Electronic Supplementary Material (ESI) for Materials Advances.

Supporting information

Binary PMMA/PVDF blend film modified substrate enables superior lithium metal anode for lithium batteries

Xiaosong Xiong, Ruoyu Zhi, Qi Zhou, Wenqi Yan, Yusong Zhu*, Yuhui Chen, Lijun Fu, Nengfei Yu*, Yuping Wu*

1. Experimental

1.1 Fabrication of PMMA/PVDF composite film coated anode

PMMA (Mw≈700,000, Aladdin Industrial Corporation, China), PVDF (Mw≈550,000, Arkema Fluorochemical Co. Ltd) and DMAc (Sinopharm Chemical Reagent Co. Ltd, China) were used as received. PMMA, PVDF (3:2, w:w) and DMAc solvent were added in a round bottom flask. Subsequently, seal the flask and mix the solution under vigorous magnetic stirring at 60℃ for 3 hours (800 rpm) to form a transparent and viscous precursor solution. The solution as obtained was then transferred into a syringe with a stainless needle. A piece of copper foil (20 × 60 cm) was washed by ethanol and deionized water for three times before directly being settled on the rolling drum as a collector for the nanofibers. After the preparation process, a voltage of 7.6 kV was applied to the solution and -0.5 kV was applied to the copper foil to start the spinning process. The distance between the needle tip and the fiber collector was kept at 15 cm, the solution pump rate was 0.08 mm/min. To prepare PMMA/PVDF film with optimal thickness, the spinning time was controlled at 5 hours. After the spinning process, the Cu foil was peeled away and then punched it to prepare electrodes with a diameter of 15 mm.

1.2 Material characterization

The contact angle analysis was carried out by an Optical Contact Angle Meter (SL200KS, Kino, USA), and a 3.0 μL droplet of the ether-based electrolyte was used in the experiment. To collect the samples for surface and cross-sectional morphology analysis, the Li-Cu half cells after deposited 1 mAh/cm^2 lithium at 1 mA/cm^2 were disassembled inside a glovebox (Universal 2440/750/900, MIKROUNA, China). The Li-deposited electrodes were firstly washed with 1,2-Dimethoxyethane (DME) to remove the residue electrolyte. After thoroughly drying, the samples were sealed in an argon-filled plastic bag and were transferred to the scanning electron microscope (SEM) quickly. SEM images were collected by using SEM (Philips XL-70) operated at an accelerating voltage of 15 kV. The diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) technique was applied to analyze the structure variation of PMMA/PVDF modified coating at different stage, The FTIR spectra at a frequency range of 4000–400 cm^{-1} with a resolution of 2 cm^{-1} were obtained by using a BRUKER ALPHA spectrometer. XPS data were obtained via Thermo Scientific ESCALAB 250Xi.

1.3 Electrochemical performance test

All cells prepared to test were assembled in CR2025 coin-type cells, 50 µL 1M LiTFSI in DME/DOL (1:1, v:v) with 2 wt.% $LiNO_3$ function as the electrolyte and a piece of Celgard 2400 porous PP membrane was utilized as the separator. In addition, the Cu current collector was washed by ethanol and deionized water for three times prior to use as the electrode.

The cycle performance testing of the Li-Cu half cells was carried out on a Lanhe battery testing station and the temperature was set to 25℃. For Li-Cu half cells, pristine copper and PMMA/PVDF modified copper (15 mm) were utilized as the working electrode with a lithium metal foil (0.4mm) as the counter electrode. During the galvanostatic cycling, a fixed amount of lithium was deposited onto the working electrode and a cut-off voltage of 0.5 V was applied for the stripping process. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) testing for Li-Cu half cells were conducted on a CHI 660e electrochemistry station at 25℃. In the CV testing process, the voltage ranged from -0.2V- 2.5V and the scan rate was 0.1 mV s^{-1}. The EIS was carried out at the open-circuit voltage with an amplitude voltage of 5 mV, and the frequency was set between 0.1 Hz-100000 Hz.

