

Supporting Information

Cycling and Failing of Lithium Metal Anodes in Carbonate Electrolyte

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Experimental Section

Electrolyte: Lithium hexafluorophosphate (LiPF₆, 1.0 M) dissolved in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume) was used as the electrolyte. Fluoroethylene carbonate (FEC) was added to the above electrolyte in a concentration of 2 wt% to prepare the electrolyte with FEC additive.

LiNO₃-modified glass fiber separator: 0.2 g of LiNO₃ was added to 10 mL of ethylene glycol dimethyl ether to form a saturated solution. Glass fiber separators (Whatman) with a diameter of 15 mm were soaked in the above solution for 2 h. The separators were then taken out and dried in vacuum overnight to fully evaporate the solvent. About 1 mg of LiNO₃ was loaded on one piece of glass fiber separator.

Cell assembly and electrochemical measurements: CR 2032 cells were assembled in an Ar-filled glove box. For Li||Cu cells with a thick Li foil electrode, a Li metal disk (450 μm in thickness) with a diameter of 13 mm and a piece of Cu foil with a diameter of 15 mm were paired. 80 μL of electrolyte was used unless mentioned otherwise. A glass fiber separator was used. An additional polypropylene layer (Celgard 3501) was introduced between the glass fiber separator and the electrode of interest, to facilitate post-cycling separation of the two. The cells were measured using a BT2143 battery analyzer (Arbin Instrument). Electrochemical Li plating at a certain current density was performed until a certain capacity was reached. It was then followed by Li stripping at the same current density with a cut-off voltage of 0.5 V vs Li⁺/Li. These processes were repeated for several cycles.

To prepare thin Li metal electrodes, a thick-Li||Cu cell was first run for 5 conditioning cycles followed by a final Li plating process. The Cu electrode with plated Li was then taken out as the thin Li metal

electrode. The thin-Li||Cu cell was cycled between -1 and 1 V.

To prepare $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes, an N-methyl-2-pyrrolidone (NMP) suspension containing $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Super P carbon black, and polyvinylidene difluoride (PVDF) in the mass ratio of 8:1:1 was coated on a Cu foil and dried in vacuum. The mass loading of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was about 28 mg cm^{-2} , which can give an areal capacity of more than 3 mAh cm^{-2} at the current density of 1 mA cm^{-2} . A Li|| $\text{Li}_4\text{Ti}_5\text{O}_{12}$ cell with a thick Li foil as the anode was first cycled between 1 and 2.5 V for 5 conditioning cycles. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode was then taken out and used as the cathode in the thin-Li|| $\text{Li}_4\text{Ti}_5\text{O}_{12}$ cell.

Materials characterization: Scanning electron microscopy (SEM) images were obtained on a Hitachi SU8230 SEM microscope. XPS spectra were obtained using a monochromatic 1486.7 eV Al K_α X-ray source on a PHI VersaProbe II X-ray Photoelectron Spectrometer with a 0.47 eV system resolution. The disassembled electrode was carefully rinsed with DEC and then dried in the antechamber of the glove box prior to characterization. For XPS measurements, the sample was transferred using an air-tight vessel to avoid exposure to air. Depth profile measurements were carried out using Ar ion sputtering at the power of $0.5 \text{ kV} \times 7 \text{ mA}$ (for the first 6 min) or $5 \text{ kV} \times 7 \text{ mA}$ (for the following 36 min) over a $3 \times 3 \text{ mm}^2$ area.

