

SUPPORTING INFORMATION

Stable Lithium metal anode enabled by in-situ formation of $\text{Li}_3\text{N}/\text{Li-Bi}$ alloy hybrid layer

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Experimental section

Preparation of the Modified Li. The oxide layer on the surface of the lithium sheet is brushed off with a toothbrush, then the lithium sheet is rolled thin with a rolling machine, and finally the lithium sheet is punched into a small round wafer with a diameter of 10 mm. The commercially Bi(NO₃)₃ (99.99%) was ordered from Aladdin (Beijing). Prepare 0.1M Bi(NO₃)₃/DMSO solution, and the magnetic stirrer was used to stir this solution overnight to ensure its complete dissolution, then add molecular sieve and seal it overnight to remove trace water from the solution. Soak the polished lithium sheet in the 0.1M Bi(NO₃)₃/DMSO solution for 30 s, take it out and transfer it to the heating table for drying at 40 °C, then raise the temperature to 200 °C to react for about 1min. After the reaction, the lithium sheet was flattened by pressing, and punched into a small round sheet with a diameter of 10 mm through a puncher, which was named BiLi₃@Li. The whole of the above experimental steps are completed in a glove box filled with argon (O₂ and H₂O levels: < 0.1 ppm).

Materials Characterization. The changes in the surface morphology of Li were observed by the scanning electron microscope (SEM, LYRA3 TESCAN). Composition changes of the reaction between bismuth nitrate and lithium were studied by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific K-Alpha). X-ray diffraction (XRD, X'Pert3 Power, PANalytical) patterns were obtained with a Cu K α radiation source ($\lambda = 0.154178$ nm). Before testing, all of the lithium flake samples need to be cleaned with pure ethylene dioxolane (DME) solvent two to three times, and then vacuum dried. Before XRD testing, the lithium sample needs to be sealed with Kapton tape for testing. While in the transfer process of other characterization tests, the samples were sealed and stored in an aluminum plastic film bag with only several seconds of exposure to the air.

Electrochemical Measurements. The CR-2016 coin-type cells were used for lithium symmetrical cell and full cell. Celgard 2400 was employed as the separator and 1 M LITFSI in the mixture of DOL/DME (1:1, v/v) with 1 wt% LiNO₃ was used as the electrolyte. In the symmetrical cell, both the positive and negative electrodes are lithium sheets (Pristine lithium and BiLi₃@Li). For full cell tests, the pristine lithium and BiLi₃@Li were used as anodes and were assembled with LiFePO₄ cathodes. Those cathodes were prepared by mixing LiFePO₄, carbon black, and polyvinylidene difluoride (PVDF) dissolved in N-methyl-2-pyrrolidone (NMP) with a mass ratio of 8:1:1 to form a slurry, and then coating it on aluminum foil. The coated foil was dried under vacuum at 110 °C for 12 h, and punched into round sheets with a diameter of 10 mm. The mass loading was ~ 3 mg/cm².

Electrochemical impedance spectroscopy (EIS) measurements were executed employing a ZIVE SP2 electrochemical workstation (WonATech Co., Ltd.) with an amplitude of 5 mV and frequency range of 1×10^5 Hz to 1×10^2 mHz. In order to realize the real-time in-situ observation of the growth of lithium dendrite during the deposition process, we adopted a transparent symmetrical cell structure. The main body of the battery is composed of two glass plates. Hollow silicon wafers are interposed in the middle to provide a certain thickness, and Kapton tape is used as the bonding adhesive to ensure the sealing property. The copper foil strips with appropriate length and width are cut to serve as wire connecting electrodes. During the test, the distance between the two lithium sheets was kept at about 1.5 mm, the current density was 5 mA cm^{-2} , and the deposition time was 1 h.

