Supporting Information Bimetallic MOFs Derivatives Enabled 3D Carbon Cloth as the Lithium-Sponge for High-Performance Lithium Metal Anode

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1 Experimental Section

Materials

The thickness of carbon cloth (CC) is 0.36 mm for hydrophilic type, purchased from Suzhou Zhengtai Rong scientific research new materials. Ferric chloride hexahydrate (FeCl₃·6H₂O, AR, 99%), Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O) , 2-Aminoterephthalic acid(C₈H₇NO₄, AR, 98%) and N,N-Dimethylacetamide (DMAC, AR, 99%) was purchased from Aladdin. Anhydrous ethanol (C₂H₆O, AR, 99.7%) was purchased from Sinopharm.

Preparation of CC@Fe₂O₃/CoFe₂O₄@Li

Part 1: The cleaning procedure for the CC is as follows: Firstly, cut the commercial CC into 14 mm diameter discs and set aside. Subsequently, the cropped CC was immersed in a mixed solution consisting of nitric acid and sulfuric acid (ratio 3:1) for 12 hours to remove surface impurities by acid treatment to minimize their adverse effects on battery performance. The treated CC is ultrasonically cleaned several times with deionized water to ensure complete removal of residual acid.

Part 2: Preparation of CC@Fe₂O₃/CoFe₂O₄ Skeleton: 1 mmol FeCl₃· $6H_2O$, 1 mmol Co(NO₃)₂· $6H_2O$, and 1 mmol 2-amino-terephthalic acid were dissolved in 15 mL of N,N-dimethylacetamide (DMAC) solution to form a homogeneous mixed system. Subsequently, the pretreated CC was immersed in the above solution and reacted under magnetic stirring conditions for 1 hour. The resulting mixture was transferred to a 100 mL autoclave reactor and subjected to a

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hydrothermal reaction at 150°C for 10 hours. At the end of the reaction, it was cooled to room temperature and the FeCo-MOFs that were not deposited on the CC were removed by washing three times with deionized water. Next, the obtained CC@FeCo-MOFs samples were dried in an oven at 80°C for 3 hours. Subsequently, it was heated to 500 °C in a muffle furnace at a ramping rate of 2 °C min⁻¹ and kept at this temperature for 2 hours for annealing treatment, and finally the CC@Fe₂O₃/CoFe₂O₄ skeleton was successfully obtained.

Part 3: Preparation of CC@Fe₂O₃/CoFe₂O₄@Li composite anodes : Lithium metal was introduced into the CC@Fe₂O₃/CoFe₂O₄ skeleton by melt injection technique. This was done by placing a lithium metal sheet under a CC@Fe₂O₃/CoFe₂O₄ skeleton and heating it to 400°C on a heating table. CC@Fe₂O₃/CoFe₂O₄@Li composite electrodes were successfully prepared after lithium was completely injected into the skeleton. The amount of Li was controlled at ~10 mg by fixing the amount of molten Li.

Materials Characterization

The crystal phases of the samples were analyzed using an x-ray diffractometer (XRD, Brook-D8 advance). The samples were surface analyzed using XPS (AXIS-ULTRA DLD). The morphology of the samples was studied by scanning electron microscopy (SU-8220) and their elemental compositions were characterized in conjunction with energy spectrum analysis (EDX). Microscopic features were further analyzed using a transmission electron microscope (Titan G2 spherical aberration-corrected TEM, FEI Corporation, 80-300 kV).