To prepare the anode electrode for Li/Li symmetric cells and Li/LFP full cells, 4 mAh/cm^2 and 1 mAh/cm^2 Li was plating on bare Cu/modified Cu in Li/Cu half cells, respectively. Then, the cells were disassembled carefully in the glove box full with Ar atmosphere. Subsequently, the obtained electrodes were washed with DME solvent to remove the Li salts on the surface. After thorough drying, two identical electrodes with 4 mAh/cm^2 Li were paired to assemble the Li/Li symmetric cells. The cathode slurry was fabricated by mixing $LiFePO_4$, conductive carbon black, poly(vinylidene difluoride) (PVDF) at a weight ratio of 8:1:1 in NMP solvent. The cathode slurry was then casting on aluminum foil by blade coating method, after air drying and vacuum drying at 80℃ overnight, the electrode foil was punched into circular piece with a dimeter of 10 mm. A piece of LFP cathode with areal mass loading of ca. 1.65 mg/cm^2 and bare Cu/modified Cu anode with 1 mAh/cm^2 Li were used to assemble the full cells. All full cells were cycled at 1C on the basis of LFP between 3 and 3.8 V at 25℃.

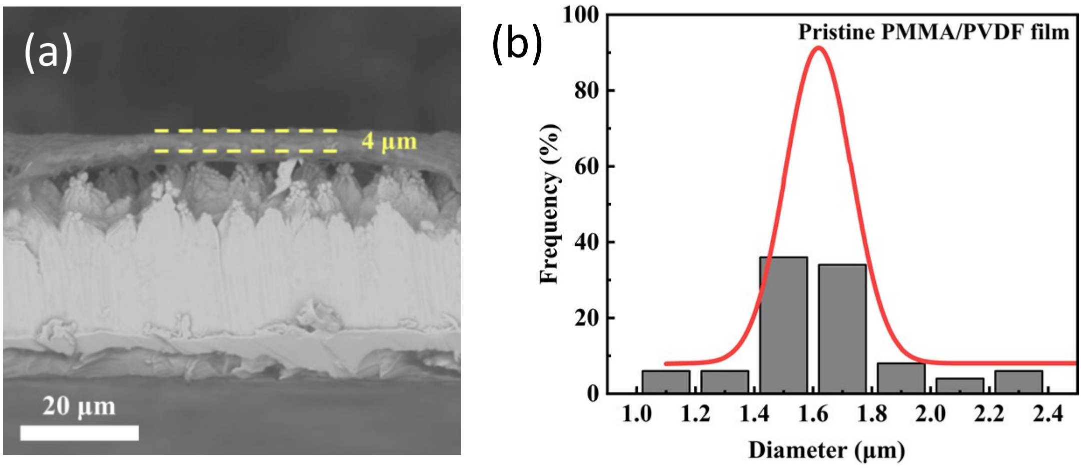


Figure S1. (a) Cross-section SEM image of the PMMA/PVDF film modified coating after cells assembly, (b) the mean diameter distribution of the PMMA/PVDF film fibers prepared by electrospinning technique.