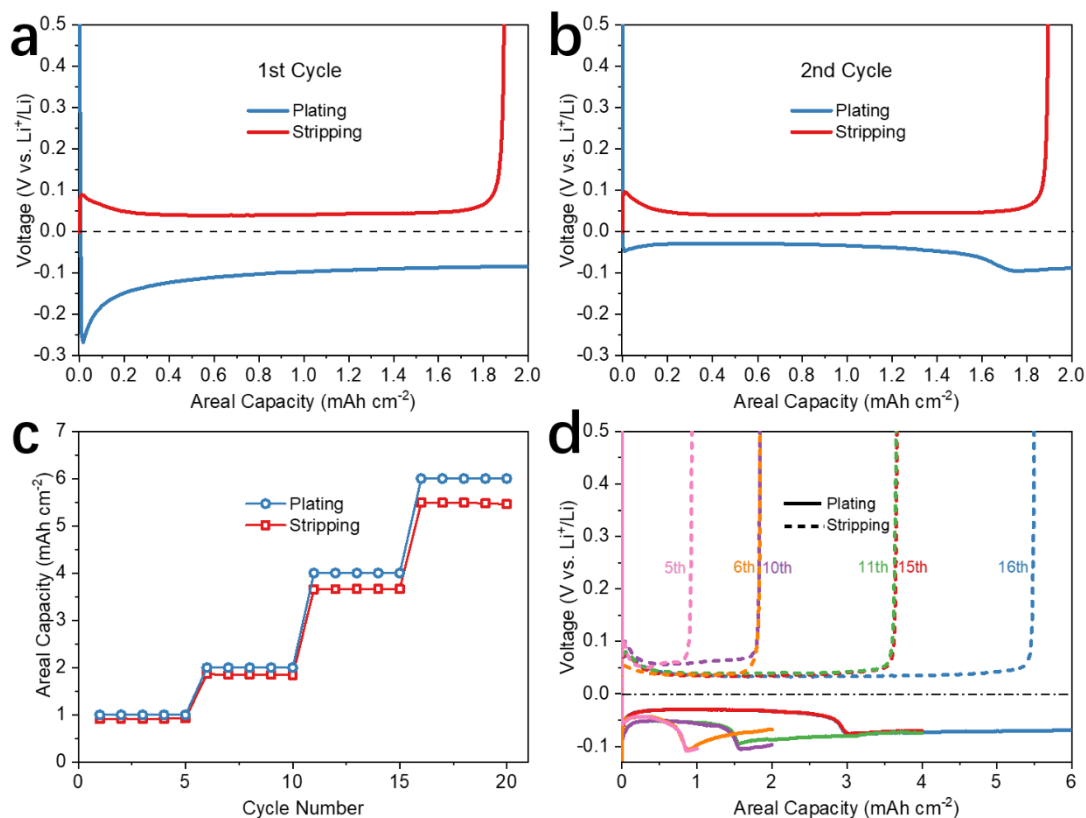


Figure S1. Li plating and stripping voltage profiles of the (a) first and (b) second cycles of a Li||Cu cell under 1 mA cm^{-2} – 2 mAh cm^{-2} conditions. (c) Li||Cu cell cycled at a fixed current density of 1 mA cm^{-2} with the Li plating/stripping capacity increased stepwise, and (d) the corresponding voltage profiles for various cycles.

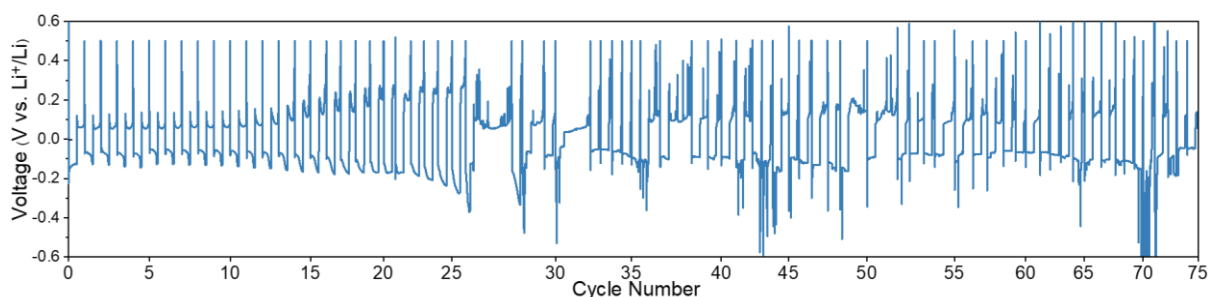


Figure S2. Voltage profiles of Li||Cu cell with $15 \mu\text{L}$ of electrolyte.

