Supplementary information for

Stable lithium metal anodes enabled by inorganic/organic double-layered alloy and polymer coating

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[b]*Shanghai Applied Radiation Institute, Shanghai University, Shanghai 200444, China. Email:* mhwu@shu.edu.cn
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Table S1 The price comparison of different metal salts for fabricating the lithiophilic alloy.

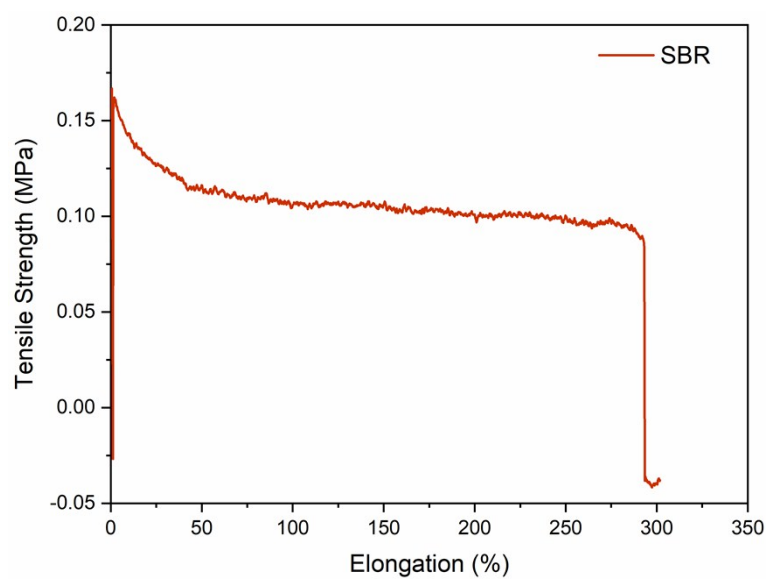| Chemicals	Brand	Price ($/g)*	Reference
$GeCl_4$	Sigma-Aldrich	21.6	1
InF_3	Sigma-Aldrich	41.6	2
$SnCl_4$	Sigma-Aldrich	9.32	3
SnTFSI	Alfa Aesar	224.6	4
$ZnCl_2$	Sigma-Aldrich	12.3	5
$InCl_3$	Sigma-Aldrich	9.2	5
$BiCl_3$	Sigma-Aldrich	3.7	5
SbF_3	Sigma-Aldrich	2.5	This work

*The price was recorded on 2019/07/26

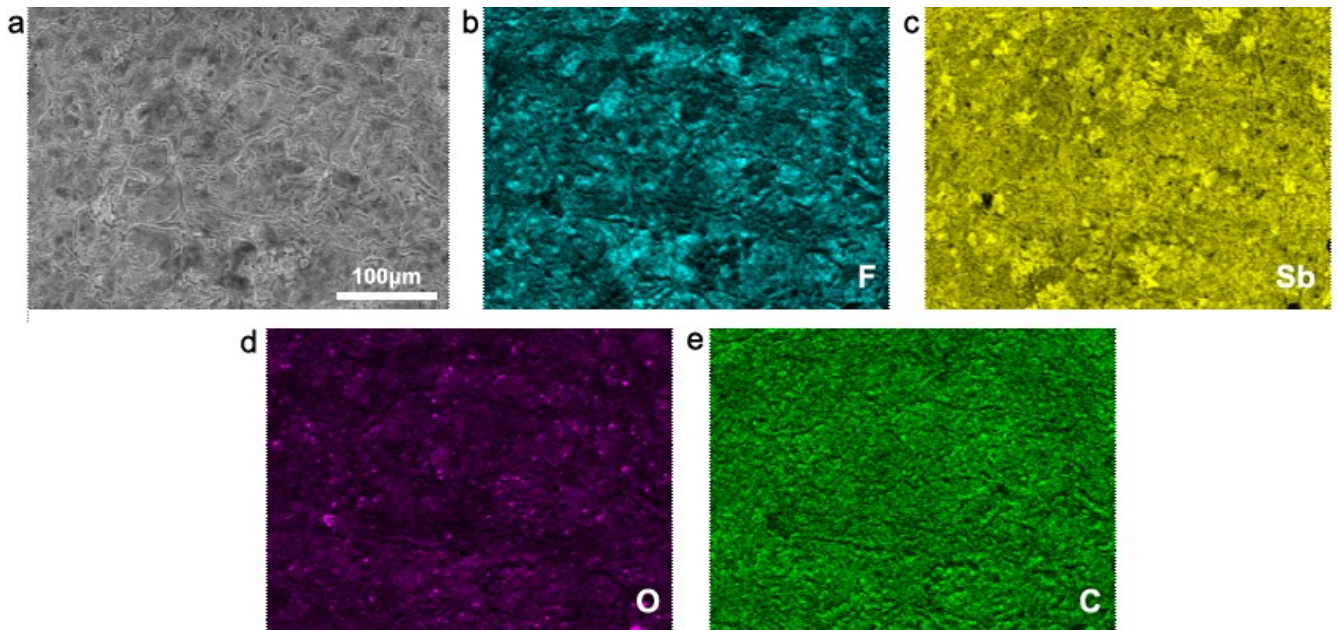**Fig.S1** The tensile strength of commercial SBR.

