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Electronic Supplementary Information

An artificial hybrid interphase endowing ultrahigh-rate and practical lithium metal anode

Anjun Hu et al.

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Part I. Supplementary Note

Note S1. Computational model and method details.

a) Surface energy.

Li₃Sb and LiF are in a cubic phase with space no. 225 (Fm-3m) with the optimized lattice constants of 6.57 and 4.08 Å, respectively, which are very close to the experimental values. In order to identify the most stable surface used for Li atom adsorption and migration, the low Miller-index surfaces (e.g., 001, 110 and 111) were taken into consideration. The stoichiometric or nonstoichiometric model with the same terminations on both sides of the slab was built for each nonpolar or polar surface, which is beneficial to avoiding the artificial dipole interactions between two periodic images. Strictly, it is difficult to calculate the surface energy of nonstoichiometric surface, which is involving in allowing the surface to exchange atom with a reservoir, namely chemical potential. However, it was suggested that the surface energy can be approximated by the following equation

$$\gamma = \left[E_{\text{unrel}}^{\text{cleav}} + E_{\text{rel}} \left(A \right) + E_{\text{rel}} \left(B \right) \right] / 2 \tag{1}$$

of which, E_{unrel}^{cleav} , $E_{rel}(A)$ and $E_{rel}(B)$ are the cleavage energy of a unrelaxed surface, the relaxed energies of symmetric slabs with A and B terminations, respectively. Furthermore, these values are calculated as:

$$E_{unrel}^{cleav} = \left[E_{slab}^{unrel}\left(A\right) + E_{slab}^{unrel}\left(B\right) - nE_{bulk}\right]/2S$$

$$E_{rel}\left(A\right) = \left[E_{slab}^{rel}\left(A\right) - E_{slab}^{unrel}\left(A\right)\right]/2S$$
(2)
(3)

$$E_{\rm rel}(R) = \left[E_{slab}^{rel}(R) - E_{slab}^{unrel}(R) \right] / 2S$$

$$(4)$$

where $E_{slab}^{rel}(A)$, $E_{slab}^{unrel}(A)$, $E_{slab}^{rel}(B)$, $E_{slab}^{unrel}(B)$ and E_{bulk} are the total energies of relaxed and unrelaxed symmetric slabs with A and B terminations, as well as the unit cell bulk, respectively. n is the number of bulk in the two slabs and S is the surface area of the cleaved plane. As shown in Fig. S1 and Table S2, the calculated surface energy of 0.07 eV/Å² for the nonpolar Li₃Sb (110) is lower than the values of LiSb- and Li₂-terminated polar Li₃Sb (001), as well as Li₃- and Sb-terminated polar Li₃Sb (111) surfaces. As for various LiF surfaces (Fig. S2), LiF (001) yields the lowest surface energy of 0.04 eV/Å², compared with the values for LiF (110), as well as F- and Li-terminated LiF (111) surfaces. Therefore, the nonpolar Li₃Sb (110) and LiF (001) were used for construction of the interfacial supercell with Li (110) and Li (001), respectively, as well as the substrate to adsorb the Li⁺.

b) Adsorption and diffusion of Li⁺.

To ensure the calculation accuracy and efficiency, the surface model of Li₃Sb (110) and LiF (001) were used as the substrate for the investigation of the adsorption and diffusion of Li⁺ on the electrolyte. As shown in left insert of Fig. 1b (right insert), four possible sites on the Li₃Sb (110) surface were considered for Li⁺ adsorption. The Li_{2nd}-top site was identified as the most stable position for the adsorbed Li⁺ with the adsorption energy of 1.04 eV. LiF (001) surface is less complicated, where three candidate positions for adsorption of Li⁺, as displayed in Fig. 1b (left insert). The F-top site is the most stable position for Li⁺ with the adsorption energy of 0.71 eV, as listed in Table S3. The charge density differences visualized in Fig. 1c evidence that the stronger interactions of Li⁺ with Li₃Sb (110) than LiF (001) surface. Bader charge analysis¹ indicates that 0.99 electrons transfer from Li⁺ to the coordinated atoms of the Li₃Sb (110) surface, while 0.39 electrons transfer at the Li₁/LiF interface. Diffusion of Li⁺ between the most stable adsorption sites were investigated via the climbingimage nudged elastic band (CI-NEB) method and shown with the energy profiles in Fig. 1d and e. The energy barrier of Li⁺ diffusion on the Li₃Sb (110) and LiF (001) surfaces are 0.06 and 0.26 eV, respectively, which are lower than that of Li (001) surface (0.39 eV), as reported by Ren et al.² Li⁺ locating on the outmost Li–Sb bond of Li₃Sb (110) and the hollow site of LiF (001) surfaces were identified as the transition states, respectively.

c) Energy calculation.

