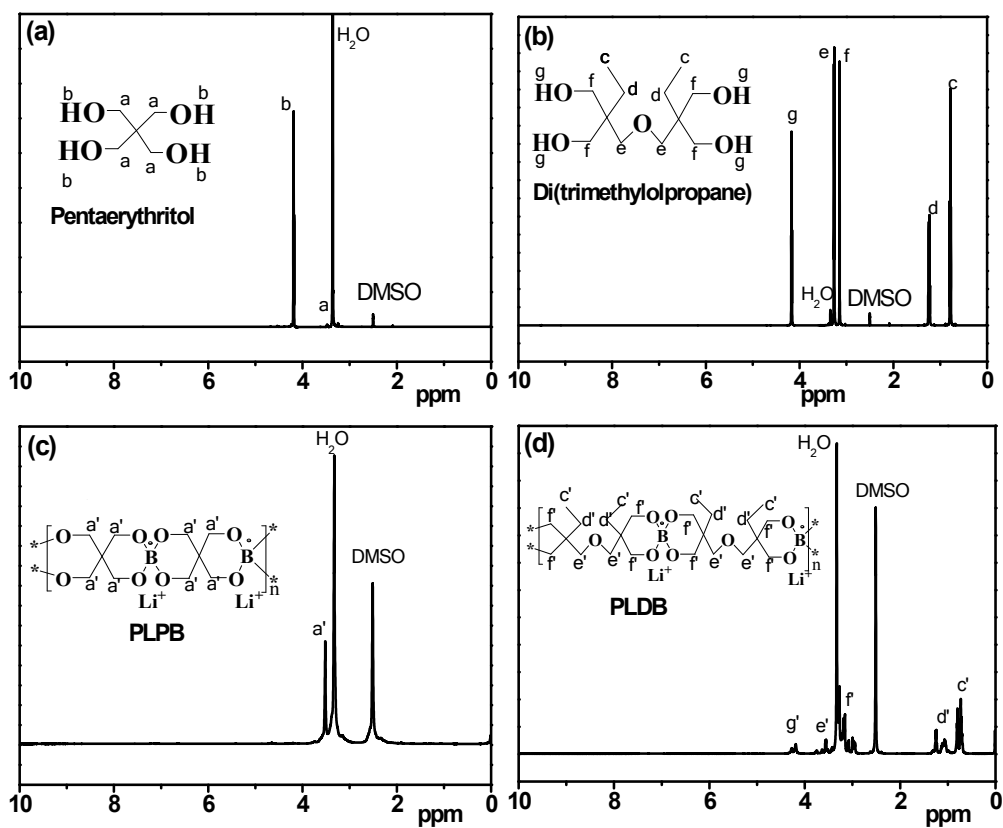


Fig. S1 ^1H NMR spectra of pentaerythritol(a), di(trimethylolpropane) (b), PLPB(c) and PLDB (d) in DMSO-d_6 .

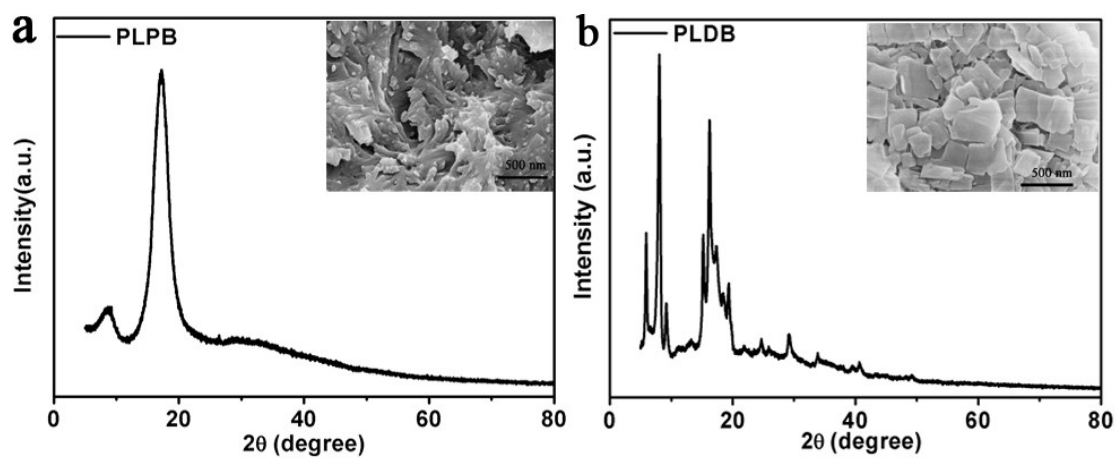


Fig. S2 XRD patterns and typical SEM images of PLPB(a) and PLDB (b).

