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Supplementary Information

3D Cu Current Collector with Biporous Structure Derived by a Phase Inversion Tape Casting Method for Stable Li Metal Anodes

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Calculation:

The specific calculation process by the Archimedes method for the porosity of P-Cu is shown as below:

The total volume of P-Cu is equal to the volume of mercury expelled, and the weight of P-Cu can be measured, hence its actual density (ρ) can be calculated. And the theoretical density of Cu (ρ_{th}) is 8.9 g cm^{-3}, therefore the porosity is calculated from $(1 - \rho/\rho_{th}) \times 100\%$.

The calculation process for Li deposits is shown as following:

The density of Li is 0.534 g cm^{-3}, and the theoretical capacity of Li is 3860 mA h g^{-1}. Assuming that Li is tiled evenly on the current collectors regardless of gaps and holes, the height of Li layer on the surface could be calculated when the deposition capacity was fixed. The result we obtained is that the height of 1 mA h cm^{-2} Li layer is 4.85 μm. Meanwhile, the proportion of Li deposited in the inner pores of P-Cu current collector to the total deposited Li can be estimated on the assumption that the Li layer on the surface is homogeneous and dense. And the maximum amount of Li accommodated in P-Cu can also be calculated in consideration of the total pore volume. In our experiments, P-Cu has a thickness of 150 μm and porosity of 56.9%. The calculated height of total Li layer is 14.55 μm when the capacity was fixed at 3 mA h cm^{-2} and 26.68 μm at 5.5 mA h cm^{-2}, while the actual heights on P-Cu current collectors are 2.0 μm and 6.6 μm, respectively. The specific calculation process is as following:

Height of Li layer = Li areal capacity × bottom surface area / (Li theoretical capacity × Li density × bottom surface area) = Li areal capacity / (Li theoretical capacity × Li density)

Height of 1 mA h cm^{-2} Li = 1.0 / (3860 ×0.534) cm = 4.85 μm

At 3 mA h cm^{-2}, the actual height on P-Cu current collector is 2.0 μm, and the proportion of Li deposited in the inner pores of P-Cu to the total deposited Li = (14.55 – 2.0) / 14.55 = 86.25%

At 5.5 mA h cm^{-2}, after the first Li plating, the height of Li layer on the surface of P-Cu was 2.5 μm, the proportion = (26.68 – 2.5) / 26.68 = 90.63%; after 30 cycles, the height increased to 6.6 μm, the proportion = (26.68 – 6.6) / 26.68 = 75.26%

The maximum amount of Li deposition = $150 \times 10^{-4} \times 1.13 \times 56.9\% \times 0.534 \times 3860 / 1.13$ mA h cm^{-2}= 17.6 mA h cm^{-2}

These values were not considered the voids and defects between the Li particles, thus, the actual accommodated Li deposits into the pores of P-Cu would be far less than 17.6 mA h cm^{-2}, and the calculated proportions of Li deposited in the pores to the total deposited Li would be much lower than those in the actual situation. In addition, the heights of Li layer on Cu foil were always significantly higher than the theoretical values, suggesting that the Li layer on Cu foil is very loose and full of defects.

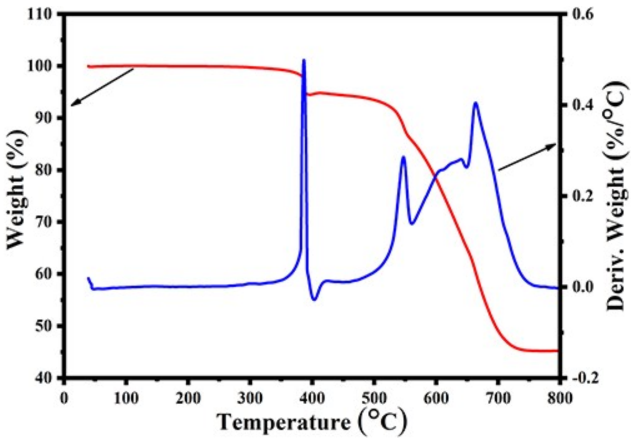

Fig. S1. DTG and TGA thermographs of the green tape containing CuO layer and graphite layer. The sample was heated at a rate of 10 °C min^{-1} in atmosphere.