Electrochemical measurements

Electrochemical measurements were made using a CR2032 coin cell. The half cells were assembled using CC@Fe₂O₃/CoFe₂O₄ as the working electrode, CC as the reference electrode, and lithium metal as the counter electrode. The symmetric cells were assembled using CC@Fe₂O₃/CoFe₂O₄@Li as the working electrode and Li foil as the reference electrode. For the full cell, CC@Fe₂O₃/CoFe₂O₄@Li was the anode (with lithium metal as the reference electrode) and LiFePO4 (LFP) was used as the cathode. LFP cathode materials were prepared by coating method. In particular, the cathode active material was 70 wt% lithium iron phosphate (LFP), which was thoroughly mixed with 20 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) binder to form a homogeneous slurry. The slurry is dispersed in NMP solvent and uniformly coated on an Al foil substrate. The coated electrode material was firstly dried at 60°C for 4 hours and then further

dried under vacuum at 120°C for 12 hours. Subsequently, the electrode material was stamped into 14 mm diameter discs using a perforating machine and compacted by means of a tablet press to ensure uniformity and denseness of the electrodes. The mass range of the compacted working electrodes was about 7.5 mg (4.88 mg·cm⁻²) to 18.9 mg (12.3 mg·cm⁻²), so the negative/positive capacity ratios (N/P ratios) are 30 and 12, respectively. To observe the surface morphology of Li after cycling, the electrodes were removed from the button cell in the glove box and then gently rinsed in DMF.

The electrolyte for the full cell consisted of a mixture of ethylene carbonate, dimethyl carbonate, and methyl ethyl carbonate (1:1:1 by volume) and contained 1 M LiPF₆. For the symmetric and half cells, the electrolyte consisted of 1 M LiTFSI mixed with equal volumes of 1,3-dioxane (DOL) and 1,2-dimethoxyethane (DME) and 1% LiNO₃ was added as an additive. The volume of electrolyte used in each cell was 30 µL.

Lithium foil was used as counter electrode material with specifications of 15.6 mm diameter and 0.42 mm thickness. The constant current charging/discharging experiments were performed on a battery measurement system (LAND CT2001A, Wuhan Jinnuo Electronics, Ltd.). Electrochemical impedance spectroscopy (EIS) measurements and cyclic voltammetry (CV) experiments were performed at room temperature on a CHI-660E electrochemical workstation (Chenhua Instruments, Shanghai, China). The EIS measurements were performed over a frequency range of 10⁶ Hz to 10⁻¹ Hz. The voltage scans of the CV tests were performed over a voltage range of 2.4V to 4.0 V, with a scan rate of 0.2 mV s⁻¹.



2 Supplementary Figures and Tables

Fig. S1. (a) XRD patterns of FeCo-MOFs. (b) XPS spectra of survey scan.



Fig. S2. Long cycling of symmetric cells with CC@Fe₂O₃/CoFe₂O₄@Li electrodes at current densities and area capacities of (a) 1 mA cm⁻²/ 1 mAh cm⁻², (b) 3 mA cm⁻²/ 3 mAh cm⁻², (c) 5 mA cm⁻²/ 5 mAh cm⁻².



Fig. S3. EIS curves before cycling.



Fig. S4. Nyquist plots of symmetric cells with different electrodes and their corresponding fitted curves. CC@Fe₂O₃/CoFe₂O₄@Li: (a) before and (b) after the 100th cycles. Bare Li: (c) before and (d) after 100th cycles.



Fig. S5. CE of the CC@Fe₂O₃/CoFe₂O₄ and CC electrode with the capacity of 1 mAh cm⁻² at different current densities (a) 1mA cm⁻², (b) 3 mA cm⁻².



Fig. S6. Rate performance of CC full cells from 0.2 C-10 C.



Fig. S7. Long cycling performance of CC@Fe₂O₃/CoFe₂O₄@Li and bare Li electrodes at 2 C.



Fig. S8. Charge-discharge curves of CC@Fe₂O₃/CoFe₂O₄ full cells at 2 C.



Fig. S9. Long cycling performance of CC@Fe₂O₃/CoFe₂O₄@Li and bare Li electrodes at 5 C.



Fig. S10. Cyclic voltammetry of CC@Fe₂O₃/CoFe₂O₄ full cells at 0.2 mV s⁻¹.



