

Supporting Information

Chromium and Molybdenum Dual-Metal Nanoclusters: Synergistic Catalysis Sulfur Redox for High Performance Li-S Batteries

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Experimental Section

Materials: Dicyandiamide (99.5%), glucose (99%), and ammonium chromate (99.5%) were purchased from Adamas-beta. Ammonium molybdate tetrahydrate (AR, 99%) was obtained from Aladdin. All chemical reagents were used as received without further purification.

Synthesis of Catalysts and Composites

Synthesis of N-C, Cr@N-C, Mo@N-C, and Cr/Mo@N-C: To synthesize N-C, 5 g of dicyandiamide and 0.25 g of glucose were dissolved in 300 mL of deionized water. The solution was then heated to 80°C under an argon atmosphere and stirred for 2 hours. After cooling, the solution was freeze-dried to obtain a homogeneous precursor. This precursor was subsequently heated at a rate of 3°C/min to 600°C and held for 2 hours. The temperature was then increased to 900°C at the same rate and held for an additional 2 hours to yield the final N-C product.

The synthesis of Cr/Mo@N-C followed the same procedure, with the addition of 7.6 mg of ammonium chromate and 8.8 mg of ammonium molybdate tetrahydrate. These metal precursors were first dissolved in 10 mL of deionized water and then mixed with the main precursor solution. The resulting Cr/Mo@N-C bimetallic nanoclusters were formed after annealing and pyrolysis.

For the synthesis of Cr@N-C and Mo@N-C, the respective metal precursors were added individually: 7.6 mg of ammonium chromate for Cr@N-C and 8.8 mg of ammonium molybdate tetrahydrate for Mo@N-C. Both were dissolved in 10 mL of deionized water and mixed with the main solution before undergoing the same pyrolysis steps as the N-C synthesis.

Synthesis of S/N-C, S/Cr@N-C, S/Mo@N-C, and S/Cr/Mo@N-C: For the preparation of sulfur cathodes, the synthesized catalyst materials (N-C, Cr@N-C, Mo@N-C, or Cr/Mo@N-C) were each mixed with sulfur powder in a 1:4 mass ratio and ground in a mortar for 1 hour. The resulting mixture was then transferred to a polytetrafluoroethylene reaction vessel, heated to 155°C under an argon

atmosphere, and maintained at this temperature for 12 hours to obtain the corresponding sulfur cathodes.

Characterizations

XRD patterns were recorded using an X'Pert3 Powder diffractometer. Morphology was determined using SEM (JSM-7800F) and TEM (JEM-F200). Specific surface areas of N-C and Cr/Mo@N-C were analyzed with a Micromeritics ASAP 2460 analyzer. Chemical composition and elemental valence states were analyzed using XPS (Thermo Scientific K-Alpha). Raman spectra were measured on an InVia Reflex Raman spectrometer with a 532 nm excitation wavelength. UV testing for LiPSs adsorption experiments was conducted using a UV-visible spectrophotometer (UV-2600i). Thermal analysis was performed with a TGA/DSC1 differential thermal analyzer. X-ray absorption spectroscopy (XAFS) studies were performed at the BL14B2 beamline of SPring-8 (8 GeV, 100 mA), Japan. The X-ray beam was monochromatized with a water-cooled Si (311) double-crystal monochromator and focused with two Rh-coated mirrors to obtain both near-edge and extended X-ray absorption fine structure spectra.

Electrochemical Measurements

The slurry was prepared by mixing 80 wt% active material (S/N-C or S/Cr/Mo@N-C), 10 wt% conductive carbon black, and 10 wt% PVDF in N-methyl-2-pyrrolidone (NMP). The slurry was then uniformly coated onto carbon paper and vacuum-dried at 60°C for 12 hours. Circular electrodes were cut, with an active sulfur loading of approximately 1.2 mg·cm⁻². CR2032 coin cells were assembled in an argon-filled glovebox. Celgard 2400 (16 mm) was used as the separator, and a metallic Li foil served as the counter electrode. 1 M LiTFSI and 1 wt% LiNO₃ solution in a 1:1 volume ratio of

DOL/DME was used for the electrolyte. For standard sulfur loading ($1.2 \text{ mg}\cdot\text{cm}^{-2}$), $30 \mu\text{L}$ of electrolyte was added per cell. For high sulfur areal loading tests ($5.5 \text{ mg}\cdot\text{cm}^{-2}$), electrodes of the same diameter were used, and $40 \mu\text{L}$ of electrolyte was added, corresponding to an E/S ratio of approximately $6.4 \mu\text{L}\cdot\text{mg}^{-1}$. After a 12-hour rest, the cells were subjected to constant current charge-discharge tests using a LAND CT3002A battery testing system within a voltage range of 1.6 V to 2.8 V at 25°C . CV curves were obtained using an AUTOLAB PGSTAT302N at a scan rate of $0.1\text{-}0.5 \text{ mV}\cdot\text{s}^{-1}$ within a voltage range of 1.6 V to 2.8 V. EIS tests were conducted on the same instrument over a frequency range of 100 kHz to 10 mHz.

