

Electronic Supplementary Information

Stable cycling of high-capacity Bi anode enabled by in-situ generated Li_3PO_4 transition layer in sulfide-based all-solid-state battery

Qin Li, Yi Cao, Geping Yin, Yunzhi Gao*

*MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage,
School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001,
China*

*Corresponding authors: Yunzhi Gao

Postal address: School of Chemistry and Chemical Engineering, Harbin Institute of Technology,
No. 92, West Dazhi Street, Harbin 150001, China.

Tel.: +86-451-86413721; fax: +86-451-86403807.

E-mail addresses: gao_yunzhihit@hit.edu.cn (Y.Z. Gao)

1. Experiments

1.1 Materials

Li_3PS_4 solid electrolytes were obtained by high-energy mechanical milling (PM 100, Retsch). The starting materials, Li_2S (99.98%) and P_2S_5 (99%) were purchased from Sigma-Aldrich and mixed in a zirconia jar (50 mL) at the stoichiometric molar ratio of $\text{Li}_2\text{S}:\text{P}_2\text{S}_5 = 75:25$ in an argon-filled glovebox. Then the mixture was ball-milled at 500 rpm under room temperature for 40 h. Li chips were purchased from MTI Corporation. Bi and BiPO_4 (99%) were also purchased from Sigma-Aldrich.

1.2 Characterization

To characterize the structural information of solid electrolyte, powder X-ray diffraction patterns (XRD) were collected on a D8 Advance using $\text{Cu K}\alpha$ radiation with LynxEye and SolX (Bruker AXS, WI). Field-emission scanning electron microscope (SEM, Hitachi SU - 70) was used to collect the morphologies of the samples. The X-ray photoelectron spectra (XPS) data were measured using a Kratos Axis 165 spectrometer with a monochromatic $\text{Al K}\alpha$ radiation source. All binding-energy values were calibrated relative to 284.8 eV of the C 1s peak.

1.3 Electrochemistry

LPS pellets (10 mm in diameter) were obtained by pressing 120 mg of the as-prepared LPS powder under 300 MPa in a polytetrafluoroethylene (PTFE) tank. The ionic conductivities of synthesized electrolyte were measured with a blocking symmetric SS/LPS/SS cell by using electrochemical impedance spectroscopy (EIS) collected on a Gamry workstation (Gamry 1000E, Gamry Instruments) with an AC amplitude of 10 mV at room temperature. The frequencies range from 1 MHz to 0.1 Hz. To assemble the all-solid-state cells, the electrode composite was obtained by hand grinding BiPO_4 , LPS and Carbon black with a weight ratio of 5:5:0.5 in the mortar. Then

the powder (~5 mg) were uniformly dispersed onto the top of the pre-pelleted LPS electrolyte (~120 mg), and then cold-pressed together in the PTFE tank under 300 MPa. After that, Li foil was attached on the other side and acted as both counter and reference electrode. Finally, the three-layered pellet was sandwiched between two stainless steel rods as current collectors. All the above preparation processes were performed in argon-filled glovebox ($O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm). Applied currents and rates were calculated based on the weight of $BiPO_4$ in the electrode. Cells were rested for 5 h prior to the test to allow the stabilization of the interface between Li and electrolyte.

2. Supplementary Figures

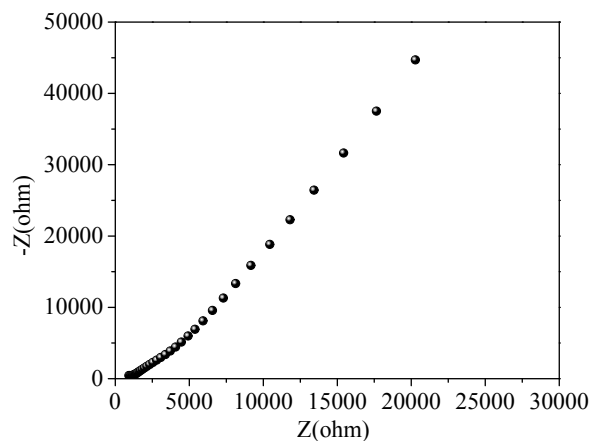


Fig. S1 The electrochemical impedance spectrum of the as-synthesized LPS solid state electrolyte.

