

Supporting Information

In-situ LiF-enriched solid electrolyte interphase from CoF₂ decorated N-doped carbon for dendrite-free Li metal anodes

Xiaopan Jin^a, Gaoxu Huang^a, Xianming Zhao^a, Guoli Chen^a, Mengjia Guan^a,
Yongsheng Li^{a, b, *}

^a Lab of Low-Dimensional Materials Chemistry, Key Laboratory for Ultrafine Materials of Ministry of Education, Frontier Science Center of the Materials Biology and Dynamic Chemistry, Shanghai Engineering Research Center of Hierarchical Nanomaterials, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China.

^b Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, School of Chemistry and Chemical Engineering, Shihezi University, Shihezi 832003, China.

Corresponding author: ysli@ecust.edu.cn

Experimental

Materials: Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and methanol (>99.9%) were purchased from Macklin Reagent Co., Ltd. 2-Methylimidazole (2-MIM) was purchased from Aladdin Reagent Co., Ltd. Polytetrafluoroethylene emulsion (PTFE) was obtained from Titan Technology Co., Ltd. All chemicals were commercially available and used as received without further purification.

Synthesis of ZIF-67: In a typical preparation procedure, 12 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 48 mmol 2-MIM were fully dissolved in 45 mL methanol, respectively. Afterwards, the above 2-MIM solution was quickly poured into the $\text{Co}(\text{NO}_3)_2$ solution followed by constant stirring for 30 min. Then the mixed solution was kept at room temperature for 16 h. The harvested ZIF-67 products were collected by centrifugation and washed with methanol for three times, and followed by drying in a vacuum oven at 60 °C overnight.

Synthesis of $\text{CoF}_2@NC$ and $\text{Co}@NC$: The as-prepared ZIF-67 powders were placed in a tubular furnace, and the temperature was heated to 400 °C with a heating rate of 2 °C min^{-1} under argon (Ar) flow. After maintaining at 400 °C for 2 h, the temperature was then raised to 800 °C with the same heating rate and held for another 2 h. After that, $\text{Co}@NC$ was obtained after the furnace cooled down to room temperature.

The fluorination of $\text{Co}@NC$ was carried out in a tubular furnace at 600 °C by fluoridation etching treatment. The above-obtained $\text{Co}@NC$ and polytetrafluoroethylene emulsion (PTFE) were placed at two separate positions of the porcelain boat, where the PTFE was placed at the upstream side and the $\text{Co}@NC$ was placed at the downstream side. Then they were heated to 600 °C in Ar atmosphere with a ramp rate of 2 °C min^{-1} . Finally, the corresponding $\text{CoF}_2@NC$ composite was obtained after cooling down to room temperature under Ar flow.

Material Characterization: The morphologies of samples were characterized by scanning electron microscope (SEM, JEOL S-4800) and transmission electron microscope (TEM, JEM-2100). Fourier-transform infrared (FTIR) spectroscopy was performed with a FTIR spectrometer (Nicolet iS50) using KBr pellets. Raman spectroscopy was acquired on a LabRAM HR with an excitation laser wavelength of

514 nm at room temperature. X-ray power diffraction (XRD) was recorded on a Bruker/D8 Focus diffractometer using Cu K α radiation ($\lambda=1.5405 \text{ \AA}$) in the 2θ range from 10° to 80° with a scan rate of 8° min^{-1} . X-ray photoelectron spectroscopy (XPS) characterization was conducted on a Thermo ESCALAB 250 spectrometer. The Brunauer–Emmett–Teller (BET) surface area and pore size distribution were measured based on the adsorption-desorption isotherm of nitrogen using a Micromeritics TriStar II 3020 analyzer.

Electrochemical measurements: All the electrochemical performances were evaluated by assembling 2032-type coin cells in the argon-filled glove box with O₂ and H₂O content below 0.1 ppm. The electrolyte used in Li|Cu cells and Li|Li symmetric cells was composed of 1 M bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,3-dioxolane/1,2-dimethoxyethane binary solvents (DOL/DME, v/v=1:1) with 2 wt% LiNO₃ as the additive. The electrolyte added in full cells was 1.0 M LiPF₆ in ethylene carbonate/diethyl carbonate solution (EC/DEC, v:v=1:1) with 10% fluoroethylene carbonate (FEC). And the volume of the electrolyte in each coin cell was 50 μL .