Li_2S_6 Symmetric Cell Measurements

The slurry was prepared by mixing 70 wt% catalyst (N-C or Cr/Mo@N-C), 20 wt% conductive carbon black, and 10 wt% PVDF in NMP. The slurry was uniformly coated onto carbon paper and vacuum-dried at 60°C for 12 hours. Circular electrodes were cut and used as both the working and counter electrodes. A Celgard 2400 separator was placed between the electrodes, and $20 \mu\text{L}$ of a 0.2 M Li_2S_6 and 1 M LiTFSI electrolyte solution (1:1 DOL/DME by volume with 1 wt% LiNO_3) was added to each side of the separator. The cells were then assembled into CR2032 coin cells. CV testing was performed using an AUTOLAB PGSTAT302N within a voltage range of -1.0 V to 1.0 V at a scan rate of $20 \text{ mV}\cdot\text{s}^{-1}$.

Li_2S Nucleation Experiment

The positive electrode and separator for the nucleation test cells were the same as those used in the symmetric cells. However, Li metal was used as the negative electrode. The electrolyte for the Li_2S nucleation test was a solution of 0.2 M Li_2S_8 and 1 M LiTFSI dissolved in a 1:1 DOL/DME mixture containing 1 wt% LiNO_3 . During the Li_2S precipitation test, the prepared cells were first discharged at

a constant current of 0.112 mA to 2.06 V. They were then discharged at a constant potential of 2.05 V until the current dropped below 10 μ A.

Figure S1. Energy dispersive X-ray spectroscopy (EDS) analysis of Cr/Mo@N-C sample.

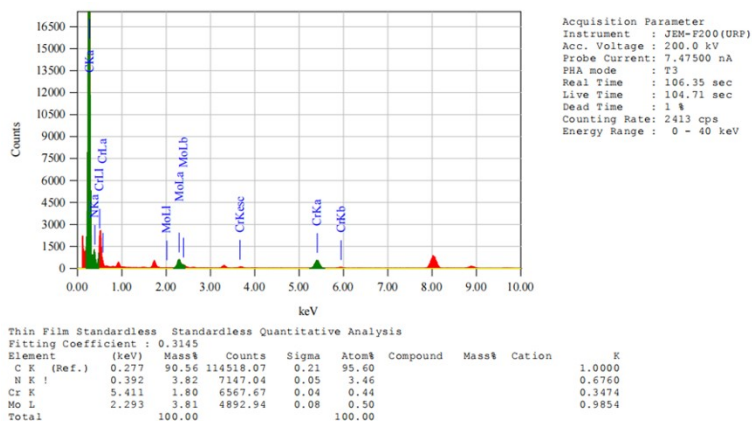


Figure S2. Characterization of the Mo@N-C electrocatalyst. (a) SEM image, (b) TEM image, (c) HRTEM image, and XPS analysis of the (d) C 1s, (e) N 1s, and (f) Mo 3d.

