Supporting Information

Nano-Cu-embedded Carbon for Dendrite-free Lithium Metal Anode

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1. Experimental Section

Materials preparation

Cu₃(BTC)₂ was rapidly prepared and purified according to the method previously reported. Typically, Cu(NO₃)₂·3H₂O (1.74 g, 7.2 mmol) and H₃BTC (0.840 g, 4.0 mmol) were dissolved in the deionized water (8 mL) and ethanol (16 mL), respectively. ZnO powder (0.293 g, 3.6 mmol) was dispersed in the deionized water (8 mL) and sonicated for 10 min to form the nanoslurry, and then was further mixed with 16 mL of N,N-dimethylformamide (DMF). Cu(NO₃)₂ solution and H₃BTC solution were added into the ZnO nanoslurry under magnetic stirring at room temperature. After 1 min, the blue product was immediately filtered and washed with ethanol (50 mL, 3 times), and then dried overnight at 120 °C. The obtained Cu₃(BTC)₂ precursor was subsequently heated at 700 °C for 3 h in N₂ atmosphere with a heating rate of 5 °C min⁻¹ to obtain the black Cu@Carbon. The obtained Cu@Carbon sample was washed with excess amounts of 0.5 M FeCl₃ (aq) followed by excess amounts of 10% (v/v) HCl (aq) and plenty of ultrapure water to remove Cu-containing byproducts. Then, the obtained pure carbon sample (denoted as Carbon) was vacuum dried at 120 °C overnight.

Material characterizations

The morphologies of the samples were characterized by scanning electron microscope (SEM, Hitachi model S-4800). As for Li-deposited Cu foil and Cu@Carbon, cells were disassembled under argon-filled glove box, and the electrodes were washed with DME solvent thoroughly before testing. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and energy dispersive spectrometer (EDS) mapping analysis were taken on a Tecnai G2 F20 S-Twin. X-ray powder diffraction (XRD) measurements were performed on a powder diffractometer (Bruker D8 Advance, Germany) with Cu Kα radiation (λ=0.15406 nm). Raman spectroscopy with a 633 nm laser excitation was conducted using a Raman spectrometer (Renishaw 1000B). X-ray photoelectron spectroscopy (XPS) analysis was performed in a Perkin-Elmer PHI 5000C ESCA instrument with Al Kα radiation. The nitrogen sorption isotherms were measured at 77 K with a Quantachrome adsorption instrument. The Brunauer-Emmett-Teller (BET) and quenched solid density functional theory (QSDFT) methods were utilized to calculate the specific surface areas and the pore size distributions.

Electrochemical measurements

Half-cells test. CR2016 coin cells were assembled with Cu foil or Cu@Carbon as working electrode and with bare Li foil as counter/reference electrode to evaluate the Coulombic efficiency. The electrolyte was 1.0 M LiTFSI (lithium bis(trifluoromethanesulphonyl) imide) in 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) (1:1 in volume) with 2 wt% LiNO₃ additive. The small current of 0.05 mA was set up at the first five cycles to remove the contaminants on the surface of electrodes and active the batteries. The Coulombic efficiency of Cu foil or Cu@Carbon were calculated by depositing Li onto Cu foil or Cu@Carbon at various current densities and capacities, followed by Li stripping up to 1 V (versus Li*/Li) for each galvanostatic cycle. The electrochemical impedance spectroscopy (EIS) measurements of the half-cells were conducted on an AUTOLAB PGSTAT302N electrochemical workstation.

Symmetric cells test. For symmetric cells, 3 mAh cm⁻² of Li was first plated on Cu foil or Cu@Carbon at 1 mA cm⁻², forming the Li@Cu or Li@Cu@Carbon anode. Two same anodes (Li@Cu, Li@Cu@Carbon, and Li foil) were reassembled into symmetric cells with the same electrolyte as above. The cells were charged/discharged with a cycling capacity of 1 mA h cm⁻² at current densities of 0.5 and 1.0 mA cm⁻².

Li-metal capacitor and battery. Li-metal capacitors were assembled pairing commercial activated carbon (AC) cathode with Li@Cu, Li@Cu@Carbon, and Li foil anodes. Prior to assemble Li-metal capacitors, planar Cu and Cu@Carbon electrodes were first pre-deposited 20 mA h cm⁻² Li in half cells. The AC cathode electrode was prepared by mixing 80 wt% AC, 10 wt% KB and 10 wt% PTFE in isopropanol, and the slurry mixture was then coated on Al foil. The electrolyte was same with the half cells (1.0 M LiTFSI and 2wt % LiNO3 in 1:1 DOL: DME). The power density (P) and energy density (E) were obtained according to the following equations:

$$P = \frac{i \times V \times 1000}{m}$$
(1)
$$E = \frac{C \times V \times 1000}{m}$$
(2)

where V is the average discharge voltage (V), i and m are the discharge current (mA) and the total mass (Kg) of active materials in both the anode and the cathode, respectively; C (mAh) is the discharge capacity.

