Promoting kinetics of polysulfides redox reactions by the multifunctional CoS/C/CNT microspheres for high-performance lithium-sulfur batteries

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The commercialization of sulfur cathodes has encountered several problems, including migration of polysulfide intermediates, low conductivity of sulfur and its discharge products, and volumetric changes in the cathode. To alleviate these problems, researchers have proposed a number of strategies, such as porous carriers, polysulfides sorbents, catalysts and conductive fillers. In this study, a novel CoS/C/CNT sulfur carrier material has been prepared by spray drying method to promote the performance of sulfur cathode according to the design idea of integrating various functions into one structure. The CoS/C/CNT can effectively adsorb polysulfides and catalyze their conversion. Simultaneously, the porous structure of the C/CNT conductive frame can improve the conductivity of the S-CoS/C/CNT composites, offer sufficient space to accommodate the necessary volume expansion of S and play a role in the physical limitation of polysulfides. Due to these multifunctional advantages in one structure, the obtained CoS/C/CNT shows a strong interaction with polysulfides and catalyzes the conversion of polysulfides. Finally, the obtained S-CoS/C/CNT composite cathode exhibits excellent electrochemical performance.

1. Introduction

With the rapid increase in demand for portable electronic devices, large-scale energy storage devices and electric vehicles, conventional lithium-ion batteries are unable to meet the need for high energy density and long cycle life. The lithium-sulfur batteries (LSBs) possess a high energy density (~2600 Wh kg\textsuperscript{-1}), a large abundance of sulfur and environmental compatibility, which is a potential next-generation energy storage system [1–4]. However, sulfur cathodes have encountered some scientific and technical problems in the commercialization process, which hinders the practical application of LSBs. First, the active substance sulfur and its discharge product lithium sulfide have poor conductivity, which limits the utilization of the active substance sulfur and reduces the rate performance of the LSBs [5–6]. Second, the dissolution and diffusion of polysulfide intermediates in the organic electrolyte during charge and discharge causes a “shuttle effect”, which reduces the utilization of the active sulfur [7]. Third, the volume change of the electrode during charging and discharging reaches 80%, resulting in destruction of the electrode structure, thereby reducing the cycle life of the LSBs [8].

In order to alleviate the above problems, the researchers have proposed a number of strategies, such as porous carriers [9,10], polysulfide sorbents [11–13], catalysts [14,15] and conductive fillers [16], which have achieved certain improvements and progress. However, in order to realize the commercialization of LSBs, there are still many problems to be solved, like loading of active materials, interaction between carriers and polysulfide intermediates, and rate performance of batteries, which require further improvement. Recently, cobalt sulfides have been widely used as a sulfur carrier because of its good electrical conductivity, strong interaction with polysulfides, and catalytic polysulfides conversion [17–21]. There are four interphases (CoS\textsubscript{2}, Co\textsubscript{2}S\textsubscript{4}, Co\textsubscript{3}S\textsubscript{4} and Co\textsubscript{3}S\textsubscript{2}) in the Co-S binary system. Co\textsubscript{3}S\textsubscript{4}, Co\textsubscript{2}S\textsubscript{4} and Co\textsubscript{2}S\textsubscript{2} have been reported to act as carriers for sulfur cathodes, adsorbing and catalyzing polysulfide intermediates [20–23]. However, studies on the adsorption and conversion of polysulfides using CoS as a carrier have rarely been reported.

The spray drying is a method of obtaining encapsulated particles from a liquid solution or slurry, which is widely used for mass...
production of various electrode materials [24–27]. Therefore, in this work, we combined the advantages of a porous conductive frame with the advantages of CoS for anchoring and catalyzing polysulfides. A new type of CoS/C/CNT with micro-size spherical particle was prepared by spray drying. Then, the CoS/C/CNT composites have been combined with sulfur by a simple hot melt method to obtain an S-CoS/C/CNT composites. The CoS/C/CNT can effectively adsorb polysulfides and catalyze their conversion. At the same time, the porous structure of the C/CNT conductive frame can improve the conductivity of the S-CoS/C/CNT composites, provide enough space to buffer the necessary volume expansion of S and play a role in the polysulfides physical limitation. Due to these multifunctional advantages in one structure, the obtained S-CoS/C/CNT composite cathode exhibits an excellent electrochemical performance.