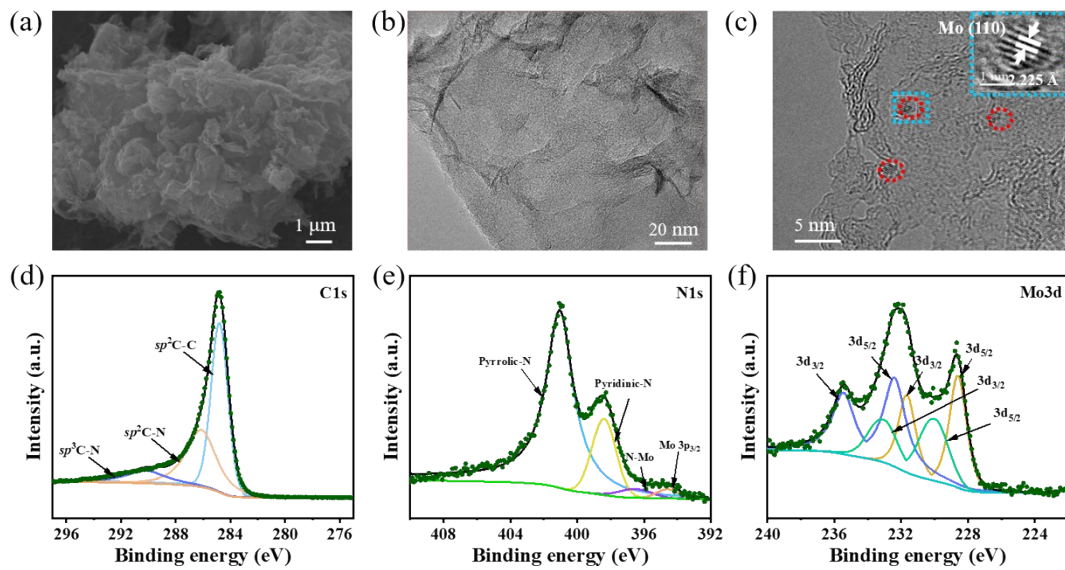


Figure S3. Characterization of the Cr@N-C electrocatalyst. (a) SEM image, (b) TEM image, (c) HRTEM image, and XPS analysis of the (d) C 1s, (e) N 1s, and (f) Cr 2p.

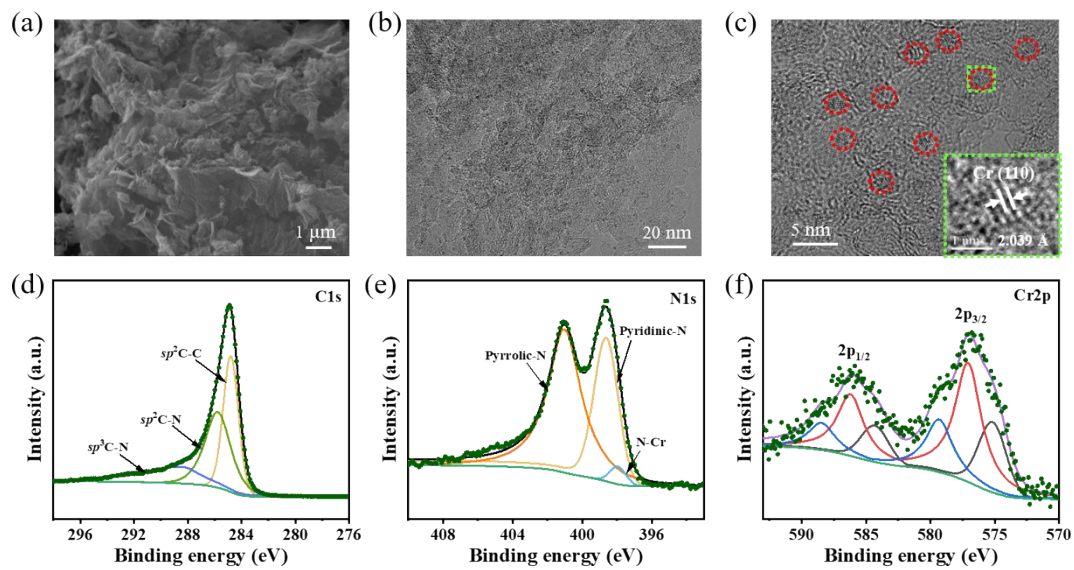


Figure S4. Characterization of the N-C electrocatalyst. (a) SEM image, (b) TEM image, and XPS analysis of the (c) C 1s and (d) N 1s.

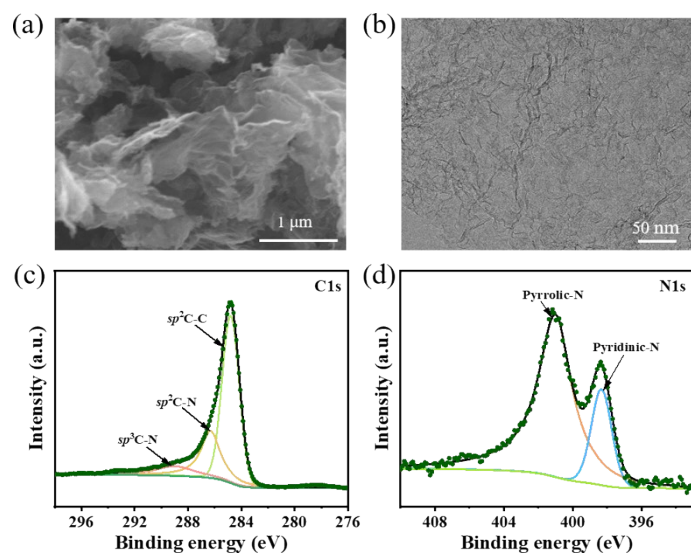


Figure S5. N₂ absorption/desorption isotherms and pore size distribution plots of N-C.

