ADVANCED ENERGY MATERIALS

Supporting Information

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3D Wettable Framework for Dendrite-Free Alkali Metal Anodes

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Table S1. Voltage hysteresis comparison of Li plating/stripping process for bare Li cell and Li-CF cell at 1 mA cm^{-2} and 3 mA cm^{-2}.

Voltage hysteresis at 1 mA cm^{-2} (mV)			Voltage hysteresis at 3 mA cm^{-2} (mV)		
Cycle index	Bare Li foil	Li-CF	Cycle index	Bare Li foil	Li-CF
1	258	72	1	737	378
2	152	63	2	492	266
10	133	60	10	352	233
100	106	72	50	252	184
200	133	89	100	256	215
300	160	95	135	349	242
372	208	100	154	1809	255

Calculation details about the energy density of full cells

We suppose a full cell delivers a total capacity of 3860 mAh. The energy density of the cell can be calculated by Equation S1:

$$E = (C \times U)/M \qquad \text{Equation S1}$$

E: Energy density of the full cell (kWh/kg)

C: Capacity of the full cell 3860 (mAh)

U: Voltage of the cell (U_2-U_1) (V)

M: Total active mass of the positive and negative electrode, respectively (m_1+m_2) (g)

U_1: Practical average discharge potential of the negative electrode (V)

U_2: Practical average discharge potential of positive electrode (V)

m_1: mass of the negative electrode to deliver 3860 mAh capacity (g)

m_2: mass of the positive electrode to deliver 3860 mAh capacity (g)

The essential data for the negative and positive electrodes are listed below:

Table S2. Essential data of typical negative materials in Li-ion and Li batteries

Electrode Material	**U_1: Practical average discharge potential (V vs. Li+/Li)**	**C_1: Practical specific capacity (mAh g^{-1})**	**m_1 (g)**
Graphite	0.1	370	10.43
Li-CF[1]	0	1430	2.70
Li	0	3860	1.00

[1] The practical capacity of the Li-CF electrode is based on the total mass of Li-CF.

Table S3. Essential data of typical positive electrode materials in Li-ion and Li batteries [1]

Electrode Material	**abbreviation**	**U_2: Practical average**	**C_2: Practical**	**m_2 (g)**

		discharge potential (V vs. Li+/Li)	specific capacity (mAh g^{-1})	
$LiCoO_2$	LCO	3.8	150	25.73
$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$	NCM	3.7	170	22.71
$LiMn_2O_4$	LMO	4.05	130	29.69
$LiMn_{1.5}Ni_{0.5}O_4$	LNMO	4.7	140	27.57
$LiFePO_4$	LFP	3.4	160	24.13
$LiCoPO_4$	LCP	4.8	130	29.69
***x*Li_2MnO_3·(1–*x*)$LiMO_2$(M=Ni, Co and Mn)**	LR-NCM	3.75	225	17.16

Table S4 Energy density calculation based on the Equation S1

Energy density (Wh kg^{-1})	LCO	NCM	LMO	LNMO	LFP	LCP	LR-NCM
Graphite	395	419	380	467	369	452.	511
Li-CF	516	562	483	599	489	572	729
Li	549	602	509	635	522	604	797