For the preparation of modified electrodes, Co@NC (CoF₂@NC) and polyvinylidene difluoride (PVDF) with a weight ratio of 9:1 were mixed in N-methyl-2-pyrrolidone (NMP) solvent to form a homogeneous slurry, followed by coating the slurry on a piece of copper foil and then dried at 60°C in a vacuum oven overnight. To measure the Coulombic efficiency (CE), Li|Cu cells were assembled using the CoF₂@NC/Cu, Co@NC/Cu, and Cu foil as the working electrodes, Celgard 2400 polypropylene as the separator and Li metal as the counter electrode, respectively. The cells were first cycled at 0.05 mA cm^{-2} in the voltage range of 0-1 V for 5 cycles to stabilize the interface then cycled under different current densities and areal capacities. To evaluate the long-term stripping/plating stability, symmetric cells were formed by depositing 6 mAh cm^{-2} of Li onto the working electrode of Li|Cu cells at a current density of 0.5 mA cm^{-2} .

LiFePO₄ (LFP, $1\text{C}=170 \text{ mAh g}^{-1}$) was used as the cathode to pair with different anodes for the full-cell testing, which was prepared by mixing commercial LFP powders with carbon black and PVDF with a weight ratio of 8:1:1 with N-methyl-2-pyrrolidone (NMP) as the solvent. The as-obtained slurry was coated on the aluminum

foil, and then dried at 110 °C for 12 h. The areal mass loading of LFP cathode was about 3.1 mg cm⁻². The assembled full cells were measured in a potential range of 2.5-4.2 V. The galvanostatic charge-discharge test was carried out on a battery test system (CT2001C, LAND). Electrochemical impedance spectroscopy (EIS) was performed on an electrochemical workstation (Chenhua, CHI 600) in the frequency range from 0.1 Hz to 100 kHz.

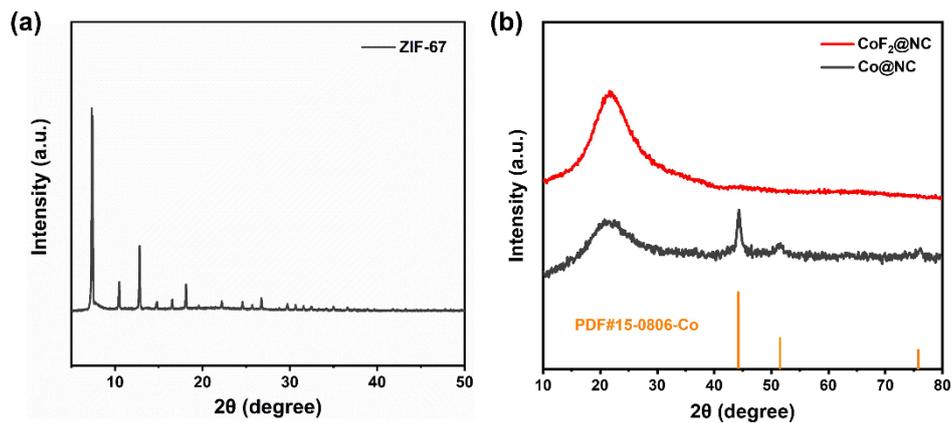


Figure S1. XRD patterns of (a) ZIF-67, (b) Co@NC and CoF₂@NC.

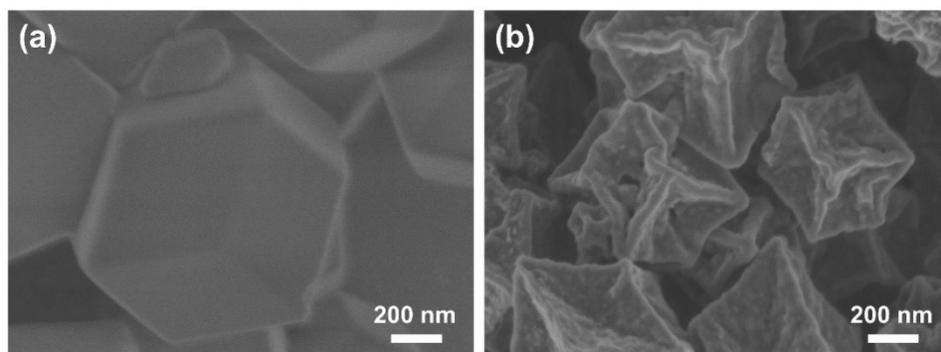


Figure S2. SEM images of (a) ZIF-67 and (b) Co@NC.

