

Electronic Supplementary Information (ESI)

Pre-carbonizing nickel-metal organic frameworks for enabling lithium–sulfur reactions

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1. Experimental Section

Synthesis of Ni-MOF.

1.329 g terephthalic acid (PTA) and 3.489 g nickel nitrate hexahydrate were dissolved in 100 mL N, N-dimethylformamide (DMF), respectively, and stirred at room temperature. Then, the two solutions above were mixed and stirred for 1 h until the liquid was homogeneous. Then, 16 mL 0.1 mol L⁻¹ sodium hydroxide solution (NaOH) was added to the mixed solution and stirred evenly. Subsequently, the mixture was charged into an autoclave and maintained at 120 °C for 24 h. After cooling to room temperature, the resulting precipitate was washed three times, alternately with DMF and alcohol. Finally, the precipitate was dried at 70 °C for 12 h to obtain Ni-MOF materials.

Synthesis of Ni@C.

Ni-MOF was heated to 600 °C at a heating rate of 10 °C min⁻¹ under argon protection, kept for 2 h, and then cooled in the furnace. The obtained carbide sample was Ni@C.

Preparation of Ni@C (or Ni-MOF) interlayers.

90 mg of Ni@C (or Ni-MOF), 90 mg of Super P and 20 mg PVDF binder were mixed in N-methyl pyrrolidone (NMP) solvent to generate a slurry, and followed by coating on one side of PP separator. After drying at 60 °C under vacuum for 12 h, the final Ni@C (or Ni-MOF) interlayers were further punched into small disks with a diameter of 19 mm prior to use.

Preparation of sulfur/carbon cathodes.

The Super P and sulfur powders were mixed with a mass ratio of 1:3. Then the mixture was sealed into a glass bottle and heated at 155 °C for 6 h under Ar atmosphere. After thoroughly grinding, sulfur/carbon composite, Super P and LA133 binder were stirred at a mass ratio of 8:1:1 until the formation of the viscous slurry. The as-prepared slurry was coated on a piece of Al foil and then dried at 60 °C under vacuum condition before punched into disks with a diameter of 13 mm. The sulfur mass content in the entire cathode was around 60 wt.%. The mass loadings were 1.4–1.6 mg cm⁻² for routine batteries and 4.8 mg cm⁻² for high-load batteries.

Preparation of coin-type LSBs.

Coin-type batteries were assembled with sulfur/carbon cathode, Ni@C (or Ni-MOF) loaded PP separator, lithium foil and electrolyte. The electrolyte was 1,2-dimethoxyethane (DME)/1,3-dioxolane (DOL) solvent (v:v=1:1) containing 1.0 mol L⁻¹ LiTFSI and 2.0 wt.% LiNO₃. The electrolyte/sulfur ratio was 15.0 μL mg_S⁻¹ for routine batteries and 7.0 μL mg_S⁻¹ for high-load batteries.

Material characterizations.

The morphology was examined using a Tescan MAIA3 model 2016 field Emission Scanning Electron Microscope. Detailed structural and elementals were observed by Tecnai G2 F20 S-Twin Transmission Electron Microscope with an accelerating voltage of 200 kV. X-ray diffraction patterns were recorded using FEI, Tecnai F20-ray Diffractometer. The ultraviolet–visible (UV–Vis) absorption spectra were recorded using a TU-1901 Dual Beam Ultraviolet–Visible Spectrometer. Observation of pore distribution and N₂ absorption and desorption of materials were performed on Quantachrome Autosorb-IQ. The inductively coupled plasma optical emission spectroscopy (ICP-OES) was characterized by ICP-OES: Agilent 5110.

Li₂S nucleation/ dissociation tests.

0.2 mol L⁻¹ Li₂S₈ solution was first attained by mixing sulfur and Li₂S at a molar ratio of 7:1 in tetraglyme solvent. Commercial carbon paper (CP) was first punched into disks with a diameter of 13 mm and then loaded with 0.2 mg of Ni@C or Ni-MOF (denoted as CP-Ni@C and CP-Ni-MOF), respectively. All the cells were assembled by using CP based cathode, lithium foil and PP separator. The as-prepared Li₂S₈ solution with a volume of 20 μL served as the catholyte, and 20 μL of Li–S electrolyte (a mixture of DME/DOL (v:v=1:1) containing 1.0 mol L⁻¹ LiTFSI and 2.0 wt.% LiNO₃) acted as the anolyte. The cells were galvanostatically discharged under 0.112 mA to 2.06 V and subsequently kept potentiostatically at 2.05 V till the current reached 10⁻⁵ A. Similarly, the Li₂S dissociation tests were first performed galvanostatically at a current of 0.112 mA to 1.7 V. Subsequently, the cells were potentiostatically charged at 2.35 V until the current was 10⁻⁵ A.