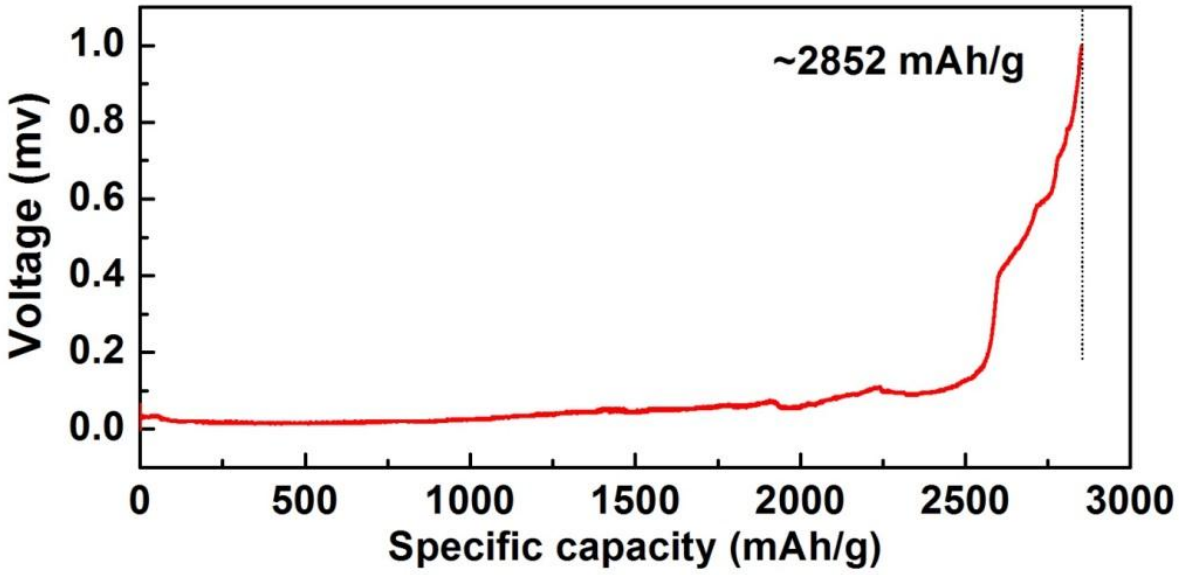

Figure S1. A Li stripping curve of the Li-CF electrode at 1 mA cm^{-2}. As shown, the Li-CF electrode delivers a capacity of 2852 mAh g^{-1} (51 mAh cm^{-2})-at a 1 V cutoff potential (based on the mass of Li).