2. Experimental section

2.1. Synthesis of CoS/C/CNT composites

0.01 mol CoSO4, 5.0 g CNT aqueous dispersion (wt% = 10%, Timesnano Co. Ltd.) and 0.8 g glucose were added into 200 mL deionized water. After vigorous stirring, a suspension was formed by adding 0.01 mol Na2S2O3. Then the suspension was spray dried at 200 °C using a BUCHI Mini Spray Dryer B-290 dryer to form black CoS/C/CNT composites precursor. The sample obtained by the spray drying process was annealed at 500 °C for 8 h (h) under Ar atmosphere at the heating rate of 5 °C min⁻¹. The product was washed with deionized water to remove Na⁺ and then dried for 12 h in a vacuum oven at 60 °C. The obtained product was labeled as CoS/C/CNT.

2.2. Synthesis of S-CoS/C/CNT composites

A simple melt-diffusion method was used to prepare the S-CoS/C/CNT composites. The S powder and CoS/C/CNT with mass ratio of 3:1 were homogeneously mixed and sealed in a glass tube under vacuum, which was heated up to 155 °C at a heating rate of 5 °C min⁻¹ for 12 h, and then naturally cooled to room temperature.

2.3. Characterization of materials

The XRD patterns of the samples were recorded by the Philips Xpert Pro Super X-ray diffract meter and Cu Kα radiation. The morphologies of CoS/C/CNT and S-CoS/C/CNT composites were characterized by scanning electron microscope (SEM) (HITACHI S-4800) and transmission electron microscope (TEM) (JEM-2100 (JEOL, Japan)). The X-ray photoelectron spectroscopy (XPS) was conducted to detect chemical state of CoS/C/CNT composites using a PHI Quantum 2000. The nitrogen adsorption–desorption isotherms were obtained at the liquid nitrogen temperature by Automatic physical and chemical adsorption (ASAP2020HD88+C, Micromeritics Instruments Corp). The thermogravimetric (TG) analysis for determining the sulfur content of S-CoS/C/CNT was performed on a SDTQ600 under a flow of N2 atmosphere.

2.4. Absorption Test

A 0.1 mol L⁻¹ Li2S6 solution was prepared by adding S and Li2S to 1,3-dioxolane/dimethoxy ethane (DOL/DME) (v:v = 1:1) according to the ratio of 5:1. The solution was then kept overnight in an Ar-filled glove box to produce a tawny Li2S6 catholyte solution. Acetylene black (AB) or CoS/C/CNT (100 mg) was added to a Li2S6 solution (5 mL), then their ability to absorb polysulfides was evaluated by standing at room temperature for 24 h.

2.5. Electrochemical measurements

A cathode slurry of the LSB was prepared by using the active material, acetylene black, PVDF (mass ratio of 7:2:1), and N-methyl pyrrolidone (NMP) as a solvent. Then, the slurry was evenly scraped on an aluminum foil and vacuum dried at 60 °C for 12 h to obtain a sulfur cathode. The areal sulfur loading was about 1 mg cm⁻² and 3 mg cm⁻². The CR2016 coin cells were used for testing to compare and analyze the differences in various electrochemical properties of LSBs. The CR2016 coin cells used the element S or S-CoS/C/CNT electrode as the cathode, the lithium foil as the anode, and the porous polypropylene (Celgard 2300) as the separator. The electrolyte was 1 M lithium bis(tri-fluoromethanesulfonyl)imide (LITFSI)/(DME + DOL) (volume ratio of 1:1) and 1 wt% lithium nitrate. The electrolyte to sulfur ratio in the cell was about 30 μL mg⁻¹ (sulfur). The cycle performances of LSBs were tested using a Wuhan Blue Electric LAND 2001 battery test system at a voltage range of 1.8–2.6 V. The cyclic voltammetry (CV) tests were carried out by Shanghai Chenhua CHI 660D electrochemical workstation at room temperature. The cyclic voltammetry curve was tested at a scan speed of 0.1 mVs⁻¹ and a voltage range of 1.5–3 V. The AC impedance was tested at an open-circuit voltage with an amplitude of 5 mV and a frequency of 100 kHz–0.01 Hz.