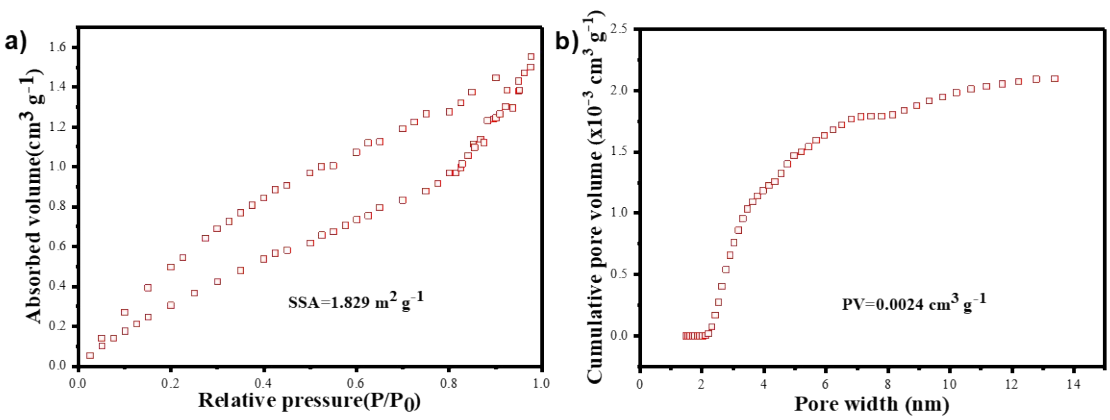

Fig. S2. (a) N_2 adsorption and desorption isotherms of P-Cu. (b) Pore volume curves of P-Cu.

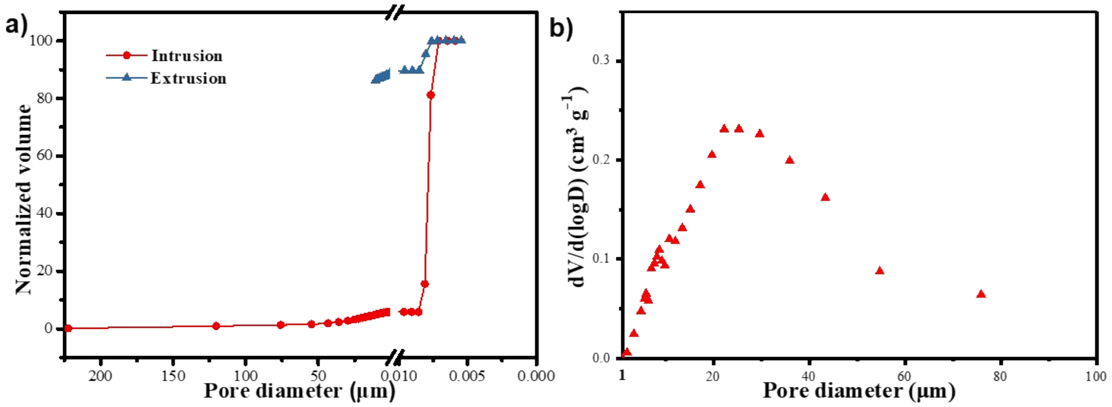

Fig. S3. (a) Cumulative pore volume-pore diameter curves of P-Cu from mercury porosimetry. (b) Pore size distribution of P-Cu from mercury porosimetry.