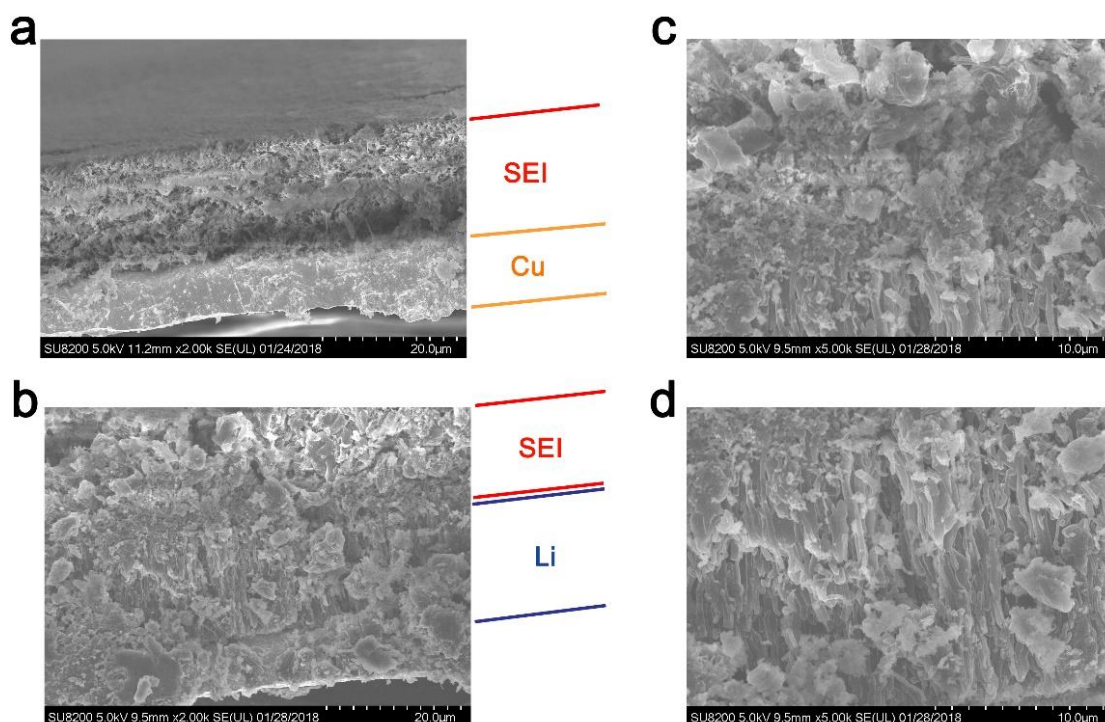


Figure S3. SEM images of Cu electrodes after (a) 5 charging-discharging cycles and (b) 5 cycles followed by another Li plating step. (c) An enlarged image of the SEI part of b. (d) An enlarged image of the Li part of b. The Li, SEI and Cu layers are distinguished based on their different textures and morphologies.

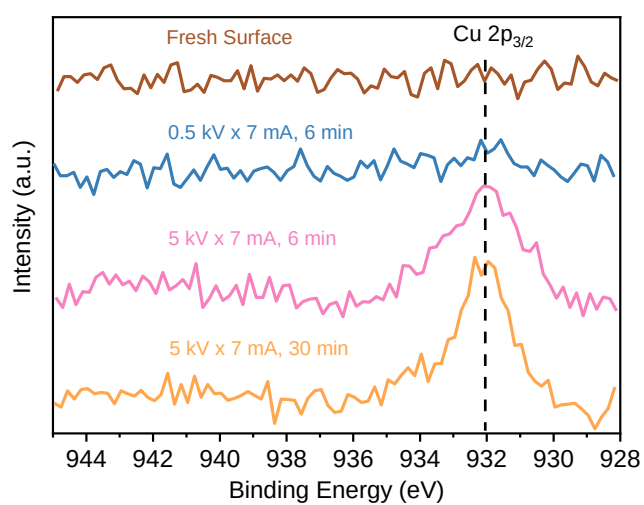


Figure S4. Cu 2p_{3/2} XPS depth profiling for the Cu electrode of a Li||Cu cell after 5 cycles under 1 mA cm⁻²–2 mAh cm⁻² conditions.