To theoretically evaluate the effect of Li₃Sb and LiF on suppression of the Li dendrites, the interfacial properties, including the formation energy (E_f), strain energy (ζ), interfacial energy (σ) and the work of adhesion (W_{adh}), were calculated for the LS/Li (LS=Li₃Sb or LiF) interfacial supercells. The formation energy is contributed from both the interfacial energy and the strain energy generated by the lattice mismatch between LS and Li. The relationship between these energies can be written as

$$\frac{E_{\rm f}}{N} = \frac{2A\sigma}{N} + \zeta$$

where A is the area of the interface and N is the number of the atoms in the interfacial supercells. The interface formation energy is defined as

$$E_{\rm f} = [E_{LS/Li} - n_{LS}\mu_{LS}^{LS-bulk} - n_{Li}\mu_{Li}^{Li-bulk}]/N$$
(5)

where $E_{LS/Li}$ is the total energy of the interfacial supercell with full relaxation of the atom positions and cellvectors, n_{LS} and n_{Li} are the numbers of the LS formula units and Li atoms in the LS and Li parts in the interfacial supercells, $\mu_{LS}^{LS-bulk}$ and $\mu_{Li}^{Li-bulk}$ are the chemical potentials of LS and Li metal, respectively. N is the total number of atoms in the supercells. As suggested by Wolverton *et al.*,³ the interfacial energy σ is then determined by

$$\sigma = [E_{LS/Li} - n_{LS} E_{LS}^{LS-bulk(c)} - n_{Li} E_{Li}^{Li-bulk(c)}] / 2A$$
(6)

where $E_{LS}^{LS-bulk(c)}$ and $E_{Li}^{Li-bulk(c)}$ are the energies of the constrained LS and Li unit bulks, respectively. In this case, pure LS and Li bulk structures were relaxed along the interfacial normal direction (c), with the in-plane lattice vectors (a and b) fixed to the fully relaxed interfacial supercells.

Furthermore, the work of adhesion (W_{adh}) of the interface, which is the cost for separating the two parts of the interface, is then expressed as

$$W_{adh} = \gamma_{LS} + \gamma_{Li} - \sigma_{LS/Li} \tag{7}$$

where γ_{LS} , γ_{Li} and $\sigma_{LS/Li}$ are the surface energies of LS and Li part, as well as the interfacial energy of the interface, respectively.

The optimized lattice constants are 3.437, 6.569 and 4.021 Å for Li, Li₃Sb and LiF unit cells, respectively. As shown in Fig. S3, The 2×1 Li₃Sb(110)/2×2 Li(110) and 4×4 LiF(001)/5×5 Li(001) supercells were thus constructed to reduce the lattice mismatch to the value of less than 5%. The full geometry optimization results in that the atoms in Li₃Sb/Li supercell experienced small perturbation, while LiF/Li underwent much more drastic distortion with the Li atomic layers bending near the interface region. Correspondingly, the calculated interface formation energy, interfacial energy and strain energy of Li₃Sb/Li are smaller than the values for LiF/Li, as listed in Table S4. Note that, the interfacial energy of 0.756 J/m² for LiF/Li is in good consistence with other theoretical result of 0.747 J/m² in Ref.⁴ The work of adhesion of Li₃Sb/Li is much higher than the value for LiF/Li, indicating that the former interface is more stable. Thus Li₃Sb is more mechanically stable to be used as a SEI component than LiF.

Note S2. Morphology of interphase layer with different amounts of SbF₃.

As a comparison, the lower SbF₃ concentration (1 mM) could not form a compact and dense lithiophilic interphase on the Li surface (Fig. S8b). Some unprotected region on the surface that allow penetration of electrolyte, resulting in the side reactions with the Li underneath. At higher SbF₃ concentrations (10 and 50 mM), rough surface with some cracks was observed (Fig. S8c and d), which result in a less dense alloy layer. The thicker layer has a higher Li⁺ barrier energy or higher impedance resulting in slow Li⁺ diffusion.⁵

Note S3. Effects of interphase layer with different amounts of SbF₃ on the battery stability.