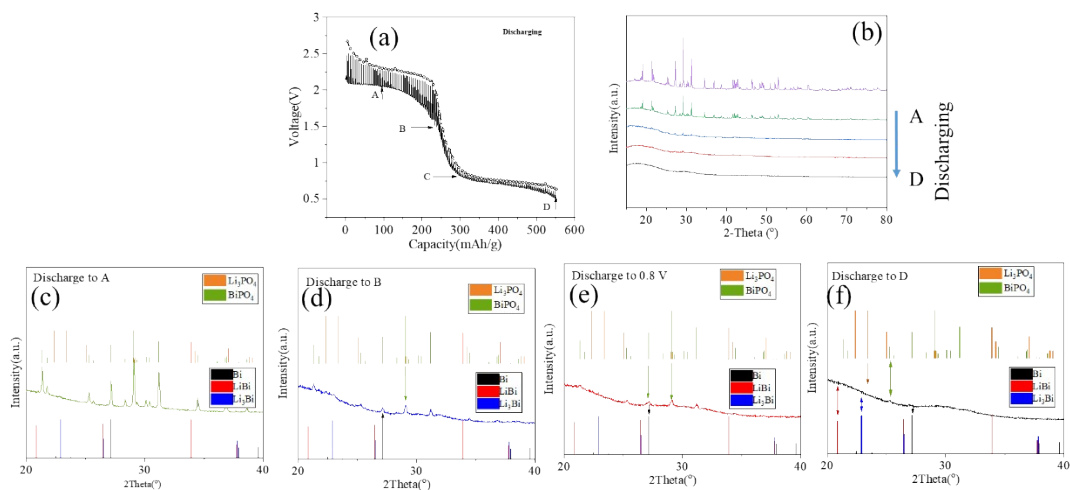


Fig. S2 (a) The discharging curve at 25 mA g⁻¹ by GITT. (b-f) XRD patterns of composite electrode at different lithiation conditions in (a).

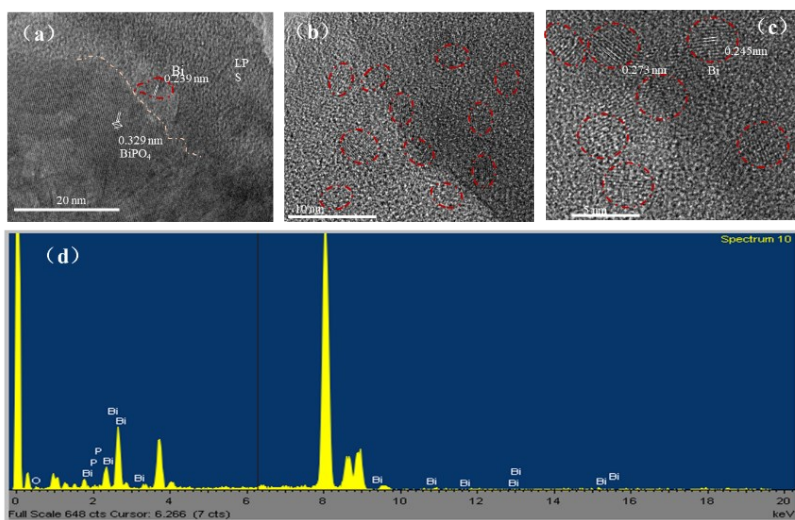


Fig. S3 TEM images of composite electrode after discharging to 2.0 V (a) and 0.8 V (b-c). (d) EDS analysis based on (c).