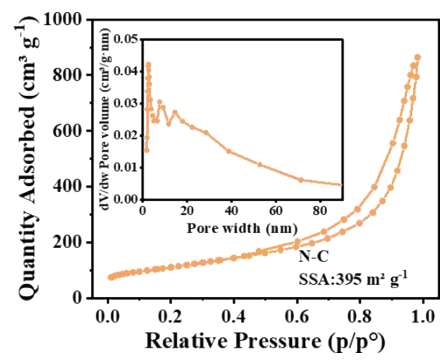


Figure S6. Potentiostatic nucleation curves of Li_2S on N-C.

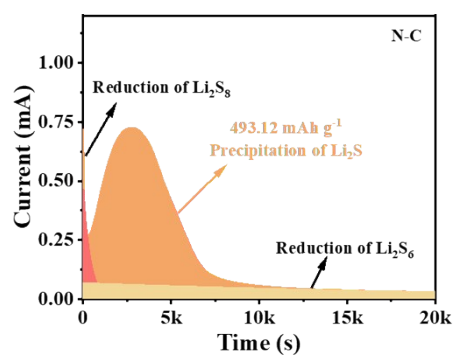


Figure S7. CV curves at different scan rates (0.1–0.5 mV s⁻¹): (a) S/N-C and (b) S/Cr/Mo@N-C.

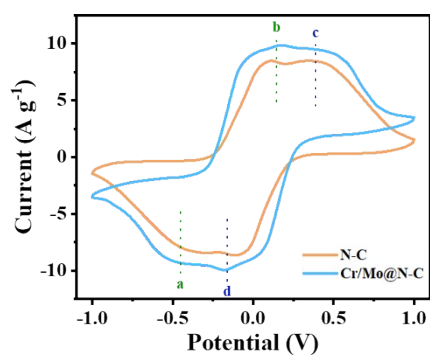


Figure S8. The UV-visible spectra absorption test of N-C and Cr/Mo@N-C on Li_2S_6 after 12 hours.

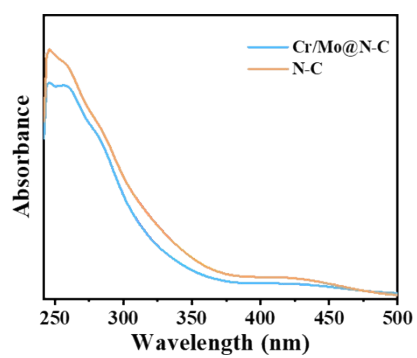


Figure S9. *In Situ* UV-Vis analysis of the N-C electrode. (a) Corresponding operando UV-Vis spectra. (b) Operando UV-Vis spectra at different depths of discharge (DOD) and states of charge (SOC). (c) Absorbance of dissolved LiPSs species at 420 nm (Li_2S_4), 480 nm (Li_2S_6), and 560 nm (Li_2S_8) during cycling.

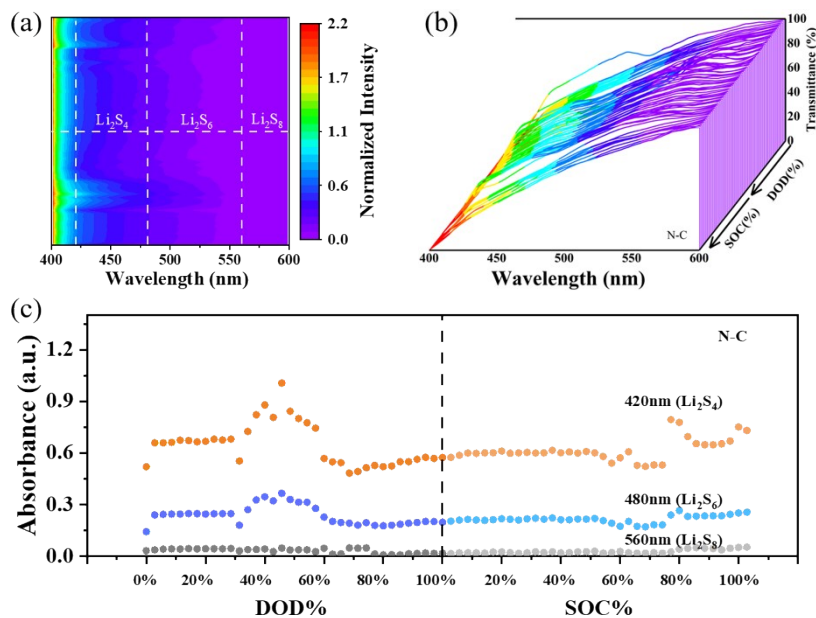


Figure S10. *Ex situ* XPS study of cycled S/Cr/Mo@N-C electrodes. (a) Mo 3d spectra and (b) Cr 2p spectra.