To find the optimized interphase layer on the Li metal, we investigated the effects of adding different amounts of SbF₃ on the battery stability. The stripping/plating measurements of Li|Li symmetric cell were carried out at 2 mA cm⁻² with capacity of 2 mA h cm⁻² (Fig. S9). The LiF/Li₃Sb-5 symmetric cell achieves stable Li deposition behavior and longest plating/stripping cycles (1100 h). The electrochemical tests of symmetric cells reveals that the Li₃Sb electrodes with thicker or thinner interphase layer have poorer cycle performance, possibly due to a frustrated Li⁺ transport in the thicker interphase layer and an insufficient suppression effect of the thinner interphase layer for dendritic Li growth. Further, the electrochemical impedance spectroscopy (EIS) was carried out to compare the charge transfer resistance (R_{ct}) of different symmetric cells (Fig. S10, Table S6). The Li₃Sb symmetric cells show two semicircles, where the first semicircle in the higher frequency range indicates the interfacial resistance of the interphase layer or resistance of Li⁺ flux through an interphase layer, and the second semicircle in the lower frequency range indicates the R_{ct} between the interphase layer and the electrolyte.^{6, 7} The symmetric cells with LiF/Li₃Sb-5 exhibits the lowest R_{ct} value of 67.1 Ω , which can be attributed to the fast Li⁺ transport with an optimized interphase layer thickness of 5 µm. The presence of an optimum amount of the SbF₃ solution stabilizes the Li anode interface and the batteries have a minimal interfacial impedance with remarkable stability during cycling. Thus, 5 µm is considered as the optimal thickness of interphase layer.

Note S4. Raman spectra of LiF/Li₃Sb-5 interphase layer.

As shown in Fig. S11, two main peaks of E_g at 103.9 cm⁻¹ and A_{1g} at 138.7 cm⁻¹ show a slight blue shift compared with those of metallic antimony in previous literature,^{8,9} which might result from partly alloyed antimony and Li₃Sb. The E_g modes are doubly degenerate in-plane vibrational modes and A_{1g} is an out-ofplane vibrational mode. The additional F_{2g} band at ~250 cm⁻¹ can be assigned to SbO_x due to the surface oxidation during the transfer process of samples.⁹

Note S5. X-ray photoelectron spectroscopy (XPS).

Taken LiF/Li₃Sb-5 as the representative, the chemical composition of the interphase layer was analyzed via XPS by Ar⁺ sputtering (Fig. 2g). The high-resolution Sb 3d XPS spectrum exhibit two main peaks at 531.2

and 538.8 eV, which are assigned to Li₃Sb. Besides, two weak peaks of SbO_x at 534.1 and 541.4 eV are also observed. With the time of Ar-ion bombardment increased, the peaks related to SbO_x species gradually decreased, while the peaks of Li₃Sb metal gradually increased. The Li 1s XPS spectrum can be deconvoluted into five peaks, which can be assigned to LiF, Li₃Sb, Li₂CO₃, LiOH, and Li₂O, respectively. In addition, after 30 min of Ar-ion bombardment, the characteristic peak of Li₂O in the lithiophilic interphase is almost disappeared, indicating that the antimony-based lithiophilic interphase can prevent the Li metal from further oxidation. In the F 3d XPS spectrum, the peak corresponding to LiF is observed at 687.5 eV.¹⁰

Note S6. Time-of-flight secondary-ion mass spectrometry (TOF-SIMS).

TOF-SIMS was measured on PHI nanoTOF II. An Ar beam (3 keV, 100 nA) was used to sputter a 500 \times 500 μ m² area for 1800 s and a Bi³⁺ beam (30 keV, 2 nA) was used to analyze a 60 \times 60 μ m² area inside the Ar sputtered area for depth profiling. The sputtering rate is 10 nm/min for SiO₂ as standard. The compositions of the antimony-based lithiophilic interphase and elemental depth distributions was further identified by time-of-flight secondary ion mass spectrometry (TOF-SIMS). As shown in Fig. S12 and S13, in the initial sputtering region, a relatively uniform distribution of secondary ions from Sb, Li and F elements is observed, demonstrating the successful formation of fluorinated antimony-based lithiophilic interphase coating on the surface of Li metal. With increasing the sputtering time, the intensity of Sb, Li and F is gradually increased, while the opposite trend is presented for C and O.

Note S7. Electrolyte wettability of the interphase layer.

The electrolyte wettability is also an important factor to evaluate the property of artificial SEI and high electrolyte wettability can promote better battery cycling performance. To probe the electrolyte wettability of the artificial SEI layer, contact angle measurements were carried out with ether-based electrolytes on bare Li and LiF/Li₃Sb-5 electrodes, respectively. The contact angle of bare Li is 14.8° (Fig. S15a), indicating moderate

wettability of bare Li in the ether-based electrolyte system. Interestingly, LiF/Li₃Sb-5 electrodes display excellent wettability, with a contact angle of almost 0° (Fig. S15b). The much-improved electrolyte wettability of Li anode with the presence of LiF/Li₃Sb-5 layer indicates that the modified Li can uptake more electrolyte. The improved electrolyte wettability is in favor of the uniform distribution of Li⁺ flux to mitigate the inhomogeneous Li deposition and reduce the nucleation barrier.¹¹

Note S8. Electronic resistivity and ionic conductivity measurement

a) Electronic resistivity.