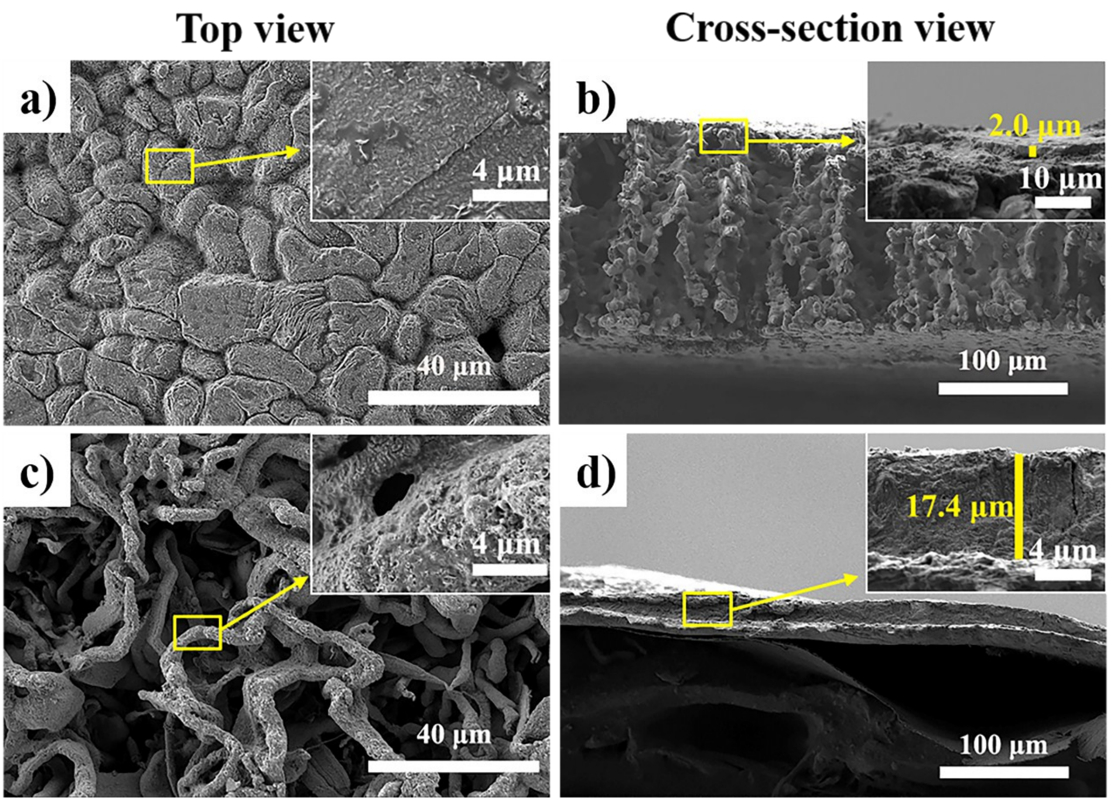

Fig. S4. SEM images of (a and b) P-Cu and (c and d) Cu foil after plating 3 mA h cm^{-2} Li at 0.6 mA cm^{-2} in the first cycle. The insets are corresponding high-magnification SEM of each image. The thickness of Li layer in (b) was 2.0 μm, while that in (d) was 17.4 μm.

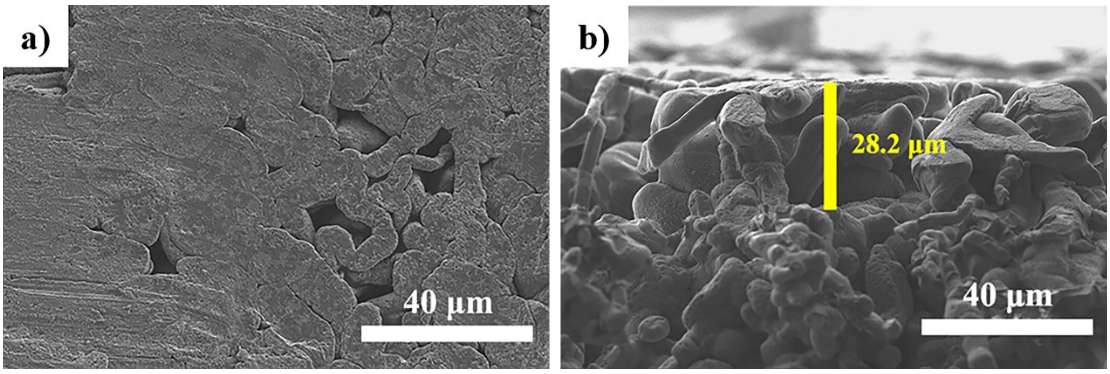

Fig. S5. (a) surface and (b) cross-section SEM images of P-Cu after plating 17 mA h cm^{-2} Li at 0.5 mA cm^{-2}. Some dendrites formed on the surface.

