Supplementary material for

Robust Pure Copper Framework by Extrusion 3D Printing for Advanced Lithium Metal Anodes

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Fig. S1 Demonstration of the important role of the introduced debinding process in air. (a) Schematic illustration of fabrication process of 3DP-Cu-Carbon without the debinding process, leading to ultimately collapse of metallic structures. (b) Schematic illustration of the fabrication process of 3DP-Cu-Carbon without he fabrication process of 3DP-Cu-Carbon without the debinding process.



Fig. S2 Digital image analysis of 3DP-Cu SEM images. (a) High contrast SEM image of 3DP-Cu. (b) Digital image analysis of 3DP-Cu SEM image elucidating interconnectivity of porous network. (c) High contrast SEM image focusing on a single Cu grain. (d) Digital image analysis of SEM image focusing on a single Cu grain, showing sub-micron and nano-sized pores.



Fig. S3 (a) N_2 adsorption-desorption isotherms and (b) the pore size distribution (BJH) of the 3DP-Cu where pore size is concentrated at ~3, 20 and 100 nm.



Fig. S4 (a) Cu 2p XPS core level spectra belonging to 3DP-CuO and 3DP-Cu samples. (b, c) Deconvoluted components of Cu $2p_{3/2}$ for (b) 3DP-CuO and (c) 3DP-Cu. TEM images showing crystal lattice structure for (d) 3DP-Cu and (e) 3DP-CuO.

Fig. S4a shows the XPS data obtained for 3DP-CuO and the reduced 3DP-Cu. The Cu 2p energy level of 3DP-Cu was made up of the main characteristic peaks corresponding to Cu $2p_{1/2}$ and Cu $2p_{3/2}$ at ~952.4 eV and ~932.5 eV respectively.^{1, 2} For 3DP-CuO, the shake-up satellite structures are at about 8-10 eV binding energies higher than that of the main Cu 2p peak for 3DP-Cu. Furthermore, the gap between the Cu2p_{1/2} and 2p_{3/2} is ~20 eV, which agrees with the standard binding energy value of CuO.¹ The fully oxidized CuO surface also exhibit intense satellite peaks at ~942.4 and ~944.6 eV (Fig. S4b, peaks S1 and S2), with these two peaks overlapping.³ Therefore, it is evident that pure metallic copper is obtained after the reduction process from 3DP-CuO from XPS analysis.



Fig. S5 (a) Cross-sectional images highlighting the differences in thickness (under different conditions) and individual strut structure retention even after 11.4 kg of load. Scale bar represents 2.5 mm. (b) Compressive stress-strain curve for 3DP-Cu. Tested samples are deformed to 65% strain without any brittle fracture or cracking. Inset demonstrating that 3DP-Cu can retain structural integrity after compression.

The greyscale cross-sectional images for micro-CT scan of 3DP Cu under different compression conditions are demonstrated in Fig. S4a. There is a clear difference in the thickness of the compressed structure, especially after subjecting 3DP-Cu to 11.4 kg load. However, the internal structural integrity is preserved, with no fractures or cracking. In Fig. S4b, a compressive stress-strain test is done, and the inset image shows that after compression, there is no brittle fracture or cracking. Plastic strain occurs from around 15% to around 30%. 3DP-Cu structure can ultimately be retained, showing mechanical stability of 3DP-Cu and it can definitely be applicable to coin cell assembly without breaking.



Fig. S6 (a) Photo demonstrating the mechanical stability of the as-deposited Cu+F127 ink after sintering in air, and then reduction in Ar/H₂ atmosphere. (b-e) Galvanostatic discharge profiles (Li plating) of high capacity of 20 mAh cm⁻² onto 3DP-Cu and Cu Coin with various current densities showing nucleation overpotential; (a) 1 mA cm⁻², (b) 3 mA cm⁻², (c) 5 mA cm⁻² and (d) 10 mA cm⁻².

The as-deposited sample is shaped into a circular coin of ~10 mm and denoted as Cu Coin (Fig. S2a). When the Cu coin is subjected to sintering in air, cracks are formed due to the expansion of Cu to CuO. After additional reduction during annealing in Ar/H_2 atmosphere, more severe cracks are induced due to the eventual shrinkage in the Cu coin. This may be attributed to the lack of space for expansion and shrinkage which the 3D printed mesh like architectures can provide. This concept will also apply to the as-deposited paste onto an external substrate for applications, illustrating the significance of 3D-printing

on mechanical stability for a free-standing crack free structure. Fig. S2b to S2e shows the performance of Li plating overpotentials of Cu coin in comparison to the 3DP-Cu.