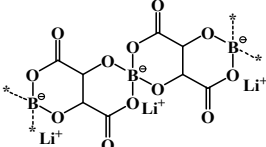
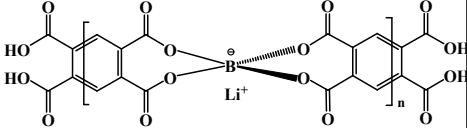
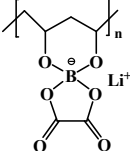
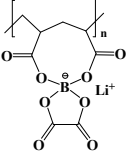
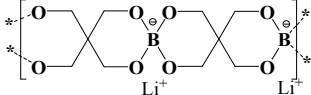
Polymeric lithium salts	Chemical structure	Molecular weight per repeating unit (g mol ⁻¹)	References
PLTB		164	Ref. 1
PPAB		268	Ref. 2
LiPVAOB		>178	Ref. 3
LiPAAOB		>234	Ref. 4
PLPB		150	

Table. S1 The molecular mass per unit of the polymeric lithium salt synthesized in recent years.

References

- 1 X. Wang, Z. Liu, C. Zhang, Q. Kong, J. Yao, P. Han, W. Jiang, H. Xu and G. Cui, *Electrochim. Acta*, 2013, **92**, 132-138.
- 2 Y. Zhang, G. Xu, Y. Sun, B. Han, T. B. W. T, Z. Chen, R. Rohan and H. Cheng, *RSC Adv.*, 2013, **3**, 14934-14937.
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- 4 Y. S. Zhu, X. W. Gao, X. J. Wang, Y. Y. Hou, L. L. Liu and Y. P. Wu, *Electrochem. Commun.*, 2012, **22**, 29-32.

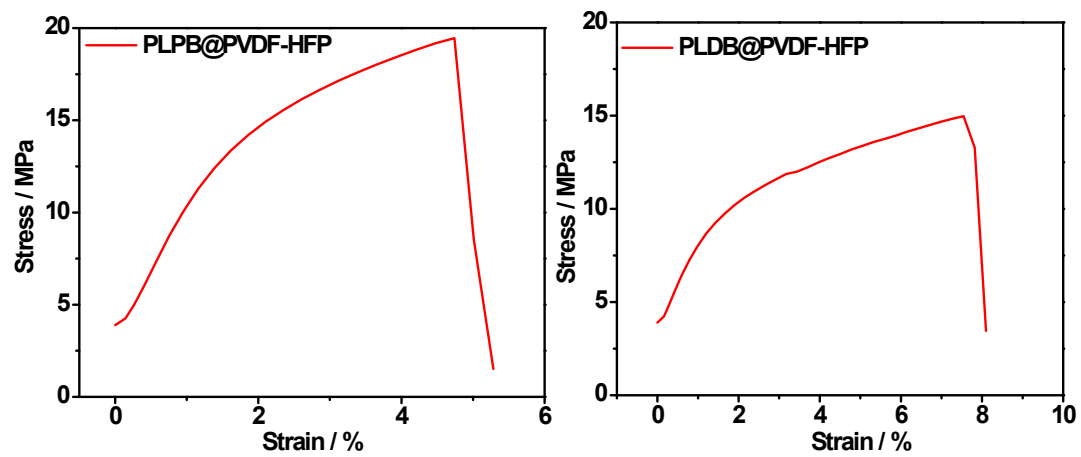


Fig. S3 Stress-strain curves for PLPB@PVDF-HFP and PLDB@PVDF-HFP, respectively.

