

## Supporting Information

### Facile preparation of a stable 3D host for lithium metal anodes

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## Experiment

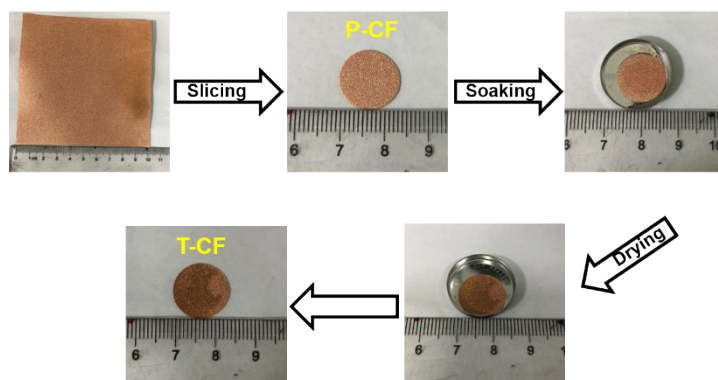
**Materials.** Li foil (400  $\mu\text{m}$ , China Energy Lithium Co., Ltd. ), Cu foams (200  $\mu\text{m}$ , 56.8  $\text{mg cm}^{-2}$ , 98% porosity, Kunshan Guangjiayuan new materials Co. Ltd), lithium nitrate ( $\text{LiNO}_3$ , Sigma-Aldrich, 99.9% ), lithium hexafluorophosphate ( $\text{LiPF}_6$ , 99%), ethylene carbonate (EC, 99%), diethyl carbonate (DEC, 99%), and fluoroethylene carbonate (FEC, 99%) were purchased from Guangzhou Tinci Materials Technology Co., Ltd.  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}$  (NCM523, Canrd Co., Ltd), commercial  $\text{LiFePO}_4$  electrode was supplied by Jiangxi Anchitech Company (China). All these materials used without further purification.

**Preparation of T-CF.** Pristine Cu foams (200  $\mu\text{m}$ , Kunshan Guangjiayuan new materials Co. Ltd) were washed by diluted hydrochloric acid solution, then alternately cleaned three times with alcohol and deionized water. After removing the Cu oxide and other impurities, the Cu foam was vacuum dried at 80  $^\circ\text{C}$  for 3 h to remove residual water. As shown in Figure S1, the resulting Cu foams were punched to 14 mm discs. Then, 100  $\mu\text{L}$  50  $\text{mg mL}^{-1}$   $\text{LiNO}_3$  aqueous solution ( $\sim 5$   $\text{mg LiNO}_3$ , which is equal to 5 wt%  $\text{LiNO}_3$  in 100  $\mu\text{L}$  electrolyte) was dispersed into P-CF and to fill it. The electrode discs was dried under vacuum at 80  $^\circ\text{C}$  for 12 h to obtain the T-CF(200  $\mu\text{m}$ , 60.2  $\text{mg cm}^{-2}$ ).

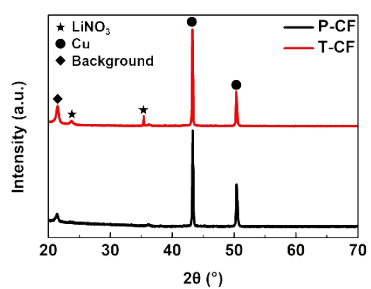
**Electrochemical measurement.** P-CF/T-CF were assembled into CR2032-type coin cells with Li foil, and they were separated by Celgard 2400 separator. The electrolyte was 1 M  $\text{LiPF}_6$  in EC/DEC (1:1) with 10%vt FEC with a certain amount of 50  $\mu\text{L}$  in coin cells. The Li-Cu half cells for Coulombic efficiency were assembled in glovebox then test at a different current density and current capacity. For further assembled full cell, Li-Cu half cells were disassembled after depositing Li at 0.5  $\text{mA cm}^{-2}$  with different areal capacity (8 or 10  $\text{mAh cm}^{-2}$ ) to obtain Cu foam deposited with Li metal (CF@Li). The NCM523 cathodes were made by blending the NCM523 powder, Super P, and PVDF (Poly (vinylidene fluoride)) at a weight ratio of 8: 1: 1, then this slurry mixture was coated on Al foil by the doctor blade way with a controlled areal mass loading is 14  $\text{mg cm}^{-2}$ . After drying in the oven at 80  $^\circ\text{C}$  overnight, these electrode foils were cut to 8 mm discs, then were paired with the different CF@Li (8  $\text{mAh cm}^{-2}$ , N/P ratio is 4), the full cells were galvanostatically cycled between 2.7-4.3V at 0.5 C before three activation cycles at 0.1 C. The commercial  $\text{LiFePO}_4$  cathode (mass loading is 17  $\text{mg cm}^{-2}$ ) was mixed of  $\text{LiFePO}_4$ , CNTs, Super P and PVDF with a weight ratio of 96.5: 1: 0.5: 2, it paired with the different CF@Li (10  $\text{mAh cm}^{-2}$ , N/P ratio is 4), and were galvanostatically cycled between 3-4V at 1 C before three activation cycles at 0.1 C. The cyclic voltammetry (CV) was measured at a scan rate of 0.1  $\text{mV s}^{-1}$  using a CHI 600D. The electrochemical impedance spectra (EIS) was acquired at the frequency range of  $10^5$  to 0.1 Hz using Solartron electrochemical workstation.

