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## Supplementary material

Surface Modified Boron Nitride as A Filler to Achieve High Thermal Stability of Polymer Solid-State Lithium Metal Batteries



Fig. S1. The SEM image of BNNS.



Fig. S2. The SEM and Elemental mapping images of BNNS.



Fig. S3. The SEM and Elemental mapping images of SiO<sub>2</sub>@BNNS.



**Fig. S4.** (a)The Photograph of BNNS nanosheets dissolving in acetonitrile. (b) The Photograph of the homogeneous electrolyte solution of SiO<sub>2</sub>@BNNS, PEO and LiTFSI in acetonitrile.



Fig. S5. Photograph of the 4%SiO<sub>2</sub>@BNNS CPE membrane.



Fig. S6. Photograph of the thickness of PLSB CPE membrane.



Fig. S7. The XRD spectra of BNNS.



**Fig. S8.** The XRD of LiTFSI. The peaks at 11.04°, 16.03°, 19.09°, 20.55°, 21.54°, 23.32°, 25.07°, 27.4°, 29.03°, 32.20°, 33.48°, 38.30° and 44.54° perfectly match to (002), (011), (201), (111), (202), (013), (113), (212), (114), (015), (115), (116) and (125) crystal planes.



Fig. S9. The EIS plots of PEO/LiTFSI/SiO<sub>2</sub>@BNNS and PEO/LiTFSI/BNNS at 60°C.



Fig. S10. FTIR spectra of SiO<sub>2</sub>@BNNS between 4000 and 500 cm<sup>-1</sup>.



Fig. S11. FTIR spectra of PLSB and PEO/LiTFSI between 1400 and 1180 cm<sup>-1</sup>.



**Fig. S12.** Cycling performance of the solid-state LiFePO<sub>4</sub>/Li battery using PEO/LiTFSI/SiO<sub>2</sub>@BNNS electrolyte at 60 °C and 0.2 C (1.0 mAh/cm<sup>2</sup>).



**Fig. S13.** Cycling performance of the solid-state LiFePO<sub>4</sub>/Li battery using PEO/LiTFSI/SiO<sub>2</sub>@BNNS electrolyte at 60 °C and 0.2 C (1.3 mAh/cm<sup>2</sup>).



Fig. S14. coin(a) and pouch (b) cell typical charge–discharge curves of solid-state LiFePO<sub>4</sub>/Li battery using PEO/LiTFSI/4 wt% SiO<sub>2</sub>@BNNS electrolyte at 1 C.



Fig. S15. (a) Cycling performance of the solid-state LiFePO<sub>4</sub>/Li battery using PEO/LiTFSI/BNNS electrolyte at 60 °C and 0.2 C. (b) Cycling performance of the solid-state LiFePO<sub>4</sub>/Li battery using PEO/LiTFSI/BNNS electrolyte at 60 °C and 1 C. (c) Cycling performance of the solid-state LiFePO<sub>4</sub>/Li battery using PEO/LiTFSI/BNNS electrolyte at 150 °C and 1 C.



**Fig. S16**. Cycling performance of the solid-state LiFePO<sub>4</sub>/Li battery using PEO/LiTFSI/SiO<sub>2</sub>@BNNS electrolyte at 150°C and 3C.