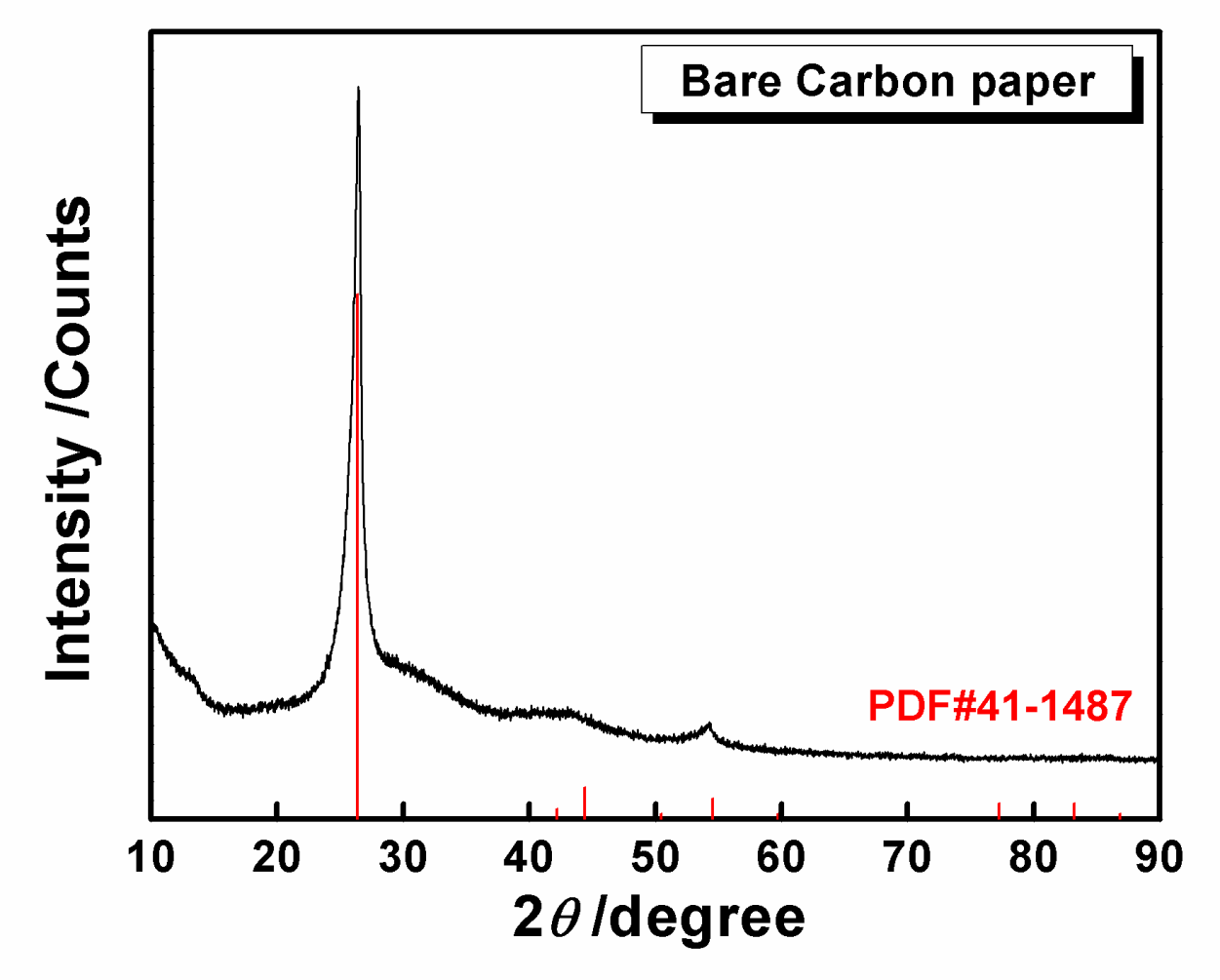

Figure S2. XRD pattern of bare CF, which corresponds well to graphitic carbon (PDF 41-1487)

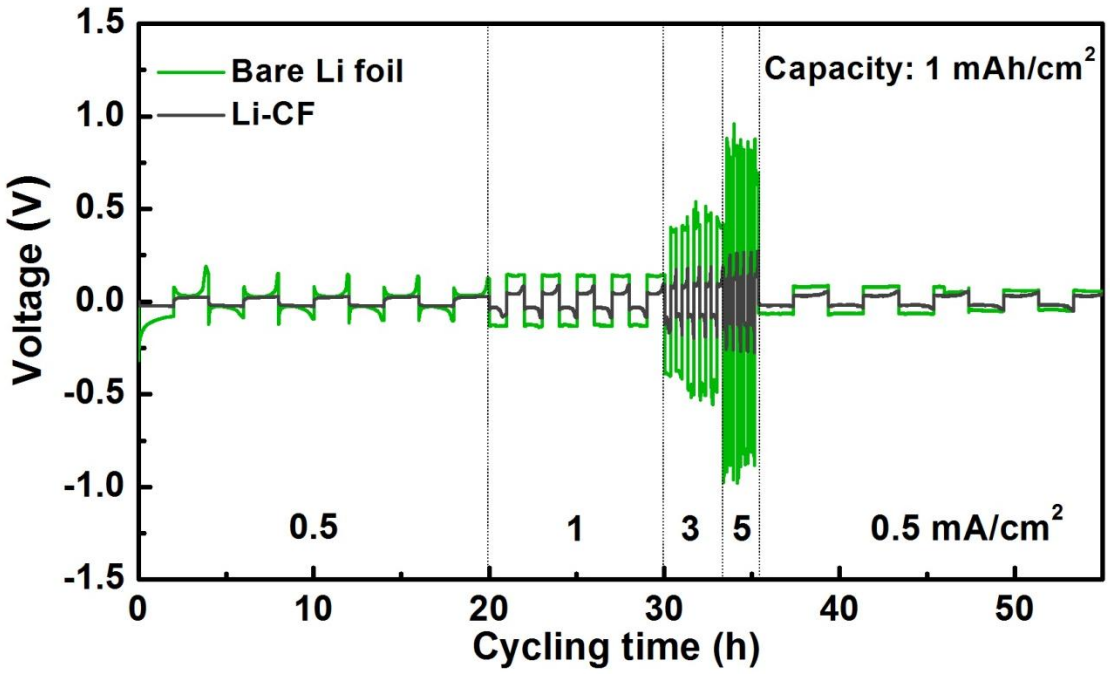

Figure S3. Rate peformance comparison of of bare Li symmetric cells (green) and Li-CF symmetric cells (black) with a cycling capacity of 1 mAh cm^{-2} at 0.5, 1, 3 and 5 mA cm^{-2} current densities