To measure the electronic resistivity of LiF/Li₃Sb-5 interphase layer, a direct current-voltage measurement was conducted by using blocking electrodes (Fig. S16). Either bare or modified Li foil are sandwiched between two stainless steel (SS) blocking electrodes. The voltage response to a direct current of 5.0 mA was recorded to calculate the electronic resistivity. The calculation formula is:

$$\rho = \mathbf{R} \cdot \mathbf{S} / \mathbf{L} = \mathbf{U} \cdot \mathbf{S} / (\mathbf{I} \cdot \mathbf{L}) \tag{8}$$

Where L is the thickness of the protecting film; I is the applied current; S is the area of the Li metal; U is the average voltage increase.

Therefore, the calculated electronic resistivity of the fluorinated lithiophilic interphase layer is around $3.8 \times 10^4 \Omega$ cm (that is, electronic conductivity, $\sigma_e = 2.37 \times 10^{-5} \text{ S cm}^{-1}$). The interphase layer renders resistive protecting layers with electronic resistivity of $\sim 3.8 \times 10^4 \Omega$ cm, which is three orders of magnitude higher than those of amorphous carbon nanosphere films ($1.3 \times 10^1 \Omega$ cm) that induce Li plating underneath the film.¹² This is also demonstrated by the polarization I-V curves that the LiF/Li₃Sb-5 electrode exhibits a much smaller I-V slope than the Li electrode (Fig. S16), implying that the artificial interphase layer of Li lowers the electronic conductivity. The electronic resistive nature of SEI is favorable to first deposit/plate Li underneath the SEI.^{13, 14}

b) Ionic conductivity.

The method of calculating ionic conductivity of an artificial SEI was based on EIS measurement of symmetrical cells assembled with LiF/Li₃Sb-5 (Fig. S10a). Ionic conductivity of the LiF/Li₃Sb-5 interphase layer can be calculated by using an equation

$$\sigma = 2L/(R \cdot S) \tag{9}$$

where L is the thickness, R is the resistance, and S is the area of SEI the layer.

Therefore, the calculated ion conductivity of the LiF/Li₃Sb-5 interphase layer is around 1.01×10^{-5} S cm⁻¹, which is much higher than that of defect-free LiF (~ 10^{-12} S cm⁻¹).² This value of ionic conductivity is large enough to diffuse lithium ion.

Note S9. Investigation of pure Li₃Sb and LiF SEI layer and the optimal ratio of Li₃Sb/LiF.

In order to demonstrate the advantage of the hybrid SEI layer, the effects of pure Li₃Sb and LiF SEI layers on the performance of Li metal anode were investigated. To construct pure Li₃Sb-modified Li metal, 5 mM of antimony nitrate (Sb(NO₃)₃) was dispersed into tetrahydrofuran (THF) solution by vigorously stirred for several hours. After being soaked for 180 s, the treated Li was rinsed using THF and dried at 60 °C to obtain pure Li₃Sb layer on Li anode. To prepare pure LiF-modified Li metal, 5 mM of ammonium fluoride (NH₄F) was dispersed into THF solution and the following procedures are the same with that of preparing pure Li₃Sb. In addition, commercial LiF layer on the Li surface was also prepared for comparison. 5 mM of commercial LiF was firstly dispersed into the THF, then 20 μ l of commercial LiF solution was dropped on the Li metal surface and dried at 60 °C to obtain pure LiF layer on Li anode. The XRD shown in Fig. S19a-c confirm the presence of single-phase Li₃Sb and LiF and the corresponding surface morphologies are presented in Fig. S11d-f. To validate the superiority of the hybrid SEI layer, the Li stripping/plating performance of different symmetric cells were conducted at 5 mA cm⁻² with capacity of 5 mA h cm⁻². As displayed in Fig. S20a-c, the symmetric cells with pure Li₃Sb, pure LiF, and commercial LiF modified Li anodes suffer a sudden voltage drop after 135 h, 90 h and 25 h, respectively, indicating an internal short-circuit and the failure of the symmetric cell. This case becomes more deteriorated under an ultra-high rate. As shown in Fig. S20d-f, at current density of 20 mA cm⁻², the voltage plateaus of the symmetric cell with pure Li₃Sb or LiF modified Li show large voltage fluctuations and constantly increased overpotential occurred at high rate, suggesting the unstable Li/electrolyte interface and the severe growth of Li dendrite. In sharp contrast, the symmetric cell with hybrid LiF/Li₃Sb-5 modified Li can deliver impressive Li plating/stripping stability over 320 h (1360 cycles) with a very low polarization of 100 mV. These results demonstrate that the fast Li⁺ diffusion kinetics of the hybrid interphase layer in our work enables not only low overpotential, but also flat and smooth cycling plateaus with a long lifespan at a high current density. In addition, the SEM images of Li deposition on the pure Li₃Sb and LiF modified Li anode were investigated at high current density of 5 mA cm⁻² with a capacity of 5 mA h cm⁻². As shown in Fig. S21a, the pure Li₃Sb layer reveals a flat and smooth morphology of lithium deposition due to the strong adsorption and the low diffusion energy of Li⁺. In addition, obvious dendrite-like morphology can be seen on the surface of pure LiF and commercial LiF modified Li anodes (Fig. S21b and c), suggesting nonuniform and uncontrolled Li nucleation and growth under high current density due to the limited ion diffusion in LiF component. In contrast, the hybrid SEI layer on the Li anode surface maintains intact and uniform after plating and the dense Li is found to be deposited underneath the hybrid SEI layer (Fig. 3f). These results further demonstrate the superiority of our hybrid SEI layer in achieving fast interfacial ion transport at high current density and suppressing the growth of Li dendrite.

