

Metallic FeCo Clusters Propelling the Stepwise Polysulfide Conversion in Lithium–Sulfur Batteries

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Experimental

1.1. Preparation of the Li₂S₆ solution

Mixed powders of Li₂S and sublimed sulphur at a molar ratio of 1:5 were dissolved into the solution containing Dioxolane (DOL)/ Dimethoxyethane (DME) (1:1, V/V). The mixture was stirring at 60 °C for 24 h to obtain the 0.2 M Li₂S₆ solution. Similarly, the 5 mM Li₂S₆ solution was prepared by following the same procedure.

1.2. Adsorption experiments

10 mg of Fe/PNC, FeCo/PNC and Co/PNC samples were put into the 5 mL of Li₂S₆ solution, and the individual system was kept for same period of time to visualize the color changes.

1.3. Physical Characterizations and Methods.

XRD patterns were recorded at 10° min⁻¹ on a Shimadzu XD-3A using filtered Cu- K α radiation ($\lambda=0.15418$ nm) generated at 40 kV and 30 mA. Scanning electron

microscopy (SEM) images were obtained using a Carl Zeiss Ultra Plus electron microscope. High-angle annular dark field scanning transmission electron microscopy (STEM) images of the prepared samples were obtained using a JEOL (JEM-2000 FX) microscope operating at 200 kV. X-ray photoelectron spectroscopy (XPS) tests were analyzed on a PHI-5702 spectrometer, and C 1 s peak at 285.0 eV was used as a reference to calibrate the binding energies.

1.4. Preparation of PNC+Li₂S₆, nano Fe/PNC+Li₂S₆, Co/PNC+Li₂S₆ and FeCo/PNC+Li₂S₆ for XPS Analysis.

Li₂S₆ solution (5 mM) was prepared by adding a mixture of lithium sulfide and sulfur powders with a molar ratio of 1:5 into DOL and DME (1:1, v/v), followed by vigorous magnetic stirring for 24 h at 60 °C in an Ar-filled glovebox. For the preparation of Fe/PNC+Li₂S₆, FeCo/PNC+Li₂S₆ and Co/PNC+Li₂S₆, the as-prepared Fe/PNC, FeCo/PNC, and Co/PNC (10 mg) was dispersed in 5mM Li₂S₆ solution of 5 mL by stand for 30 min. The precipitate of Fe/PNC+Li₂S₆, FeCo/PNC+Li₂S₆ and Co/PNC+Li₂S₆ was collected and dried under vacuum overnight.

1.5. Li-S Cell Assembly and Electrochemical Testing

To prepare the cathode, a mixture of S@FeCo/PNC (or S@Fe/PNC or S@Co/PNC) (70 wt %), Super P carbon (20 wt %), and PVDF (10 wt %) binder was casted onto a current collector (diameter = 10 mm) with NMP and dried at 60 °C overnight in a vacuum oven to remove solvent. The routine mass loading of sulfur in the electrode is about 1 mg cm⁻². Coin cells (2032 type) with stainless steel as the current collector were

assembled in an Ar-filled glovebox, using Celgard 2400 as separator and Li metal (thickness: 0.45 mm) as anode. The electrolyte contains 1.0 M LiTFSI and 0.1 M LiNO₃ electrolyte additive dissolved in DOL and DME (1:1, v/v). The electrolyte/sulfur (E/S) ratio is about 40 μL mg⁻¹ unless otherwise noted. During electrochemical performance testing, both the current rate setting, and specific capacity calculation were referenced to the mass of sulfur in the cathode (1 C = 1675 mA h g⁻¹). The cells were tested on a Neware battery system with a voltage window of 1.7–2.8 V. CV measurements and EIS testing were performed on a CHI 650D electrochemical analyzer (CH Instruments). The scan rate and voltage range of the CV measurements were 0.1 mV s⁻¹ and 1.7–2.8 V, respectively. For the EIS testing, the frequency range was from 100 kHz to 10 mHz. All the electrochemical tests were performed at ambient temperature.

