Facilitating redox kinetics of sulfur species by cobalt-nitrogen co-doped porous hollow carbon for high-performance Li-S battery

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Abstract. The shuttle effect of polysulfides is the main obstacle restricting the development of lithium-sulfur batteries. However, most efforts focused on physical adsorption and polar adsorption cannot fundamentally solve the problem of sluggish conversion of polysulfides, especially for high sulfur loading. Herein, a cobalt-nitrogen co-doped porous hollow carbon sphere (Co-CN) is synthesized in one step. The porous conductive carbon spheres can realize a rapid charge transfer, mitigate volume expansion during cycling and enhanced physical adsorption for polysulfides. Nitrogen and cobalt doping provide chemisorption and catalysis for the restriction and conversion of polysulfides. Furthermore, liquid Li2S8 polysulfide was used as sulfur source to guarantee high sulfur loading and fast redox kinetic. Benefiting from the triple effect of physical adsorption, chemical adsorption and catalysis, the Co-CN@Li2S8 cell with sulfur loading of 5.15 mg cm⁻² delivers a high reversible initial capacity of 1499 mAhg⁻¹ at 0.1C and 880.9 mAhg⁻¹ after 100 cycles. More excitingly, the capacity decay rate was only 0.012% per cycle at 1C over 1000 cycles, indicating excellent long cycle stability. This work provides a facile and effective route for Co-CN as a sulfur host in lithium-sulfur battery.

1. Introduction

Lithium-sulfur batteries (LSBs), with high available specific capacity (1675 mAh g⁻¹) and energy density (2567 Wh kg⁻¹), low cost and environmentally friendly, have been considered as the most promising candidate. [1] However, there are still some significant obstacles hindering its commercialized application. [2] i) The large volume variation occurred during the reaction is up to 80%, causing a huge deformation and a loss of active materials. ii) The high insulation of S/Li2S makes charge transfer difficult, resulting in low sulfur utilization. iii) The "shuttle reaction" of intermediate polysulfides (LiPS) (Li2Sn, 4 ≤ n ≤ 8), in which the soluble polysulfides can easily migrate from cathode to anode and react with Li, inducing low coulombic efficiency and rapid capacity fading. iv) the poor redox kinetics of S species, resulting in large overpotentials and poor rate capability.

Extensive researches have been devoted to address the aforementioned issues and achieved remarkable results. A well-known strategy is to encapsulate sulfur or LiPS with porous conductive matrixes, [3-5] such as mesoporous structures, hollow structures, graphene, carbon nanotubes, etc. As early as 2009, Nazar et al. [6] proposed mesoporous carbon (CMK-3) host, and then the solution has
focused on the restriction and adsorption of active substances. However, the weak physical confinement cannot effectively inhibit the shuttle effect for long periods of time. Problems such as loss of active material, capacity attenuation, cycle instability, and low coulombic efficiency still exist. Therefore, another effective strategy is introducing new active sites, such as doped carbon materials or polar conductive compounds, to form strong chemical adsorption between host and LiPS was another effective strategy. [7,8] Duan et al.[9] use heteroatom-doped graphene as a model system to explore electrocatalytic SRR, and show that nitrogen and sulfur dual-doped graphene considerably reduces the activation energy to improve kinetics. However, strong chemical adsorption cannot fundamentally solve the problem of sluggish conversion of polysulfides, especially for high sulfur loading.[10] Recently, incorporate active materials with catalytic functions (Ni, Co, Fe, etc.) in carbon nanostructures enhance the LiPS conversion efficiency.[11] For example, Liu et al.[12] designed a sulfur host with CNTs intercalated to etallic cobalt and N-doped carbon(Co-N-C/CNTs), resulting in significant improvement of electrochemical performance. However, the previously reported Co/C composites is metal-organic skeleton, which could not provide large enough space, and the traditional melt perfusion method has a low sulfur loading, which could not reach the practical application standard. [13]