In addition, by changing the mole ratio of SbF₃/Sb(NO₃)₃ or SbF₃/NH₄F precursor solvents, we can control the mole ratio of Li₃Sb and LiF in hybrid layer. To investigate the effects of Li₃Sb/LiF ratios on the cycling stability, the Li stripping/plating performance of different symmetric cells were carried out at high current density of 5 mA cm⁻² with a capacity of 5 mA h cm⁻², as shown in Fig. S22. Unfortunately, all symmetrical cells with different ratios of Li₃Sb/LiF obtained by changing the content of SbF₃/Sb(NO₃)₃ or SbF₃/NH₄F precursor solvents show short circuit with less than 90 h. At an optimum ratio of 4:3 (Li₃Sb/LiF), the symmetrical cell can be operated stably for 88 h, which surpasses the results of those with other ratios. Despite of this, its cycling stability is far behind that of LiF/Li₃Sb-5 modified Li anode obtained by SbF₃ precursor as the sole source rather than introducing another sources of metal halides or fluorine.

Note S10. Coin-type Li-S full cell performance

To further understand the effect of artificial hybrid SEI-modified Li on the electrochemical reaction of Li–S batteries, the cyclic voltammetry (CV) were conducted at a scan rate of 0.05 mV s⁻¹ within the voltage range of 1.7 to 2.7 V. Due to the presence of artificial SEI layer on Li surface, an initial activation process is required for the electrochemical reaction of sulfur and modified Li.¹⁵ Therefore, the CV results of both batteries with different anodes were obtained after activation. As presented in Fig. S23, two distinct reduction and oxidation peaks can be clearly observed, indicating that the surface modification of artificial hybrid SEI layer on Li anode shows no influence on the electrochemical reactions. During the cathodic scan, two reduction peaks at 2.32 and 2.01 V can be observed, corresponding to the reduction of element sulfur into soluble polysulfides and then to solid lithium sulfides (Li₂S₂/Li₂S).^{16,17} During the subsequent anodic scan, an oxidation peak appears at 2.39 V and followed by a shoulder peak at 2.44 V, which is attributed to the conversion of lithium sulfide into polysulfides and then to element sulfur. In addition, ΔE_1 and ΔE_2 are used to record the exact

redox potential difference reflecting the conversion of polysulfide to elemental sulfur and the conversion between lithium sulfide and polysulfide, respectively.¹⁵ It is noticed that the values of ΔE_1 and ΔE_2 of the battery with modified Li anode is lower than that with bare Li anode, indicating that the electrochemical reaction of Li–S battery becomes easier due to the high Li⁺ conductivity of the artificial hybrid LiF/Li₃Sb-5 layer.