The Li⁺ diffusion rates were calculated based on the classic Randles-Sevcik equation:

$$I_p = (2.686 \times 10^5) n^{1.5} A D_{Li^+}^{0.5} C_{Li^+} v^{0.5}$$

Where, I_p is the current peak; n is the number of electron transfer ($n=2$); A is the electrode area ($A=1.13 \text{ cm}^2$); D_{Li^+} is the coefficient of Li⁺ diffusion rates; C_{Li^+} is the Li⁺ concentration in the electrolyte ($0.0002 \text{ mol cm}^{-3}$); v is the scan rate.

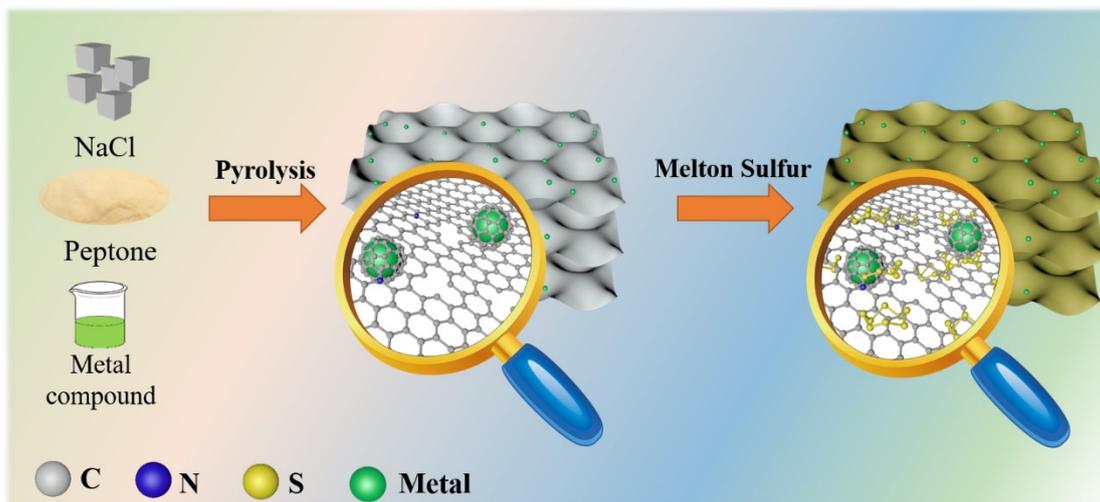


Fig. S1. Schematic illustration for the synthesis of S@Fe/PNC and S@Co/PN samples.

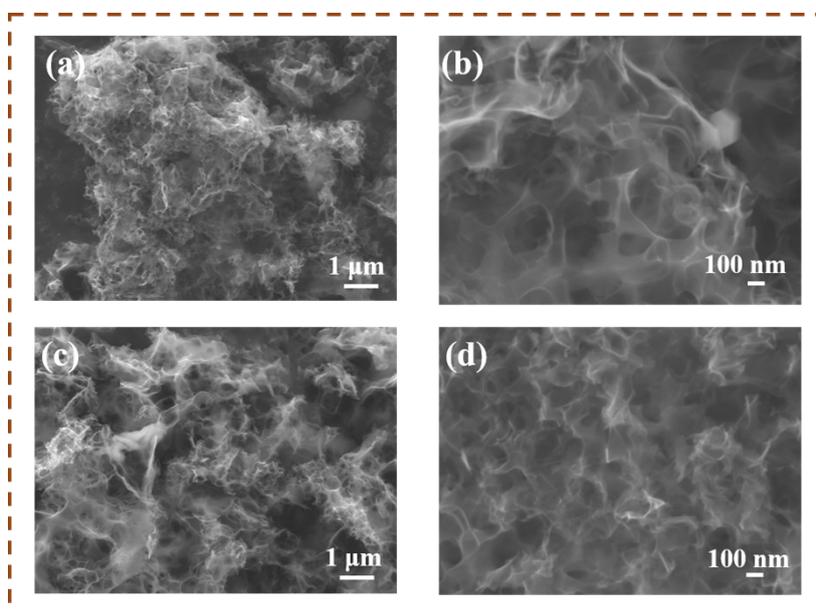


Fig. S2. SEM images of (a, b) Fe/PNC and (c, d) Co/PNC sample.