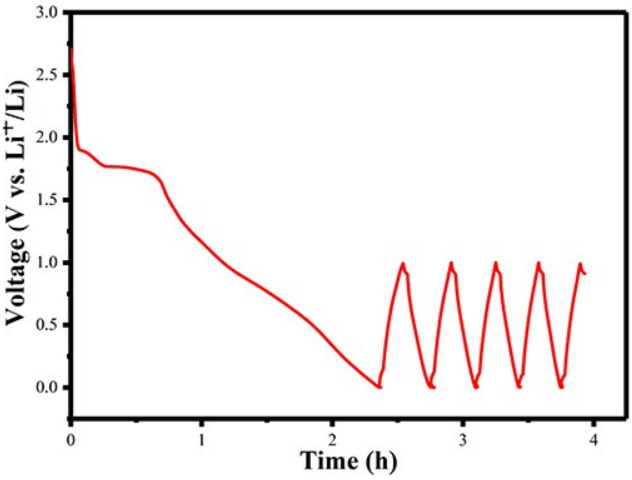

Fig. S6. Voltage-time profile during initial activation process. The batteries were first cycled between 0–1 V (vs. Li^+/Li) at 50 µA for five cycles to remove contamination and stabilize the interface.

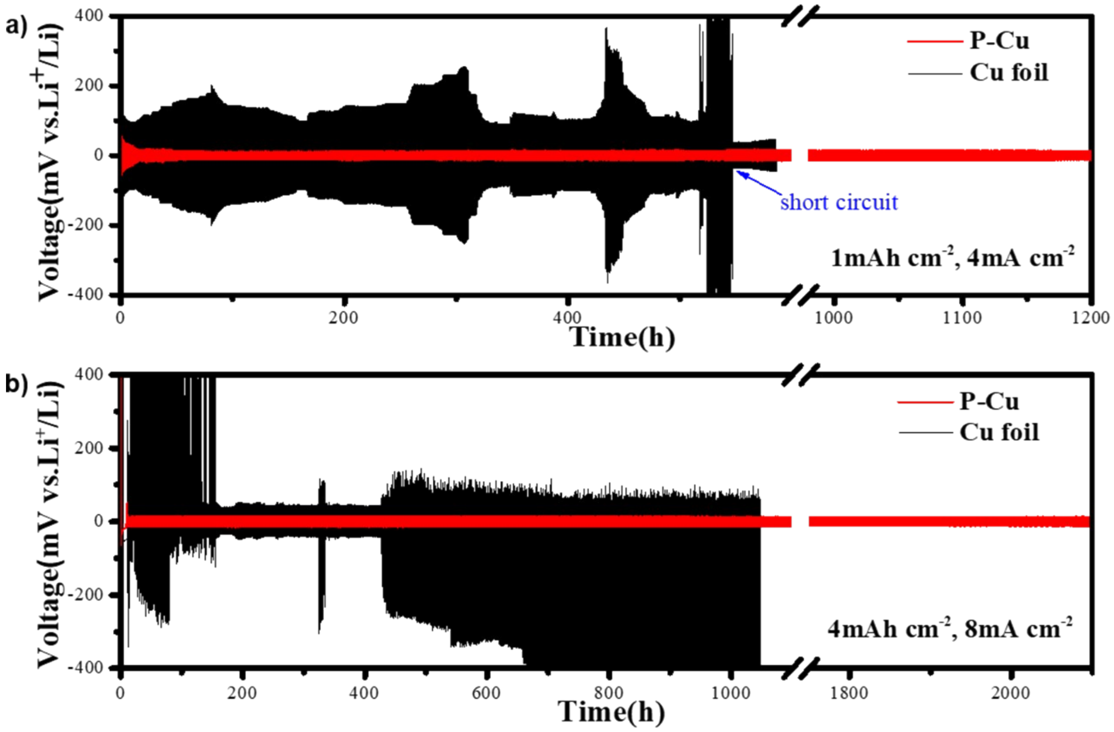

Fig. S7. (a) Long-term cycling performance comparison of P-Cu and Cu foil with Li plating/stripping capacity of 1 mA h cm^{-2} at 4 mA cm^{-2} in symmetric cells. (b) Long-term cycling performance comparison of P-Cu and Cu foil with Li plating/stripping capacity of 4 mA h cm^{-2} at 8 mA cm^{-2} in symmetric cells.