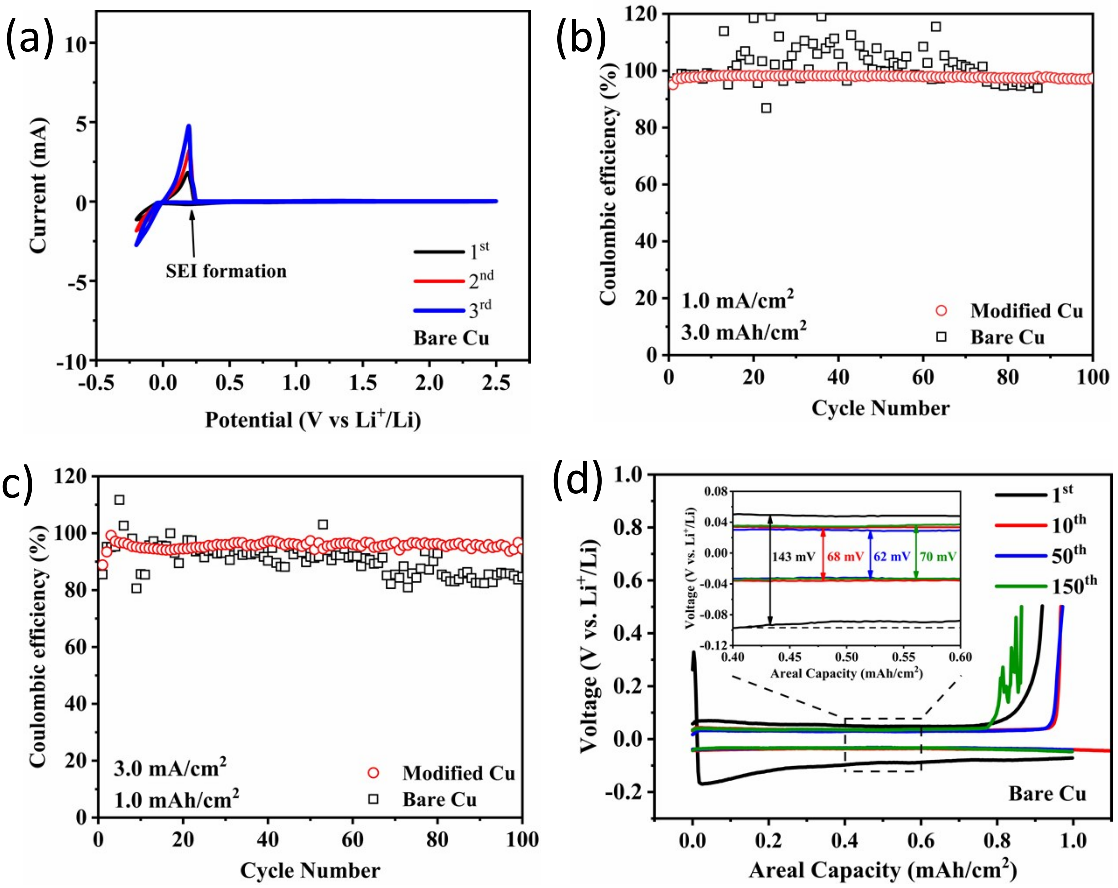


Figure S2. (a) Cyclic voltammetry curve of Li/bare Cu half cell for the initial 3 cycles, (b-c) coulombic efficiency of Li/bare Cu and Li/modified Cu at 3.0 mA/cm^2 (1.0 mAh/cm^2) (b) and 1.0 mA/cm^2 (3.0 mAh/cm^2) (c).

Table S1. Fitting equivalent circuit model and impedance parameters of half cells.

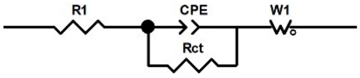
	R_s (Ω)		R_{ct} (Ω)	
	1st	40th	1st	40th
Modified Cu	3.656	7.721	45.84	5.975
Pristine Cu	7.066	7.224	94.35	28.45

Table S2. Summary of recent literature reports on the Li/Cu cycling performance using polymer coating.