For LiFePO₄//Li full cell, full cells were comprised of LiFePO₄ as the cathode, 20 mA h cm⁻² of deposited Li metal on Cu@Carbon or planar Cu as the anode. The LiFePO₄ is synthesized as reported in our previous work.^{S1} The LiFePO₄ cathode was prepared by mixing the active material LiFePO₄, super carbon, and polyvinlidene fluoride (PVDF) in a weight ratio of 8:1:1 on aluminum foil. The electrolyte used in full cells is the same with that in half cells. The full cell using Li foil as anode was prepared at the same condition for comparison.

Density Functional Theory (DFT) Calculations

The geometries of all the structures presented in the present work were fully optimized by applying the density functional theory (DFT) B3LYP⁵² functional along with the 6-311G^{*53} basis set. The optimized geometries are followed by frequency calculations to confirm that the optimized structures are indeed minima on the potential energy surface with no imaginary frequencies. Spin multiplicity numbers are 1 for normal graphene; 2 for Cu-embedded grapheme and Li adsorbed on normal graphene; and 3 for Li adsorbed on Cu-embedded graphene. The adsorption binding energy (E_b) of Li atom on normal graphene is defined as

$$\mathbf{E}_{b} = E_{Li+graphene} - E_{graphene} - E_{Li} \tag{3}$$

where $E_{Li+graphene}$, E_{Li} and $E_{graphene}$ represent the total energies of the Li bound to the graphene structure, the Li atom and the graphene structure, respectively.

For the case of Li adsorbed on Cu-embedded graphene, the adsorption binding energy (E_b) of Li adatom is defined as

$$\mathbf{E}_{b} = E_{Li+Cu-graphene} - E_{Cu-graphene} - E_{Li} \tag{4}$$

where ELi+Cu-graphene is the total energy of Li adsorbed on Cu-embedded graphene, and ECu-graphene is taken as the total

energy of Cu-embedded graphene.

A negative E_b indicates an exothermic reaction process and shows that the product configuration is more stable. All

calculations were conducted using the Gaussian 09 program.^{S4}

2. Supporting Figures and Tables:



Fig. S1 Schematic illustration of the fabrication of $Cu_3(BTC)_2$ and Cu@Carbon.

Fig. S2 SEM images with different magnifications for the as-prepared $Cu_3(BTC)_2$.

Fig. S3 XRD patterns of the simulated $Cu_3(BTC)_2$ and the as-prepared $Cu_3(BTC)_2$.

Fig. S4 EDX elemental mappings of Cu₃(BTC)₂ showing the presence of Cu, C, and O elements. Scale bar is 200 nm.

Fig. S5 XRD patterns of Cu@Carbon.

Fig. S7 XPS spectra of Cu@Carbon for (a) Cu $2p_{3/2}$ and (b) C 1s peaks.

Fig. S8 Nitrogen adsorption-desorption isotherm at 77K (inset: the corresponding pore size distribution) of

Cu@Carbon.

Fig. S9 Voltages profiles of Cu@Carbon electrode at 0.5 mA cm⁻² for 1.0 mAh cm⁻².

Fig. S10 Nyquist plots of Cu@Carbon electrode after 1, 20, 50, and 100 cycles at 0.5 mA cm⁻² for 1.0 mAh cm⁻².

Fig. S11 Voltage profiles of the Li plating/stripping on the Cu@Carbon electrode at the 100th cycle under different

capacities with a current density of 1.0 mAh cm⁻².

Fig. S12 Rate capability profiles of the Li@Cu@Carbon symmetric cell.

Fig. S13 SEM images of (a-c) Cu@Carbon anode after stripping (a) 1.0 mAh cm⁻², (b) 2.0 mAh cm⁻², and (c) 3.0 mAh cm⁻² from Li@Cu@Carbon. The morphology can return to the initial geometry along with the stripping capacity increase from 1.0 to 3.0 mA h cm⁻².

