Supporting Information



Fig. S1 Additional details about the DFT simulations. Electron density difference of a Li atom absorbed on LiF (001) surface at (a) stable and (b) saddle-point configurations. The isosurface value is 0.0003 e/a_0^3 with a_0 being the Bohr radius. Electron accumulation and depletion are represented by red and blue isosurfaces, respectively.



Fig. S2 SEM image of the thickness of the coated LiF layer. It shows a thickness about 150nm from a 20-minute deposition using radio-frequency magnetron sputtering.



Fig. S3 Electrochemical performance of symmetrical cells using 50 nm LiF-coated electrodes or 500 nm LiF-coated Li electrodes. (a and b) Voltage profiles obtained from galvanostatic cycling of cells using 50nm LiF-coated electrodes (a) and 500 nm LiF-coated Li electrodes (b) at current density of 1 mA cm⁻² for a total capacity of 1 mAh cm⁻².



Fig. S4 SEM images of patterned 500 nm LiF-coated Li anodes after Li deposition.



Fig. S5 SEM images of patterned LiF-coated Li foil before (a) and after cycling (b and c).



Fig. S6 SEM images of bare Li electrode after cycling. (a to d) Morphologies of Li electrodeposition at different resolutions.



Fig. S7 SEM images of LiF-coated Li electrode after cycling. (a to d) Morphologies of Li electrodeposition at different resolutions.



Fig. S8 XPS spectra of F and Li signals. (a to d) F signals of bare Li foil before (a) and after (b) cycling, and F signals of LiF-coated Li foil before (c) and after (d) cycling. (e to h) Li signals of bare Li foil before (e) and after (f) cycling, and Li signals of LiF-coated Li foil before (g) and after (h) cycling. The XPS analysis was performed from the surface film on the lithium metal electrode. Depth profiles are all arranged from top (0 nm) to a depth of 200 nm with an increment of 20 nm.



Fig. S9 SEM images of bare Cu electrode and LiF-coated Cu electrode after cycling. (a and b) Morphologies of Li deposition on bare Cu electrode using PC (a) or DOL/DME (b) electrolyte. (c and d) Morphologies of Li deposition on LiF-coated Cu electrode using PC (c) or DOL/DME (d) electrolyte.



Fig. S10 Discharge capacities of Li/LTO and LiF-coated Li/LTO cells at different chargedischarge rates. (a and b) Discharge capacities of Li/LTO (red) and LiF-coated Li/LTO (blue) cells with PC (a) or EC/DEC (b) electrolyte from 0.2 C to 10 C.