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Spray drying-assisted preparation FeS_x/C/CNT composite for energy storage and conversion performance



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ABSTRACT

Transition metal sulfides are widely used in energy storage and conversion due to their exclusive physical and chemical performance. In this work, $FeS_x/C/CNT$ composites have been prepared by spray drying assisted and then calcined in an Ar atmosphere. As lithium-ion battery anodes and electrode material for supercapacitor, the $FeS_x/C/CNT$ composites display the excellent reversible capacity, capacitance and cycle stabilities. Cyclic voltammetry at different scan rates indicate that the Faraday electrochemical reaction and surface capacitance behavior occur simultaneously when the $FeS_x/C/CNT$ composites act as anode material for lithium ion battery. Cycling under 200 mA g⁻¹ current density for 100 times, the Coulomb efficiency is still about 99% while the capacity is about 630 mAh g⁻¹. At the current density of 1, 2, 3 and 5 A g⁻¹, the specific capacitances of the $FeS_x/C/CNT$ composites are expected to become anode materials for high-performance lithium-ion batteries and electrode materials for high-performance supercapacitors.

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1. Introduction

Over the past 40 years, researches on energy storage appliances like lithium-ion batteries and supercapacitors have made tremendous progress. However, in order to meet the needs of high-end equipment, the power density, energy density and lifetime of energy storage and conversion devices will need to be further improved [1]. The above electrochemical performance is closely related to the properties of electrode materials [2–5]. For example, specific capacity and operating voltage are primarily determined by the electrode material properties. Therefore, the main challenge in advancing energy storage and conversion devices is to find suitable electrode materials. Among many electrode materials, transition metal sulfides (TMSs) have attracted increasingly attention due to their unique physical and chemical properties [6]. TMSs deliver enormous advantages in low cost, high theoretical capacity and environmental friendliness so that they are widely applied in lithium-ion batteries and supercapacitors [7–12].

Like other TMS, the cyclic performance of iron sulfide is also poor, because polysulfide dissolution causes loss of active materials, and volume expansion/contraction occurs during the lithiation/ delithiation process [13,14]. Active material coating can alleviate the decay of iron sulfide cycle performance to some extent. Compared with commercial cathodes material for rechargeable LIB, Tan et al. [15] reported a new type of core-shell nano FeS₂@Ndoped graphene cathode material, it exhibited more stable cycling performance, higher specific power and specific energy. This is due to the nano-sized FeS₂ which shortens the Li ion diffusion path, and the mechanical strength of the N-doped graphene shell can enhance the structural stability of the active material, meanwhile, it also optimizes the electron conductivity. Xu et al. [16] successfully

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synthesized a FeS₂ nanocrystals@hierarchical porous carbon (HPC) with pre-prepared HPC. After 100 cycles at 1C, the specific capacity of FeS₂@HPC is as high as 720 mAh g⁻¹. This is because HPC with an interconnected macroporous carbon capsules and microporous shell can provide effective buffering effect on the volume change of FeS₂ and restrain the growth of FeS₂ to obtain nanoscale particles, and inhibit the loss of active substances during cycling.

In general, one-dimensional nanostructures exhibit distinctive performance that make them suitable for use as active materials for LIBs. For example, Zhu et al. [17] prepared FeS₂@C fiber electrodes by electrospinning. FeS₂@C fiber electrode exhibited excellent electrochemical property and had the potential for application in energy storage systems. This is because one-dimensional structures have many advantages. First, the one-dimensional structure allows adaptation to lithiation/delithiation volume changes in a particular direction. Second, the interspace assembled between adjacent structures can be used as a channel for the electrolyte, making it easier for the electrolyte to diffuse into the inner area of the electrode, and finally extending the battery's life. Third, compared to the bulk counterparts, the larger surface/volume ratio of the nanostructure array can offer more active sites, and significantly shorten the diffusion path of lithium ions.

Herein, we report a novel approach to fabricate $FeS_x/C/CNT$ composites with the assistant of spray drying. The $FeS_x/C/CNT$ composite/lithium battery exhibits improved electrochemical performance including superb cycling stability and high specific capacity. And the capacitor of the $FeS_x/C/CNT$ composite exhibits good capacitive characteristics including high rate performance and excellent specific capacitance. The $FeS_x/C/CNT$ composites are easy to prepare, with superb lithium storage performance and capacitance characteristics, and therefore have broad application prospects in energy storage and conversion.