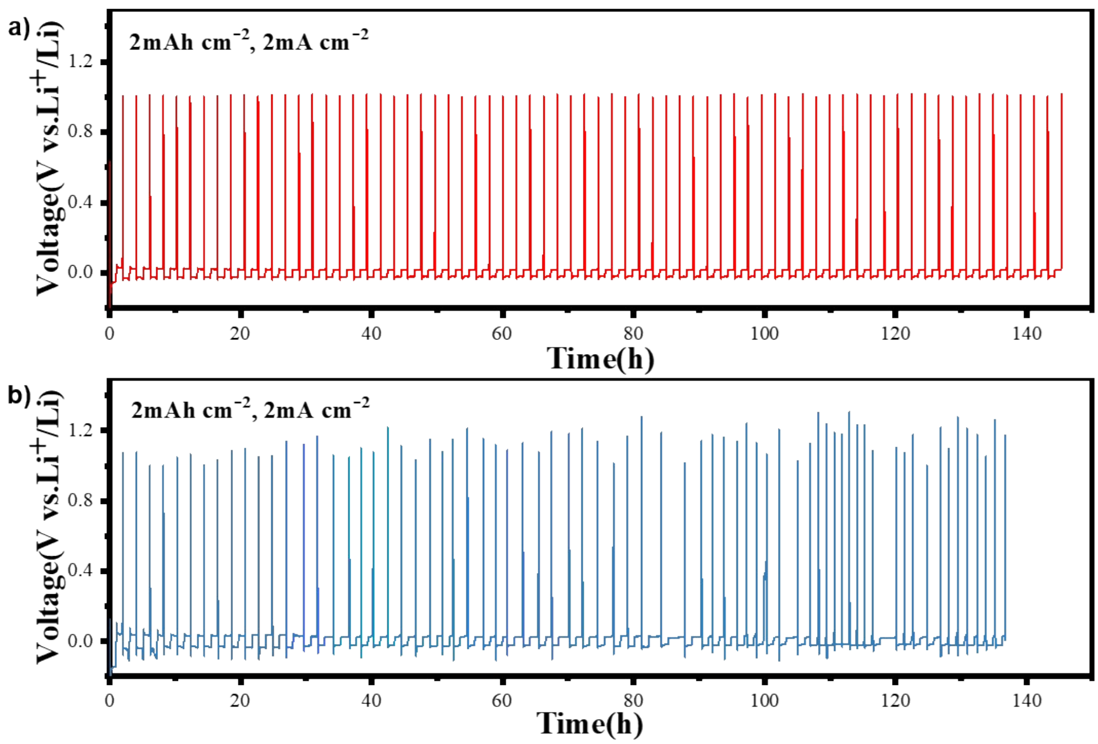

Fig. S8. Voltage profiles of Li plating/stripping on (a) P-Cu and (b) Cu foil current collectors at 2 mA cm^{-2} with a plating capacity of 2 mA h cm^{-2}.