Assembly of symmetric cells.

Symmetric cells were assembled by applying CP-Ni@C (CP-Ni-MOF) as the working and counter electrodes, and 20 μL of Li₂S₆ solution with a concentration of 0.2 mol L⁻¹ as the electrolyte. Cyclic voltammetry (CV) tests were conducted between –1 to 1 V at a scan rate of 50 mV s⁻¹.

Adsorption tests.

To obtain Li₂S₆ solution (3 mmol L⁻¹), the lithium sulfide and sublimed sulfur at a molar ratio

of 1:5 was dissolved in 1,2-dime-thoxyethane (DME) solvent. The Ni@C and Ni-MOF interlayers were placed in the caps of headspace bottles filled with 2 mL of 3 mmol L⁻¹ Li₂S₆ solution, respectively, and inverted into a large sample bottle filled with 2 mL of DME. The devices were placed in an argon-filled glove box.

Electrochemical tests.

The galvanostatic discharge and charge processes, rate capacities and cycle performances of LSBs were measured within the voltage window of 1.7–2.8 V on the NEWARE CT4008 Battery Testing System. Electrochemical impedance spectroscopy (EIS) curves in the frequency range of 10⁵ to 10⁻² Hz and CV curves were collected on a Metrohm Autolab G204 electrochemical workstation.

2. Figures

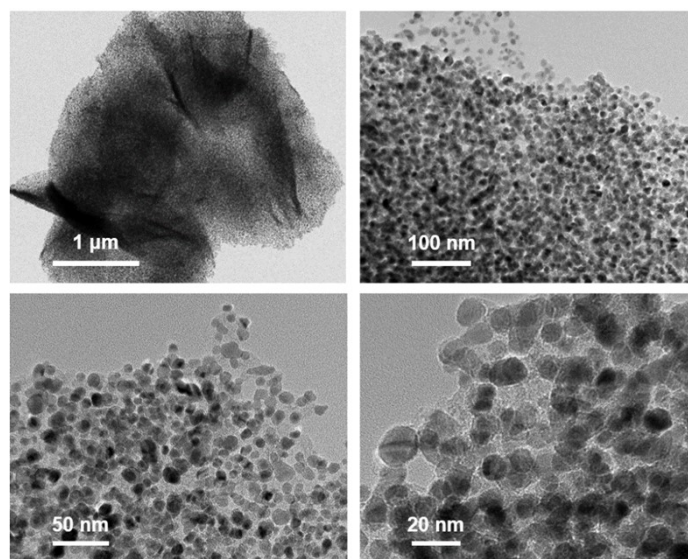


Fig. S1 TEM images of Ni@C.

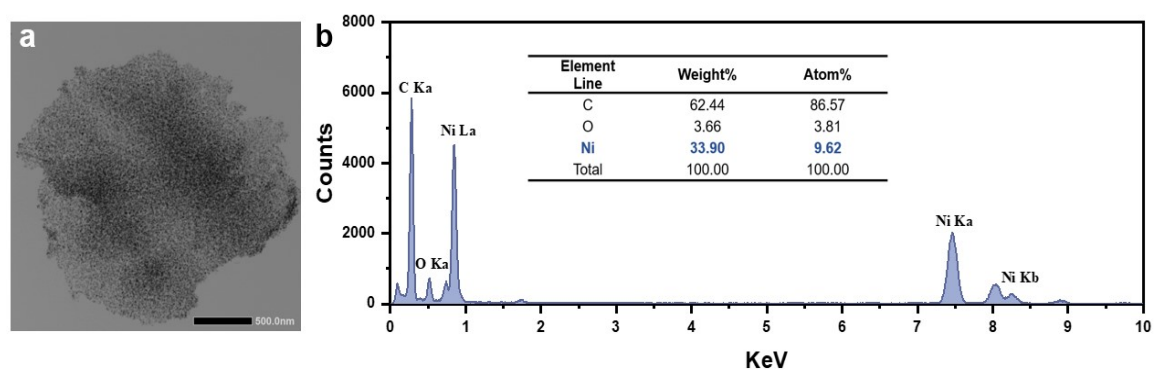


Fig. S2 (a) STEM and (b) elemental compositions of Ni@C.