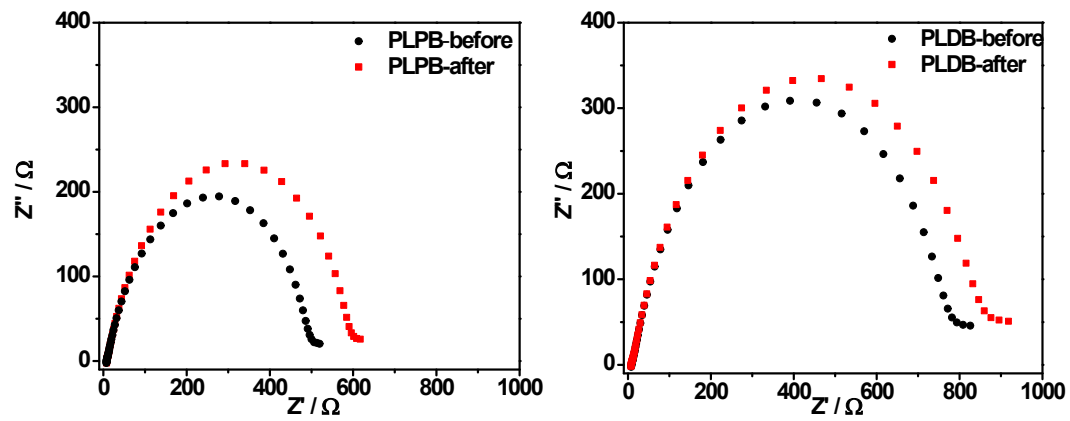


Fig. S4 AC impedance of Li/EC/DMC-PLPB@PVDF-HFP/Li cell (left) and Li/EC/DMC-PLDB@PVDF-HFP/Li cell (right) before and after polarized with a potential difference of 10 mV at room temperature.

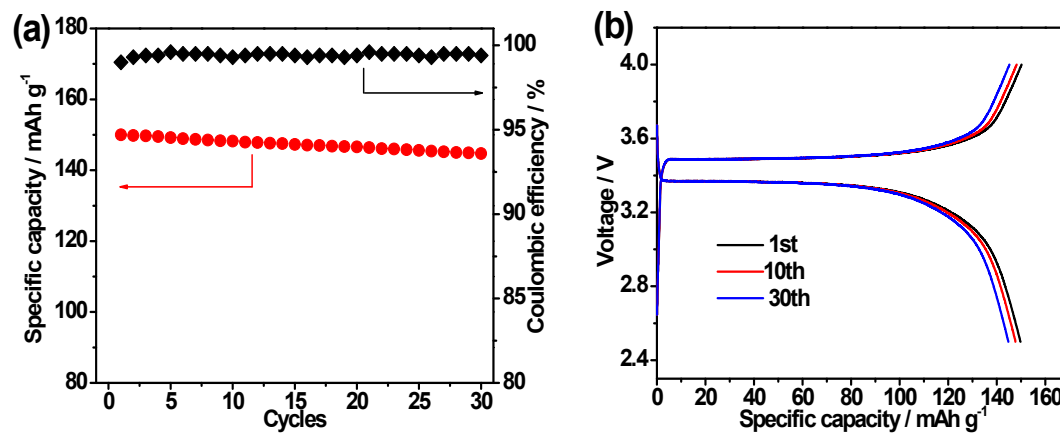


Fig. S5 Cycling performance of the Li/ PC swollen PLPB@PVDF-HFP /LiFePO₄ batteries at 120°C (a), charge and discharge profiles of the Li/ PC swollen PLPB@PVDF-HFP /LiFePO₄ batteries at 120°C (b).

The Li//EC/DMC-PLDB@PVDF-HFP//LiNi_{0.5}Mn_{1.5}O₄ half coin cells (2032-type) were assembled by sandwiching the EC/DMC swollen PLDB@PVDF-HFP membrane between lithium metal foil and LiNi_{0.5}Mn_{1.5}O₄ electrode. The LiNi_{0.5}Mn_{1.5}O₄ electrode was composed of 80 wt. % LiNi_{0.5}Mn_{1.5}O₄, 10 wt. % PVDF and 10 wt. % carbon black. All assembly of cells was carried out in an argon-filled glove box. After cell assembly, the cells were laid down on one side for 12 h and then on the other side for another 12 h to impregnate the porous composite electrodes and their interfaces with electrolyte. The charge/discharge performance was recorded on a LAND battery test system. The galvanostatic charge/discharge behavior of Li//EC/DMC-PLDB@PVDF-HFP//LiNi_{0.5}Mn_{1.5}O₄ cells were conducted at 0.1C over the range of 3.5–5.0 V.