The symmetric battery consists of two identical electrodes as the working and counter electrodes, and a solution containing Li2S6 as the electrolyte. The AB or CoS/C/CNT materials were used as the identical working and counter electrodes (mass ratio of the above materials to PVDF binder = 9:1). The electrolyte including about 0.5 M Li2S6 which was prepared by adding Li2S and S (mole ratio of 1:5) into DOL/DME (v:v = 1:1). The CV test was conducted on a electrochemical workstation (CHI 660D) at a scan rate of 50 mV s⁻¹ in a voltage window of −0.5 to 0.5 V.

3. Results and discussion

The syntheses and battery reaction mechanism of S-CoS/C/CNT are illustrated in Scheme 1. As shown in Scheme 1a, the preparation process of S-CoS/C/CNT is as follows. First, the CNT suspension was evaporated at 155 °C to obtain S-CoS/C/CNT composites precursor. The sample obtained by the spray drying process was annealed at 500 °C for 8 h (h) under Ar atmosphere at the heating rate of 5 °C min⁻¹. The product was washed with deionized water to remove Na⁺ and then dried for 12 h in a vacuum oven at 60 °C. The obtained product was labeled as CoS/C/CNT.

The obtained CoS/C/CNT composites were not destroyed, most of the sulfur melts into the CoS/C/CNT composites, the C, S and Co elements are uniformly distributed throughout the spherical structure (Fig. 1g). The C and CNT penetrate through the entire spherical structure of the CoS/C/CNT, providing an electron transport path, which is beneficial to improve the conductivity of electrode. The XRD pattern in Fig. 2a shows that the Co and S binary compounds are present in the form of CoS (JCPDS 065-8977). At the same time, the high resolution TEM images in Fig. S1 also demonstrate a distinct lattice spacing of 0.296 nm corresponding to the (1 0 0) plane of CoS. Next, the CoS/C/CNT composites were mixed with sulfur powder by melt-diffusion method at 155 °C to obtain S-CoS/C/CNT composites. After heat treatment, the overall morphology of the CoS/C/CNT composites are not destroyed, most of the sulfur melts into the necessary volume expansion of S and play a role in the polysulfides physical limitation.
the porous hollow CoS/C/CNT structure, and a small amount of sulfur adheres to the surface of the CoS/C/CNT structure or scatters in the composite material (Fig. 1d, e, and h). This may be the reason for the fast decay of the electrochemical performance in the first few cycles. The XRD pattern in Fig. 2a shows that the diffraction peaks of the S-CoS/C/CNT composites are consistent with that of pure S. However, the corresponding diffraction peaks of CoS is not found in the S-CoS/C/CNT composites, which further indicates that S is almost completely integrated into the CoS/C/CNT composites. To further demonstrate the melting of S into the porous hollow CoS/C/CNT structure, a linear EDX scan is performed and the results are shown in Fig. 1c and f. It can be seen that the internal sulfur content is significantly increased after the mixing of CoS/C/CNT composites with S, which further demonstrates the entering of S into the porous hollow CoS/C/CNT structure, and it also demonstrates that the S, Co and C elements are evenly distributed in the bulk phase of the microsphere. The content of sulfur in the samples has been investigated by TG [28]. The results are shown in Fig. 2b. We infer that the content of sulfur in the S-CoS/C/CNT composites is about 59.2%.