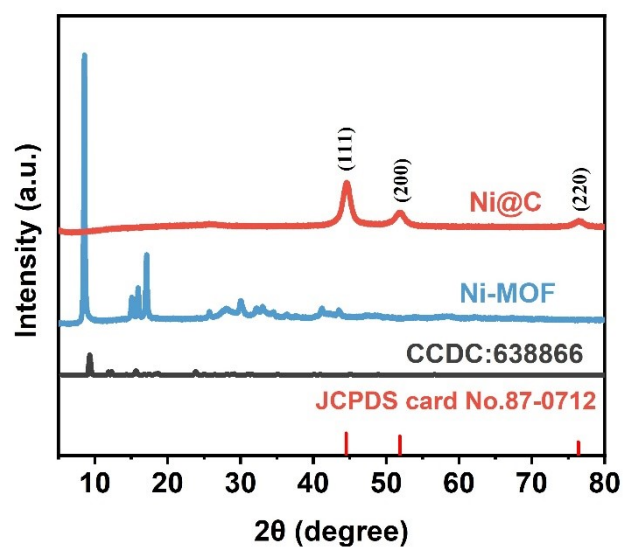


Fig. S3 XRD patterns of Ni-MOF and Ni@C.

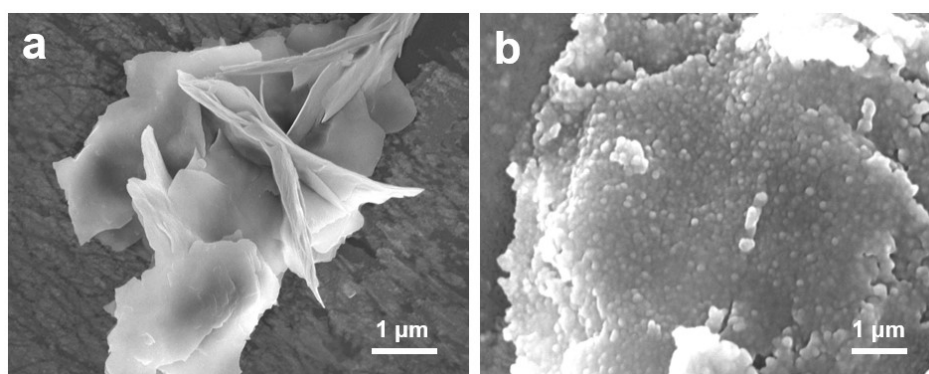


Fig. S4 SEM images of (a)Ni-MOF and (b)Ni@C.

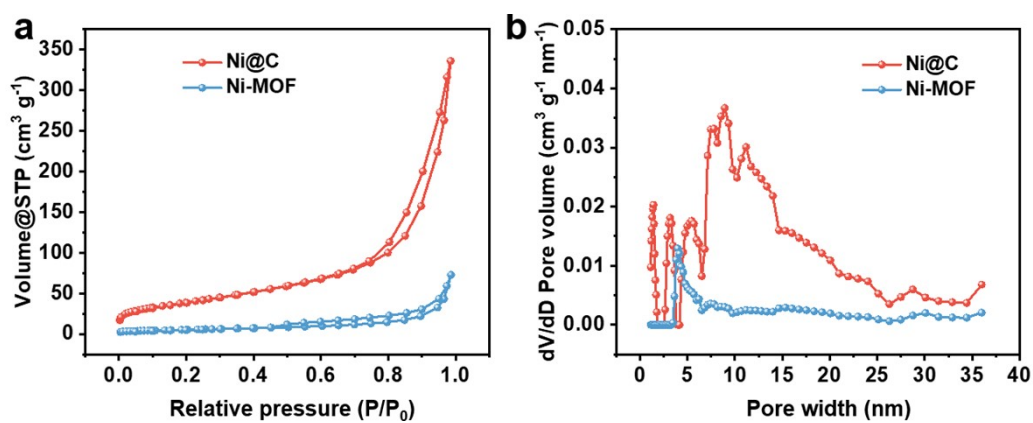


Fig. S5 (a) N_2 adsorption and desorption isotherms and (b) pore size distribution curves of Ni@C and Ni-MOF.