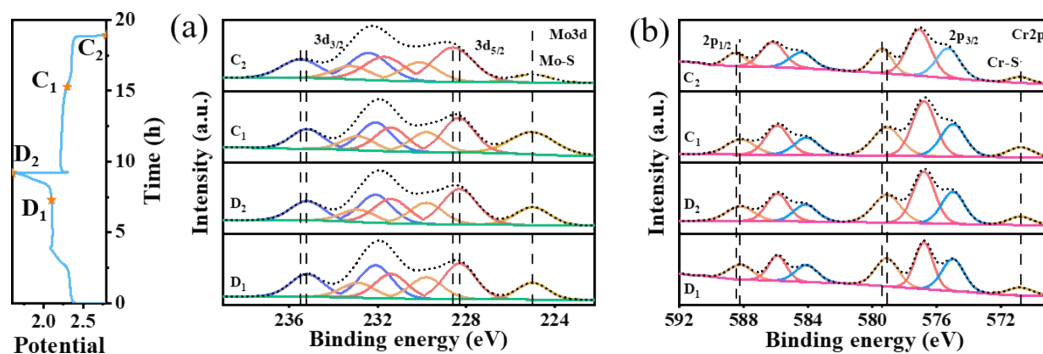


Figure S11. S 2p spectra at different states of charge and discharge.

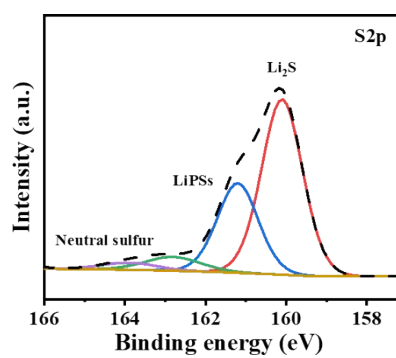


Figure S12. SEM image of S/Cr/Mo@N-C.

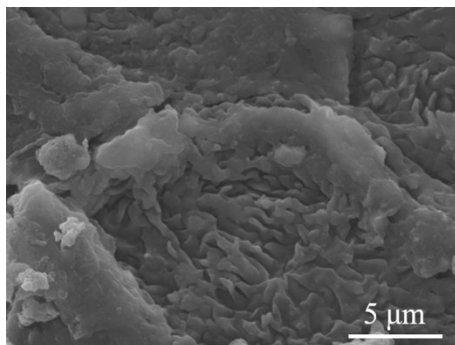


Figure S13. SEM image of the S/Cr/Mo@N-C electrode and corresponding elemental mapping images.

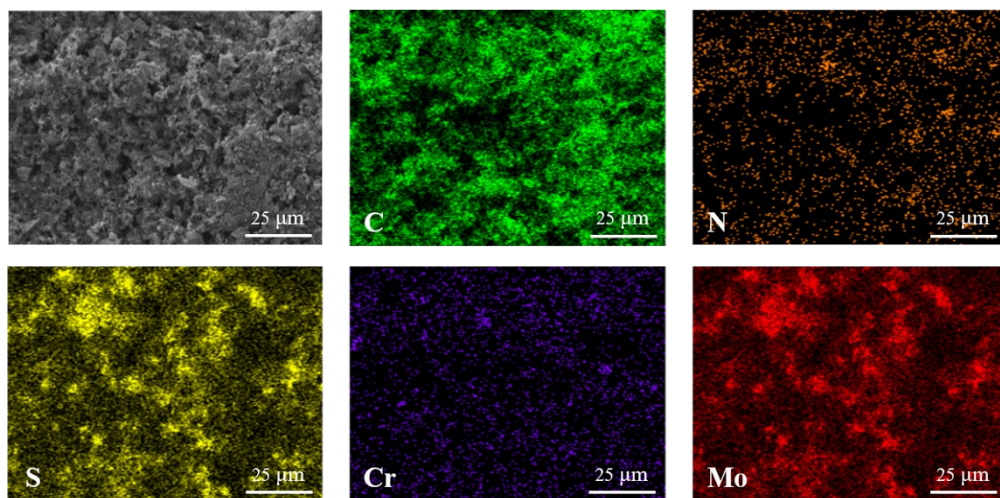


Figure S14. XRD patterns of S/N-C and S/Cr/Mo@N-C.

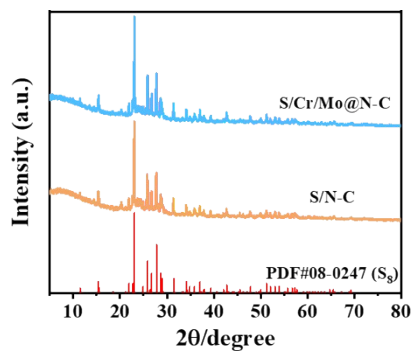


Figure S15. Raman spectra of S/N-C and S/Cr/Mo@N-C.