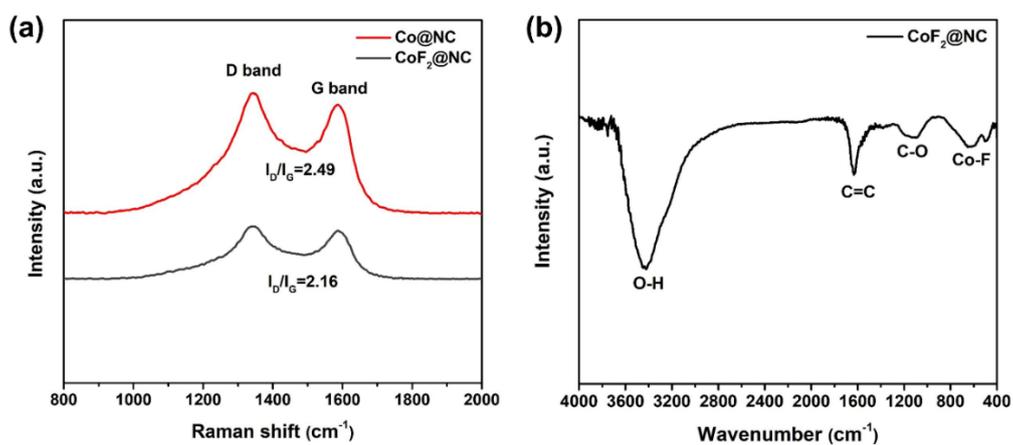


Figure S3. (a) Raman spectra of Co@NC and CoF₂@NC, and (b) FTIR spectrum of CoF₂@NC.