Herein, a cobalt-nitrogen co-doped porous hollow carbon sphere(Co-CN) was prepared in one step, liquid Li2S8 catholyte was used as sulfur source to obtain Co-CN@Li2S8 electrode. The composite offers enough free space, large specific surface area, strong conductive network, polar covalent bonds and catalysis, inhibiting the shuttle effect of polysulfides through physical adsorption, chemical adsorption and catalysis. Li2S8 polysulfide was used as sulfur source to guarantee high sulfur loading and fast redox kinetic.[14] Benefiting from these unique structure and chemical properties, the obtained Co-CN@Li2S8 battery with sulfur loading of 5.15mg cm−2 exhibits an high capacity of 1499 mAhg−1 at 0.1C and an ultralow capacity fading of 0.012% per cycle over 1000 cycles at 1C. Our work provides a novel and facile approach for high-performance lithium-sulfur battery.

2. Experimental

2.1. Preparation of porous CN and Co-CN hollow spheres

Co-CN hollow spheres: 3 mL ammonia aqueous solution (27 wt %), 60 mL ethanol, 20 mL deionized water and 5.6 mL TEOS were mixed and stirred for 30 min. Subsequently, 0.3 g F127, 0.4 g resorcinol and 1 mL formaldehyde (40wt %) were added and stirred for 30 min. Then 2.25ml silane and 0.1g CoCl2·6H2O was slowly injected into the above mixed solution and stirred for 24h continually. Next, heated at 120℃ for 24 h by hydrothermal and carbonize at 700℃ for 3 hours with the heating rate of 2℃ min−1 under flowing N2 gas. After that, the SiO2 template was removed by etching with HF for 48 hours to obtain Co-CN hollow spheres.

CN hollow spheres: CN hollow spheres were obtained according to the same approach as Co-CN hollow spheres without silane and CoCl2·6H2O.

2.2. Preparation of Li2S8 catholyte

The Li2S8 catholyte was prepared by mixing 1.345g sulfur and 0.275g Li2S in DOL/DME (1:1 in volume) co-solvent with 2wt % LiNO3 additive in a 10ml vial. The suspension was continuous stirring at 80°C for 12h in an argon-filled glove box to form 4.8M-Li2S8 catholyte. (All concentration of Li2S8 calculated based on elemental S)

2.3. Characterization

The microstructures and morphology of materials is characterized by TEM (JSM-2100F). Energy dispersive spectrometer mapping (EDS mapping) images are recorded with JEM-2100 HR. XRD spectra were examined to analyls crystallographic structure by PANalytical X-pert diffractometer (PANalytical, Netherlands) with Cu Kα (40 kV and 40 mA). X-ray photoelectron spectra (XPS) were carried out with Thermo escalab 250Xi X-ray Photoelectron Spectrometer. N2 adsorption and desorption isotherms were tested by Micromeritics Tristar instrument. The specificifc surface area and the pore size distribution was
calculated by the BJH (Barret-Joyner-Halenda) and BET (Brunauer Emmet and Teller) multipoint method.

2.4. Electrochemical measurements
CR2025-type coin cells were assembled in an argon-filled glovebox (<0.01 ppm H2O, < O2). The Co-CN@Li2S8 cathode was fabricated by dispersing 80 wt% Co-CN sample, 10 wt% conductive carbon black and 10 wt% PVDF in NMP solvent to form a homogeneous slurry. Then spread the slurry uniformly on the aluminum foil. Drop 30 μL 4.8 M Li2S8 catholyte into the sample (corresponding to sulfur loading of 5.15 mg cm⁻²) and 10 μL LiTFSI catholyte solution. Celgard 2400 membrane and Li foil was used as the separator and anode. The CN@Li2S8 were obtained according to the same approach, which was used as a control cathode. Cyclic voltammetry (CV) curves and electrochemical impedance spectroscopy (EIS) tests were obtained via a CHI 660E electrochemical workstation. Galvanostatic charge discharge (GCD) tests were performed using a LAND CT-2001A cell test system at room temperature.