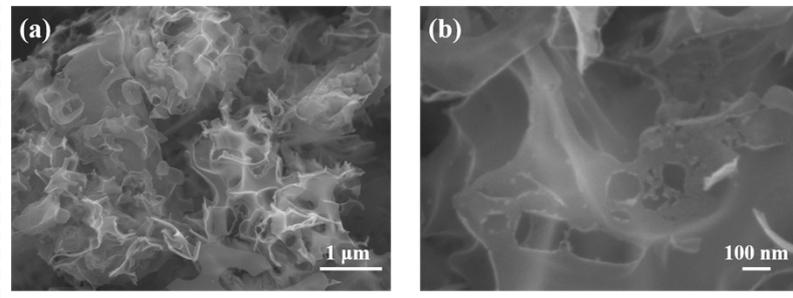


Fig. S3. (a, b) SEM images of the PNC sample.

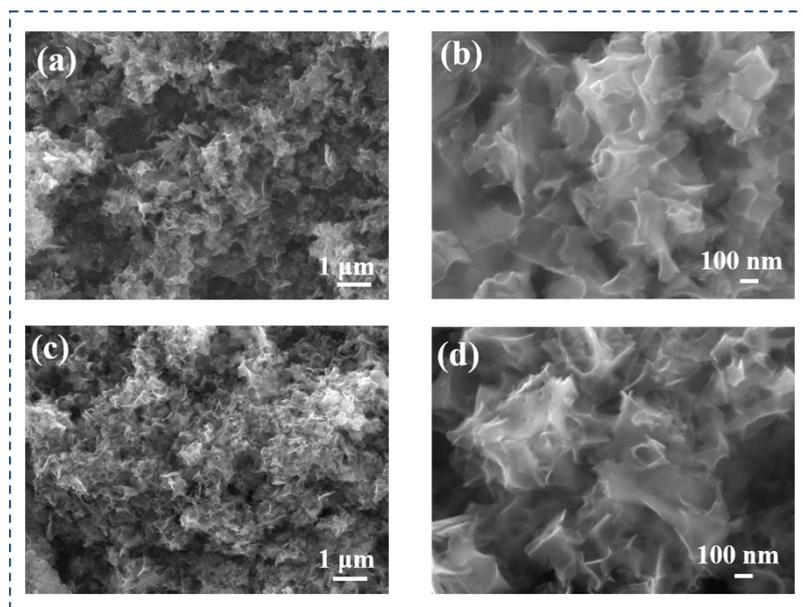


Fig. S4. SEM images of (a, b) S@Fe/PNC and (c, d) S@Co/PNC samples.

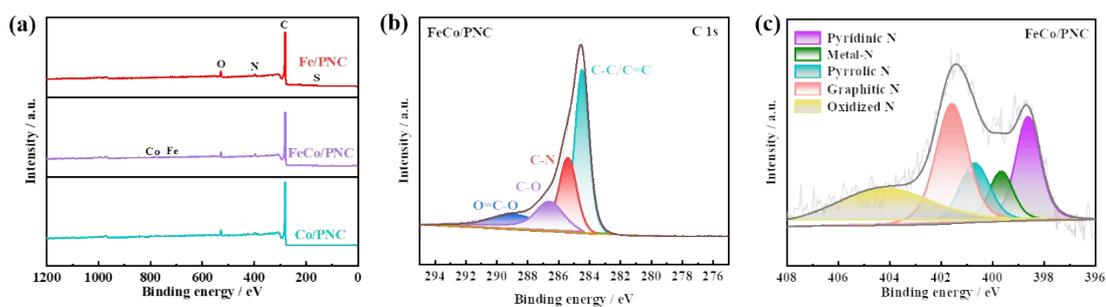


Fig. S5. (a) XPS survey spectra of Fe/PNC, FeCo/PNC and Co/PNC samples. The high-resolution XPS spectra for (b) C 1s, (c) N 1s of FeCo/PNC sample.