The original charge-discharge voltage profiles of the LiNi_{0.5}Mn_{1.5}O₄/Li batteries employing EC/DMC-PLDB@PVDF-HFP as electrolyte at room temperature was shown in Fig. S6. As depicted in Fig. S6, the EC/DMC-PLDB@PVDF-HFP based Li/LiNi_{0.5}Mn_{1.5}O₄ cells exhibited stable charge-discharge profiles from the 1st cycle to the 20th cycle. The capacity loss in the first 20 cycles was acceptable considering the low charge-discharge current of 0.1C. The coulombic efficiency was about 96%, meaning that some modifications were still needed in further research.

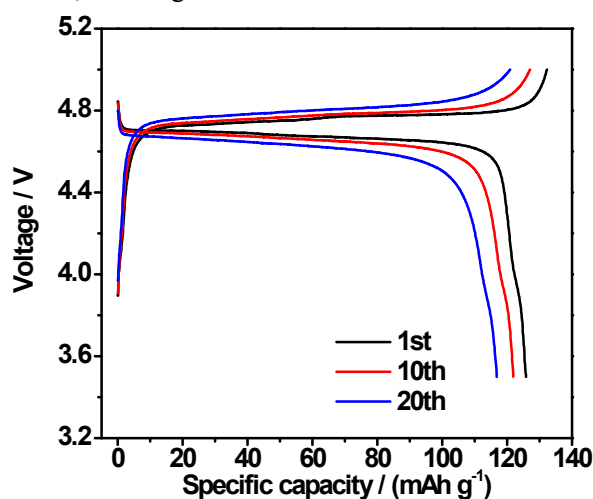


Fig. S6 Charge and discharge profiles of the Li//EC/DMC swollen PLDB@PVDF-HFP//LiNi_{0.5}Mn_{1.5}O₄ batteries at room temperature.

The electrochemical stability of PLPB and PLDB was measured in a three-electrode setup using

linear sweep voltammetry (LSV). A 200 mg sample of PLPB or PLDB along with 10 mg PVDF-HFP was dispersed in 4 mL DMSO solvent to prepare a homogeneous ink. The mass ratio of lithium salt and PVDF-HFP is as high as 20:1 to ensure that the detected electrochemical signal was mainly from the lithium salts. After that, a 5 μ L drop of ink was put onto a 0.07 cm² glassy-carbon disk electrode and dried at 60°C in a vacuum oven for 12 h to remove the solvent. The PLPB and PLDB coated glassy carbon electrode as well as the pristine glassy carbon electrode (control sample) were used as working electrode, respectively, while lithium sheets were used as counter- and reference electrodes. Herein, 1 M LiPF₆ in EC:DEC (3:7, by wt.) was used as electrolyte owing to its superior electrochemical stability⁵. The measurements were conducted with a scan rate of 1 mV s⁻¹ through a CHI660C Electrochemical Workstation (Shanghai, China) in the voltage range of 2.0V-6.0 V.

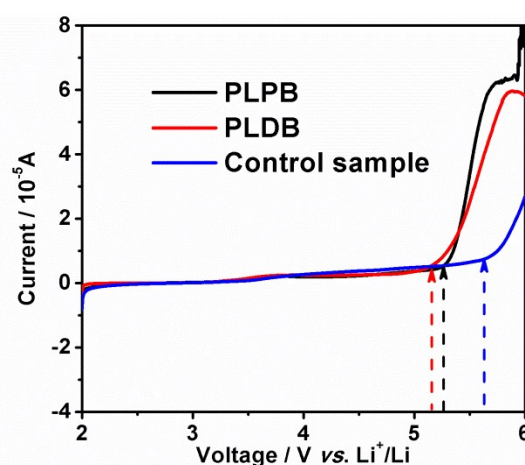


Fig. S7 Linear sweep voltammetry of PLPB, PLDB and control sample measured in a three-electrode setup at a scan rate of 1 mV s⁻¹. (electrolyte: 1 M LiPF₆ EC:DEC)

The electrochemical stability of PLPB and PLDB was measured in a three-electrode setup, where the kinetic factors might be minimized. As shown in Fig. S7, the control sample started to decompose at about 5.75 V, which is in good agreement with the electrochemical stability window of 1 M EC:DEC- LiPF₆ reported in Ref. [5]. The limiting potential for PLPB and PLDB was about 5.25 V and 5.15 V respectively, demonstrating the better thermodynamically stability of PLPB than PLDB.

Ref. [5] Pia Janssen et al., *Electrochim. Acta*, 2014, **125**, 101–106.