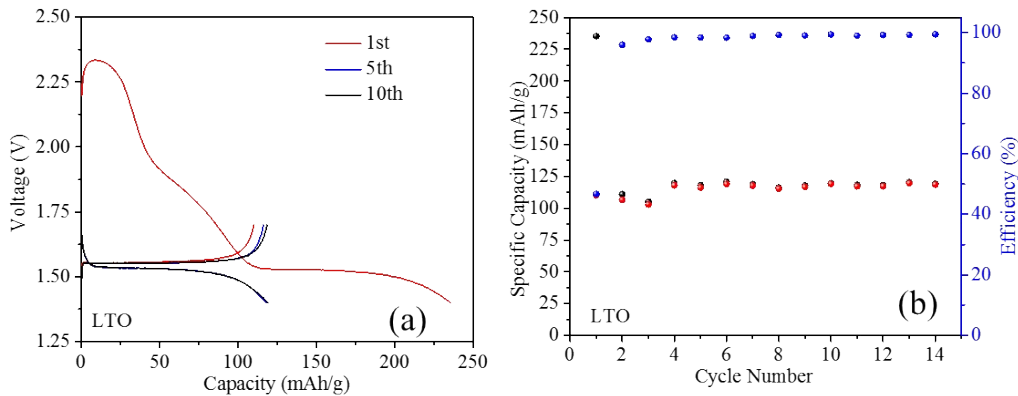


Fig. S4 a) Charge/discharge curves of LTO in different cycles at 0.05 C at room temperature. (b) Corresponding cycling performance of the cell.

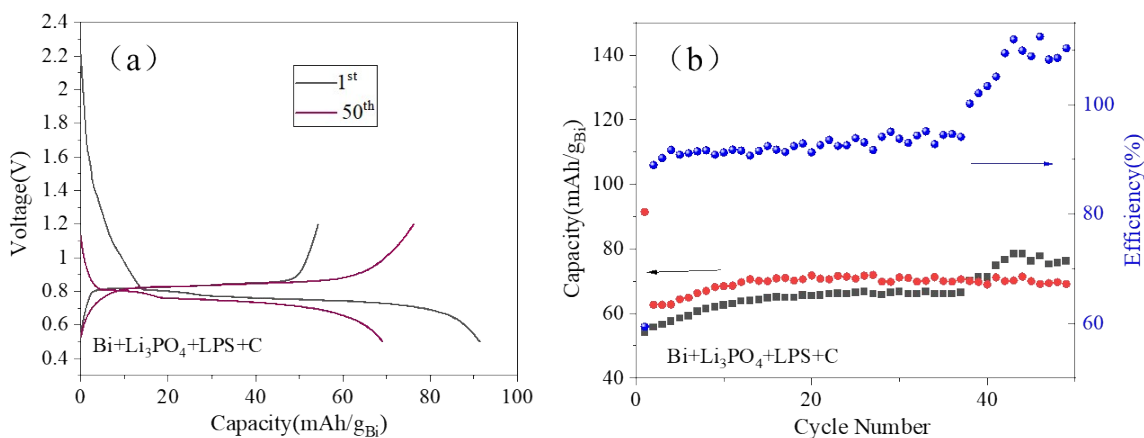


Fig. S5 Typical voltage profiles (a) and corresponding cycling performance at a rate of 25 mA g⁻¹ (b) of the Bi electrode mixed with Li₃PO₄ powder.