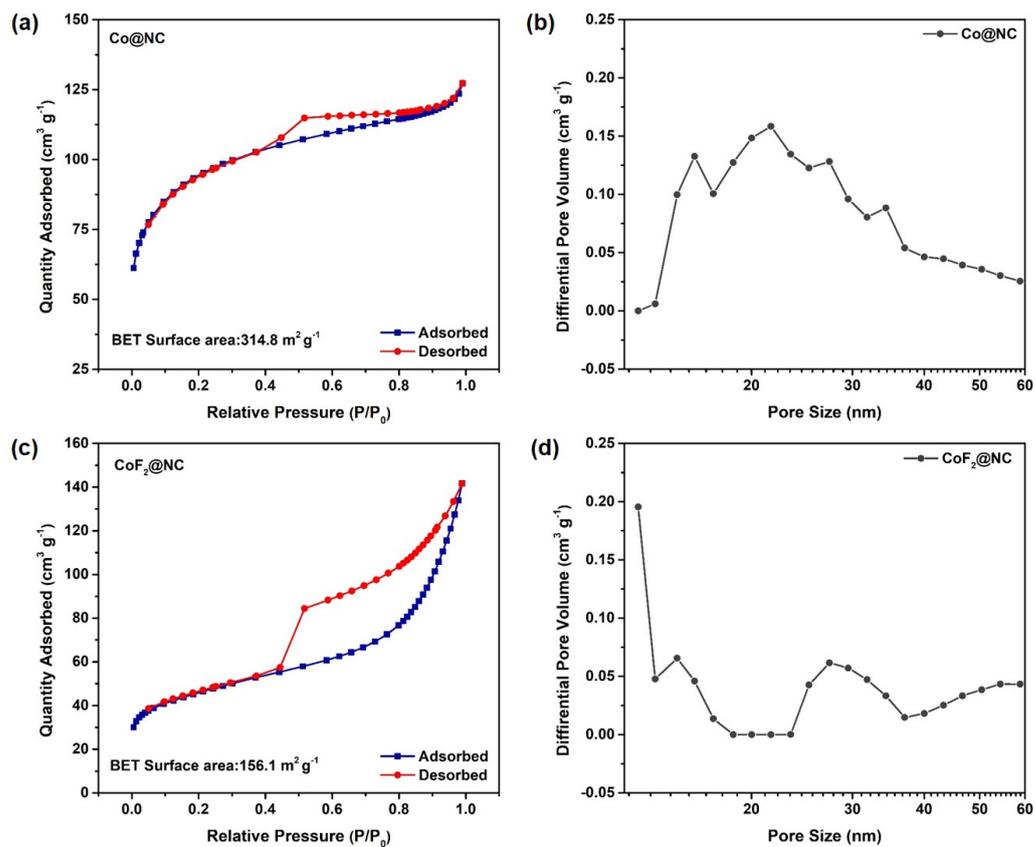


Figure S4. N₂ adsorption-desorption isotherms of (a) Co@NC and (c) CoF₂@NC, pore size distribution curves of (b) Co@NC and (d) CoF₂@NC.

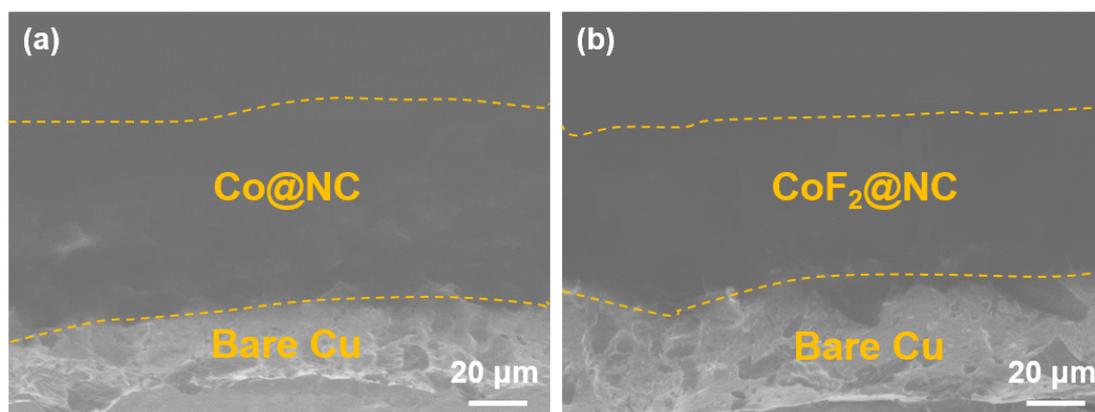


Figure S5. Cross-section SEM images of (a) Co@NC and (b) CoF₂@NC.

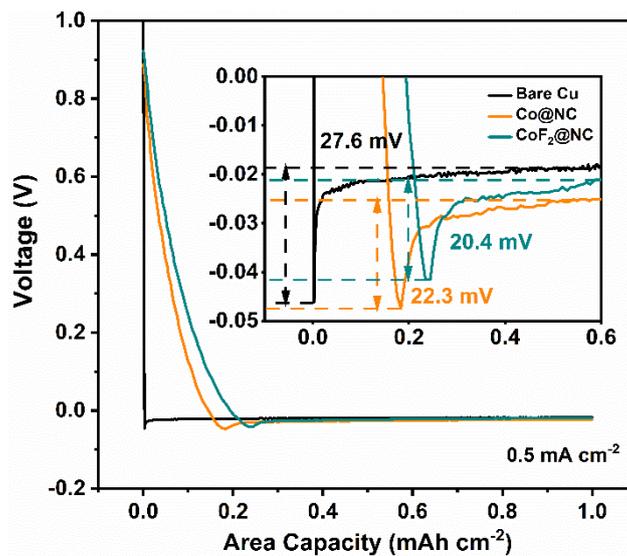


Figure S6. Nucleation overpotentials of CoF₂@NC/Cu, Co@NC/Cu, and bare Cu substrates at 0.5 mA cm⁻² and 0.5 mAh cm⁻².