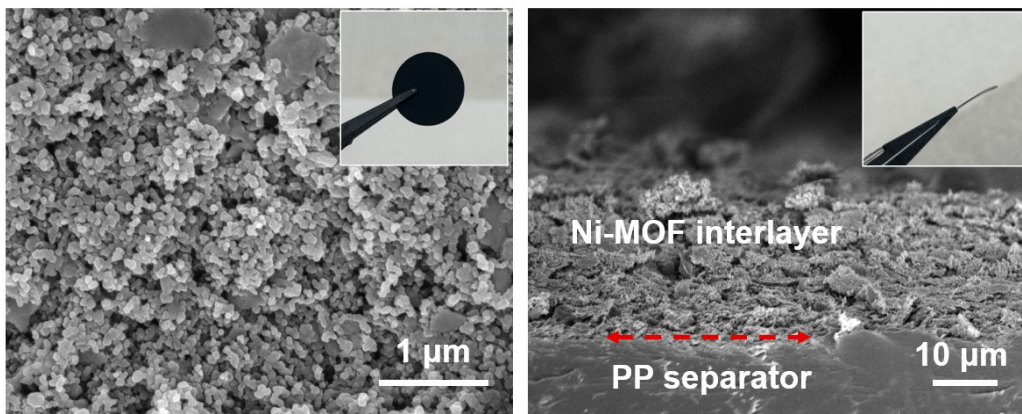


Fig. S6 The planar and cross-sectional SEM images and digital photographs (insets) of the Ni-MOF interlayer.

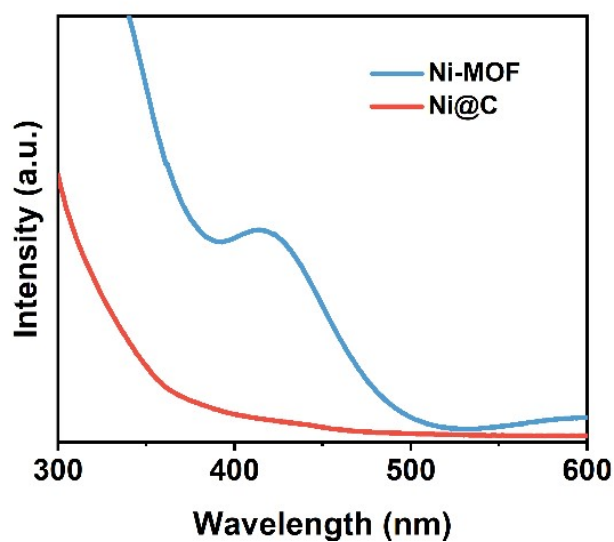


Fig. S7 UV-Vis absorption spectra of the Li_2S_6 solution after adsorption tests.