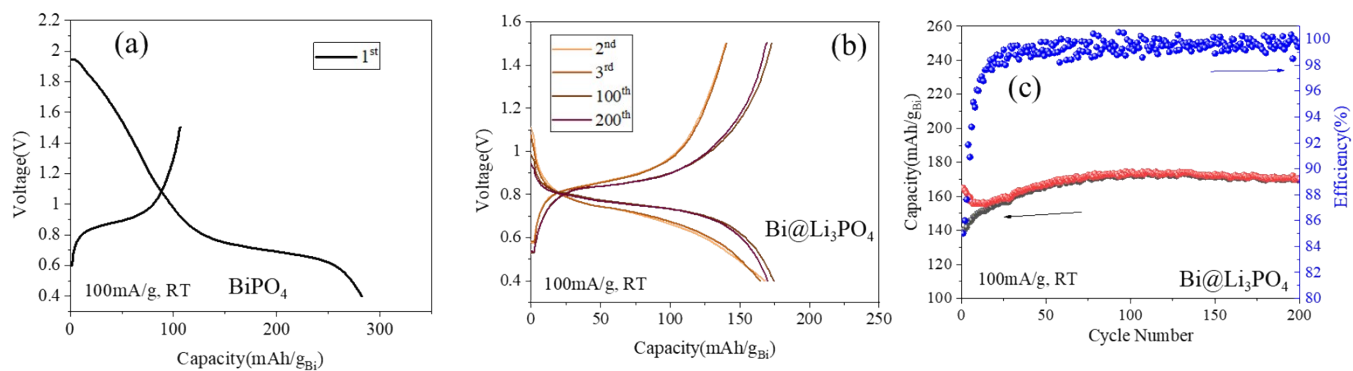


Fig. S6 (a) The initial cycle at 100 mA g⁻¹ at room temperature of BiPO₄ composite. The typical voltage curves (b) and corresponding cycling performance (c) of Bi@Li₃PO₄ electrode.

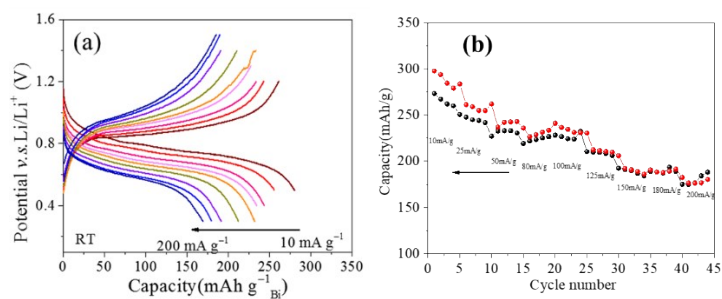


Fig. S7 (a) Typical voltage profiles of the composite electrode at various rates. (b) Cycling performance of the composites at various rates.

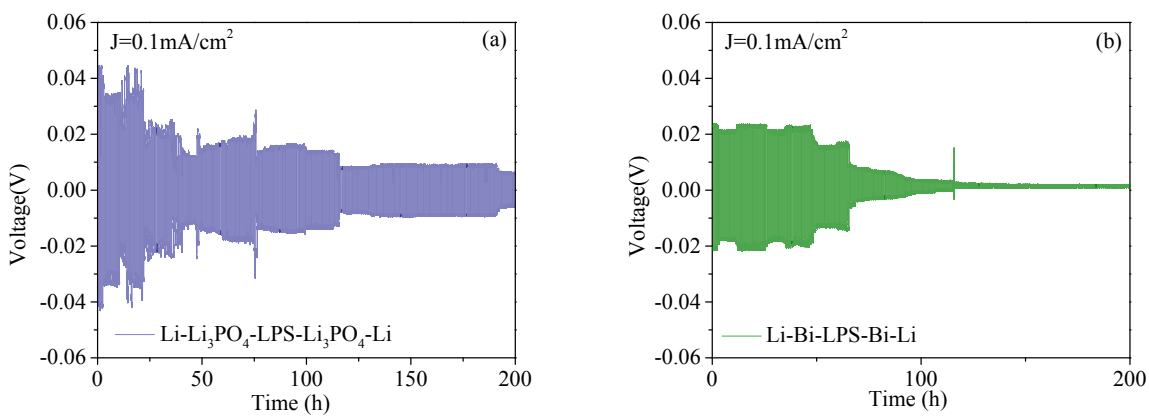


Fig. S8 Galvanostatic cycling of the Li-Li cells at constant current density of 0.1 mA cm^{-2} with Li_3PO_4 (a) and Bi (b) interlayer. The time for each charge and discharge is 0.5 h.