**Characterizations.** X-ray diffraction XRD patterns were collected by PANalytical X'pert PRO-DY2198 with Cu K $\alpha$  radiation. The scanning electron microscopy (SEM) images of the deposited metallic Li were observed by using Nova Nano SEM 450. Noticeably, the electrodes were obtained by disassembling the Li-Cu half cells in the glovebox with  $\text{H}_2\text{O}$  and  $\text{O}_2$  below 0.1 ppm and gently risen with DEC to remove the Lithium salts and electrolytes before observed. The X-ray photoelectron spectroscopy (XPS) measurement applied to the SEI was implemented on a VG MultiLab 2000 system (Thermo VG Scientific).

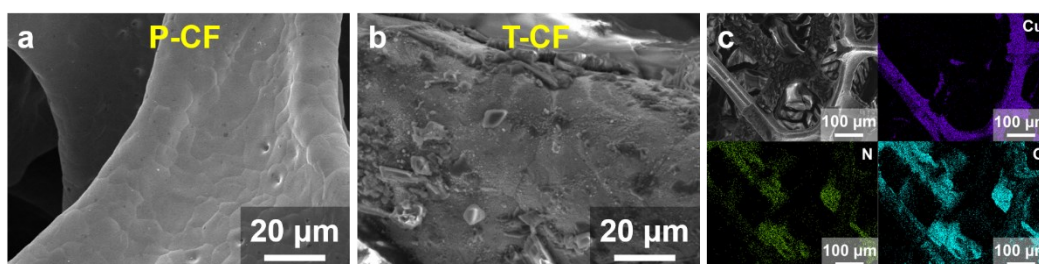
## Supporting Figures



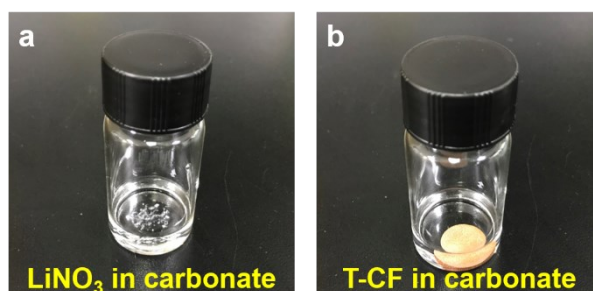
**Figure S1.** Photographs of the preparation process of T-CF.



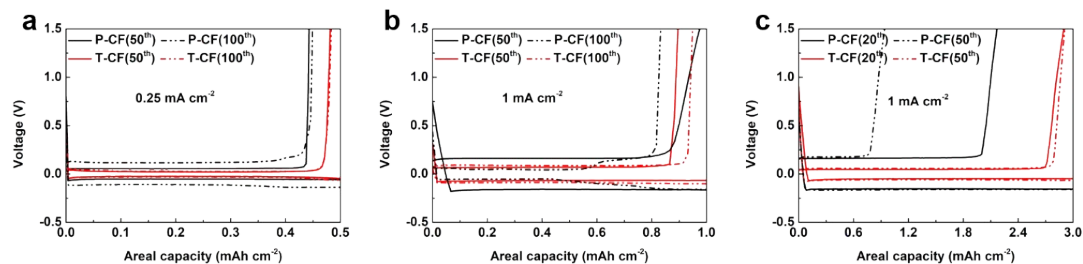
**Figure S2.** XRD patterns of P-CF and T-CF.