Methods	Prepared Materials	Current density - deposition capacity (mA/cm^2)-(mAh/cm^2)	Life-span (cycles)	Average Coulombic efficiency (%)	Electrolyte 1 M LiTFSI in DOL and DME (v:v= 1:1)	Reference
Electrospinning technique	PVDF/ PMMA	1.0-1.0 1.0-3.0 3.0-1.0	260 100 100	98.2 97.8 95.6	50 µL, 2 wt% LiNO$_3$ additive	This work
Spin coating	branched oleic acids, diethylene triamine and urea	1.0-1.0 1.0-3.0	180 80	97.0 97.7	75 µL, 1 wt% LiNO$_3$ additive	[1]
Doctor blade coating	Silly Putty (Dow Corning 3179 Dilatant Compound)	1.0-1.0 1.0-2.5 3.0-1.0	120 40 70	97.0 97.5 Above 90	60 µL, 1 wt% LiNO$_3$ additive	[2]
Doctor blade coating	styrene butadiene rubber and Cu$_3$N	1.0-1.0	150	97.6 (20th-70th)	60 µL, 1 wt% LiNO$_3$	[3]
Doctor blade coating	β-PVDF	1.0-0.5 1.0-2.0	200 250	~98.0 98.7	3 wt% LiNO$_3$	[4]
Electrospun technique	K$^+$ doped Nafion	1.0-1.0 1.0-3.0	100 100	98.5 97.0	20 µL, 1 wt% LiNO$_3$	[5]
Impregnation method	Polydopamine/Cu^{2+}	1.0-1.0	260	90.0	/ 0.1 M LiNO$_3$	[6]
Stirred deposition	Polydopamine	1.0-1.0	100	96.0	1 wt% LiNO$_3$	[7]
Electrospinning technique and magnetron sputtering	poly (vinylpyrrolidone)/carbon	1.0-1.0	~100	98.0	30 µL, 1 wt% LiNO$_3$	[8]
Doctor blade coating	quaternized polyethylene terephthalate (q-PET)	1.0-1.0	＞300	98.0	/ 2 wt% LiNO$_3$ additive	[9]
Doctor blade coating	poly(vinylidene-*co*-hexafluoropropylene) PVDF-HFP/LiF	1.0-1.0	＞60	96.3	/ 2 wt% LiNO3 additive	[10]

References:

1. G. Y. Zheng, C. Wang, A. Pei, J. Lopez, F. F. Shi, Z. Chen, A. D. Sendek, H. W. Lee, Z. D. Lu, H. Schneider, M. M. Safont-Sempere, S. Chu, Z. N. Bao and Y. Cui, *Acs Energy Letters*, 2016, **1**, 1247-1255.
2. K. Liu, A. Pei, H. R. Lee, B. Kong, N. Liu, D. Lin, Y. Liu, C. Liu, P.-c. Hsu, Z. Bao and Y. Cui, *Journal of the American Chemical Society*, 2017, **139**, 4815-4820.
3. Y. Liu, D. Lin, P. Y. Yuen, K. Liu, J. Xie, R. H. Dauskardt and Y. Cui, *Advanced Materials*, 2017, **29**, 1605531.
4. J. Luo, C.-C. Fang and N.-L. Wu, *Advanced Energy Materials*, 2018, **8**, 1701482.
5. M. Hu, Y. Yuan, Y. Liu, L. Tian, Y. Zhang and D. Long, *Electrochimica Acta*, 2019, **302**, 301-309.
6. Q. Meng, H. Zhang, Y. Liu, S. Huang, T. Zhou, X. Yang, B. Wang, W. Zhang, H. Ming, Y. Xiang, M. Li, G. Cao, Y. Huang, L.-z. Fan, H. Zhang and Y. Guan, *Nano Research*, 2019, **12**, 2919-2924.
7. Y. He, H. Xu, J. Shi, P. Liu, Z. Tian, N. Dong, K. Luo, X. Zhou and Z. Liu, *Energy Storage Materials*, 2019, **23**, 418-426.
8. S. Huang, L. Tang, H. S. Najafabadi, S. Chen and Z. Ren, *Nano Energy*, 2017, **38**, 504-509.
9. W. Zhang, H. L. Zhuang, L. Fan, L. Gao and Y. Lu, *Science Advances*, 2018, **4**, eaar4410.
10. R. Xu, X. Q. Zhang, X. B. Cheng, H. J. Peng, C. Z. Zhao, C. Yan and J. Q. Huang, *Advanced Functional Materials*, 2018, **28**, 1705838.