Fig. S2 The SEM image (a) and EDS mapping images of Li|Li-Sb-alloy electrode: (b) F, (c) Sb, (d) O, and (e) C.
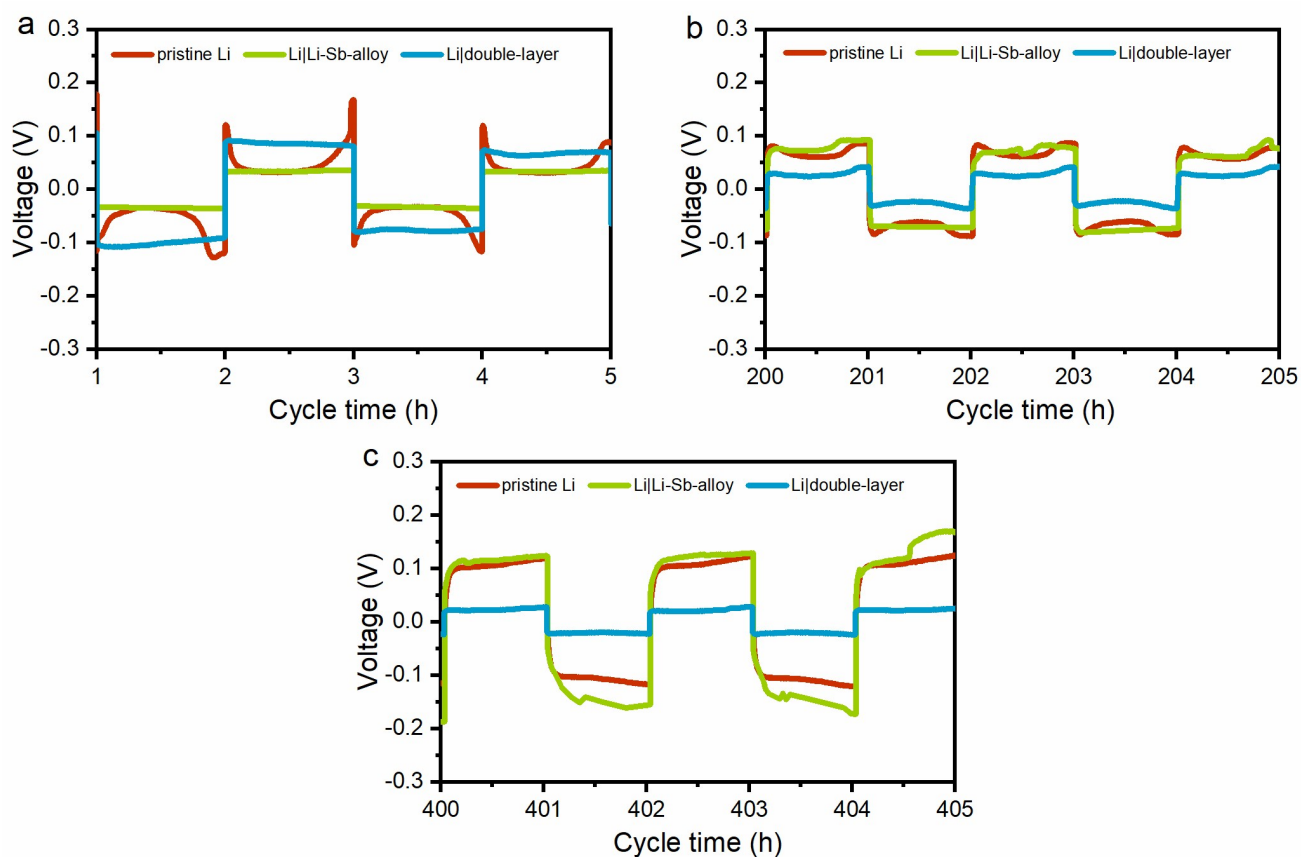
Fig. S3 Enlarged views for cycling performance of Li|Li symmetric cells containing pristine Li, Li|Li-Sb-alloy, and Li|double-layer under current density of 1 mA cm^{-2} for 1 h at different cycling times: (a) 1-5 h, (b) 200-205 h, and (c) 400-405 h. The electrolyte was 1 M LiPF$_6$ in EC/DEC (1:1, v/v).