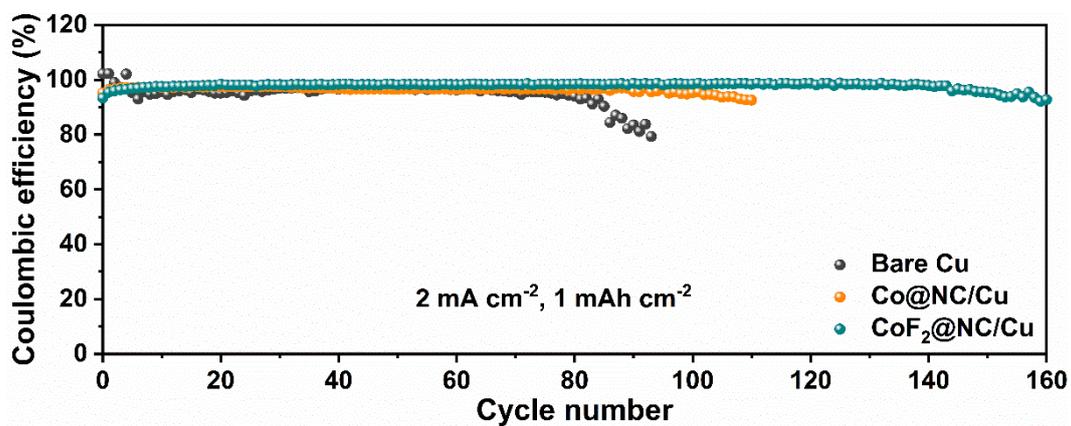


Figure S7. Coulombic efficiency of the Li|Cu cells with bare Cu, Co@NC/Cu and CoF₂@NC/Cu electrodes at 2 mA cm⁻² and 1 mAh cm⁻².

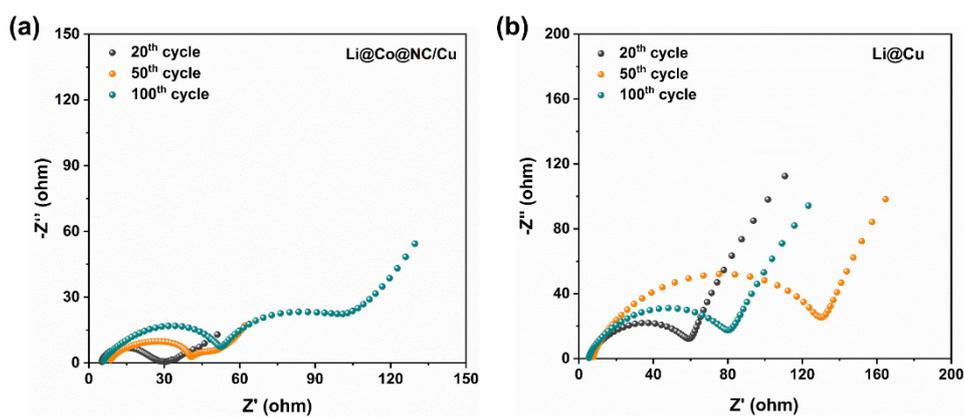


Figure S8. Nyquist plots the symmetric cells with (a) Li@Co@NC/Cu and (b) Li@Cu anodes at various stages.