Fig. S7 Coulombic efficiency evaluation at 3DP-Cu at high areal capacities of (a) 7.5 mAh cm⁻², (b) 15 mAh cm⁻², at current density of 1 mA cm⁻². Electrochemical performance of the symmetric cells using the Li@3DP-Cu, Li@Cu Coin and bare Li foil electrodes.



Fig. S8 Coulombic efficiency evaluation of 3DP-Cu and Cu coin at current density of 1 mA cm⁻² (a), 3 mA cm⁻² (b), 5 mA cm⁻² (c) and 10 mA cm⁻² (d) for a plating capacity of 5 mAh cm⁻². (e) Galvanostatic cycling profiles of the as-deposited Cu Coin at the current rate of 1 mA cm⁻² with a limited capacity of 1 mAh cm⁻².



3 mA cm⁻²

5 mA cm⁻²

10 mA cm⁻²

Fig. S9 SEM images of plated 3DP-Cu at high current densities of (a) 3 mA cm⁻², (b) 5 mA cm⁻² and (c) 10 mA cm⁻², for an areal capacity of 20 mAh cm⁻².



Fig. S10 Schematic showing the plating mechanism on the 3DP-Cu and bare Cu foil, and the corresponding SEM image of initial Li nucleation growth at a rate of 1 mA cm⁻² with a plated capacity of 2.5 mAh cm⁻² to 10 mAh cm⁻². (a,b) On the 3DP-Cu filament surface. (c,d) On the bare Cu foil surface.



Fig. S11 Galvanostatic discharge profiles (Li plating) of high capacity of 20 mAh cm⁻² onto 3DP-Cu and bare Cu foil with various current densities showing nucleation overpotential; (a) 1 mA cm⁻², (b) 3 mA cm⁻², (c) 5 mA cm⁻² and (d) 10 mA cm⁻².



Fig. S12 (a,b) Coulombic efficiency evaluation of 3DP-Cu and bare Cu Foil at current density of 2 mA cm^{-2} (a) and high current density of 3 mA cm^{-2} (b), for a plating capacity of 5 mAh cm^{-2} . (c,d) Li plating/striping profiles measured at 1 mA cm^{-2} (c) and 2 mA cm^{-2} (d) for 5 mAh cm^{-2} , respectively. (e, f) Li plating/striping profiles measured at 1 mA cm^{-2} (e) and 2 mA cm^{-2} (f) for 5 mAh cm^{-2} at different cycles, with the insets showing enlargements of the low voltage range.



Fig. S13 Impedance plots for the cells with a) the 3DP-Cu electrode and b) the bare Cu foil after 5 cycles at 1 mA cm⁻² for 5 mAh cm⁻².

The major resistance is from the SEI layer formed along the interfacial surface between deposited Li layer on Cu current collector and liquid electrolyte. The magnitude of resistance is hypothesised to be proportional to the surface area of Li deposition layer. 3DP-Cu exhibited the ability of forming a even layer, while bare Cu foil would possess a rough layer with a much larger surface area due to the Li dendrite formation. Therefore, resistances should be larger for the bare Cu foil due as compared to 3DP-Cu.

The semicircle in the EIS should represent information of two components: SEI layer between plated Li and the liquid electrolyte, and the liquid electrolyte itself. The latter should be roughly the same for two types of Cu collectors since the used electrolyte is the same. Therefore, a smaller semicircle could depict a smaller SEI impedance and therefore a flatter SEI layer.



Fig. S14 Coulombic efficiency evaluation of 3DP-Cu and Cu foil at high areal capacities of (a) 7.5 mAh cm⁻², (b) 15 mAh cm⁻², at current density of 1 mA cm⁻². (c) Coulombic efficiency evaluation of 3DP-Cu at a higher areal capacity of 20 mAh cm⁻² and the high current density of 5 mA cm⁻². Corresponding SEM images of Li plated 3DP-Cu after 200 h of cycling at areal capacities of (d) 7.5 mAh cm⁻², (e) 10 mAh cm⁻², (f) 15 mAh cm⁻² and (g) 20 mAh cm⁻².



Fig. S15 (a) XRD data of 3DP-Cu after durability cycles of 5, 10 and 20 mAh cm⁻² at a current density of 1 mA cm⁻². (b) SEM image and (c) EDX Cu elemental mapping of 3DP-Cu after durability cycle of 20 mAh cm⁻² at current density of 1 mA cm⁻².