Table S2 The comparison between double-layer protected lithium foils and other treated lithium foils reported in the previous literatures.

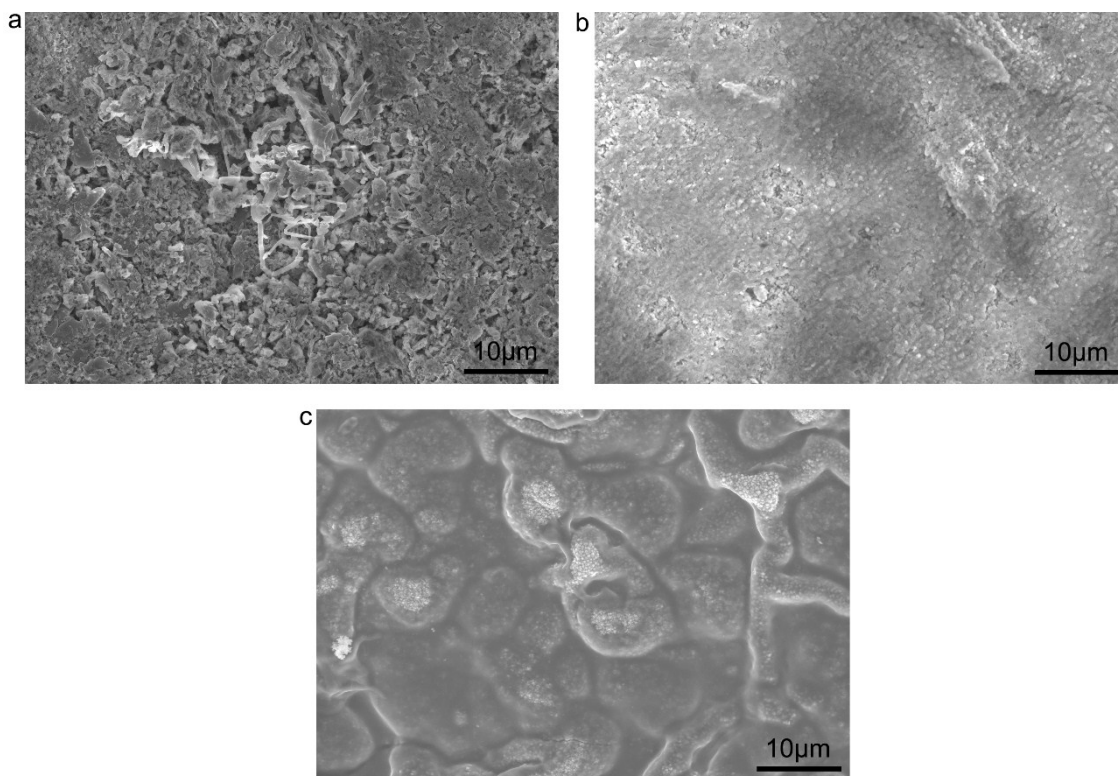| Electrolyte	Modifications/treatments	Current density & capacity	Plating/Stripping time	Overpotential	Reference
1M LiPF$_6$ EC/DMC (1:1, v/v) with 60 mM InF$_3$	InF$_3$ treated Li	1 mA cm^{-2}, 1 mA h cm^{-2}	400 h	167 mV	2
1M LiPF$_6$ EC/DMC (1:1, v/v)	PECA & LiNO$_3$ treated Li	1 mA cm^{-2}, 1 mA h cm^{-2}	400 h	74 mV	6
1M LiPF$_6$+0.2 M SiCl$_4$ in PC	SiCl$_4$ treated Li	1 mA cm^{-2}, 1 mA h cm^{-2}	100 h	86 mV	7
1M LiPF$_6$ in EC/DMC/DEC (1:1:1, v/v/v)	PAA treated Li	1 mA cm^{-2}, 1 mA h cm^{-2}	250 h	120 mV	8
1 M LiPF$_6$ in EC/DEC (1:1, v/v)	carbonized wood as Li host	1 mA cm^{-2}, 1 mA h cm^{-2}	330 h	86 mV	9
1.3 M LiPF$_6$ in EC/DEC (3:7, v/v) with 0.01 mg/mL carbon dots	carbon dots as electrolyte additives	1 mA cm^{-2}, 1 mA h cm^{-2}	250 h	122 mV	10
1M LiPF$_6$ EC/EMC/DMC (1:1:1, v/v/v)	zinc phosphate treated Li	1 mA cm^{-2}, 1 mA h cm^{-2}	500 h / 600 h	130 mV / 280 mV	11
1 M LiPF$_6$ in EC/DEC (1:1, v/v)	SbF$_3$ & SBR double layer protected Li	1 mA cm^{-2}, 1 mA h cm^{-2}	500 h	21 mv	This work