2. Results and discussion

A schematic diagram of spray drying assisted synthesis of FeS_x/ C/CNT is shown in Fig. 1. Spray drying is to atomize the dispersion or solution in a drying room, and the moisture is quickly evaporated by contact with hot air, so as to obtain a black powder. Therefore, as shown in Fig. 1, the iron source FeSO₄, the sulfur source Na₂S₂O₃, and the carbon sources glucose and CNT are made into a dispersion, and the nearly spherical precursor FeS_x/C/CNT is obtained by a spray drying method. Then, the precursor FeS_x/C/CNT is calcined under a high temperature and inert atmosphere to obtain a final product FeS_x/C/CNT.

Fig. 2a reveals the XRD patterns of FeS_x/C/CNT. The diffraction pattern of FeS_x/C/CNT displays several diffraction peaks at 30.2°, 34.3° , 44.3° , 53.6° (2 θ), respectively, corresponding well with the Fe₇S₈ standard card (JCPDS No. 01-071-0647). The diffraction peak at 26.4° is weak, probably because CNT is less abundant and is

encapsulated in the near-spherical particles, and the carbon formed by the carbonization of glucose is amorphous. The samples of FeS_x/ C/CNT is further characterized by *Raman* microscopy (Fig. 2b). The peaks at 1360 cm⁻¹ and 1590 cm⁻¹ are the characteristic D-band and G-band of graphite, respectively [3]. However, almost no peak of FeS_x is found, indicating that FeS_x is well wrapped by carbon. In order to characterize the pore structure of FeS_x/C/CNT, a BET analysis is performed, and the results are shown in Fig. 2c and d. The BET surface area of FeS_x/C/CNT is 203.2 m² g⁻¹ and the pore diameter of FeS_x/C/CNT is mainly concentrated at 9.0 nm. This facilitates the entry of the electrolyte, thereby facilitating the transport of ions.

The morphology of $\text{FeS}_x/C/\text{CNT}$ is shown in Fig. 3. Fig. 3a displays an SEM image of $\text{FeS}_x/C/\text{CNT}$ at low magnification, the diameter of $\text{FeS}_x/C/\text{CNT}$ spheres is a few microns. Fig. 3b shows an SEM image of $\text{FeS}_x/C/\text{CNT}$ at high magnification, the surface of $\text{FeS}_x/C/\text{CNT}$ spheres is rough, and a small amount of CNT are homogeneously distributed on them, indicating that the $\text{FeS}_x/C/\text{CNT}$ sphere is formed by the accumulation of primary nanoparticles, amorphous carbon and CNT. Fig. 3c displays the SEM elemental mapping of $\text{FeS}_x/C/\text{CNT}$, C, Fe and S are evenly distributed and mainly concentrated on the spherical particles, indicating that FeS_x in the $\text{FeS}_x/C/\text{CNT}$ is well wrapped by C/CNT and the $\text{FeS}_x/C/\text{CNT}$ has a good conductive skeleton.

The characterization of lithium storage performance was performed by assembling CR2016-type coin cells. Fig. 4a shows the 1st, 5th, 50th and 100th charge-discharge curves of the battery at a current density of 200 mA g⁻¹. It can be observed that there is a large polarization gap in the first few cycles, and then the polarization decreases little and little along with two stable discharge plateaus at about 1.7 V and 1.5 V. As the cycle progresses, the discharge curve platform changes from two (1.7 V and 1.5 V) to one (1.7 V), which depends on the kinetics of the system [18]. At the same time, two charge plateaus at around 2.2 V and 1.8 V only appear in the first cycle, and then the plateau at 2.2 V gradually disappears after several cycles, leaving the plateau at around 1.8 V exist. This is consistent with the charge and discharge mechanism in the first cycle of Li/FeS₂ batteries previously reported by Fong and Zhang et al. [13,18–21], as follows:

Discharge:

$$FeS_2 + 2Li^+ + 2e^- \rightarrow Li_2FeS_2 \tag{1}$$

$$Li_2FeS_2 + 2Li^+ + 2e^- \rightarrow 2Li_2S + Fe$$
(2)

Charge:

$$Fe + 2Li_2S \rightarrow Li_2FeS_2 + 2Li^+ + 2e^-$$
(3)

$$\text{Li}_2\text{FeS}_2 \rightarrow \text{Li}_{2-x}\text{FeS}_2 + x\text{Li}^+ + xe^- \tag{4}$$



Fig. 1. Schematic diagram of the preparation of FeS_x/C/CNT.



Fig. 2. (a) The XRD patterns, (b) Raman spectrum, (c) Isothermal absorption and desorption curve and (d) Pore size distribution of FeS_x/C/CNT.