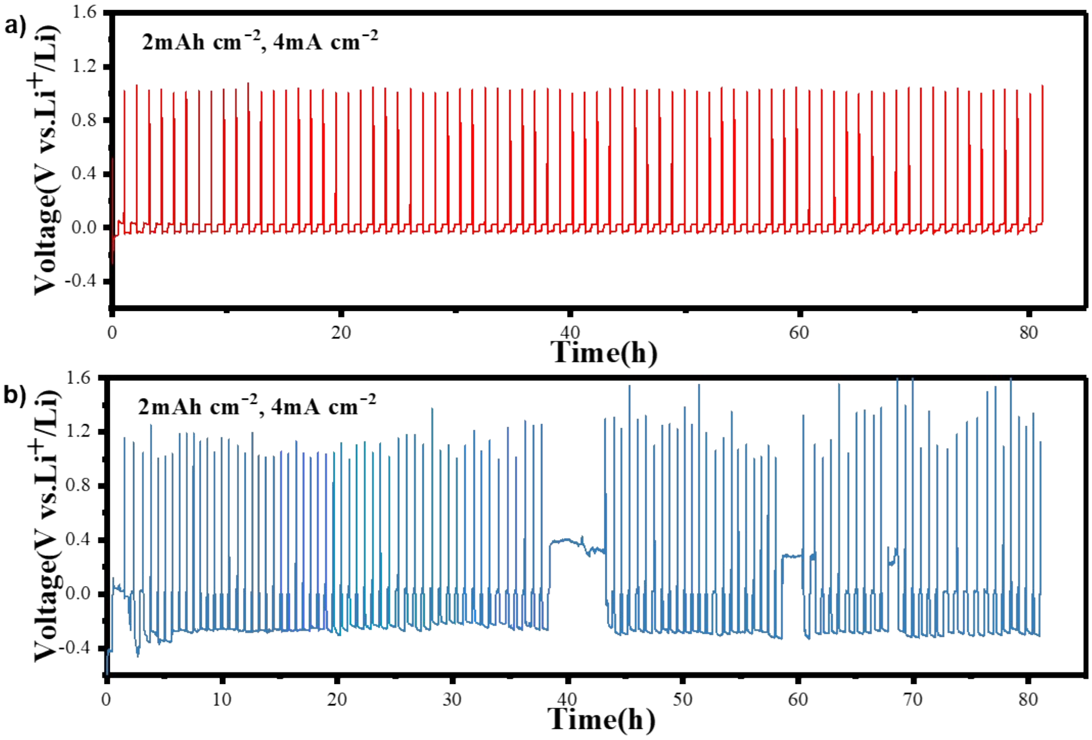

Fig. S9. Voltage profiles of Li plating/stripping on (a) P-Cu and (b) Cu foil current collectors at 4 mA cm^{-2} with a plating capacity of 2 mA h cm^{-2}.

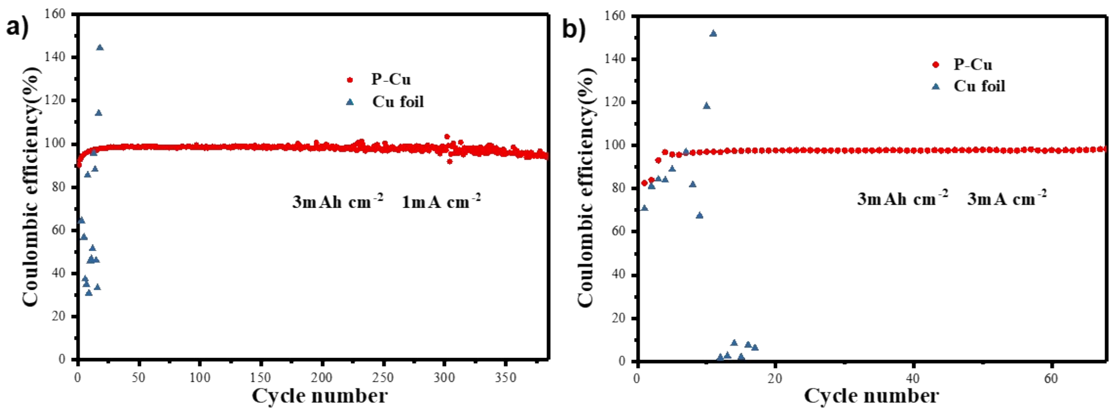

Fig. S10. CE comparison of Li deposition on P-Cu and Cu foil with current densities of (c) 1 mA cm^{-2} and (d) 3 mA cm^{-2} for a total of 3 mA h cm^{-2} Li.

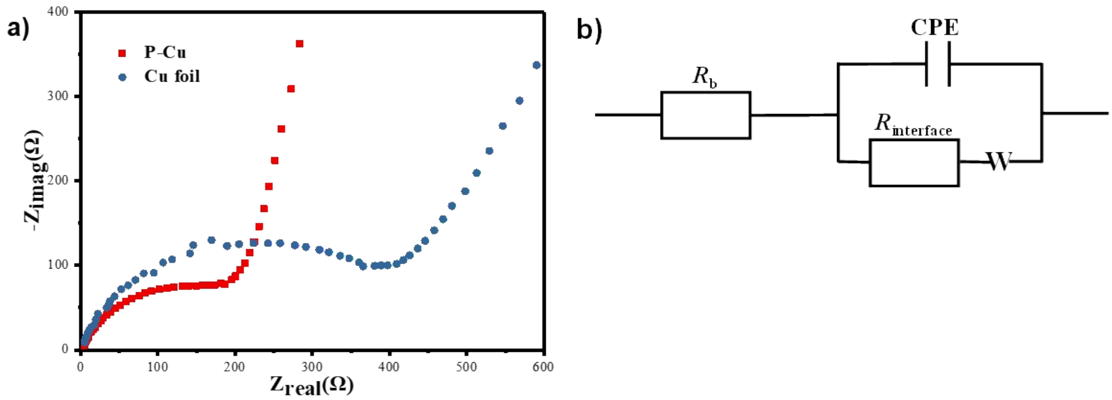

Fig. S11. (a) Nyquist plots and (b) equivalent circuit diagram of fresh symmetric cells using P-Cu@Li electrode and Cu foil@Li electrode.