Voltage hysteresis is the sum derived by adding the maximum value of the stripping/plating overpotential at each cycle.[2] A stable and minute increase in voltage hysteresis can be observed for the Li-CF electrodes during long-term cycling up to 100 mV (372th cycle) for 1 mA cm^{-2} and 255 mV (154th cycle) for 3 mA cm^{-2}. In contrast, the voltage hysteresis of the bare Li foil experiences a sharp decrease from 258 mV (1st cycle) to 133 mV (10th cycle) followed by an increase from 106 mV (100th cycle) to 208 mV (372th cycle) at 1 mA cm^{-2}. The bare Li foil also shows a dramatic increase from 252 mV (50th cycle) up to 1809 mV (154th cycle) at 3 mA cm^{-2}, suggesting continuous and excessive SEI formation induced by poor plating and stripping behavior.

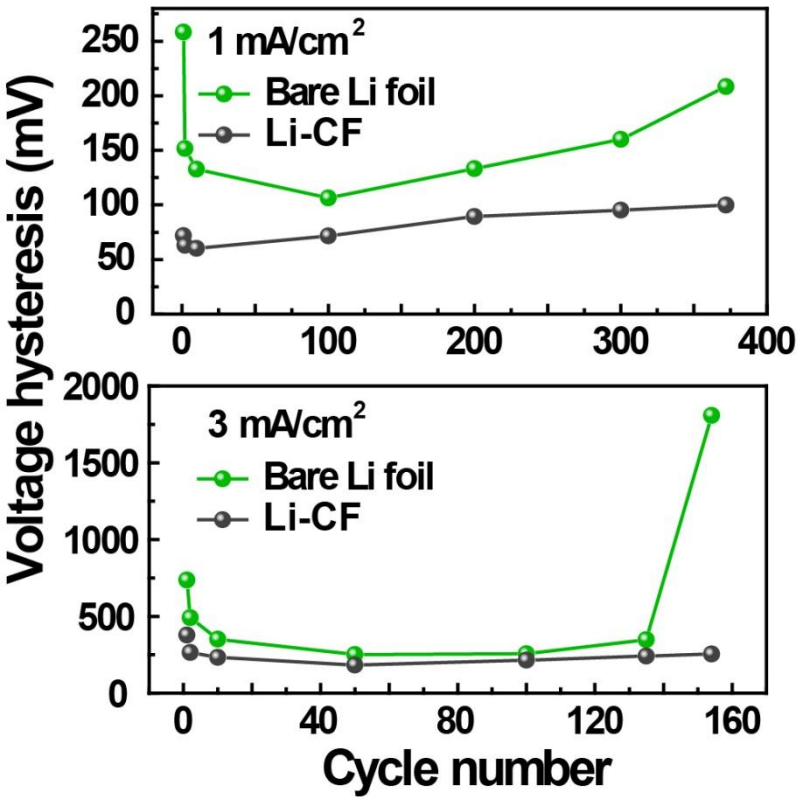

Figure S4. Comparison of the voltage hysteresis for a bare Li cell (green) and Li-CF cell (black) at 1 mA cm^{-2} (for selected cycle 1, 2, 10, 100, 200, 300 and 372) and 3 mA cm^{-2} (for selected cycle 1, 2, 10, 50, 100, 135 and 154).