To validate the superiority of the LiF/Li₃Sb-5 for lithium metal batteries, Li–S full cells were assembled by using LiF/Li₃Sb-5 modified Li anode paired with C/S cathodes. The galvanostatic charge/discharge behaviors of the Li–S cells based on bare Li and LiF/Li₃Sb-5 anodes at current density of 0.5 C were investigated (Fig. S24). The cycling stability of the LiF/Li₃Sb-5 based battery shows capacity retention of 72% after 100 cycles which is superior to the battery with the Li anode (66% after 100 cycles). Especially at high current density of 3 C, the LiF/Li₃Sb-5 based Li–S battery shows significant improvements in both the initial capacity and cycling stability compared with the bare Li-based Li–S battery (Fig. S25). The LiF/Li₃Sb-5 exhibits a higher average Coulombic efficiency (99.7%) than that of the battery using bare Li (97.2%) during 100 cycles, suggesting the good stability of the modified Li anode at ultrahigh current density due to the fast interfacial ion transport. In addition, a smooth flat surface was observed without any dendrites for the LiF/Li₃Sb-5 anode (Fig. S26a), while the bare Li surface is rough with porous dendrites for the bare Li anode after 100 cycling (Fig. S26b). This further also demonstrates that effectiveness of the high-strength interphase layer for suppressing the growth of Li dendrite.

Note S11. Pouch cell assembly and specific energy evaluation

a) Pouch cell assembly.

To assemble the 0.4 Ah-level pouch cell, S/C composite (areal S loading of 6 mg cm⁻² at single side) cathode was prepared and cut to be 3 cm by 4 cm and the active materials were carefully removed from tab areas to

expose the Al foil. The Al tab was riveted on the four pieces of as-prepared S/C cathode and a Ni tab was riveted on the three pieces of LiF/Li₃Sb anode (100 um) by ultrasonic welding. After that, two double-sided S cathode, separator, and Li anode were alternatively stacked together with two pieces of single-sided S cathode as the outer layer, the simplified pouch-cell configuration is shown in the Fig. S27. The total S loading is 432 mg. Then, ~1.3 mL of electrolyte ($E/S = 3 \ \mu L \ mg^{-1}$) was injected into the stack and the package was sealed under vacuum. 1 M LiTFSI in DME:DOL (1:1, v/v) with 2% LiNO₃ was used as the electrolyte. All pouch cells were assembled in an glovebox filled with argon gas (<0.1 ppm O₂ and <0.1 ppm H₂O).

b) Specific energy evaluation.

To evaluate the potential practical application of our pouch cell, the energy density (in Wh kg⁻¹) of the pouch cell was evaluated by the following equation:

 $E_g = VC / \sum m_i$

(10)

where E_g is the cell specific energy (Wh kg⁻¹), V is the average output voltage (V), C is the output capacity (mAh), and m_i are the weight (kg) of each component in the pouch cell, respectively, excluding packaging. The E_g of the as-assembled 0.4 Ah-level pouch cell was calculated to be 325.28 Wh kg⁻¹.

Part II. Supplementary Figure



Fig. S1 Surface energies $(eV/Å^2)$ of Li₃Sb surfaces.



Fig. S2 Surface energies (eV/Å²) of LiF surfaces.



Fig. S3 Side-view of the fully relaxed supercells of Li₃Sb(110)/Li(110) and LiF(001)/Li(001) interfaces.



Fig. S4 Optical images of SbF_3 dissolved in DME. No precipitations were observed even after resting for 10 days, indicating the dispersion stability of SbF_3 dissolved in DME solution. Taken 5 mM of SbF_3 as the representative.



Fig. S5 Ternary Phase diagram showing the phase equilibrium of the Li-Sb-F.



Fig. S6 Optical images of (a) bare Li, (b) treated Li with SbF₃, and (c) different concentrations of interphase

layer on Li.



Fig. S7 Three-dimensional (3D) element reconstruction of the various secondary ions after Ar sputtering.



Fig. S8 The SEM images of (a) bare Li, (b) LiF/Li₃Sb-1, (c) LiF/Li₃Sb-10, and (d) LiF/Li₃Sb-50.



Fig. S9 The voltage profiles of symmetric cells with (a) bare Li, (b) LiF/Li₃Sb-1, (c) LiF/Li₃Sb-5, (d) LiF/Li₃Sb-10, and (d) LiF/Li₃Sb-50 at 2 mA cm⁻² at 2 mA h cm⁻². (f) Corresponding discharge terminmal voltage.



Fig. S10 (a) Nyquist plots of LiF/Li₃Sb symmetric cells at fresh conditions and (b) corresponding equivalent circuit model.



Fig. S11 Raman spectra of the antimony-based lithiophilic interphase, taken LiF/Li₃Sb-5 as representative.



Fig. S12 TOF-SIMS depth profiles of various secondary ion species obtained by Ar-ion sputtering.