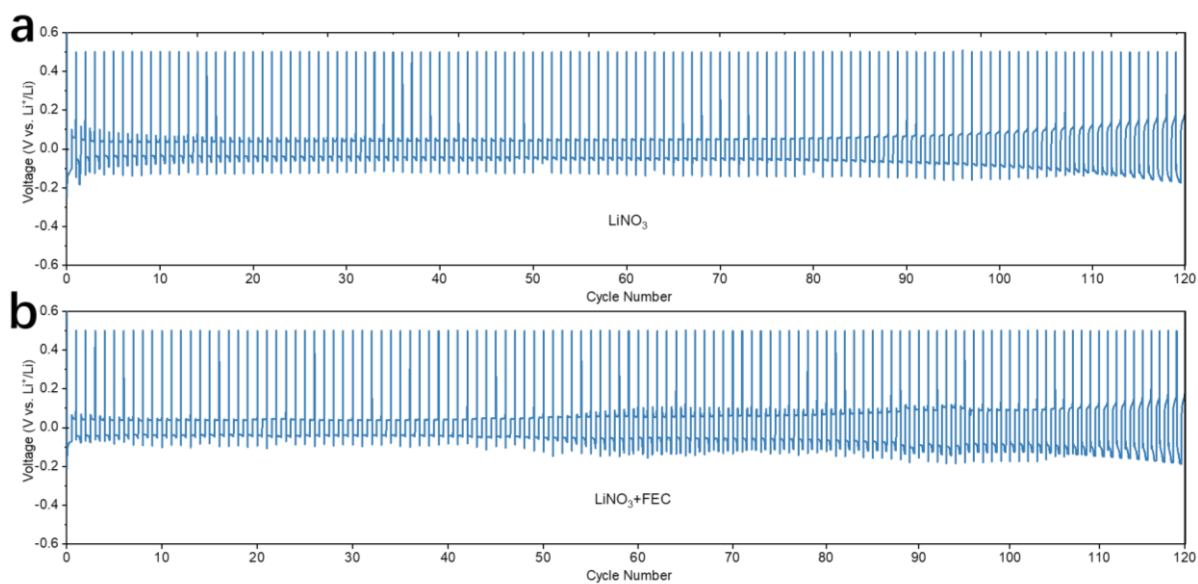


Figure S5. Charging-discharging voltage profiles of Li||Cu cells using (a) LiNO₃ additive and (b) LiNO₃+FEC additives.