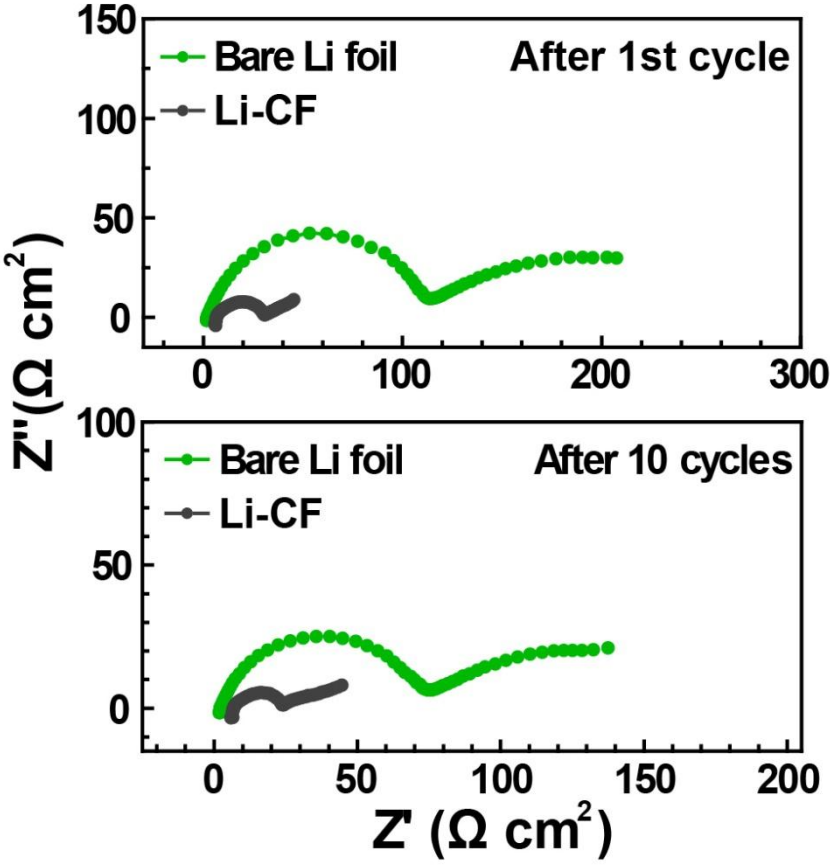

Figure S5. Areal impedance spectroscopy of a bare Li cell (green) and Li-CF cell (black) before cycling and after 10 galvanostatic cycles at 1 mA cm^{-2}.

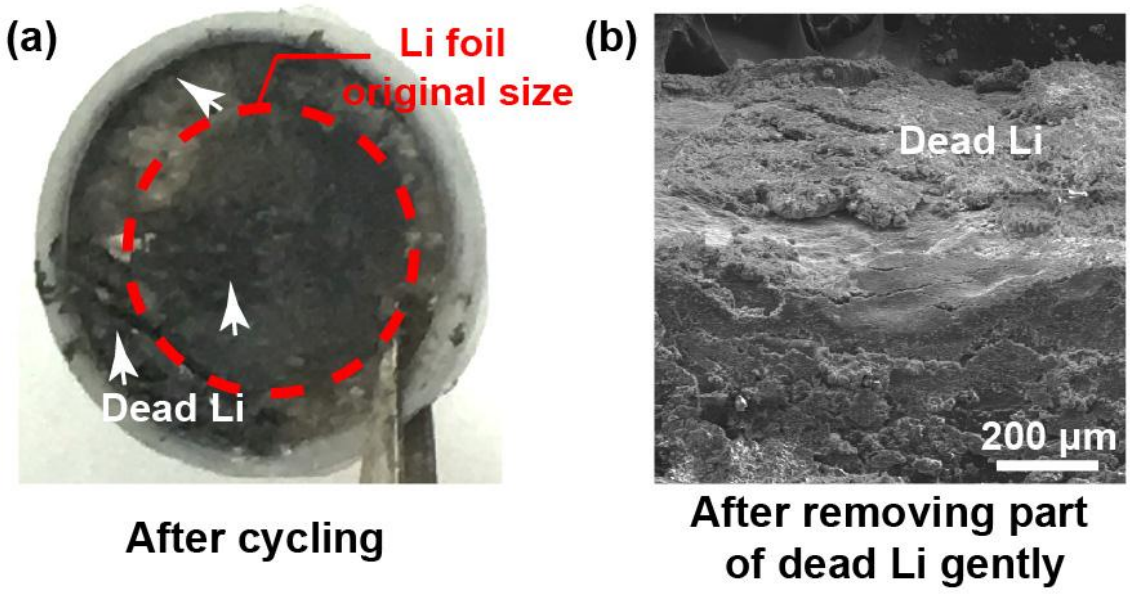

Figure S6. (a, b) Digital and SEM images of the bare Li foil after 744 hours of cycling. The zoomed-in SEM image shows the morphology of the Li foil after gently removing dead Li. The residual dead Li can easily detach from the bulk electrode which leads to severe capacity fade.