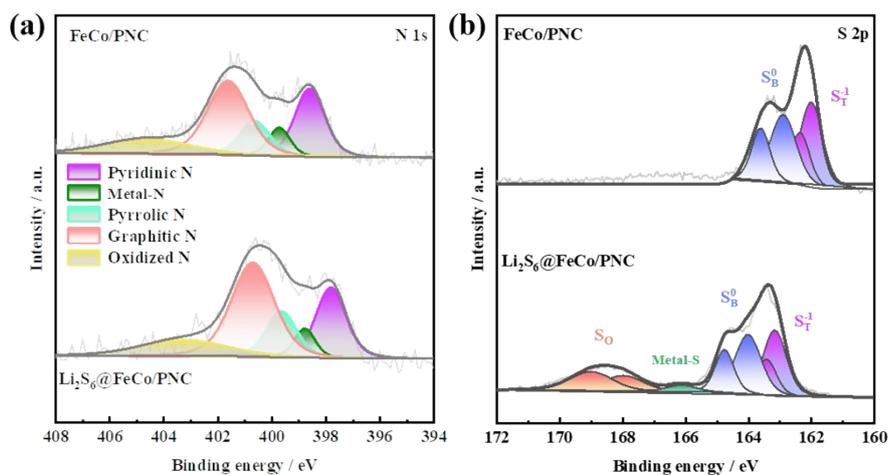


Fig. S6. (a, b) N 1s and S 2p of FeCo/PNC and S@FeCo/PNC composites before and after absorption.

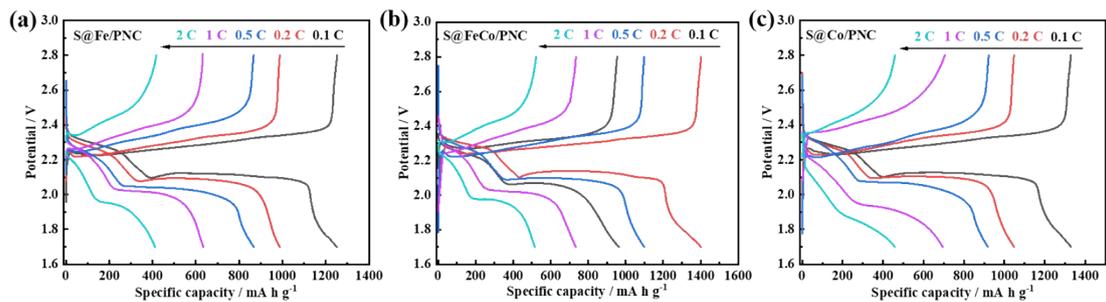


Fig. S7. (a-c) The discharge-charge profiles of S@Fe/PNC, S@FeCo/PNC and S@Co/PNC samples from 0.1 to 2.0 C.