The nitrogen adsorption/desorption isotherms and pore size distribution of the CoS/C/CNT and S-CoS/C/CNT composites have been obtained by nitrogen absorption/desorption test (Fig. 3). The CoS/C/CNT composites present a typical V isotherm with a distinct hysteresis loop according to the IUPAC classification, indicating the existence of mesoporous nanostructures. After hot melt compounding sulfur, the BET surface area of the CoS/C/CNT composites is sharply reduced from 182 to 1 m$^2$ g$^{-1}$, and the mesopores of $\sim$15 nm disappear, indicating the melting of S and the immersion of S in the pores of the CoS/C/CNT composites.

The electrochemical performance of S-CoS/C/CNT electrode has been characterized by the CV and galvanostatic charge/discharge test. As a comparison, the electrochemical properties of pure sulfur are also tested as a control. The galvanostatic charge/discharge curves of the S-CoS/C/CNT and S at 500 mA g$^{-1}$ in the potential range from 1.8 to 2.6 V are illustrated in Fig. 4a. The S-CoS/C/CNT delivers a higher initial discharge capacity (up to 1031mAh g$^{-1}$) than the S. The charge/discharge curves of the S-CoS/C/CNT and S have two discharge platforms and two charging platforms. The higher voltage discharge platform at about 2.3 V represents the reduction of S$^8$ to long-order polysulfides [29]. The lower voltage discharge platform is at approximately 2.1 V, corresponding to the reduction of long-order polysulfides to Li$_2$S$_2$ or Li$_2$S [30]. The charge platforms are at approximately 2.2 V and 2.35 V, corresponding to the oxidation of Li$_2$S or Li$_2$S$_2$ to long-order polysulfides and the oxidation of polysulfides to S, respectively. The voltage difference of charge and discharge plateau ($\Delta$E) of the S-CoS/C/CNT at a half capacity (0.17 V) is lower than that of S (0.25 V), suggesting the polarization of the S-CoS/C/CNT is lower than that of S. The CV curves of the S-CoS/C/CNT and S at 0.1 mV s$^{-1}$ in the potential range from 1.5 to 3.0 V are shown in Fig. 4b. All the CV curves display typical features of LSB with two reduction peaks and one overlaid oxidation peak [31], which corresponds to the galvanostatic charge/discharge curves. The redox peaks potential of the S-CoS/C/CNT is closer to the quasi-equilibrium potentials than the S, demonstrating less polarization and a faster electrochemical reaction of the S-CoS/C/CNT than the S [21]. At the same time, the oxidation peak of the S-CoS/C/CNT is broader than that of S, indicating that the conversion from Li$_2$S or Li$_2$S$_2$ to polysulfides and eventually to sulfur is relatively easy. That is, the S-CoS/C/CNT has an efficient electrocatalytic effect.

The electrochemical performance has been further studied by testing long-term cycling stability and rate capability. As shown in Fig. 4c and d, the cycle performance and rate performance of the S-CoS/C/CNT are better than that of S, especially at high current density.
When cycling at the current density of 500 mA g\(^{-1}\), the initial specific discharge capacity of the S-CoS/C/CNT is 1031 mAh g\(^{-1}\), which is much higher than 945 mAh g\(^{-1}\) of S-CoS, and 761 mAh g\(^{-1}\) of sulfur. During the cycle, the capacity in the first 5 cycles decays fast, and then the capacity decays slowly with the cycle. The specific discharge capacities of the S-CoS/C/CNT, S-CoS and sulfur are 638, 523 and 487 mAh g\(^{-1}\) after 100 cycles, respectively, that is, the capacity retention rates (relative to the fifth circle) are 81%, 66.7%, and 65.9%, respectively. Their Coulombic efficiencies gradually approach to ~100% after the first 5 cycles. The S-CoS/C/CNT delivers specific capacity of ~830, ~680, ~530, ~390 and ~700 mAh g\(^{-1}\) at 200, 500, 1000, 2000 and 200 mA g\(^{-1}\), respectively, higher than that of S, especially at high current density. The cycle performance comparison between S-CoS/C/CNT and pure S with high loading (S-CoS/C/CNT = 3.1 mg cm\(^{-2}\), pure S = 2.5 mg cm\(^{-2}\)) is shown in Fig. S2a. It can be seen that the S-CoS/C/CNT also exhibits better cycle performance than S under high sulfur loading. At the same time, the long cycling performance was shown in Fig. S2b, which shows that the S-CoS/C/CNT delivers a stable capacity of 450 mAh g\(^{-1}\) at 0.5 A g\(^{-1}\) after 300 cycles. In addition, the electrochemical performance of S-CoS/C/CNT is better than that of other metal sulfides, as summarized in Table S1. Even though S-CoS/C/CNT has a sulfur content as high as 70%, it has better cycle stability than pure sulfur (Figs. S3 and S4).