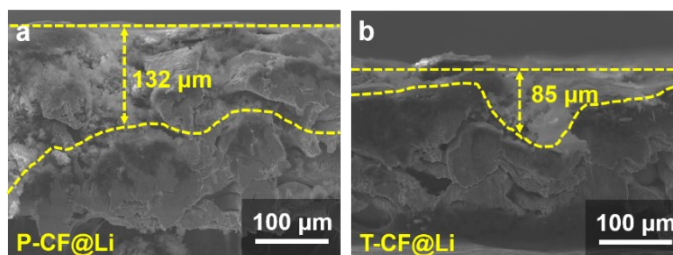
**Figure S3.** SEM images of (a) P-CF and (b) T-CF. (c) The corresponding EDS spectrum of T-CF (Cu, N, O).



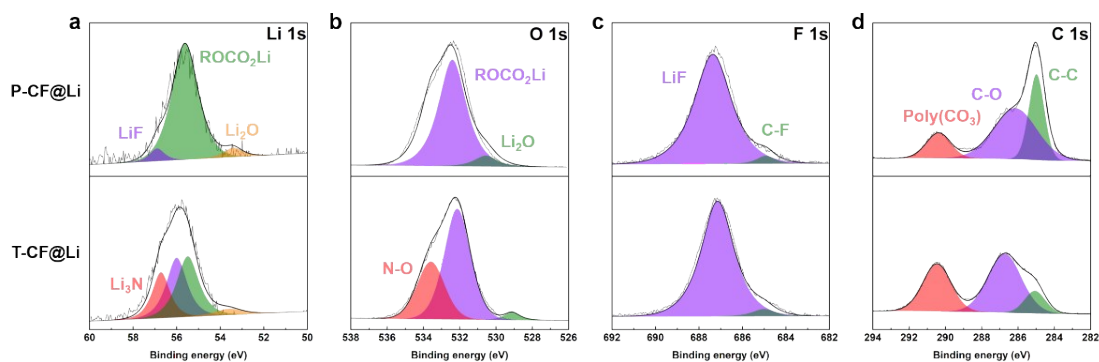
**Figure S4.** Photographs comparison of a) pure LiNO<sub>3</sub> and b) T-CF in carbonate electrolyte.



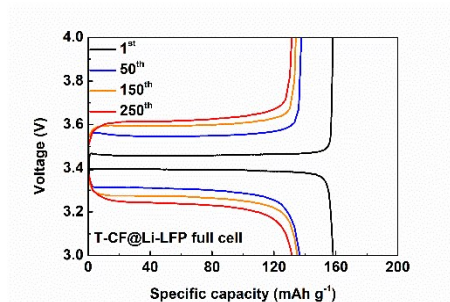
**Figure S5.** The comparison of Li-Cu half cells voltage profiles during cycling at (a)  $0.25 \text{ mA cm}^{-2}$  for  $0.5 \text{ mAh cm}^{-2}$ , (b)  $1 \text{ mA cm}^{-2}$  for  $1 \text{ mAh cm}^{-2}$ , and (c)  $1 \text{ mA cm}^{-2}$  for  $3 \text{ mAh cm}^{-2}$ .



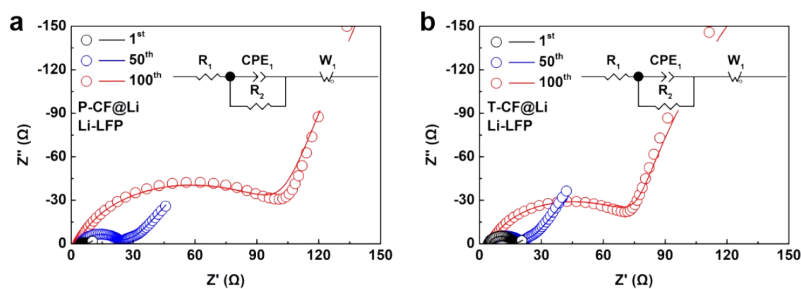
**Figure S6.** SEM cross-sectional images of cycled (a) P-CF@Li and (b) T-CF@Li. (Cycled condition:  $1 \text{ mA cm}^{-2}$ ,  $1 \text{ mAh cm}^{-2}$  after 50 cycles)