3. Results and discussion

![Fig 1.](image1)

Transmission electron microscope (TEM) was used to analyze the microstructures and morphology of Co-CN sample. As shown in Fig.1a, A uniform hollow spherical structure with the diameter of ~50nm and the thickness of ~2nm can be observed, which can offer conductive network and enough space to contain active substances and alleviate volume expansion. The energy-dispersive X-ray spectroscopy (EDS) spectra (Fig.1b) confirms N and Co were distributed on the hollow spheres uniformly, which is beneficial to provide more reaction sites and accelerate ion transfer.

![Fig 2.](image2)

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The crystallographic structures of Co-CN was examined by XRD (Fig. 2a). The Co-CN@GO contained a broad diffraction peak between 15° and 30°, corresponding to the (002) plane of graphite. The peaks at 44.2°, 51.6° and 75.9° correspond to the (111), (200) and (220) crystal planes of cobalt (PDF#15-0806), respectively, confirming the cobalt has been successfully loaded on carbon spheres. N\textsubscript{2} adsorption and desorption measurements were shown in Fig. 2b. The specific surface area of CN and Co-CN was 189.6 m\textsuperscript{2}/g and 311.2 m\textsuperscript{2}/g, respectively. Co-CN sample has higher specific surface area owning to Co doping, resulting in a high sulfur loading and S utilization rate.[15] The surface chemistry was analyzed by X-ray photoelectron spectroscopy (XPS). Co, N, C and O elements can be observed in Fig. 2c. Co peak at 779.1 eV was increased compared with CN, further indicating the progress Co doping had been completed.

Electrochemical performance was used to evaluate the feasibility of Co-CN@Li\textsubscript{2}S\textsubscript{8} and CN@Li\textsubscript{2}S\textsubscript{8} electrodes. 30 μL 4.8 M Li\textsubscript{2}S\textsubscript{8} catholyte was used as sulfur source, corresponding to sulfur loading of 5.15 mg cm\textsuperscript{-2}. Fig. 3a and 3b exhibit the cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) curves of three electrodes at 1.5-2.8 V (vs Li/Li\textsuperscript{+}). As shown in Fig. 3a, all electrodes present two representative cathodic peaks and one broad oxidation peak. The former peaks were the reduction of sulfur to long-chain LiPS and the formation of short-chain insoluble Li\textsubscript{2}S\textsubscript{2}/Li\textsubscript{2}S, the latter corresponded to the oxidation of Li\textsubscript{2}S\textsubscript{2}/Li\textsubscript{2}S into LPSs. Co-CN@Li\textsubscript{2}S\textsubscript{8} electrode shows stronger current peaks, indicating the better redox activity of lithium polysulfide. And a lower polarization occurs (\(\Delta V\)) was observed in the Co-CN@Li\textsubscript{2}S\textsubscript{8} electrode, indicating an easier electrochemical redox reaction and faster electronic transfer after Co-doped.[16] Fig. 3b shows the GCD curves of three electrodes at 0.1C. The Q\textsubscript{b}/Q\textsubscript{a} ratio in the GCD curves can reflect the conversion kinetics of polysulfides. Co-CN@Li\textsubscript{2}S\textsubscript{8} electrode has a higher value of Q\textsubscript{b}/Q\textsubscript{a}, further indicating that Co doping can catalyze the conversion of polysulfides and accelerate electron transfer rate. Cycling performance and columbic efficiency of the two electrodes were evaluated in Fig. 3c-e. As shown in Fig. 3c, CN@Li\textsubscript{2}S\textsubscript{8} cell delivers initial and final discharge capacities of 1312.1 and 395.9 mAhg\textsuperscript{-1} at 0.1C, indicating a serious capacity fading (30\% retention). In sharp contrast, Co-CN@Li\textsubscript{2}S\textsubscript{8} cells were capable of delivering a steady discharge capacity of 1499 mAhg\textsuperscript{-1} and 880.9 mAhg\textsuperscript{-1} over 100 cycles respectively. Fig. 3d depicts the rate capability of
the two cells from 0.1 to 2 C. The Co-CN@Li2S8 cell delivers reversible capacities of 1509.5, 1085.7, 758.2 and 494.5 mAh g\(^{-1}\) at 0.1C, 0.5C, 1C and 2C, respectively. When the current density drops to 0.1 C, the high reversible capacity of 1406.2 mAh g\(^{-1}\) can be attained (93% retention), meaning a good reversible rate performance. However, the CN@Li2S8 cell without Co doping shows rather poor reversible rate, only 75% reversible capacity. Fig. 3e shows the long-term cycling performance of Co-CN@Li2S8 cell at 1C. The cell delivers a initial capacity of 878 mAh g\(^{-1}\) and retains 768.8 mAh g\(^{-1}\) after 1000 cycles, showing 88% capacity retention rate and only 0.012% decay per cycle, demonstrating excellent stability in large rate cycle.