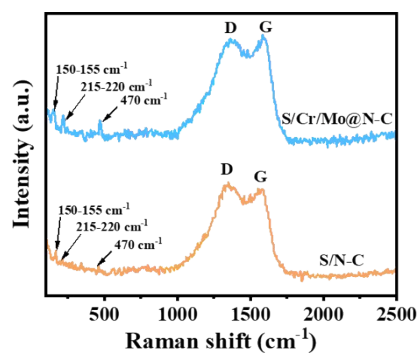


Figure S16. TGA curves of (a) S/N-C and (b) S/Cr/Mo@N-C.

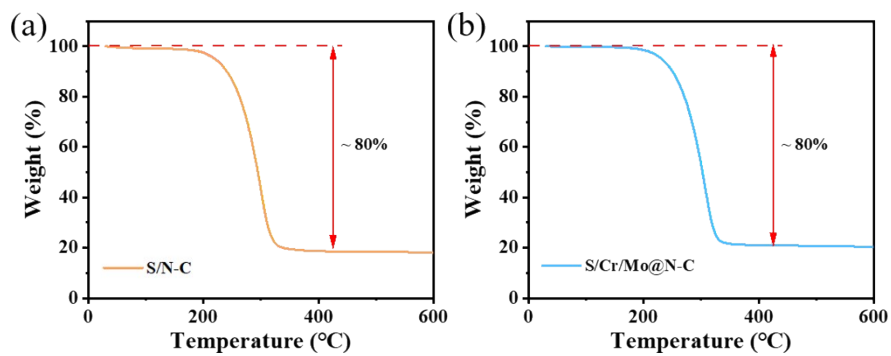


Figure S17. GITT curves of S/N-C and S/Cr/Mo@N-C.

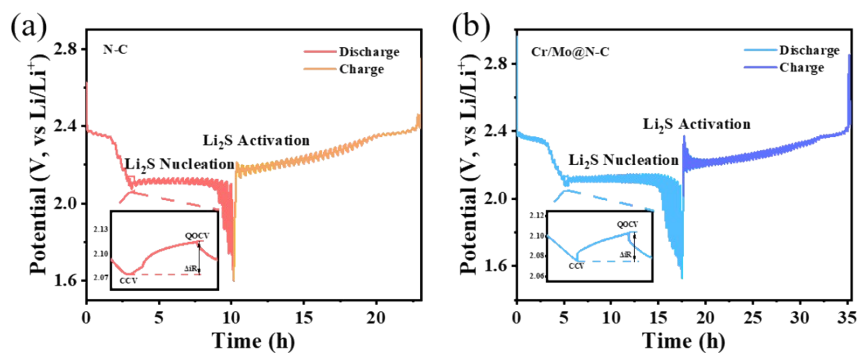


Figure S18: CV curves of (a) N-C and (b) Cr/Mo@N-C, with a voltage range of 1.6-2.8 V and a scan rate of 0.1 mV s^{-1} .

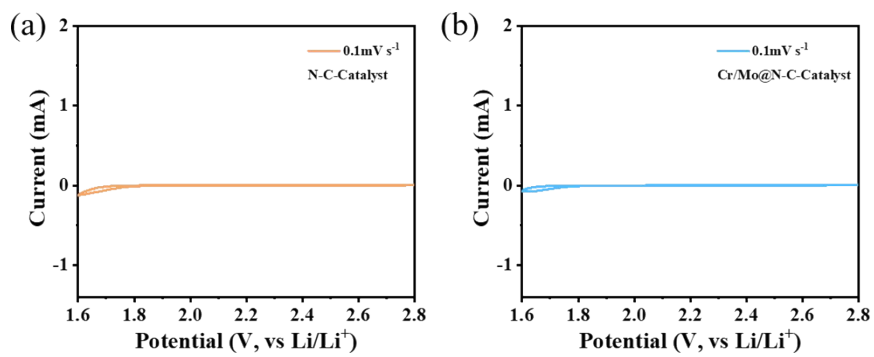


Figure S19. EIS curves of Li-S batteries with different positive electrodes after 20 cycles.

