Reduced Graphene Oxide-Wrapped FeS₂ Composite as Anode for High-Performance Sodium-Ion Batteries

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Highlights

- Reduced graphene oxide-wrapped FeS₂ (FeS₂/rGO) composite was synthesized by a facile two-step method.
- The integral reduced graphene oxide networks not only connect the FeS₂ nanoparticles but also prevent them from aggregating.
- As anodes for sodium-ion batteries, the FeS₂/rGO composite delivers high specific capacity and good cycling stability.

Abstract
Iron disulfide is considered to be a potential anode material for sodium-ion batteries due to its high theoretical capacity. However, its applications are seriously limited by the weak conductivity and large volume change, which results in low reversible capacity and poor cycling stability. Herein, reduced graphene oxide-wrapped FeS₂ (FeS₂/rGO) composite was fabricated to achieve excellent electrochemical performance via a facile two-step method. The introduction of rGO effectively improved the conductivity, BET surface area, and structural stability of the FeS₂ active material, thus endowing it with high specific capacity, good rate capability, as well as excellent cycling stability. Electrochemical measurements show that the FeS₂/rGO composite had a high initial discharge capacity of 1263.2 mAh g⁻¹ at 100 mA g⁻¹ and a high discharge capacity of 344 mAh g⁻¹ at 10 A g⁻¹, demonstrating superior rate performance. After 100 cycles at 100 mA g⁻¹, the discharge capacity remained at 609.5 mAh g⁻¹, indicating the excellent cycling stability of the FeS₂/rGO electrode.

Keywords
FeS₂ · Reduced graphene oxide (rGO) · Enwrapping structure · Anode material · Sodium-ion battery
1 Introduction

Sodium-ion batteries (SIBs) have been considered to be promising candidates for large-scale energy storage systems, electric vehicles, and other portable devices because of their outstanding electrochemical performance and inexpensive characterization. As the most important parts of SIBs, electrolytes and electrodes have been extensively investigated. It has been demonstrated that polymer electrolytes (such as gel polymer electrolytes and ceramic electrolytes) may be desirable alternatives for liquid electrolytes because of their modularity and reliability in electrochemical devices [1, 2]. Various cathodes, including oxides (such as transition metal oxides), transition metal fluorides (typically FeF3), polyanionic compounds (such as NaFePO4, NaVPO4F, NaM2(PO4)3, NASICON compounds), Prussian blue analogues, and organic electrodes, have displayed outstanding sodium storage performance [3]. Meanwhile, significant progress has been achieved in the area of anodes for SIBs. It has been revealed that carbon-based materials, alloys, and metal oxides/sulfides are promising anode materials for SIBs [4-6]. Among these materials, iron sulfides, such as FeS2 [7-9], FeS [10] and Fe1-xS [11, 12], have attracted much attention due to their advantages of abundant reserves, non-toxicity, low cost, and high theoretical capacity (894 mAh g\(^{-1}\) for FeS2, based on the conversion reaction of FeS2 + 4Na ↔ 2Na2S + Fe). However, the intrinsically low conductivity and notable volume change during the charge-discharge process greatly restrain its rate performance and cycling stability, restricting its further commercialization.

To solve these problems, Chen's group tuned an electrolyte and applied a higher voltage cutoff to improve the electrochemical performance of Na/FeS2 and Li/FeS2 cells [13, 14]. Numerous studies have revealed that constructing nanostructured materials can greatly reduce the electron/ion transport pathways and effectively buffer the large volume expansion during electrochemical processes, thus improving the reversibility and rate capability of FeS2 anode materials [15, 16]. Moreover, the combination of a carbon or a polypyrrole (ppy) modification strategy to form a coating or an embedded structure (such as FeS2/C [17-20], ppy@MoO3 [21-23], ppy@V2O5 [24]) would help prevent aggregation and improve the conductivity of the electrode materials, thus enhancing the cycling and rate performance. For example, Liu et al. designed FeS2@C nanoboxes and obtained discharge capacity of 511 mAh g\(^{-1}\) at 100 mA g\(^{-1}\) after 100 cycles [25]. Graphene is a highly conductive ultrathin nanosheet, with a large surface area and high flexibility, which is commonly used as modification material. In previous studies, FeS/ reduced graphene oxide (rGO) [26], FeS2/rGO [27], Fe3O4/ rGO [28], Fe2O3/rGO [29], and LiFePO4/rGO [30, 31] composites have been fabricated and used in lithium-ion batteries (LIBs). It is demonstrated that enwrapping anode materials in a conductive network is a favorable strategy to enhance the rate capability. However, the FeS2/graphene composite with an enwrapping structure for SIBs has not been reported.