Fig. S4 Top-view SEM images of (a) pristine Li, (b) Li|Li-Sb-alloy, and (c) Li|double-layer after cycling for 100 h. The electrolyte was 1 M $LiPF_6$ in EC/DEC (1:1, v/v).
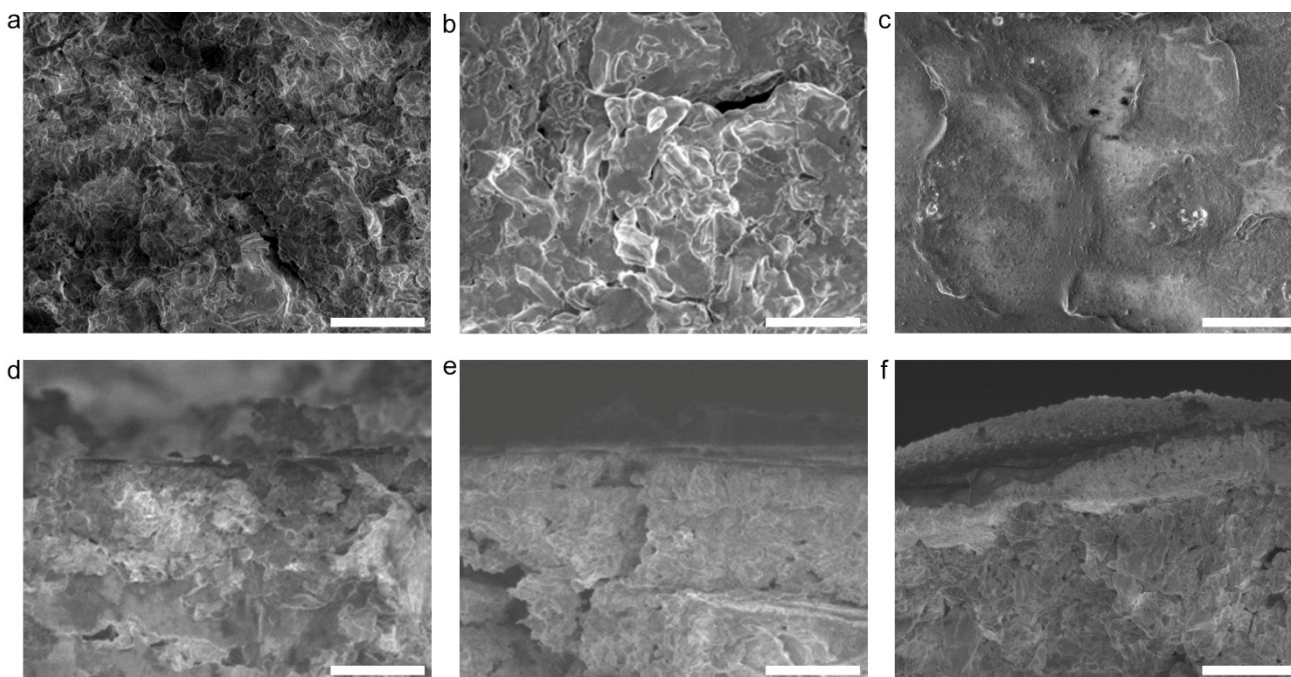
Fig. S5 Top-view SEM images of (a) pristine Li, (b) Li|Li-Sb-alloy after cycling for 400 h and (c) Li|double-layer after cycling for 500 h. Cross-sectional SEM images of (d) pristine Li, (e) Li|Li-Sb-alloy after cycling for 400 h and (f) Li|double-layer after