Fig. S14 Optimized structure of H-saturated graphene. Top view (left) and side view (right). C atoms are colored grey, H atoms are white. Bond distance is in angstrom. The calculated C-C distance in normal graphene is 1.42 Å, which is in good agreement with the C-C bond length in bulk graphite.^{S5}

Fig. S15 Optimized structure of Cu-embedded graphene. Top view (left) and side view (right). Grey, white and orange balls denote C, H and Cu atoms, respectively. Bond distance is in angstrom. The geometrical optimization of Cu-graphene reveals that the Cu-substituted carbon ring is slightly distorted from planarity, and an average distance between Cu and its neighboring carbon atoms is 1.85 Å, being similar to previous report for Cu-graphene (1.83 Å).⁵⁶

Fig. S16 Frontier orbitals HOMO of (a) normal graphene and (b) Cu-embedded graphene.

Fig. S17 The rate capability of AC//Li@Cu@Carbon, AC//Li@Cu, and AC//Li cells at various current densities from 0.2

to 20.0 A g⁻¹.

Fig. S18 SEM images of (a) AC//Li@Cu@Carbon, (b) AC//Li@Cu, and (c) AC//Li anodes after cycles.

Fig. S19 Voltage profile comparison of Li@Cu@Carbon, Li@Cu, and bare Li anodes at (a) 1.0 C, (b) 2.0 C, and (c) 5.0 C.

Fig. S20 Capacity retention as a function of the cycle number for the present Li-metal battery and different LFP based

Li-metal batteries described in the literature.

Strategies	Current density (mA cm ⁻²)	Deposition capacity (mAh cm ⁻²)	Coulombic Efficiency (%)	Cycling number	Ref.
3D TiC/C core/shell nanowire	1	1	98.5	100	22
	5	1	94.8	50	25
Nitrogen-doped graphene	1	1	98	180	26
	2	1	98	50	26
Porous Cu with vertically aligned microchannels	1	3	98.5	200	27
3D porous polymelamine-formaldehyde	1	3	97.5	120	28
	5	1	95.6	100	
3D porous Cu	1	1	97.5	200	29
Metallic Ni form	1	1	90	100	30
Polyimide-clad copper grid	0.5	0.5	~99	150	
	0.5	1	~90	150	31
3D porous Cu	0.5	1	97.5	100	32
3D Cu current collector	1	1	97	140	33
3D Carbon Paper	0.5	3	~89.7	150	34
	0.5	4	~93.1	100	
Graphitized carbon fibers	0.5	8	98	50	35
CNT paper	1	5	97.5	100	36
CNT sponge	1	2	98.5	90	37
Crumple graphene	1	0.5	97	50	38
Graphene oxide	1	1	90	160	40
Nitrogen-doped graphene	0.5	1	96	200	41
CuO@Cu	0.5	1	94	200	46
quaternized polyethylene terephthalate	1	1	98	100	47
	5	1	95	90	
AgNP/carbon nanofiber	0.5	1	~98	50	49
Cu@Carbon	0.25	1	99.3	200	
	0.5	1	98.7	200	
	2	1	98.1	200	This
	5	1	97.7	200	work
	1	1	98.5	200	
	1	4	98.2	200	

Table S1. Comparison of the Coulombic efficiency of Li metal anodes with different porous structures.

Table S2. Comparison of galvanostatic cycling performance of symmetric cells with different porous structures for Li metal anodes.

Strategies	Current density (mA cm ⁻²)	Deposition capacity (mAh cm ⁻²)	Cycling time (h)	Ref.
Li-ion conductive nanocomposite electrode	1	1	200	22
3D TiC/C core/shell nanowire	0.5 1	1	800 400	23
MnO₂/G foam	1	1	1600	24
Nitrogen-doped graphene	1	0.042	12.6	26
Porous Cu with vertically aligned microchannels	1	1	200	27
3D porous polymelamine-formaldehyde	2	1	350	28
3D porous Cu	1	1	400	29
Metallic Ni form	1	1	200	30
Polyimide-clad copper grid	0.2	0.5	500	31
3D porous Cu	0.5	1	1200	32
	1	1	600	
3D Cu current collector	0.2	1	1000	33
3D Carbon Paper	1	2	1500	34
Graphitized carbon fibers	1	1	1000	35
Crumple graphene	0.5	1	750	38
Layered reduced graphene oxide	1	1	222	39
Graphene oxide	1	1	320	40
Nitrogen-doped graphene	1	1	1454	41
hollow Li foam	1	1	320 80	44
3D porous carbon	3	1	53	45
CuO@Cu	0.5	0.5	700	46
quaternized polyethylene terephthalate	3	1	100	47
AgNP/carbon nanofiber	0.5	1	500	49
Ag/Carbon Fibe	1	1	400	50
Cu@Carbon	0.5	1	2000	This
	1	1	2000	work

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