To investigate what factors improve the electrochemical properties of the S-CoS/C/CNT, theoretical calculation, the polysulfides adsorption, variable scan rate CV and a symmetric cell using S-CoS/C/CNT have been investigated, respectively. The adsorption energy \(E_{\text{ads}}\) for Li\(_2\)S\(_6\) on CoS (0 0 1) plane and Graphite is defined as the equation \(E_{\text{ads}} = E_{\text{sub}} + E_{\text{Li}_2\text{S}_6} - E_{\text{sub-Li}_2\text{S}_6}\), the \(E_{\text{sub}}, E_{\text{Li}_2\text{S}_6}\) and \(E_{\text{sub-Li}_2\text{S}_6}\) represent the energy of substrate, Li\(_2\)S\(_6\) and substrate-Li\(_2\)S\(_6\)). Fig. S5a and b shows that the adsorption energy of Li\(_2\)S\(_6\) on CoS (0 0 1) plane is 6.38 eV, which is higher than that of Li\(_2\)S\(_6\) on Graphite (0.84 eV). This is consistent with the polysulfides adsorption test (Fig. S5c). In the polysulfides adsorption test, the color of the added CoS/C/CNT changes from brownish yellow to nearly colorless. However, the color of the polysulfides solution is almost unchanged with the addition of AB. This
visually demonstrates a strong interaction between CoS/C/CNT and polysulfides, which can effectively improve long-term cycle performance of the battery. The CoS/C/CNT has been performed XPS test before and after the polysulfides adsorption, and the results are shown in Fig. 5d–f. The Co 2p$_{3/2}$ spectra of CoS/C/CNT have broad peaks and satellite peaks before and after polysulfide adsorption, respectively. For CoS/C/CNT after the polysulfides adsorption, the Co 2p$_{3/2}$ peak narrows and satellite peak becomes stronger, indicating that electrons are transferred from Li$_2$S$_6$ to CoS. In summary, the polysulfides adsorption experiments and XPS analysis prove that the CoS/C/CNT can well immobilize polysulfides, alleviate the problem of diffusion and shuttle of polysulfides and facilitate long-term cycle stability of the battery.

To confirm the diffusion coefficient of Li$^+$ in the S-CoS/C/CNT electrode, CV having different scan rates of 0.1–0.9 mV s$^{-1}$ have been studied, and the results are shown in Fig. 6a and b. The diffusion coefficient of Li$^+$ can be roughly calculated by the classical Randles-Sevcik equation according to the CV at different scan rates [23]:

$$I_p = 0.4463nFAC(nF D/RT)^{1/2}$$

(1)

where $I_p$ represents the peak current, C is concentration of Li$^+$ (mol cm$^{-3}$), $\upsilon$ is scan rate (V s$^{-1}$), $D$ represents Li$^+$ diffusion coefficient (cm$^2$ s$^{-1}$), $n$ is the number of electrons transferred, $F$ is the Faraday’s constant (96,485 C mol$^{-1}$) and $A$ represents electrode area (1.14 cm$^2$). The $C$, $n$, $F$ and $A$ act as constants. Thus, the value of the diffusion coefficient of Li$^+$ will be positively correlated to the slope of the curve $I_p \sim \upsilon^{1/2}$. We take $\upsilon^{1/2}$ as the horizontal axis and $I_p$ of anode peaks as the vertical axis, the obtained curves are shown in Fig. 6c. The slope of the S-CoS/C/CNT (104.16) is higher than that of sulfur (67.26), demonstrating that diffusion coefficient of Li$^+$ in the S-CoS/C/CNT is greater than the S. Fast diffusion of Li$^+$ enhances the kinetics of polysulfides redox reactions, thereby inhibiting the shuttle effect of polysulfides.