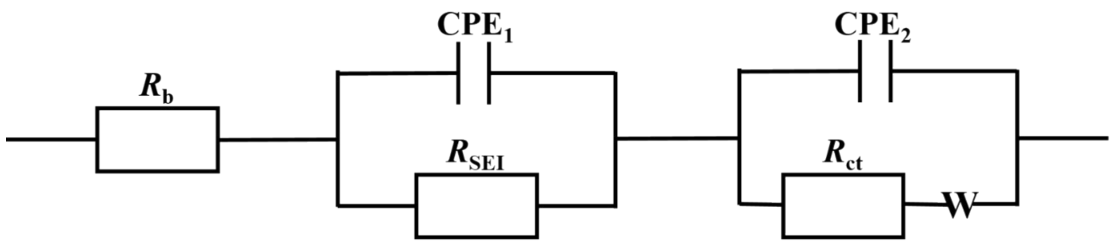

Fig. S12. Equivalent circuit diagram for Nyquist plots in **Fig. 6e-f**.

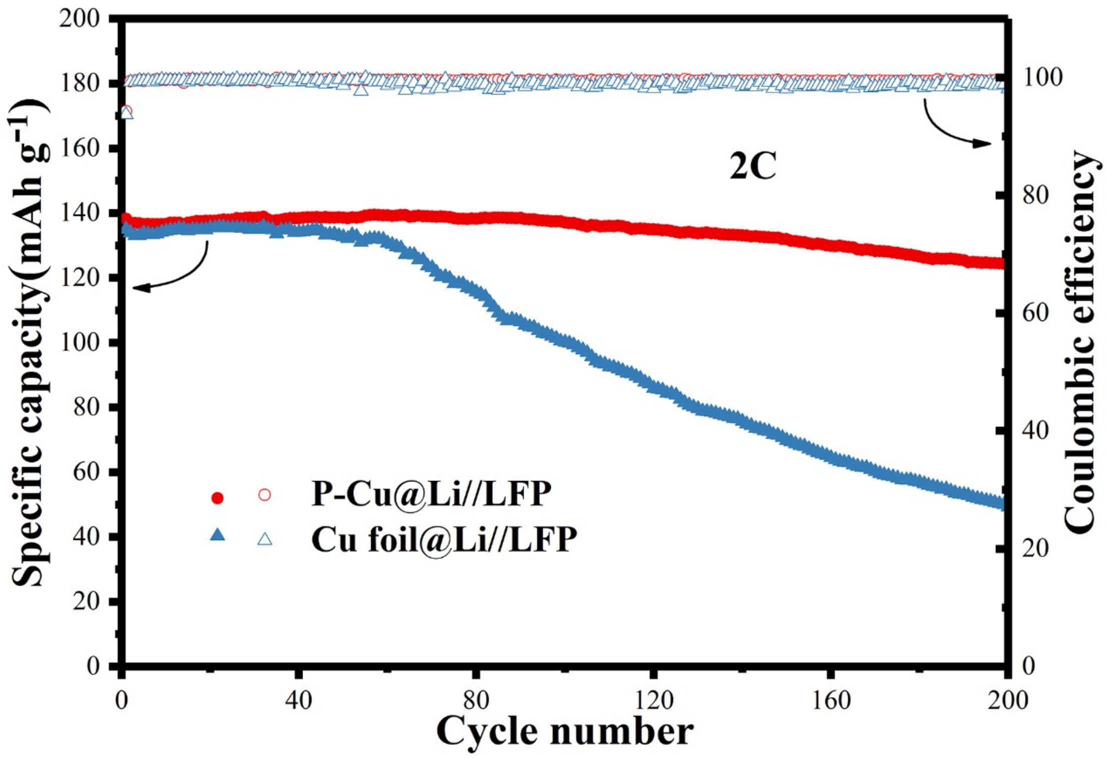

Fig. S13. Cycling performance of P-Cu@Li//LFP and Cu foil@Li//LFP full cells at 2C.

Table S1. Electrochemical impedance fitted parameters for **Fig. 6e-f** with an equivalent circuit model shown in **Fig. S12**.