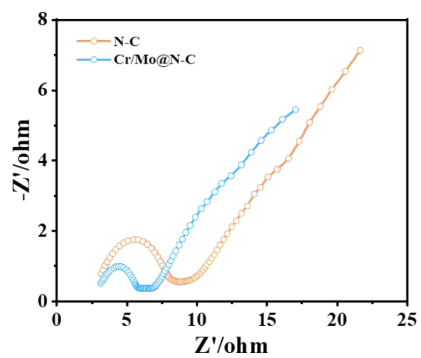


Figure S20. Cycling performance of high-loading S/Cr/Mo@N-C electrodes at 0.1 C.

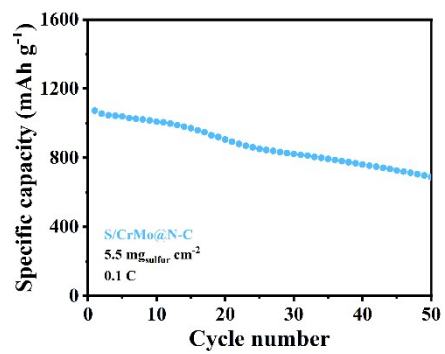


Figure S21. Pouch cell performance. (a) Optical photograph of a pouch cell with an S/Cr/Mo@N-C cathode. (b) Cycling performance of the corresponding pouch cell.

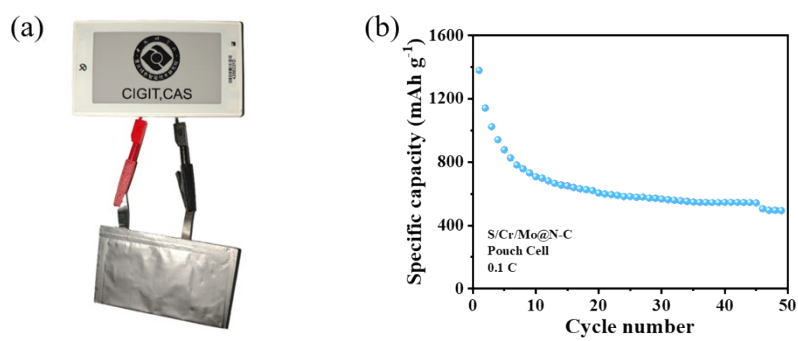


Figure S22. Optical photographs of electrode morphology for S/N-C and S/Cr/Mo@N-C cathodes after cycling.

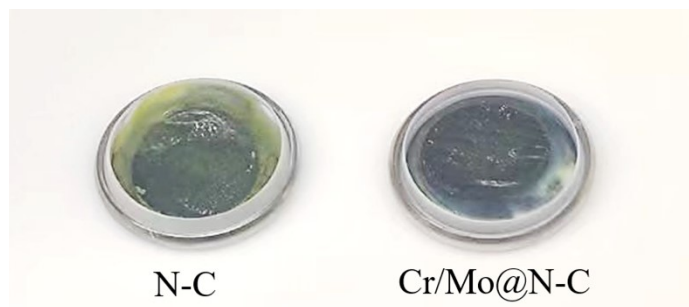


Figure S23. SEM images of the electrode surfaces after cycling: (a) N-C and (b) Cr/Mo@N-C.

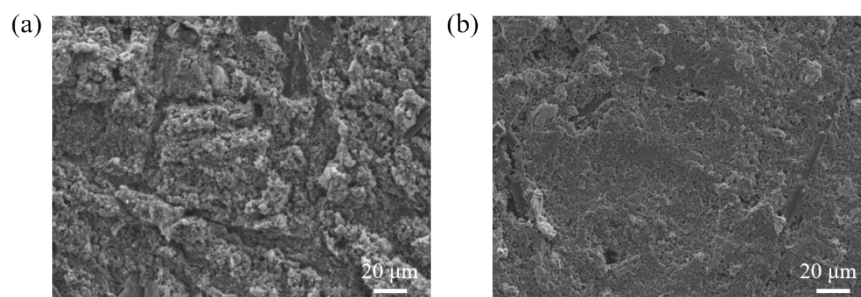


Table S1. EXAFS fitting parameters at the Cr K-edge for various samples.

| Sample | Shell | CN ^a | R(\AA) ^b | $\sigma^2(\text{\AA}^2)$ ^c | $\Delta E_0(\text{eV})$ ^d | R factor |
|------------------|---------|-----------------|--------------------------------|---------------------------------------|--------------------------------------|----------|
| Cr foil | Cr-Cr | 8* | 2.50 \pm 0.01 | 0.0048 \pm 0.0023 | 4.5 \pm 1.4 | 0.0012 |
| CrO ₂ | Cr-O | 6* | 1.91 \pm 0.01 | 0.0043 \pm 0.0025 | 4.7 \pm 2.4 | 0.0114 |
| | Cr-Cr | 3.0 \pm 1.0 | 3.00 \pm 0.01 | 0.0062 \pm 0.0042 | 5.0 \pm 2.4 | |
| CrO ₃ | Cr=O | 3* | 1.61 \pm 0.01 | 0.0059 \pm 0.0028 | 6.1 \pm 1.6 | 0.0140 |
| | Cr-O-Cr | 2.0 \pm 0.1 | 1.79 \pm 0.01 | 0.0073 \pm 0.0023 | 6.0 \pm 2.2 | |
| Cr/Mo@N-C | Cr-N | 2-3 | 1.75 \pm 0.3 | 0.003–0.008 | 0–5 | < 0.03 |
| | Cr-Cr | 1 | 3.0 \pm 0.3 | 0.008–0.015 | | |