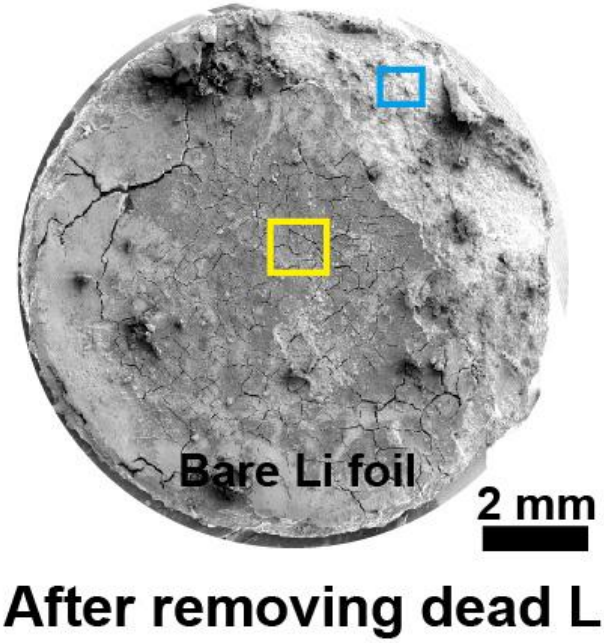

Figure S7. Top view SEM image of the bare Li foil after washing away dead Li. The exposed surface shows cracks and crevices. The marked yellow and blue rectangles are in accordance with the description in Figure 3e and 3f, respectively.

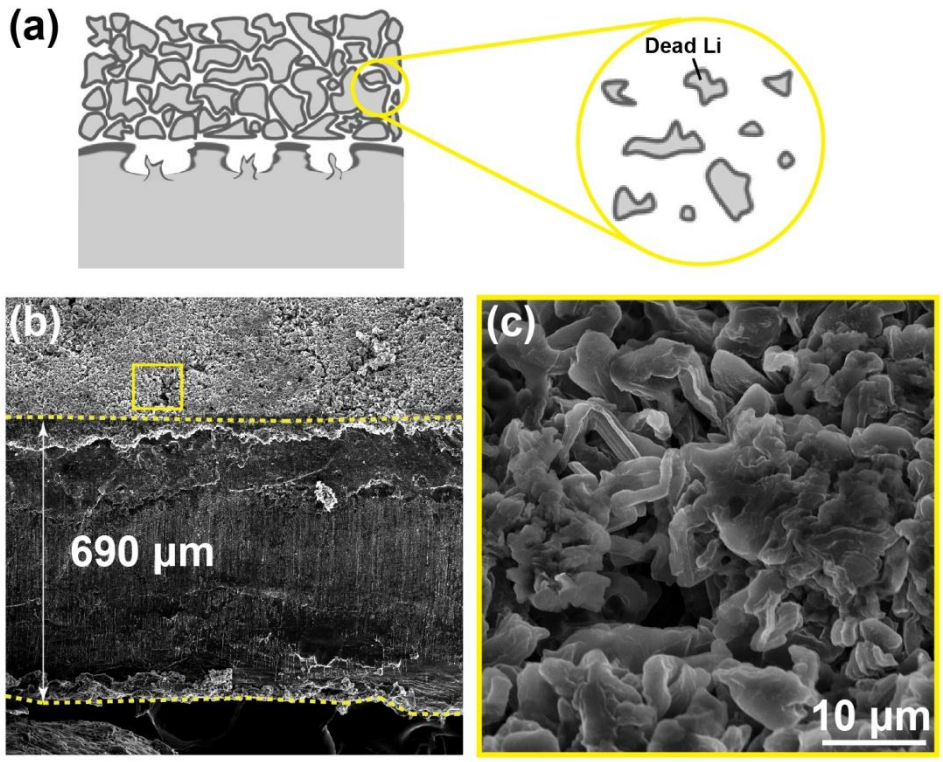

Figure S8. Schematic illustration and cross-sectional SEM image of the bare Li foil after plating 10 mAh cm^{-2} of Li. The bare Li foil gives a fluctuated profile, indicating uneven Li deposition on the surface of the planar Li foil.