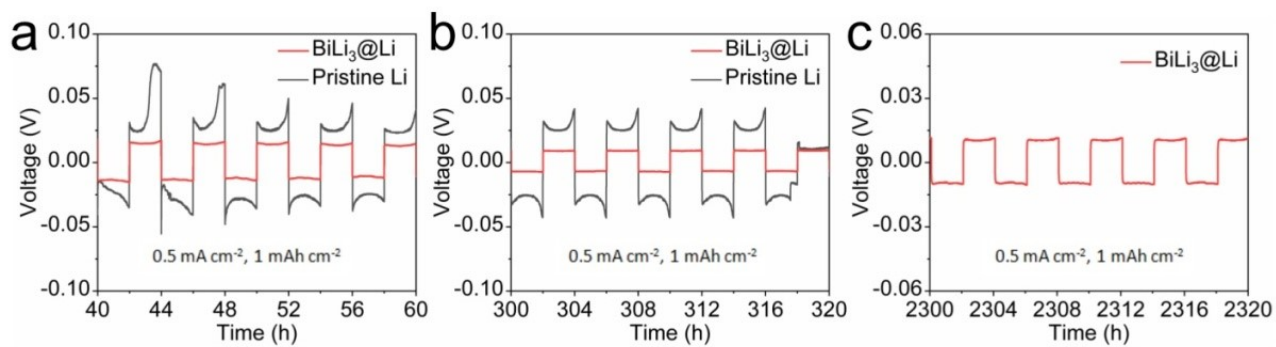


Fig. S1. The enlarge view of some turns during the cycle of the symmetric cell with pristine Li electrodes and BiLi₃@Li electrodes.

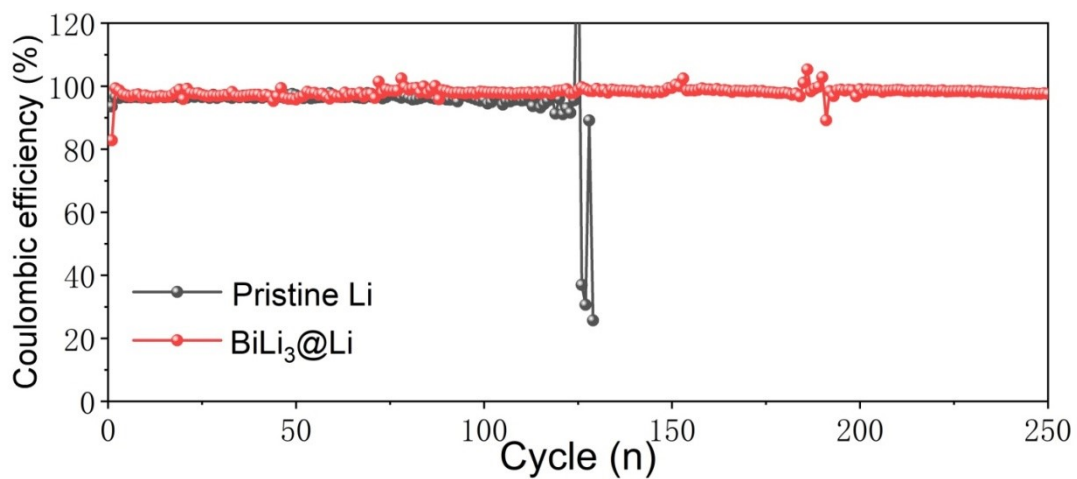


Fig. S2. Electrochemical Li|Cu half cells test. The Coulombic efficiency of Li|Cu cells with pristine Li and BiLi₃@Li at current density of 1 mA cm⁻².