Fig. S11. (a) Rate performance of the CC@Fe₂O₃/CoFe₂O₄@Li electrodes at 0.2 C-10 C. (b)Long cycling performance of CC@Fe₂O₃/CoFe₂O₄@Li at 2 C (Ether electrolyte: 1M LiTFSI/DOL-

Fig. S12. SEM cross-sectional image of the electrode after full cell cycling (LFP: 12.3 mg cm²)

Fig. S13. (a) Deposition mechanism diagram of intermittent (uniformly grown) conductive frameworks (b) Schematic of lithium deposition from $CC@Fe_2O_3/CoFe_2O_4@Li$ and bare Li electrodes.

Possible mechanisms and intermittent lithiophilic model (Fig. S13)

In order to elucidate the mechanism of enhancement of bimetallic oxide penetration rate and its modulation on the deposition behavior of "lithium sponge", we have drawn a schematic diagram of the mechanism for the construction of a synergistic strategy for two-component lithiophilic materials (Fig. S13a): the construction of intermittent lithiophilic skeletons arranged at atomic-level intervals by MOFs derivatives (Fe₂O₃ and CoFe₂O₄) to form the alternating structure of A (e.g., CoFe₂O₄) and component B (e.g., Fe₂O₃). The design achieves spatial and temporal separation of lithium deposition at the micro and molecular scales the A site preferentially induces lithium nucleation and consumes localized Li⁺, and then drives the subsequent uniform deposition of Li⁺ in the B site after lowering the concentration of Li⁺ in the electrolyte. This process both avoids localized lithium stacking and makes full use of the backbone nucleation sites to synergistically

regulate the Li⁺ flux and interfacial electric field distribution. This intermittent deposition model has been well validated by our previous works ^[1-3]. This model both improves the lithium enrichment problem at the top of the electrode caused by the homogeneous lithophilic model and maintains the active site utilization more effectively than the gradient lithophilic model, thus providing a new way to achieve high area capacity. In addition, the results further confirm the mechanism: the lithium percolation rate of the composite anode is enhanced to 2 s (compared to 30 s for pure CC), and Figure S13b shows that it achieves a uniform dendrite-free deposition (compared to a disordered one for the bare electrode), corroborating the optimization of the percolation behavior by the nucleation site modulation.

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[3] T. Wei, Y. Zhou, C. Sun, X. Guo, S. Xu, D. Chen and Y. Tang, An intermittent lithium deposition model based on CuMn bimetallic MOF derivatives for composite lithium anode with ultrahigh areal capacity and current densities, *Nano Res.*, 2023, **17**, 2763-2769.

	R_s/Ω	Error/%	R_{int}/Ω	Error/%	R_{total} / Ω
Li foil (before)	4.163	1.87	229.95	0.81	234.113
CC@Fe ₂ O ₃ /CoFe ₂ O ₄ @Li (before)	6.716	1.45	83.63	2.24	90.346
Li foil (after)	2.136	0.58	13.12	1.54	15.256
CC@Fe ₂ O ₃ /CoFe ₂ O ₄ @Li (after)	2.359	3.29	3.904	5.93	6.299

Table S1 Electrochemical impedance fitting results of symmetric Li cells with different electrodes

Table S2 Corresponding Equivalent Circuits					
	Bare Li	Li-Mn ₂ O ₃ -NF			
Before cycling	Rs Rf Rct CPE1 CPE2	Rs Rf Rct			
After cycling	Rs Rf Rct W ₁ CPE1 CPE2	$\begin{array}{c cccc} Rs & Rf & Rct & W_1 \\ \hline & & & & \\ \hline & & & & \\ CPE1 & CPE2 \end{array}$			

In the Nyquist diagram, the semicircles in the high-frequency and low-frequency regions are closely related to the formation process of the solid electrolyte interface (SEI) layer on the electrode surface and the charge transfer reaction process at the electrode/electrolyte interface, respectively. Rs: electrolyte resistance; Rf: surface film resistance; Rct: charge transfer resistance; CPE: constant phase element; W₁: Warburg element (Warburg impedance). Rint=Rf+Rct, representing interfacial resistance between the electrode and the electrolyte.