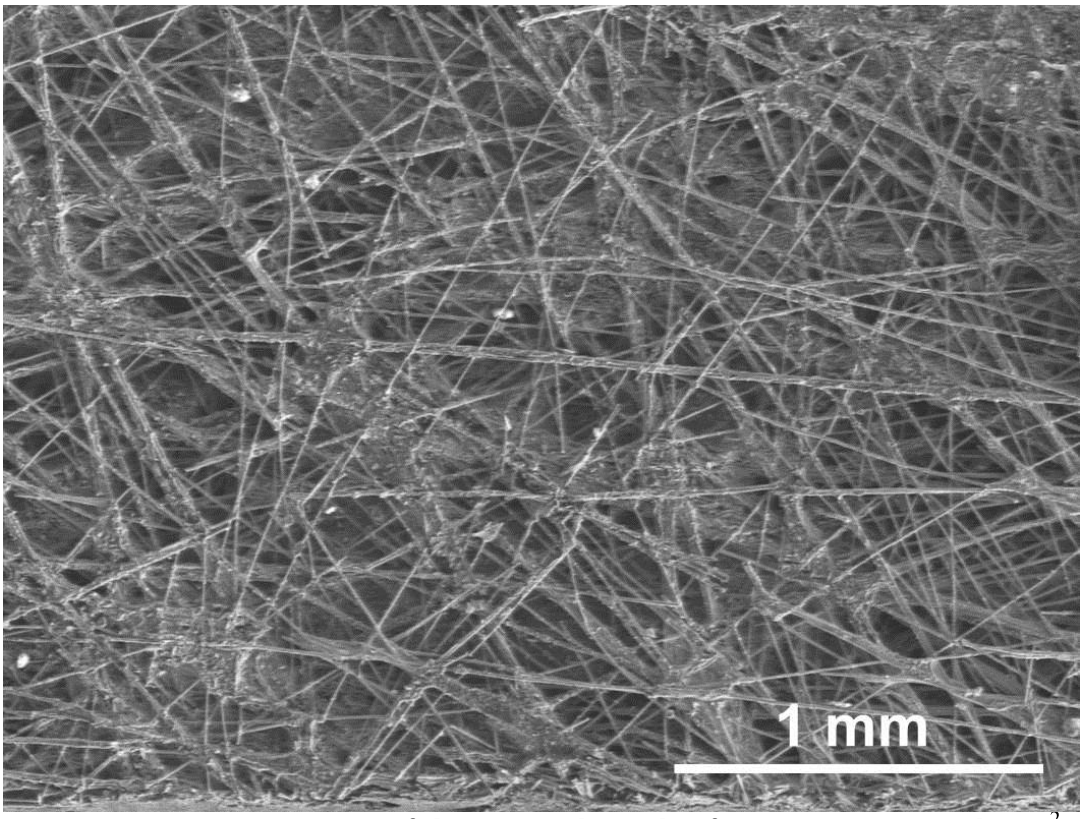

Figure S9. Top-view SEM image of the Li-CF electrode after stripping 10 mAh cm^{-2} of Li, showing a stable CF framework with the anticipated porous structure.