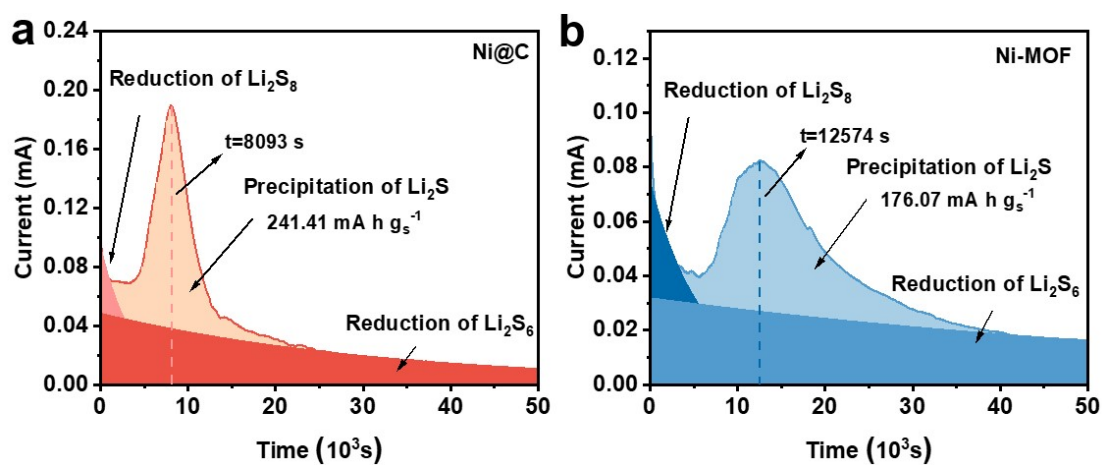


Fig. S8 (a,b) Li_2S nucleation curves on Ni@C and Ni-MOF.

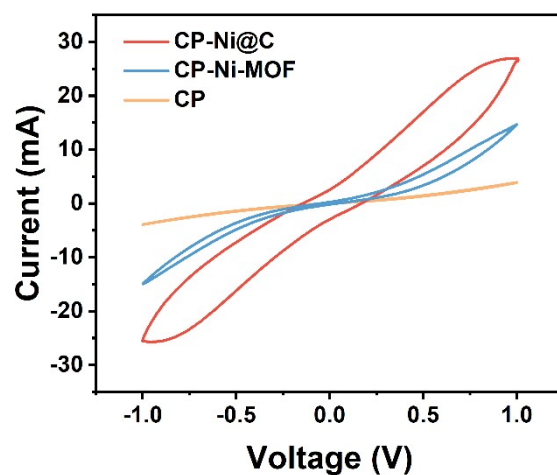


Fig. S9 Polarization curves of symmetrical cells with CP, CP-Ni@C, and CP-Ni-MOF.

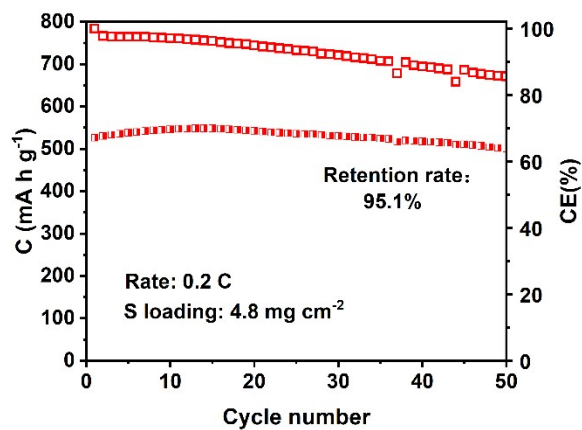


Fig. S10 Cycling stability of the battery with Ni@C interlayer at a mass loading of 4.8 mg cm^{-2} at 0.2 C.

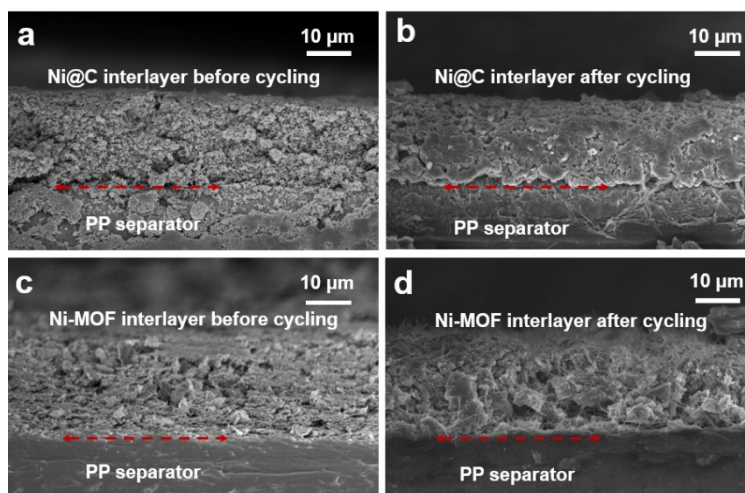


Fig. S11 SEM images of Ni@C and Ni-MOF interlayers before and after 100 cycles at 1.0 C.

3. Table

Table. S1. ICP-OES results of Li in cathode powder with regard to Ni@C before and after discharge at 1.0 C.

	Before discharge	After discharge
The content of Li (wt.%)	0	1.3

Note: the cycled cathode powder was collected at the end of the discharge procedure.