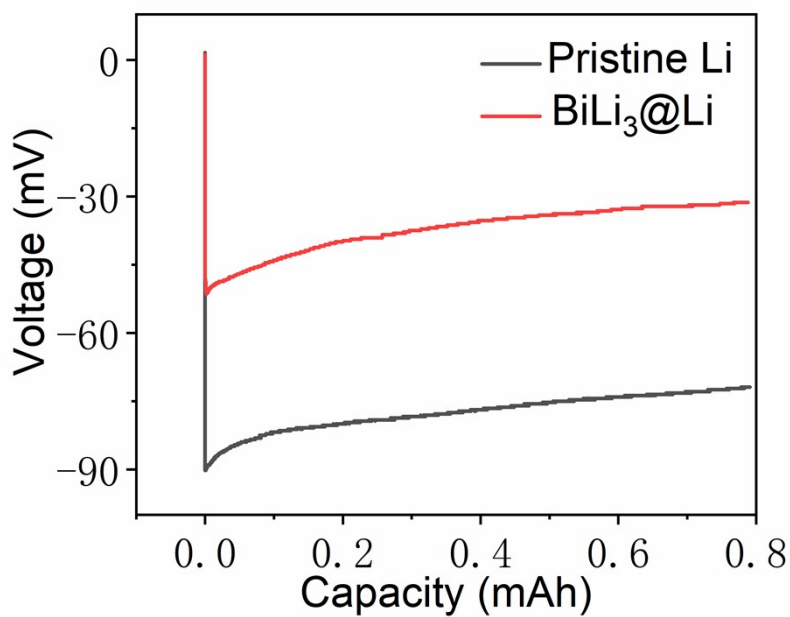


Fig. S3. The polarization curves of the pristine Li and BiLi₃@Li symmetric cells at 1 mA cm⁻².

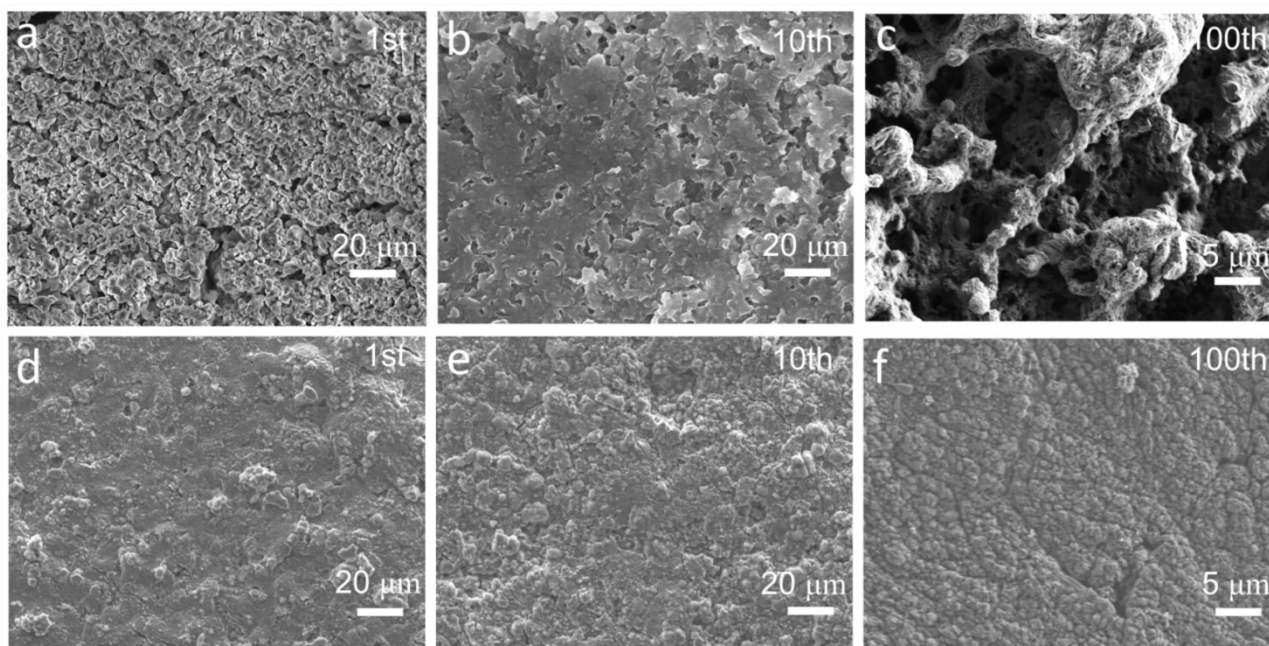


Fig. S4. Top-view SEM images of (a-c) the pristine Li electrodes and (d-f) BiLi₃@Li electrodes after 1, 10, 100 cycles, respectively.