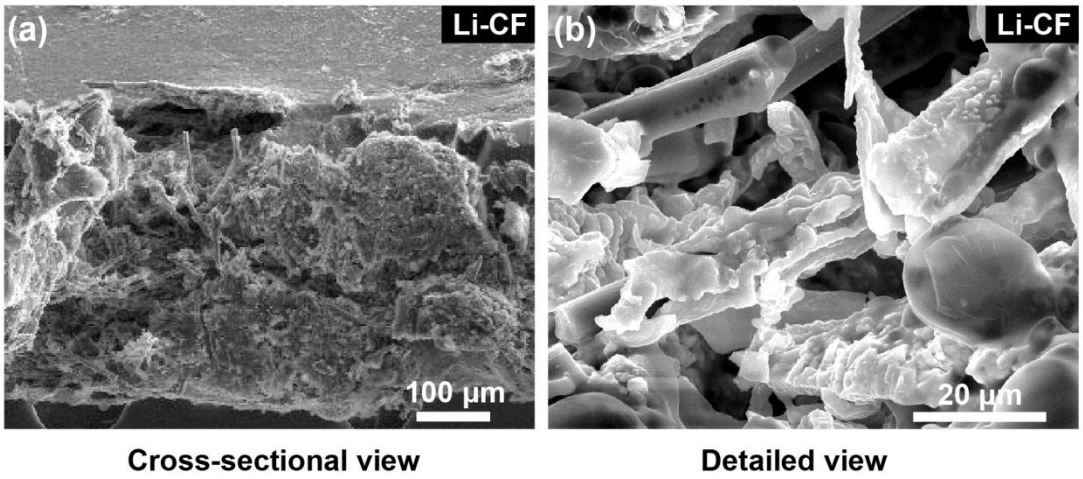

Figure S10. Cross-sectional and zoomed-in SEM images of the Li-CF electrode after plating 10 mAh cm^{-2} of Li. Re-deposition into the porous CF framework indicates good accommodation of the infinite volume change.

We fabricated Li-CF|Celgard|Li cells to be tested at an ultrahigh current density of 10 mA/cm^2 with a capacity of 1 mAh/cm^2. After 10 cycles, we opened the cells and gently washed the electrodes with ethyl methyl carbonate solvent to remove any lingering Li salts before detailed characterization. Optical microscopy of bare Li foil (**insets of Figure S11a**) reveals a black surface and SEM images in **Figure S11a-b** present a porous irregular surface, which indicates severe formation of dead Li and pulverization. In sharp comparison, no obvious dead Li is observed on the surface of the Li-CF electrode (**insets of Figure S11c**). The Li-CF electrode shows a ribbed texture on the modified carbon fibers with mossy Li at the junctions (**Figure S11c-d**). This result confirms the high reversibility and stability of the modified metallic anodes by utilization of the 3D CF framework.

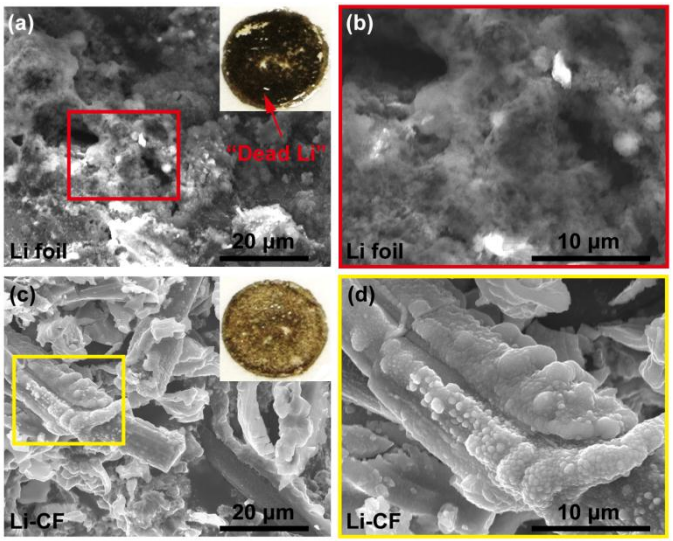

Figure S11 SEM images of the (a-b) bare Li foil and (c-d) Li-CF electrodes after cycling for 10 cycles at 10 mA cm^{-2}; the insets of (a) and (c) are optical photos of bare Li foil and Li-CF electrodes after opening the cells.

Reference:

[1] E. J. Berg, C. Villevieille, D. Streich, S. Trabesinger, P. Novák, J. Electrochem. Soc. 2015, 162, A2468.

[2] Z. Liang, D. Lin, J. Zhao, Z. Lu, Y. Liu, C. Liu, Y. Lu, H. Wang, K. Yan, X. Tao, *Proc. Natl. Acad. Sci. U. S. A.* **2016**, 113, 2862.