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Supporting Information

Super-slippery Graphene Film Enables Highly Reversible Superdense Deposition of Lithium Metal Anode

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Experimental section

Materials synthesis

The stacked graphene nanosheet film (SGNF) on lithium metal via mechanical rollpress and Lithium stripping method. The clean lithium foil is divided into four equal parts and the graphite powder is dispersed on the lithium foils evenly. The mass percentage of lithium metal and graphite powder is 10:1. Stacking the four lithium foils together and roll them back to 100 μ m to mix graphite powder into lithium metal. Repeat the steps of cutting, stacking, rolling and cutting the Li foil multiple times (20 times in this work). Continuously peel off graphite to obtain graphene arrange inside the lithium metal by shear force. To structure the SGNF on lithium metal, symmetric cells were assembled, and stripping Li capacity of 1 mAh cm⁻² at 1 mA cm⁻². After lithium was stripped, the top graphene sheets stack with each other to form SGNF. All the preparation process was operated in an argon atmosphere glovebox.

Materials characterizations

The morphology image was obtained by scanning electron microscopy (SEM, JSM7900F, Japan) and transmission electron microscopy (TEM, Tecnai G2 20ST, America).

Raman spectroscopy (DXR3, America) was used to characterize the defects of graphite G-1 and G-2. X-ray photoelectron spectroscopy (XPS, K-Alpha, America) was used to characterize the type and content of elements in anode. The morphology, size, and thickness of graphene were investigated atomic force microscope (AFM, Bruker Dimension ICON, Germany).

Tribological tests

Graphite G-1 and G-2 were dispersed in N-Methylpyrrolidone (NMP) at a concentration of 3 wt%. G-1/NMP, G-2/NMP and NMP extract 5 mL solution for friction test samples, respectively. Tribological tests (Bruker UMT-2, Germany) in reciprocating friction mode during 3600s were conducted with an GCr15 steel ball (6-mm) as the frictional pairs and a stainless-steel disk as the bottom pallet. Oscillation amplitude, frequencies and load were set at 2 mm ,1 Hz and 2N, respectively.

Electrochemical measurements

The electrochemical performance was performed in a CR2025 cell system. The symmetric cells were assembled with the Li metal electrodes (bare Li, G-1-Li or G-2-Lii), Celgard 2320 was used as separator, and 1M lithium bis(trifluoromethane)sulfonimide (LiTFSI) in Dioxolane/1,2-Dimethoxyethane (DOL/DME, 1:1 by volume) solvent. Galvanostatic discharge-charge tests were measured by using a LAND battery measurement system. Before the cycling test, all symmetric cells were rested for 12 h. The full cells were assembled with LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM) as the cathode, bare Li metal, G-1-Li or G-2-Li as anode and 1 M LiPF₆ in Ethylene carbonate/Diethyl carbonate/ Ethyl methyl carbonate (EC/DEC/EMC,1:1:1 by volume) as the electrolyte. All the assembly processes were conducted in a glove box (H2O, O2 < 0.1 ppm). The NCM cathode electrodes were prepared by mixing 80 wt% active materials, 10 wt% conductive carbon

black, and 10 wt% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidinone (NMP) to form a slurry. The mixture slurry was coated on Al foil and then dried at 80 °C for 12 h in vacuum. The cathodes were cut into disks with a diameter of 10 mm before use. The areal mass loading of the NCM cathode is 1.8 mg/cm², which corresponds to an areal capacity of 0.36 mAh/cm². To form SGNF on the graphene-Li composite anode, 1 mAh cm⁻² of Li was stripped from the anode surface via symmetric cell before the assemble of full cells. For the G-2-SGNF-Li//NCM full cell, the thickness of anode is 100 µm and the ratio of lithium metal to graphene is 10:1. Therefore, the N/P ratio is less than 55. The performance of the full cells was conducted on a LAND battery test system with a voltage window between 2.5 and 4.3 V under a rate of 1C. All the electrochemical tests were performed at 25 °C temperature.

Li-ion flux simulation

The simulation of Li-ion flux (current density) on spherical SGNF for Li plating was performed by COMSOL Multiphysics with implemented finite element solver. The physics model used was "Electrodeposition, Tertiary Nernst-Planck". The diffusion coefficient of Li+ in the electrolyte was set to 1×10^{-5} cm² s⁻¹. The simulation results of the Li-ion flux in this work were collected after 0.1 seconds of simulation time. The simulation cell geometry in COMSOL of the Li-ion flux for Li plating on Li anode with uneven deposition induced bumps was presented in Fig.S10.



Fig. S1. SEM image of commercial graphite used in this work. (a)(b) G-1, (c)(d) G-2.



Fig. S2. TEM image of commercial graphite used in this work (a)(b) G-1, (c)(d) G-2.



Fig. S3. Scheme for construct graphene nanosheets in Li metal by mechanical roll-press method.



Fig. S4. Statistical calculations of (a) G-1 and (b) G-2. (c) Diameters and thicknesses of corresponding graphene nanosheets.



Fig. S5. The COF-Time curve of the NMP.



Fig. S6. Morphology of the plated (a) and stripped (b) bare-Li anode after 10 cycles by SEM.



Fig. S7. Lithium deposition of G-1-SGNF-Li anode and G-2-SGNF-Li anode after different cycles.



Fig. S8. Cross-sectional SEM images for the (a) bare Li anode and (b) G-2-SGNF-Li anode after plating different capacity of Li metal under 1 mA cm⁻².



Fig. S9. C 1s, F 1s and O 1s High-resolution XPS spectra of the SEI on (a)-(c) Li anode, and the SGNF on (d)-(f) G-1-SGNF-Li anode and (g)-(i) G-2-SGNF-Li anode after 100 cycles at the depth of 10 nm.

In conventional lithium metal anodes, a higher F content often results from excessive electrolyte decomposition due to poor interfacial stability. The introduction of G-2 effectively constructs a stable SGNF on the lithium anode surface. SGNF as a protective layer, significantly reducing direct contact between the lithium metal and the electrolyte. As a result, the decomposition of F-containing electrolyte (LiFSI) is minimized, leading to a lower F content in the SEI. It is generally believed that the presence of more inorganic component LiF in SEI is beneficial for the stability of lithium metal interface, but its content does not completely determine the quality and structure of SEI. In our study, the G-2-SGNF provides a mechanically robust and ionically conductive interface, which effectively suppresses lithium dendrite growth and side reactions. This structural stability compensates for the lower LiF content, ensuring excellent cycling performance.



Fig. S10. Simulation cell geometry of the Li-ion flux for Li plating on Li anode with uneven deposition induced bumps.



Fig. S11. Rate performance of the G-2-SGNF-Li||NCM full cell and bare-Li||NCM full cell at various rates from 0.2 to 5C.

Elements	Li	С	F	0
Li	47.5%	6.8%	24.2%	21.5%
G-1-SGNF-Li	44.4%	6.7%	25.9%	23.0%
G-2-SGNF-Li	46.0%	8.4%	12.5%	33.1%

Table S1. Percent contents of different elements in the SEI.