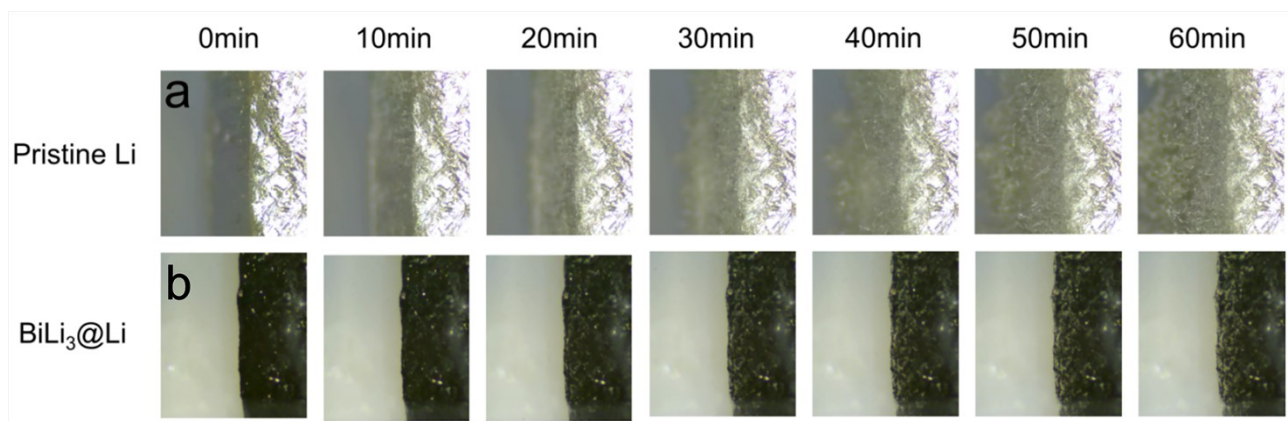


Fig. S5. In situ optical microscopy observation of Li deposition on (a) the pristine Li and (b) BiLi₃@Li electrodes at 5 mA cm⁻², respectively.

Table S1 Comparison of Plating/Stripping Hours of This Work with Previous Reports

artificial layer type	electrolyte	density/capacity (mA cm ⁻² /mAh cm ⁻²)	plating/stripping (hours)	ref.
Li ₃ Bi/Li ₃ N protective layer	1 M LiTFSI DOL/DME (1:1, v/v) with 1 wt% LiNO ₃	0.5/1	~2400	this work
		1/1	~1200	
		2/1	~800	
Li-Sb alloy/Li ₃ N double layer	1 M LiPF ₆ EC/DMC/FEC (1:1:0.2, v/v)	1/1	~550	1
Li ₃ N protective layer via plasma activation	1 M LiPF ₆ EC/DEC (1:1, v/v)	0.5/1	~500	2
Li-Sb alloy protective layer	1 M LiTFSI DOL/DME (1:1, v/v)	0.5/1	~1200	3
		2/1	~250	
		5/1	~150	
composite aphroid layer with Ag particle/carbon fiber	1 M LiTFSI DOL/DME (1:1, v/v)	1/1	~290	4
Li ₃ N-rich SEI via plating of Mg ₃ N ₂	1 M LiTFSI DOL/DME (1:1, v/v) with 1 wt% LiNO ₃	1/1	~290	5
LiI protective layer	1 M LiPF ₆ EC/DEC (1:1, v/v)	1/1	~700	6
Li-Zn alloy layer by e-beam evaporation	1 M LiFSI in DME	1/1	~900	7
		2/1	~1000	
		2/2	~300	
amorphous Li ₃ PO ₄ thin film SEI	1 M LiPF ₆ EC/DEC/DMC (1:1:1, v/v)	0.5/0.5	~900	8
		1/1	~300	
Li-In alloy/LiF biphasic layer	1 M LiPF ₆ EC/DMC (1:1, v/v)	1/1	~400	9
	1 M LiTFSI DOL/DME (1:1, v/v)	1/1	~1000	

Table S2. Impedance results of the pristine Li and BiLi₃@Li symmetrical cells.

		R_s (Ω)	R_{ct} (Ω)
Before cycle	BiLi ₃ @Li	6.1	270.21
	Pristine Li	2.04	380.02
After 1 cycle	BiLi ₃ @Li	8.23	35.97
	Pristine Li	8.7	63.09

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