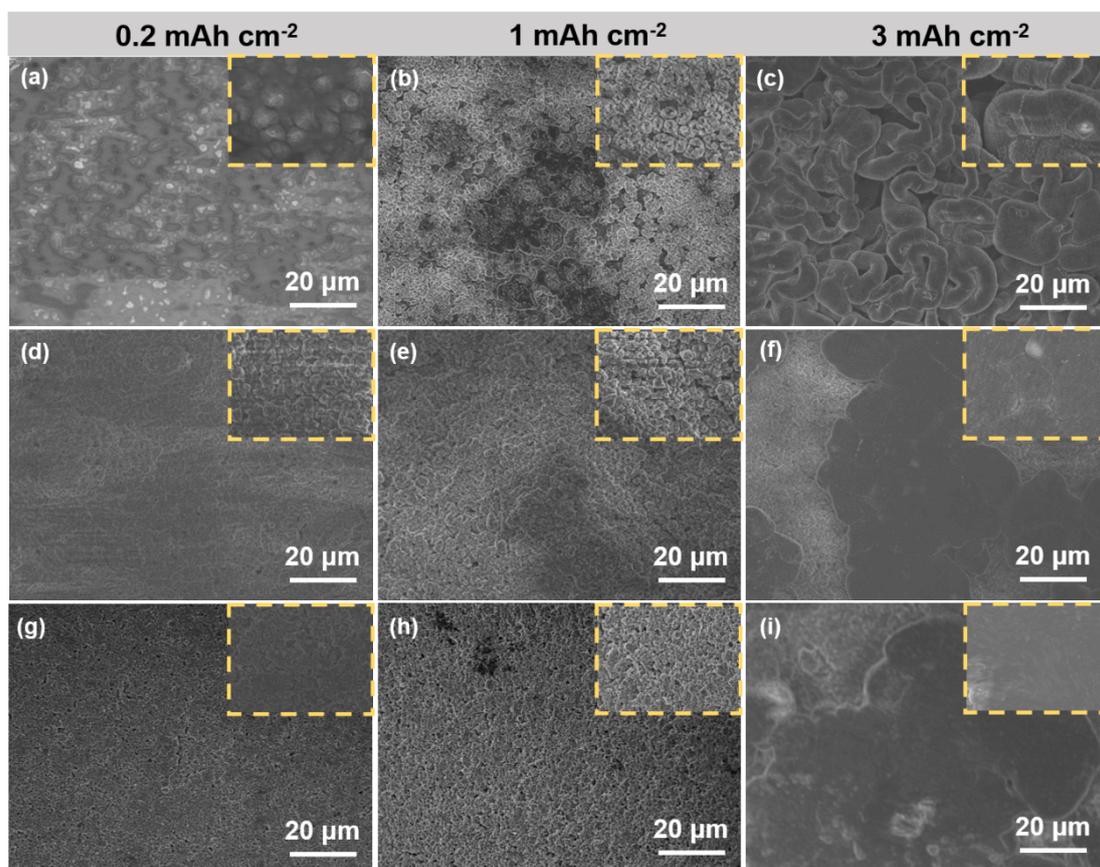


Figure S9. Top-view SEM images of Li deposition morphology with capacities from 0.2 to 3 mAh·cm⁻² on the (a-c) bare Cu, (d-f) Co@NC, and (g-i) CoF₂@NC.

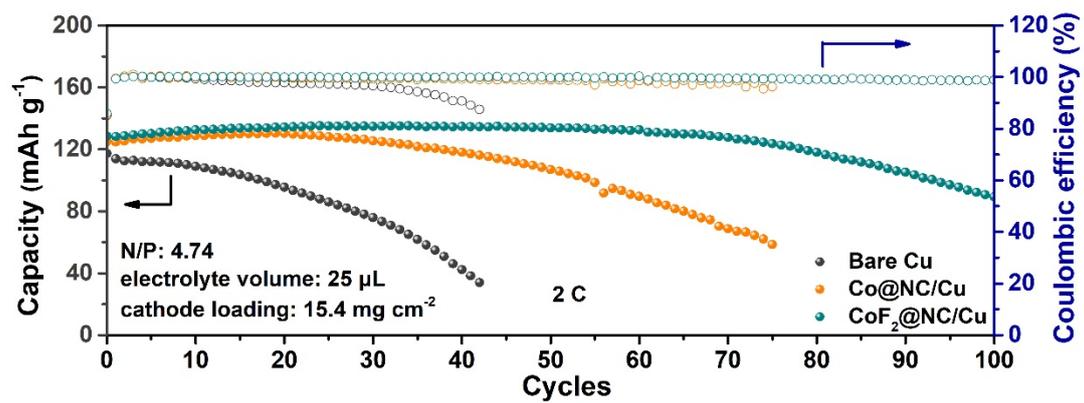


Figure S10. Cycling performance of LFP full cells with CoF₂@NC/Cu, Co@NC/Cu, and bare Cu current collectors the rate of 2 C.