 $Li_{2-x}FeS_2 \to FeS_y + (2-y)S + (2-x)Li^+ + (2-x)e^-$ (5)

The CV curves of FeS_x/C/CNT electrode are shown in Fig. 4b, which are carried out from 1.0 to 3.0 V at the different scan rate of 0.2, 0.4, 0.6 0.8 and 1.0 mV s⁻¹. Under the sweep speed of 0.2 mV s^{-1} , three reduction peaks can be observed on the first curve, at 2.08 V, 1.55, and 1.39 V, respectively. The phase transition from FeS_x to FeS_2 is at 2.08 V, and the peaks at 1.55 and 1.39 V can be attributed to the conversion reaction of FeS₂ to form Fe and Li₂S [16]. At the same time, during the first anodic scan, two oxidation peaks appear at 1.90 and 2.30 V, respectively. The first oxidation peak (1.90 V) is the oxidation of Fe and Li₂S to intermediate FeS_x [16] and the second oxidation peak (2.30 V) suggests the over potential of Li₂S. The CV is consistent with the voltage profile of the galvanostatic cycling tests. As the scan rate increases, the reduction peak shifts to a lower voltage, indicating an increase in the energy barrier and polarization of the electrode. The oxidation curve becomes more complicated and shows a complex reaction in the subsequent delithiation process.

Fig. 6a shows the cycle performances of $FeS_x/C/CNT$ electrode at 0.2 A g⁻¹. For $FeS_x/C/CNT$ electrode, the capacity stands on about 630 mAh g⁻¹ among 100 cycles. The $FeS_x/C/CNT$ electrodes not only show better cycling performance, but also show higher reversible capacity. The long cycle performance at high current density is displayed in Figure S1. The $FeS_x/C/CNT$ electrodes show excellent long-cycle performance. After 500 cycles at the current of 0.5 A g⁻¹, the capacity remains at 370 mAh g⁻¹, and the coulomb efficiency still remains at about 100%. The rate performance at different current densities are shown in Figure S2. At current densities of 0.1, 0.2, 0.5, 1.0, 2.0, and 0.1 A g⁻¹, the discharge capacities of $FeS_x/C/CNT$

electrode are 635, 580, 345, 290, 260 and 590 mAh g⁻¹, respectively. The electrochemical impendence spectroscopy (EIS) of FeS_x/C/CNT electrode after cycling was carried out (Figure S3). The high frequency semicircle in the Nyquist plot is related with the charge transfer resistance of the electrode. The charge transfer resistance is 54 Ω after 10 cycles. This shows that the FeS_x/C/CNT electrode has a smaller charge transfer resistance and better charge transfer kinetics. The reason why FeS_x/C/CNT electrode has excellent lithium storage performance is that its unique near-spherical C/CNT porous structure can provide favorable transport paths for Li ions and electrons, inhibit the dissolution of polysulfide intermediates and alleviate the volume effect.

To understand the charge storage mechanism of the $FeS_x/C/CNT$ electrode, further analysis was performed based on the data of the CV under different sweep speeds (Fig. 4c and d). We can classify electrochemical reactions into diffusion control insertion or surface capacitance processes according to the above CV data and the following chemical equation [22]:

$$\mathbf{i}(\mathbf{V}) = a\nu^b \tag{6}$$

where the i is a function of the voltage (V) related with sweep speed (v) along with adjustable parameters (a and b). When the value of b is greater than or equal to 1.0, it indicates that the i originates from capacitive effect. When the b value is less than or equal to 0.5, it indicates that the i originates from the diffusion-controlled reaction. When the b value is between 0.5 and 1.0, it indicates that the i is controlled by both the capacitive effect and the diffusion-controlled reaction. Therefore, based on equation (6), we can get equation (7), so the value of b is the slope of a plot of log i versus log



Fig. 3. The morphology of FeS_x/C/CNT. (a) and (b) SEM images, (c) SEM elemental mapping.

(7)

υ.

 $\log\,i = b\,\log\,\upsilon + \log\,a$

The current i of the CV curves (Fig. 4b) at the peak 1 and peak 2 is selected, and then log i is plotted against log υ , and the results are shown in Fig. 4c. It can be seen from the figure that at the peak 1 and peak 2, the b values are 0.76 and 0.83, respectively, indicating that the FeS_x/C/CNT electrode have both the capacitive effect and the diffusion-controlled reaction [23–25].