cycling for 500 h. The electrolyte was 1 M LiTFSI in DOL/DME (1:1, v/v). The white scale bars are 5 μm.
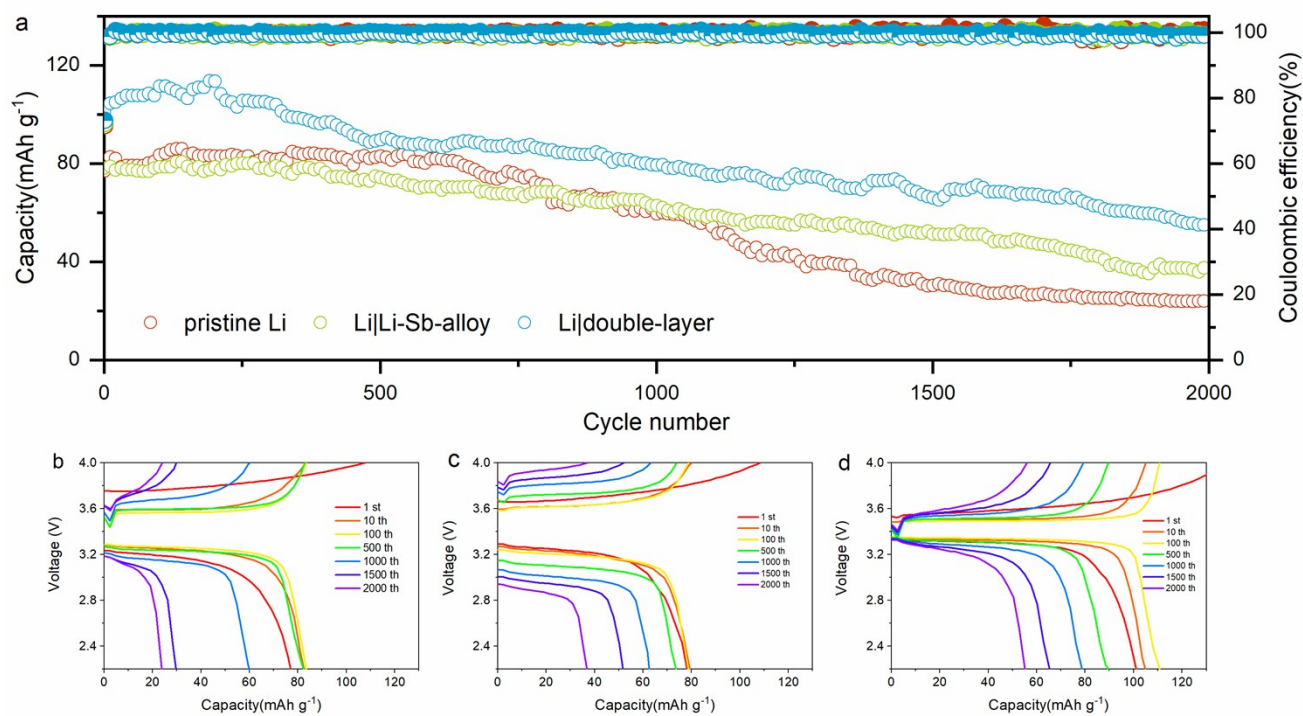
Fig. S6 (a) Cycling performance of Li|LiFePO$_4$ full cells containing the pristine Li, Li|Li-Sb-alloy, and Li|double-layer at 5C (1C = 170 mA g^{-1}). Charge/discharge curves of the Li|LiFePO$_4$ cells containing (b) pristine Li, (c) Li|Li-Sb-alloy, and (d) Li|double-layer. The electrolyte was 1 M LiPF$_6$ in EC/DEC (1:1, v/v).