Fig. S13 TOF-SIMS mappings of LiF/Li₃Sb-5 electrodes before and after Ar consecutive sputtering for 1800s. The TOF-SIMS spectra were collected over time from the ejected secondary ions sputtered by Ar; and the relative intensity is also related to the weight of the ejected ions.



Fig. S14 Force-displacement plots of (a) bare Li and (b) the LiF/Li₃Sb-5 layer. It gives the force curves as a function of tip-surface distance during the indentation loading and unloading cycle.



Fig. S15 The contact angle measurement of (a) bare Li and (b) LiF/Li_3Sb-5 with ether electrolyte.



Fig. S16 Measurement of d.c. conductivity of bare Li and LiF/Li₃Sb-5 using blocking electrodes. Voltage response of bare Li and LiF/Li₃Sb-5 to an applied current of 5.0 mA.



Fig. S17 LSV curves of symmetric cells with bare Li and LiF/Li₃Sb-5 at 100 mV s⁻¹ within a voltage range of -0.2 to 0.2 V.



Fig. S18 Nyquist plot of symmetric cells with (a) LiF/Li₃Sb-5 and (b) bare Li after 10 and 100 cycles. (c) corresponding equivalent circuit model. (d) R_{ct} of bare Li and LiF/Li₃Sb-5.



Fig. S19 XRD of (a) pure Li₃Sb, (b) pure LiF, and (c) commercial LiF modified Li anodes. SEM images of

(d) pure Li₃Sb, (e) pure LiF, and (f) commercial LiF modified Li anodes.



Fig. S20 Voltage profiles of symmetric cells with (a,c) pure Li₃Sb, (b,d) pure LiF, and (c,f) commercial LiF modified Li anodes.



Fig. S21 SEM images of Li deposition on (a) pure Li₃Sb, (b) pure LiF, and (c) commercial LiF modified Li anodes after plating 5 mAh cm⁻² at 5 mA cm⁻².



Fig. S22 Voltage profiles of symmetric cells Li_3Sb/LiF with different the ratio at 5 mA cm⁻² for 5 mA h

 cm^{-2} .



Fig. S23 CV curves of Li–S batteries with bare Li and modified Li at a scan rate of 0.05 mV s⁻¹.



Fig. S24 Charge and discharge curves at different cycles of Li–S batteries with (a) bare Li and (b) LiF/Li₃Sb-5

at 0.5 C. (c) cycling performance of Li–S batteries with bare Li and LiF/Li₃Sb-5 at 0.5 C.



Fig. S25 (a) Cycling performance of Li–S cells with bare Li and LiF/Li₃Sb-5 at 3 C. (b) The corresponding average Coulombic efficiency.



Fig. S26 SEM images of (a) bare Li and (b) LiF/Li_3Sb-5 after 100 cycles.



Fig. S27 The actual pouch cell configuration.



Fig. S28 SEM image of a large-scale commercial lithium belt treated by 5 mM of SbF₃.

Part III. Supplementary Tables

Alloy	Li diffusivity (cm ² s ⁻¹)	Ref.
Li (self-diffusion)	7.65×10 ⁻¹¹	[18]
	6.12×10 ⁻¹¹	[19]
Li ₁₃ Sn ₅	5.01×10 ⁻⁵ -7.59×10 ⁻⁴	[20]
Li ₂₂ Sn ₅	1.9×10 ⁻⁷ -5.9×10 ⁻⁷	[21]
	6.58×10 ⁻⁵ -1.91×10 ⁻⁴	[20]
Li ₂₂ Si ₅	5.13×10 ⁻⁵ -7.24×10 ⁻⁵	[22]
Li ₃ Bi	1.0×10 ⁻⁶ -3.0×10 ⁻⁶	[23]
LiZn	4.0×10 ⁻⁷ -4.0×10 ⁻⁸	[21, 24]
Li–In (47–62 at % Li)	4.73×10 ⁻⁷ -3.98×10 ⁻⁵	[25]
Li _x Ag (x=4.7–5.0)	$0.12 \times 10^{-8} - 4.0 \times 10^{-8}$	[26]
Li–Mg (β-phase)	≈10 ⁻⁸	[27]
	≈10 ⁻¹¹	[28]
	≈2.3×10 ⁻¹¹	[29]
Li ₃ Sb	2.0×10 ⁻⁴	[30]

Table S1. Summary of lithium diffusivity in various Li-rich alloy.