Furthermore, the contribution of surface capacitance and diffusion-controlled capacitance in the total charge storage of $FeS_x/C/CNT$ electrode can be distinguished according to the method of Dunn et al. [24] The specific formula is as follows:

$$i(V) = K_1 v + K_2 v^{1/2} \tag{8}$$

, where the i is a function of voltage (V), K_1 and K_2 represent constants, and υ is the sweep speed. In this equation, $K_1 \upsilon$ and $K_2 \upsilon^{1/2}$ represent the surface capacitive element and diffusion-controlled reactions, respectively. Dividing both sides of formula (3) by $\upsilon^{1/2}$ at the same time gives the following formula (4):

$$i(V) / v^{1/2} = K_1 v^{1/2} + K_2 \tag{9}$$

Therefore, when $i/v^{1/2}$ is plotted against $v^{1/2}$ at a certain potential, a straight line is obtained with a slope of K_1 and an intercept of K_2 . The current i of the CV curves (Fig. 4b) at the peak 1 and peak 2 is selected, and then $i/v^{1/2}$ is plotted against $v^{1/2}$, and the results are shown in Fig. 4d and Table 1. It can be seen that at the peak 1, the ratios of the surface capacitive element and diffusion-controlled reactions (0.6 mV s⁻¹) are 56.4% and 43.6%, respectively. And at the peak 2, the ratios of the surface capacitive element and diffusion-controlled reactions (0.6 mV s⁻¹) are 61.3% and 38.7%, respectively, which indicates FeS_x/C/CNT electrode undergoes both diffusion-controlled reactions and surface capacitance reactions [23–25].

The charge storage mechanism of $\text{FeS}_x/\text{C/CNT}$ electrode for lithium storage undergoes both diffusion-controlled reactions and surface capacitance reactions. Therefore, $\text{FeS}_x/\text{C/CNT}$ as active material of capacitor is performed, the results are shown in Fig. 5 and Fig. 6b. The specific capacitances of the $\text{FeS}_x/\text{C/CNT}$ composite at the current density of 1, 2, 3 and 5 A g⁻¹ are 617.5, 508.0, 436.1 and 365.0 F g⁻¹, respectively (Fig. 5). Under different sweep speeds, the CV curve of capacitor changes steadily (Fig. 6b).



Fig. 4. (a) Charge-discharge curves at 0.2 A g⁻¹, (b) CV curves, (c) the corresponding log i ~ log υ scatters and linear fitting of the CV curves (Fig. 4b) at the peak of 1 and 2, (d) the corresponding $i/\upsilon^{1/2} \sim \upsilon^{1/2}$ scatters and linear fitting of the CV curves (Fig. 4b) at the peak of 1 and 2, (d) the

Table 1The ratios of the surface capacitive element and diffusion-controlled reactions.

	Slope (k ₁)	Intercept (k ₂)	Ratio of the surface capacitive element $(k_1\upsilon)(0.6\mbox{ mV s}^{-1})$	Ratio of the diffusion-controlled reactions $(k_2 \upsilon^{1/2})(0.6\mbox{ mV}\mbox{ s}^{-1})$
Peak 1	-5.77	-3.45	56.4%	43.6%
Peak 2	5.48	2.68	61.3%	38.7%

3. Conclusions

In summary, the near-sphere composite FeS_x/C/CNT can be synthesized by a facile spray drying assisted method and subsequent high temperature calcination in an inert atmosphere. Test results reveal that as-prepared FeS_x/C/CNT displays the excellent lithium storage performance and capacitance performance. The discharge capacity of LillFeSx/C/CNT batteries can maintain about 630 mAh g^{-1} among 100 cycles at the current density of 0.2 A g^{-1} and 370 mAh g^{-1} after 500 cycles at the current density of 0.5 A g^{-1} , respectively. At the same time, the FeS_x/C/CNT electrodes also display outstanding rate characteristics, which means LillFeSx/C/ CNT batteries can obtain 635, 580, 345, 290, 260 and 590 mAh g⁻¹ at current densities of 0.1, 0.2, 0.5, 1.0, 2.0, and 0.1 A g^{-1} , respectively. The charge storage mechanism of FeS_x/C/CNT electrode for lithium storage is investgated using CV at different scan rate, indicating that FeSx/C/CNT electrode undergoes both diffusioncontrolled reactions and surface capacitance reactions.