The symmetrical cells are assembled on two CoS/C/CNT electrodes with or without Li$_2$S$_6$ electrolyte and two AB electrodes with Li$_2$S$_6$ electrolyte. The CV measurements of these symmetrical cells have been performed and the results are shown in Fig. 6d. As shown in Fig. 6d, the current response of CoS/C/CNT symmetrical cell is higher than that of the AB cell, demonstrating that the CoS/C/CNT not only absorbs polysulfides, but also facilitates the electrochemical conversion of polysulfides [7,19]. After disassembling the battery after 50 cycles, the SEM characterization of the S and S-CoS/C/CNT electrodes (Fig. S5) shows that the surface of pure S electrode leads to serious agglomeration due to dissolution/deposition of sulfur species on the cathode surface. Impressively, there is no agglomeration of sulfur species in the S-CoS/C/CNT electrode, the morphology of the electrode is maintained well-preserved, which shows that the CoS/C/CNT composites can fix sulfur species well during the cycle. Such substantially facilitated charge transfer is further verified by the EIS spectra of the S-CoS/C/
Fig. 4. The electrochemical performance of S and S-CoS/C/CNT electrode (the S loading is about 1 mg): Charge/discharge curves (a), CV curves (b), cycle performance at the current of 500 mA g\(^{-1}\) (c) and rate performance (d).

Fig. 5. The adsorption binding energies of Li\(_2\)S\(_6\) on graphite and CoS (0 0 1) (a, b), the optical photo of Li\(_2\)S\(_6\) adsorption on AB and pristine CoS/C/CNT (c) and the XPS spectra of Co 2p\(_{3/2}\) of the pristine CoS/C/CNT and the CoS/C/CNT powder separated from the adsorption test (d, e, f).
CNT and S electrodes before and after cycling, and the symmetrical cells (Figs. S6–S8). The quasi-semicircles in the Nyquist plots can be attributed to the Rct at the electrode-polysulfides interfaces. It is clear that the semicircle diameter of the S-CoS/C/CNT electrode is smaller than that of S (Fig. S6) or the semicircle diameter of the CoS/C/CNT with Li2S6 is smaller than that of AB (Fig. S7). This indicates that charge transfer at the CoS/C/CNT-polysulfides interface is much faster than at the AB-polysulfides interface, further accelerating the redox kinetics of the liquid-phase polysulfides by introducing conductive CoS/C/CNT mediators. At the same time, it can be seen from Fig. S8 that the impedance of S electrode after cycling is much larger than that of the CoS/C/CNT composites electrode, which is caused by the agglomeration of sulfur species on the electrode surface, which is consistent with the SEM results.

4. Conclusion

We have fabricated the multifunctional CoS/C/CNT composites as sulfur host by simple spray drying method, which enables the LSBs to achieve high capacity, superior cycle performance and rate performance. This is because the CoS/C/CNT combine porous hollow host, conductive agent, adsorbent and catalyst into one structure. Firstly, the porous structure of the C/CNT conductive frame can facilitate the electronic transmission of the S-CoS/C/CNT electrodes, provide sufficient space to buffer the necessary volume expansion for S, and play a role in the physical limitation of polysulfides. At the same time, the CoS/C/CNT can effectively adsorb polysulfides and catalyze their conversion. In summary, the method of constructing multifunctional host materials is one of the best strategies for improving the cathode performance of LSBs in the future.

Declaration of Competing Interest

The authors declared that there is no conflict of interest.

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Appendix A. Supplementary material

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References