References

1. K. Liao, S. Wu, X. Mu, Q. Lu, M. Han, P. He, Z. Shao and H. Zhou, *Adv. Mater.*, 2018, **30**, 1705711.

2. Q. Pang, X. Liang, I. R. Kochetkov, P. Hartmann and L. F. Nazar, *Angew. Chem., Int. Ed.*, 2018, **57**, 9795-9798.

3. Z. Jiang, L. Jin, Z. Han, W. Hu, Z. Zeng, Y. Sun and J. Xie, *Angew. Chem., Int. Ed.*, 2019, **58**, 11374-11378.

4. Z. Tu, S. Choudhury, M. J. Zachman, S. Wei, K. Zhang, L. F. Kourkoutis and L. A. Archer, *Nat. Energy*, 2018, **3**, 310-316.

5. X. Liang, Q. Pang, I. R. Kochetkov, M. S. Sempere, H. Huang, X. Sun and L. F. Nazar, *Nat. Energy*, 2017, **2**, 17119.

6. Z. Hu, S. Zhang, S. Dong, W. Li, H. Li, G. Cui and L. Chen, *Chem. Mater.*, 2017, **29**, 4682-4689.

7. Q. Zhao, Z. Tu, S. Wei, K. Zhang, S. Choudhury, X. Liu and L. A. Archer, *Angew. Chem., Int. Ed.*, 2018, **57**, 992-996.

8. N.-W. Li, Y. Shi, Y.-X. Yin, X.-X. Zeng, J.-Y. Li, C.-J. Li, L.-J. Wan, R. Wen and Y.-G. Guo, *Angew. Chem., Int. Ed.*, 2018, **57**, 1505-1509.

9. Y. Zhang, W. Luo, C. Wang, Y. Li, C. Chen, J. Song, J. Dai, E. M. Hitz, S. Xu, C. Yang, Y. Wang and L. Hu, *Proc. Natl. Acad. Sci. U. S. A.*, 2017, **114**, 3584-3589.

10. D. Hong, Y. Choi, J. Ryu, J. Mun, W. Choi, M. Park, Y. Lee, N.-S. Choi, G. Lee, B.-S. Kim and S. Park, *J. Mater. Chem. A*, 2019, 2019, **7**, 20325-20334.

11. X. Wang, J. Zhuang, M. Liu, C. Wang, Y. Zhong, H. Wang, X. Cheng, S. Liu, G. Cao and W. Li, *J. Mater. Chem. A*, 2019, **7**, 19104-19111.