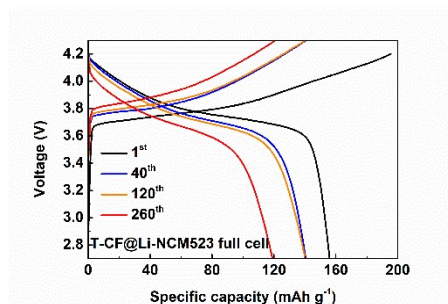
**Figure S7.** XPS spectrum comparison of (a) Li 1s, (b) O 1s, (c) F 1s, and (d) C 1s.



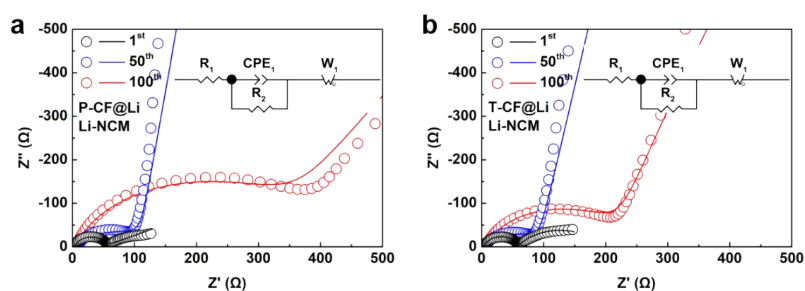
**Figure S8.** Voltage profile of T-CF@Li-LFP full cell.



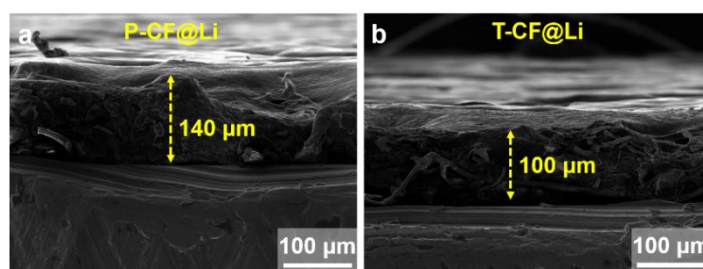
**Figure S9.** EIS plot comparison of Li-LFP full cells during cycling a) P-CF@Li and b) T-CF@Li. The inset figure is the corresponding equivalent circuit.



**Figure S10.** Voltage profile of T-CF@Li-NCM523 full cell.



**Figure S11.** EIS plot comparison of Li-NCM523 full cells during cycling a) P-CF@Li and b) T-CF@Li. The inset figure is the corresponding equivalent circuit.



**Figure S12.** SEM cross-sectional images of cycled in Li-NCM523 full cells after cycling (a) P-CF@Li and (b) T-CF@Li.

### Supporting Note

#### The estimated specific capacity of the composite anode.

For the P-CF@Li deposited 10 mAh cm<sup>-2</sup> Li, the specific capacity can be calculated as

$$x = \frac{10 \text{ mAh cm}^{-2}}{\frac{10 \text{ mAh cm}^{-2}}{3860 \text{ mAh g}^{-1}} \times 1000 + 56.8 \text{ mg cm}^{-2}} \times 1000 = 168 \text{ mAh g}^{-1}$$

(1)

Similarly, the T-CF@Li deposited 10 mAh cm<sup>-2</sup> Li, the specific capacity can also be calculated as

$$x = \frac{10 \text{ mAh cm}^{-2}}{\frac{10 \text{ mAh cm}^{-2}}{3860 \text{ mAh g}^{-1}} \times 1000 + 60.2 \text{ mg cm}^{-2}} \times 1000 = 159 \text{ mAh g}^{-1}$$

(2)

It's worth noting that the specific capacity of composite anode can be significantly improved by using lighter 3D host (carbon fiber, 3D graphene, or carbon nanotubes, etc.), and deposited more metallic Li.