Table S2. EXAFS fitting parameters at the Mo K-edge for various samples.

| Sample | Shell | CN^a | R(Å)^b | σ²(Å²)^c | ΔE₀(eV)^d | R factor |
|------------------|--------------|-----------------------|-------------------------|---|---------------------------------------|-----------------|
| Mo foil | Mo-Mo | 8* | 2.73±0.02 | 0.0058±0.0022 | 3.5±1.4 | 0.0024 |
| | Mo-Mo | 6* | 3.15±0.01 | 0.0064±0.0026 | 3.6±1.5 | |
| MoO ₂ | Mo-O | 6* | 2.00±0.01 | 0.0028±0.0028 | 3.7±2.4 | 0.0031 |
| | Mo-Mo | 3.0±1.0 | 2.65±0.01 | 0.0068±0.0052 | 4.8±2.4 | |
| MoO ₃ | Mo=O | 2* | 1.70±0.01 | 0.0029±0.0005 | 5.1±1.6 | 0.0140 |
| | Mo-O | 4* | 1.95±0.01 | 0.0043±0.0013 | 6.0±2.2 | |
| | Mo···Mo | 4* | 3.40±0.01 | 0.0095±0.0010 | 6.7±2.5 | |
| Cr/Mo@N-C | Mo-N | 2-3 | 1.51±0.01 | 0.0070±0.0035 | 0-5 | < 0.05 |
| | Mo-Mo | 1 | 3.4±0.01 | 0.008-0.015 | | |

Table S3: Comparison results of conductivity tests.

$$\sigma = \frac{1}{\rho}$$

" σ represents the electrical conductivity, and ρ represents the electrical resistivity."

| Conductivity (S cm⁻¹) | 4 Mpa | 8 Mpa | 12 Mpa | 15 Mpa |
|---|--------------|---------------|---------------|---------------|
| N-C | 2.004 | 4.016 | 5.348 | 6.289 |
| Cr@N-C | 2.907 | 4.184 | 5.682 | 6.623 |
| Mo@N-C | 5.988 | 10.309 | 13.514 | 17.544 |
| Cr/Mo@N-C | 8.547 | 14.706 | 20.121 | 24.038 |

Table S4: ICP-OES/MS Quantification of Metal Loadings in the Catalysts.

The calculation formula is:

$$C_x \left(\frac{\mu\text{g}}{\text{kg}} \right) = \frac{C_0 \left(\frac{\mu\text{g}}{\text{L}} \right) * f * V_0(\text{mL}) * 10^{-3}}{m(\text{g}) * 10^{-3}} = \frac{C_1 \left(\frac{\mu\text{g}}{\text{L}} \right) * V_0(\text{mL}) * 10^{-3}}{m(\text{g}) * 10^{-3}}$$

$$W(\%) = \frac{C_x \left(\frac{\mu\text{g}}{\text{kg}} \right)}{10^9} * 100\%$$

| Sample Mass m _o (g) | Con- stant Volu- me V _o (mL) | Test Eleme- nt | Test Solution Element Concentra- tion C _o (μg/L) | Diluti- on Facto- r f | Element Concentration in Original Digestion Solution C ₁ (μg/L) | Element Mass Fraction in Sample C _x (μg/kg) | Element Content in Sample C (μg/kg) | Element Content in Sample W (%) |
|-----------------------------------|--|----------------------|--|--------------------------------|---|---|--|---|
| | | | 174.042 | | 17404.208 | 20050931.336 | | |
| 0.0217 | 25 | Cr | 174.097 | 100 | 17409.731 | 20057293.894 | 20048362.9 | 2.00% |
| | | | 173.920 | | 17391.998 | 20036863.479 | | |
| | | | 30.993 | | 30993.102 | 35706338.940 | | |
| 0.0217 | 25 | Mo | 31.050 | 1000 | 31049.883 | 35771754.608 | 35749666.1 | 3.57% |
| | | | 31.049 | | 31049.145 | 35770904.839 | | |