	P-Cu current collector			**Cu foil current collector**		
	R_b [Ω cm^2]	R_{SEI} [Ω cm^2]	R_{ct} [Ω cm^2]	R_b [Ω cm^2]	R_{SEI} [Ω cm^2]	R_{ct} [Ω cm^2]
1st	2.78	7.98	30.83	3.94	50.22	22.68
2nd	2.72	6.77	22.15	3.65	21.54	26.36
5th	2.84	4.38	14.07	8.44	37.24	11.13
20th	2.84	3.30	7.64	10.64	147.91	345.78
100th	2.57	1.57	2.75	16.80	89.42	109.88

Table S2. Comparison of symmetric cells' electrochemical performances of as prepared P-Cu with other porous Cu current collectors.

Materials	Electrolytes	Current density [mA cm^{-2}]	Capacity [mA h cm^{-2}]	Cycling time [h]	Hysteresis [mV]
Cu with vertically aligned micro channels[1]	1 M LiTFSI in DOL/DME (1:1) with 1% $LiNO_3$	1	1	200	~ 20
Chemical dealloyed Cu[2]	1 M LiTFSI in DOL/DME (1:1) with 1% $LiNO_3$	0.2	1	1000	~ 30
Cu mesh[3]	1 M LiTFSI in DOL/DME (1:1) with 1% $LiNO_3$	0.5	1	200	~ 60
Cu with a submicron-sized skeleton[4]	1 M LiTFSI in DOL/DME (1:1) with 1% $LiNO_3$ and 0.005M Li_2S_6	0.2	0.5	600	< 50
Free-standing Cu nanowires[5]	1 M LiTFSI in DOL/DME (1:1) with 1% $LiNO_3$ and 0.005M Li_2S_8	1	2	550	~ 40
Micro compartmented Cu[6]	1 M LiTFSI in DOL/DME (1:1) with 1% $LiNO_3$	0.2	0.5	500	~ 100
Graphene@Cu foam[7]	1 M LiTFSI in DOL/DME (1:1) with 2% $LiNO_3$	0.5	1	2000	~ 20
VA-CuO-Cu[8]	1 M LiTFSI in DOL/DME (1:1) with 1% $LiNO_3$	0.5	0.5	700	~ 25
Our sample: P-Cu	**1 M LiTFSI in DOL/DME (1:1) with 2% $LiNO_3$**	**2**	**1**	**2200**	**~ 18**
		4	**1**	**1200**	**~ 25**
		8	**4**	**2100**	**~ 30**

Table S3. Comparison of half cells' electrochemical performances of as-prepared P-Cu with other porous Cu current collectors.

Materials	Electrolytes	Current density [mA cm^{-2}]	Capacity [mA h cm^{-2}]	Cycle number	Coulombic efficiency [%]
Cu with vertically aligned micro channels[1]	1 M LiTFSI in DOL/DME (1:1) with 1% $LiNO_3$	1	3	200	98.5
Chemical dealloyed Cu[2]	1 M LiTFSI in DOL/DME (1:1) with 1% $LiNO_3$	1	1	140	97
Cu mesh[3]	1 M LiTFSI in DOL/DME (1:1) with 1% $LiNO_3$	0.5	1	100	97.5
Cu with a submicron-sized skeleton[4]	1 M LiTFSI in DOL/DME (1:1) with 1% $LiNO_3$ and 0.005M Li_2S_6	0.5	1	50	98.5
Free-standing Cu nanowires[5]	1 M LiTFSI in DOL/DME (1:1) with 1% $LiNO_3$ and 0.005M Li_2S_8	1	2	200	98.6
Micro compartmented Cu[6]	1 M LiTFSI in DOL/DME (1:1) with 1% $LiNO_3$	0.5	0.5	150	99
Graphene@Cu foam[7]	1 M LiTFSI in DOL/DME (1:1) with 2% $LiNO_3$	2	1	150	97.4
VA-CuO-Cu[8]	1 M LiTFSI in DOL/DME (1:1) with 1% $LiNO_3$	1	1	180	94
Our sample: P-Cu	**1 M LiTFSI in DOL/DME (1:1) with 2% $LiNO_3$**	**2**	**2**	**200**	**97.6**
		4	**2**	**62**	**97.1**
		1	**3**	**385**	**97.8**
		3	**3**	**68**	**97.2**

Supporting References

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