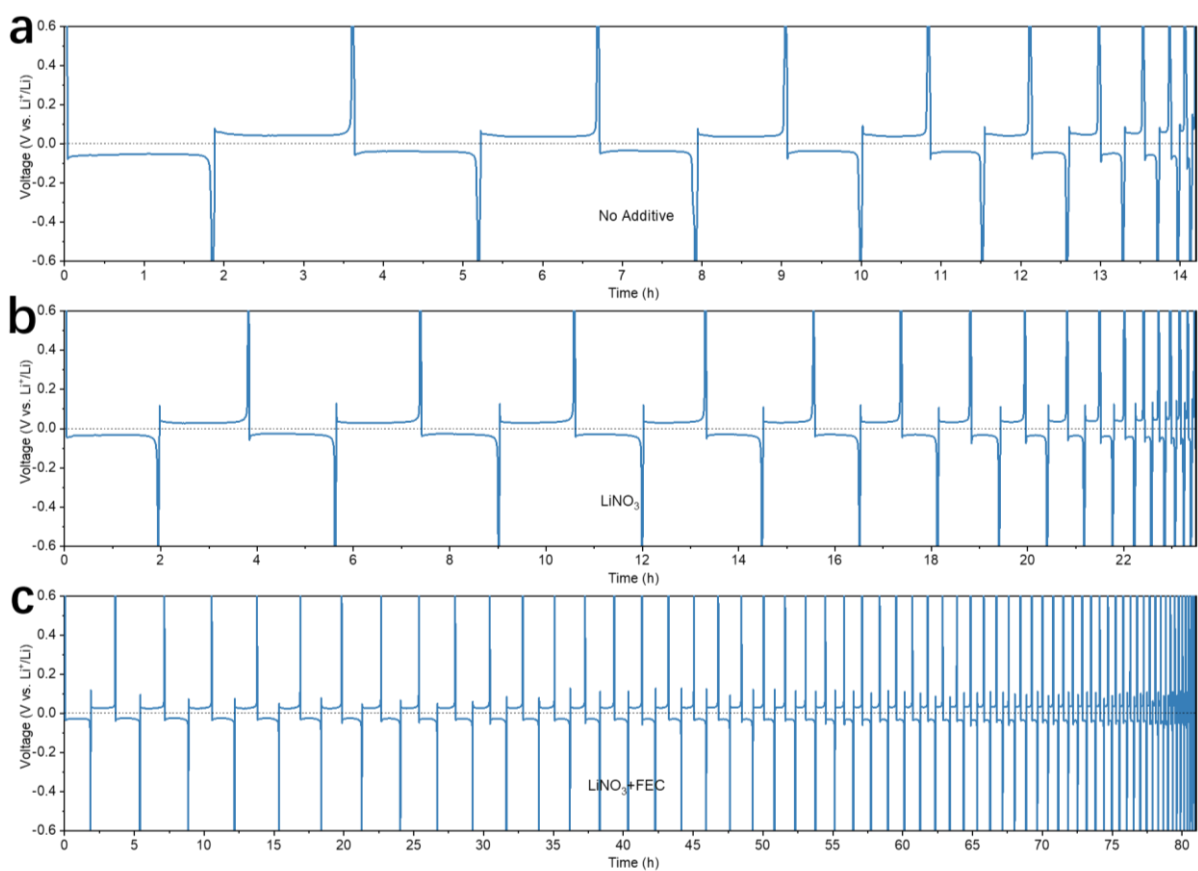


Figure S6. Charging-discharging voltage profiles of thin-Li||Cu cells using (a) no additive, (b) LiNO₃ additive and (c) LiNO₃+FEC additives.

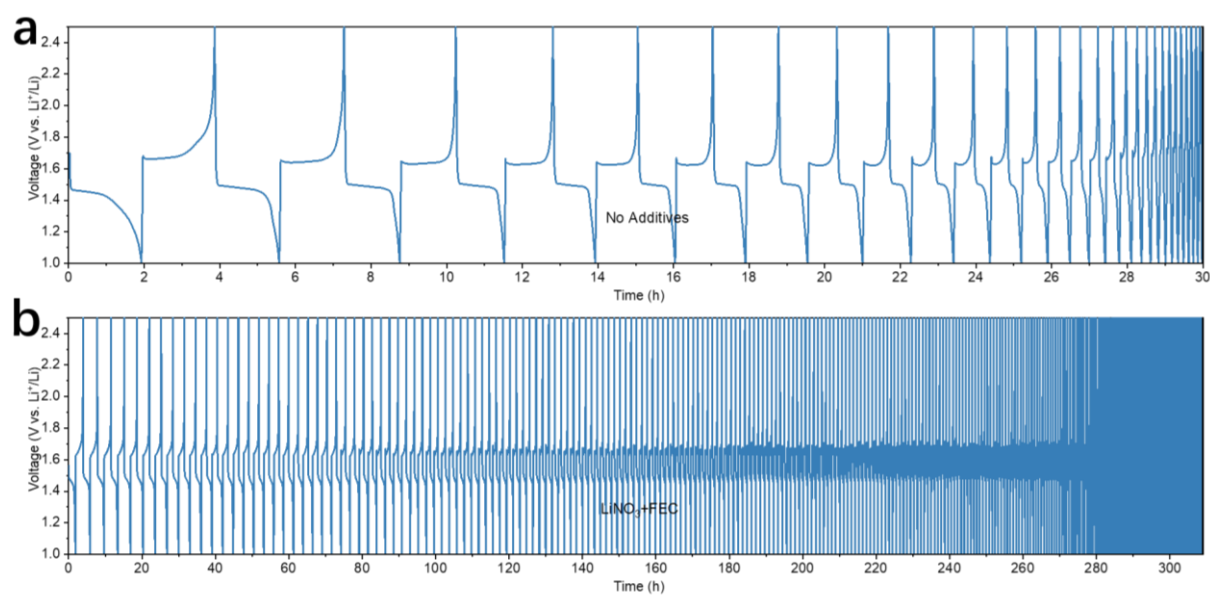


Figure S7. Charging-discharging voltage profiles of thin-Li||Li₄Ti₅O₁₂ cells using (a) no additive and (b) LiNO₃+FEC additives.