Fig 4. (a) Comparison of the electrochemical impedance spectra of CN@Li2S8 cell and Co-CN@Li2S8 cell. (b) The relationship between \(Z'\) and \(\omega^{-1/2}\) of the two cells at a very low frequency region.

The interface stability of the electrode can also be confirmed by electrochemical impedance spectroscopy (EIS) in Fig. 4. All impedance data are fitted with the equivalent circuit shown in the inset of Fig. 4a. The resistances (Rct) of CN @ Li2S8, and Co-CN@Li2S8 cells were 162.1 and 185.7 \(\Omega\), respectively. The lower resistance in Co-CN@Li2S8 cell mainly ascribes to the Co,N doping and porous hollow structure, providing faster charge transfer rate.[17] Fig. 4b exhibit the relationship of the three electrodes between \(Z'\) and \(\omega^{-1/2}\). The Li-ion diffusion coefficient (\(D_{Li}\)) is calculated according to Eq (1):

\[
D_{Li} = \frac{R^2 T^2}{2 A^2 n^4 F^4 C^2 \sigma^2}, \quad Z' = \frac{R_e + R_{ct}}{\sigma} + \sigma \omega^{-1/2}
\]

where R, T, A, n, F, C and \(\omega\) refer to the gas constant, the Kelvin temperature, the area of electrode, the number of transferred electrons per molecule, the concentration of Li-ions and the angular frequency, respectively. The \(\sigma\) is the slope of \(Z' \sim \omega^{-1/2}\) after linear fitting. As shown in Fig. 4b, the \(\sigma\) of Co-CN@Li2S8 and CN@Li2S8 cell are 3.12 and 3.8. The lower value corresponds to higher \(D_{Li}\), implying the faster lithium ions diffusion and excellent electrochemical performance, which is in good agreement with the above result shown in Fig. 3, attributing to the cobalt doping which accelerates the kinetic transformation.[18]

4. Conclusion

In summary, we designed cobalt-nitrogen co-doped porous hollow carbon sphere (Co-CN) as a host of Li-S battery. The porous hollow structure of Co-CN provides enough space for volume expansion during cycling and large conductive network for ion/mass transmission. More importantly, the doping of Co and N offers strong chemisorption and catalytic ability for LiPS, which effectively inhibits the dissolution and diffusion of LiPS and promotes the electrochemical transformation of long-chain lithium polysulfides. Benefiting from both advantages, the Co-CN@Li2S8 cell (sulfur loading: 5.15 mg cm\(^{-2}\)) delivers a high reversible initial capacity of 1490 mAh g\(^{-1}\) and 880.9 mAh g\(^{-1}\) after 100 cycles at 0.1C, almost 100% coulomb efficiency. More excitingly, the Co-CN@Li2S8 cell has a excellent long cycle
stability over 1000 cycles (only 0.012% capacity decay per cycle) under current density of 1C. This work provides a facile and cost-effective route for the scalable synthesis of Li-S battery.

Conflicts of interest
There are no conflicts to declare.

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