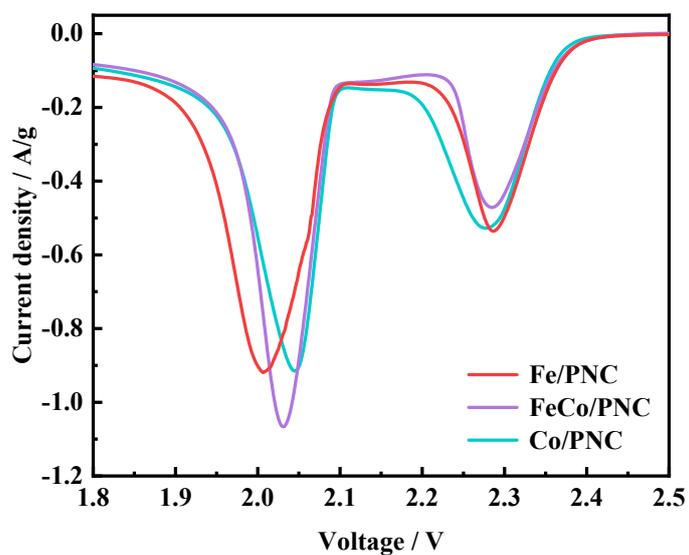


Fig. S8. LSV between 1.8 and 2.8 V at a scan rate of 0.1 mV s⁻¹

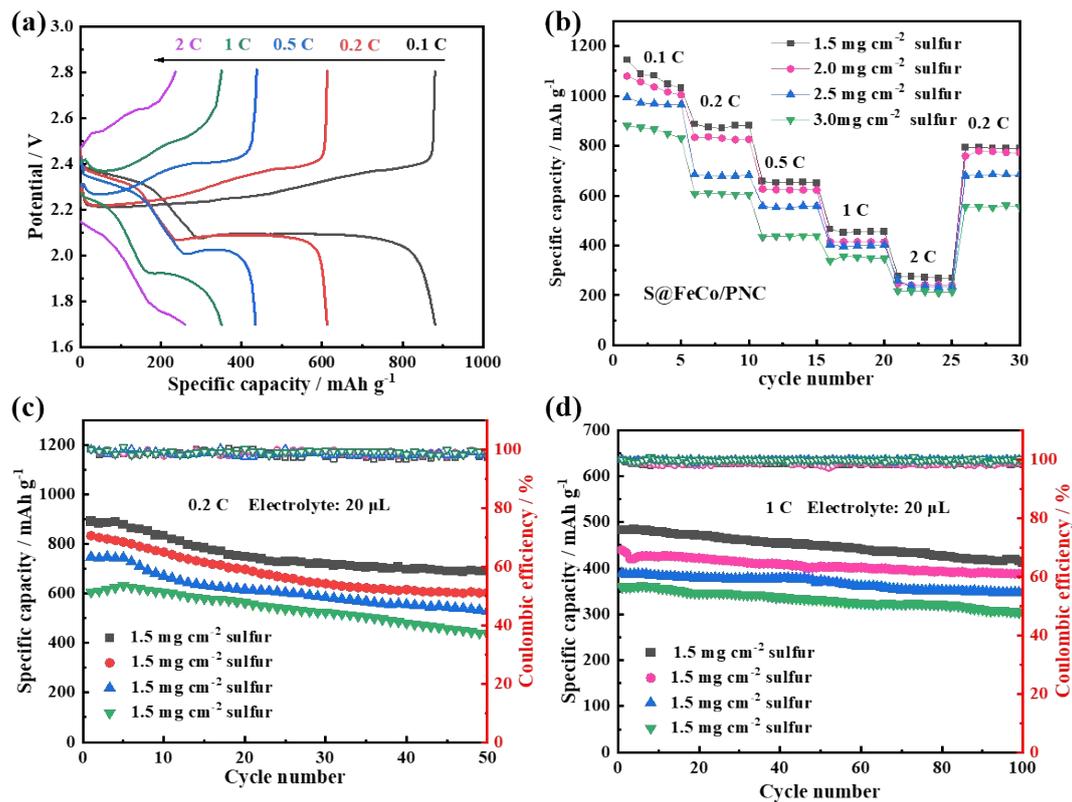


Fig. S9. (a) The discharge-charge profiles, (b) rate capability, the cycling performance of FeCo/PNC electrode at (c) 0.2 C and (d) 1 C with 20 μL electrolyte.