Li ₃ Sb		LiF		
surface	surface energy	surface	surface energy	
(001)-LiSb term.	0.12	(001)-LiF term.	0.03	
(001)-Li ₂ term.	0.13	(110)-LiF term.	0.09	
(110)-Li ₃ Sb term.	0.07	(111)-F term.	0.58	
(111)-Li ₃ term.	0.18	(111)-Li term.	0.57	
(111)-Sb term.	0.19			

Table S2. Summary of the surface energies (eV/Å²) of the various Li_3Sb and LiF surfaces.

Li ₁ /Li ₃ Sb (110)		Li ₁ /LiF (001)	
model	E _{ads} (eV)	model	E _{ads} (eV)
Li _{1st} -top	0.72	F-top	0.71
Li _{2nd} -top	1.04	Li-top	0.14
Sb _{1st} -top	0.92	Hollow	0.22
Sb _{2nd} -top	0.66		

Table S3. The adsorption energies (E_{ads}) of Li^+ on the substrates.

Table S4. The calculated formation energy (E_f), strain energy (ζ), interfacial energy (σ) and the work of adhesion (W_{adh}) for the interfacial supercells.

interface	E _f (kJ/mol)	ζ (kJ/mol)	σ (J/m²)	W _{adh} (J/mol)
Li ₃ Sb(110)/Li(110)	0.892	0.018	0.159	1.513
LiF(001)/Li(001)	7.475	0.163	0.756	0.236

Chemicals	Price (\$/g)*	Reference
InBr ₃	11.4	[31]
InI ₃	59	[31]
InCl ₃	9.42	[13]
BiCl ₃	3.7	[13]
SnCl ₄	9.62	[32]
TiCl ₄	50.8	[32]
GeCl ₄	22.2	[33]
InF ₃	42.6	[31]
BiF ₃	8.76	[2]
SbF ₃	0.798	This work

Table S5. The price comparison of different metal salts for fabricating the lithiophilic alloy.

* The price was obtained from Sigma-Aldrich (Shanghai) Trading Co., Ltd on Dec.1 in 2020.

symmetrical cells	R_s/Ω	R_{int} / Ω	R_{ct}/Ω
LiF/Li ₃ Sb-1	2.9	224.1	615.6
LiF/Li ₃ Sb-5	2.4	96.5	67.1
LiF/Li ₃ Sb-10	2.8	99.4	82.4
LiF/Li ₃ Sb-50	3.8	127.2	180.3

 Table S6. Impedance results of LiF/Li₃Sb symmetric cells at initial state.

symmetrical cells	bare Li	LiF/Li ₃ Sb-5	
	R _s R _{ct}	R _s R _{ct}	
10 cycles	3.5 2.1	1.9 1.6	
100 cycles	4.1 10.4	2.1 2.0	

 Table S7. Impedance results of bare Li and LiF/Li₃Sb-5 symmetric cells at different states.

 Table S8. Comparison of maximum current density of our LiF/Li₃Sb-5 with the reported modified SEI in symmetric cells.

Modified SEI	Maximum current / capacity (mA cm ⁻² / mAh cm ⁻²)	Cycle life (hours)	Ref.
Graphite fluoride-LiF	10/1	33	[34]
N-organic/Li ₃ N	3/6	300	[35]
LiZn/Li ₃ PO ₄	5/1	140	[36]
Li–Hg alloy	12/12	200	[37]
Al-Li alloy/LiCl	20/1	100	[38]
Li ₃ N/LiF/organic composite	10/1	100	[39]
UiO-66-ClO ₄	5/1	300	[40]
Poly(vinyl alcohol)	5/2	200	[41]
Li-Nafion/LiCl	8/1	120	[42]
PVDF-HFP/LiF	2/2	200	[43]
polyacrylonitrile	10/1	200	[44]
hybrid polyurea film	5/1	85	[45]
PTCDI	10/1	300	[46]
Mg@C ₆₀	3/1	180	[47]
Li alginate	3/1	120	[48]
This work	20/2	320	

Tech.	Areal S loading (mg cm ⁻²)	E/S ratio (µL mg ⁻¹)	Energy density (Wh kg ⁻¹)	Cycle number	Capacity retention (%)	Ref.
Intercalation-type Mo ₆ S ₈	6.9	1.2	366	10	~82%	[49]
Mesoporous carbon nanotube aerogel	10.0	7.8	~200	20	84.6%	[50]
Cell design	6	2.5	313	22	~30%	[51]
LiTFSI in TMS/TTE electrolyte	1.77	2.97	298	40	49%	[52]
VS4@RGO	5	7	118	50	82%	[53]
Interconnected carbon fabrics	7.56	2.7	315.98	51	80.3%	[54]
This work	6	3	325.28	60	91.5%	

Table S9. Comparison of the pouch cell performance of our work with previously reported works.

Part IV. Supplementary References

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