4. Experimental

4.1. Raw materials and synthesis

In this work, the FeS_x/C/CNT composite was prepared under spray drying, FeSO₄ was used as iron source, Na₂S₂O₃ was used as a sulfur source, carbon source derived from CNT dispersion and glucose, along with deionized water. In typical synthesis route, 0.01 mol FeSO₄, 0.4 g glucose and 0.25 g CNT dispersion were added into a beaker containing 100 ml of deionized water and treated with ultrasonic and magnetic stirring to evenly distribute, then 0.01 mol Na₂S₂O₃ was added into the beaker. The mixed dispersion was spray dried to obtain the FeS_x/C/CNT composite precursor at 200 °C under a working gas of nitrogen. The precursor powders were collected and placed in a tube furnace under an argon atmosphere, kept at $500 \degree C$ for 5 h with $5 \degree C \min^{-1}$ heating speed, and then naturally cooled to 25 °C. Eventually, the FeS_x/C/CNT target products were obtained by washing the calcined powders with deionized water and ethanol for three times and dried in a vacuum oven at 60 °C overnight.



Fig. 5. The capacitor performance of $\text{FeS}_x/\text{C/CNT}$ composite: (a) 1 A g⁻¹, (b) 2 A g⁻¹, (c) 3 A g⁻¹ and (d) 5 A g⁻¹.



Fig. 6. (a) The cycle performances of FeSx/C/CNT electrode at 0.2 A g⁻¹ and (b) The capacitance performance at different sweep speeds.

4.2. Characterization of materials

The X-ray diffraction (XRD) patterns were tested with a Rigaku Miniflex 600 (Rigaku Corporation, Japan) instrument. Hitachi S-4800 (Hitachi, Japan) scanning electron microscope (SEM) and 200 kV JEM-2100 (JEOL, Japan) were used to analyze the sample's morphological information, elemental spectra, and selected area electron diffraction (SAED) patterns. Elemental analysis tests were performed with a Vario EL III elemental analyzer. 5–10 mg of the dried sample was placed in an Al_2O_3 pot, heated from 35 °C to 800 °C under a nitrogen flow at 10 °C min⁻¹, and tested the weight loss curve of the sample to analyze the components in the sample content. A nitrogen adsorption-desorption isotherms were obtained by an automatic physicochemical adsorption device (ASAP2020HD88 + C, Micromeritics Instruments Corp) at liquid nitrogen temperature.

4.3. Electrochemical measurements

The characterization of lithium storage performance was performed by assembling CR2016-type coin cells. The FeS_x/C/CNT composite, acetylene black (AB), and polypropylene fluorides (PVDF) were mixed in N-methyl-2-pyrrolidene (NMP) at a weight ratio of 80:10:10. The coin battery consists of the FeS_x/C/CNT composite electrode, lithium metal counter electrode, separator and electrolyte. The electrolyte was 1 M bis(trifluoromethane sulphonyl)imide (LiTFSI) dissolved in a mixture solution of 1,2-Dimethoxyethane (DME) and 1,3-dioxolane (DOL) at 1:1 vol ratio. The battery constant current charge and discharge tests and the cyclic voltammetry curve tests were performed in a voltage range of 1.0–3.0 V.

The performance of the capacitor is characterized by a threeelectrode system. 80 parts by weight of the $FeS_x/C/CNT$ composite, 10 parts by weight of the AB, and 10 parts by weight of binder polytetrafluoroethylene (PTFE) were mixed to prepare a powder slurry. And a saturated calomel electrode was used as a reference electrode, and a platinum electrode was used as a counter electrode to form a three-electrode system. The electrolyte was 3 mol L⁻¹ KOH, and the test current densities were 1 A g⁻¹, 2 A g⁻¹, 3 A g⁻¹ and 5 A g⁻¹, respectively, and the charge-discharge cut-off voltage limit was $-1.2 \sim -0.4$ V.

5. Credit author statement

I have made substantial contributions to the conception or design of the work; or the acquisition, analysis, or interpretation of data for the work. I have drafted the work or revised it critically for important intellectual content; and I have approved the final version to be published. I agree to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved. All persons who have made substantial contributions to the work reported in the manuscript, including those who provided editing and writing assistance but who are not authors, are named in the Acknowledgments section of the manuscript and have given their written permission to be named.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Yiyong Zhang: Formal analysis, Writing - review & editing. Mingsheng Xu: Formal analysis. Ying Wang: Writing - review & editing. Shuangshuang Lin: Writing - review & editing. Linlin Ji: Data curation. Xue Li: Formal analysis. Yingjie Zhang: Funding acquisition. Jinbao Zhao: Funding acquisition, Supervision.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at

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