Fig. S16 (a) Long-term cycling performance at 0.1C ($1C = 180 \text{ mA g}^{-1}$ with LiFePO₄ cathode) and (b) rate capability of the LFP|Li@3DP-Cu and LFP|Li Foil full cells.

Note S1: The reason for choosing Pluronic F127 as the hydrogel in the DIW ink system.

Pluronic is a copolymer of poly(ethylene oxide) and poly(propylene oxide) in a 2:1 ratio. Poly(propylene oxide) is versatile in a way where the temperature and amount of water controls its hydrophobic or hydrophilic behaviour.^{4, 5} The gelation process is due to polypropylene domains adsorbing onto the surface of the copper particles, exposing the poly(ethylene oxide) chains in the water to form a gelation network.^{6, 7} Therefore, on the condition that volume fraction of the copper particles is optimal, interparticle interactions will not dominate the gelation network, thus particles can be suspended homogenously within the polymer network to form a self-standing ink.⁴

Note S2: Influence of other factors in electrochemical performance.

Diameter of printed filaments can also be controlled by using different nozzle sizes for DIW. By 3D printing a thicker diameter, it is expected that it would have a slightly poor performance compared to a thinner diameter. This is due to the less overall surface area for Li deposition, therefore leading to smaller areal capacity. It will also limit the performance for Li plating/stripping. In addition, there is a consideration for optimizing the filament size for a crack-free 3DP-Cu structure. For a fully filled structure (as seen by the as-deposited sample), the expansion and shrinkage will cause cracks to form, limiting electrochemical performance. However, if the diameter of the filament is too thin, the whole structure will then lack overall mechanical stability, making the thin filaments easier to crack under compression during cell assembly. Therefore, the diameter of $\sim 200 \,\mu\text{m}$ is chosen for this study.

Anode substrates	Areal capacity	Current density	Reference
	(mAh cm ⁻²)	(mA cm ⁻²)	
3DP-Cu	20	10	This study
Compact 3D Copper with	2	1	8
Uniform Porous Structure			
Free-Standing Copper	7.5	1	9
Nanowire Network			
Hierarchically Bicontinuous	1	3	10
Porous Copper as			
Advanced 3D Skeleton			
for Stable Lithium Storage			
Self-supported, three-	1	2	11
dimensional porous copper film			
3D Cu with a submicron skeleton	2	0.5	12
3D Porous Cu Current	2	1	13
Collector/Li-Metal			
Composite Anode			
Three-dimensional pie-like Copper	2	1	14

Table S1. Comparison of the performances for the copper-based lithium metal anodes

Table S2. Summary of time per cycle for Coulombic Efficiency cycling measurements

	10h/cycle	15h/cycle	20h/cycle	30h/cycle	40h/cycle
1 mA cm ⁻²	5h/charge or	7.5h/ charge or	10h/ charge or	15h/ charge or	20h/ charge or
	discharge discharge		discharge	discharge	discharge
	3.33h/cycle	5h/cycle	6.67h/cycle	10h/cycle	13.33h/cycle
3 mA cm ⁻²	1.67h/ charge	2.5h/ charge or	3.33h/ charge	5h/ charge or	6.67h/ charge
	or discharge	discharge	or discharge	discharge	or discharge
	2h/cycle	3h/cycle	4h/cycle	6h/cycle	8h/cycle
5 mA cm ⁻²	1h/ charge or	1.5h/ charge or	2h/ charge or	3h/ charge or	4h/ charge or
	discharge	discharge	discharge	discharge	discharge
	1h/cycle	1.5h/cycle	2h/cycle	3h/cycle	4h/cycle
10 mA cm ⁻²	0.5h/ charge	0.75h/ charge	1h/ charge or	1.5h/ charge	2h/ charge or
	or discharge	or discharge	discharge	or discharge	discharge
	1	1	1	1	

A summary of the cycle time corresponding to the respective current densities and specific areal capacities for C.E evaluation is stated in detail in Table S2.

Table S3	. Summary o	f time per	cycle for	symmetric	cell cycling	measurements
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Time of one cycle (Symmetric Cell)	1 mAh cm ⁻²		
1 mA cm ⁻²	2h/cycle		
	1h/charge or discharge		
10 mA cm ⁻²	0.2h/cycle		
	0.1h/ charge or discharge		

The individual cycle time corresponding to the respective current densities for symmetric cell cycling is listed in Table S3.

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