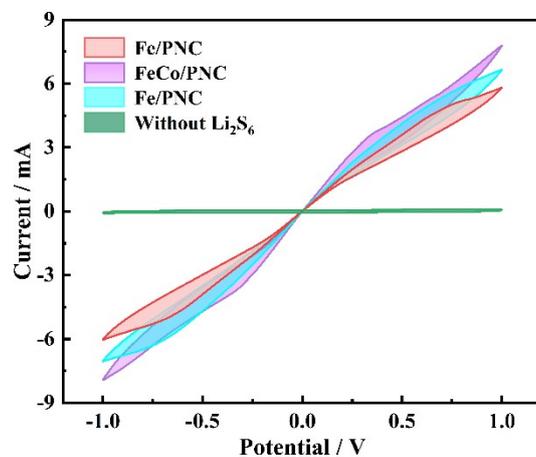


Fig. S10. CV curves of Li_2S_6 symmetric cells of S@Fe/PNC, S@FeCo/PNC and S@Co/PNC samples.

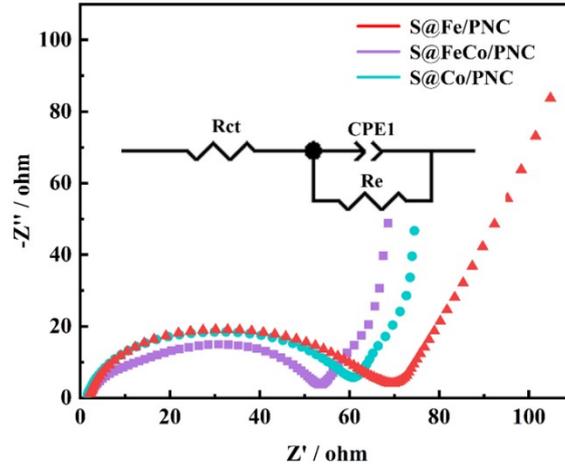


Fig. S11 EIS Nyquist plots and corresponding equivalent circuit diagram of S@Fe/PNC, S@FeCo/PNC and S@Co/PNC samples.

Table S1. Physical properties of Fe/PNC, FeCo/PNC and Co/PNC samples.

| Sample | Specific Surface Area / m ² g ⁻¹ | Pore Volume / cm ³ g ⁻¹ |
|-----------|---|--|
| Fe/PNC | 355 | 0.92 |
| Fe Co/PNC | 437 | 0.99 |
| Co /PNC | 610 | 1.06 |

Table S2. Elements content of three host materials (Fe/PNC, FeCo/PNC and Co/PNC).

| Sample | C | N | O | Fe | Co |
|--|-------|------|------|------|------|
| PNC | 92.95 | 3.05 | 3.62 | 0.38 | / |
| nano Fe ₃ O ₄ /PNC | 93.09 | 3.02 | 3.45 | 0.21 | 0.23 |
| Fe ₃ O ₄ /PNC | 93.36 | 2.90 | 3.32 | / | 0.42 |

Table S3. Li-S performance comparison of Fe/Co composite with results reported in literature.

| Sample | Sulfur loading of cathode | Initial capacity (mAh g ⁻¹ , at n C) | Decay (per cycle, %) | Ref. |
|---------|------------------------------|--|-------------------------|------|
| SC-Co | 63% | 1130 (0.5 C) | 0.086 | 1 |
| Co-CNCS | 74.5% | 1290 (0.2 C) | 0.029 | 2 |
| Co-Fe-P | 70% | 1118 (0.2 C) | 0.043 | 3 |
| Co/PNC | 60% | 1105 (0.2 C) | 0.064 | 4 |

| | | | | |
|---------------------------|-------|--------------|-------|------------------|
| FeCo-C | 70% | 1250 (0.2 C) | 0.073 | 5 |
| NC-CoS₂ | 68.7% | 1150 (0.1 C) | / | 6 |
| Fe-PNC | 70% | 1138 (0.1 C) | / | 7 |
| FeCo/PNC | 71.1% | 1405 (0.1C) | 0.045 | This work |

References

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