Here, we report a two-step method for the preparation of a novel rGO-wrapped FeS2 (FeS2/rGO) composite for SIBs. Structural and morphological characterization revealed that the FeS2 nanoparticles are evenly surrounded in the interconnected rGO networks. The composite displayed superior sodium storage performance even at high charge-discharge current densities.

2 Experimental

2.1 Materials Synthesis

FeS2/rGO was synthesized via a hydrothermal method, followed by a sulfurization process. All chemicals were of analytical grade and used without further purification.

**Synthesis of Fe3O4/rGO composite** In a typical synthesis, 0.04 g of graphene oxide was dispersed in 65 mL of deionized water by sonication. Then, 0.4 g of Fe(NO3)3·9H2O was dissolved in the above suspension and stirred for 4 h at 70 °C. Following this, 5 mL of N2H4·H2O was added to the above system, and the solution was sealed in a 100-mL Teflon-lined stainless-steel autoclave for hydrothermal reaction at 150 °C for 6 h. Finally, the rGO-wrapped Fe3O4 composite was collected by centrifugation, washed with water and ethanol three times, and dried at 70 °C in a vacuum for 12 h.

**Synthesis of FeS2/rGO Composite** The as-prepared Fe3O4/rGO and sulfur powder in a weight ratio of 1:2 were mixed and pressed into a small tablet and sealed in a small quartz tube under Ar atmosphere. Then, the quartz tube was heated at 150 °C for 2 h and subsequently at 550 °C for 6 h in a quartz tube reactor. After cooling down and washing with CS2 to remove the residual sulfur powder, the final FeS2/rGO composite was obtained. For comparison, FeS2 nanoparticles were prepared using the same method without the addition of rGO.

2.2 Materials Characterization

The crystal structures of the as-prepared samples were characterized by powder X-ray diffraction (XRD) using Cu Ka radiation. The morphologies were investigated using field-emission scanning electron microscopy (SEM) on a JEOL JSM-7500FA system and transmission electron
weight ratio of 8:1:1. A solution of 1 M NaClO4 in ethylene carbonate/propylene carbonate (v/v = 1/1) with 5 wt% fluoroethylene carbonate additive was used as the electrolyte. Cyclic voltammetry (CV, 0–2.5 V, 0.1 mV s−1) tests and electrochemical impedance spectroscopy (EIS, with 5 mV amplitude in a frequency range from 100 kHz to 0.01 Hz at open-circuit potential) tests were conducted on a Biologic VMP-3 electrochemical workstation. The galvanostatic charge–discharge curves, cycling performance, and rate capabilities of the electrode materials were tested on a LAND Battery Test System, in an atmosphere (Fig. 3a). Both the samples display a minor weight loss (∼ 6–8%) under 200 °C, which is due to the vapor of the residual water in the materials. Then a large weight loss of about 35% is observed in the range 400–500 °C for pure FeS2, which corresponds to the conversion of FeS2 to Fe2O3. (The theoretical weight loss is about 42%.) For FeS2/rGO, a more significant weight loss of about 42% is observed between 400 and 600 °C, which may be caused by the phase change of FeS2 to Fe2O3 and rGO to carbon dioxide. Based on the thermogravimetric analysis, the weight content of FeS2 in the FeS2/rGO composite can be calculated to be about 79.1%. According to the above analysis, the FeS2/rGO composite contains integral nanostructures, with the FeS2 nanoparticles enwrapped in the 3D rGO networks. This unique structure endows the composite with high structural stability and super electron conductivity, which may be beneficial for the cycling stability and rate performance of the FeS2 electrode material for sodium storage.

Figure 4a, b shows the cyclic voltammetry (CV) curves of pure FeS2 and the FeS2/rGO composite at a scan rate of 0.1 mV s−1 between 0 and 2.5 V (vs. Na/Na+). During the initial cathodic scan, a large peak appears at 1.0 V and a broad peak appears at 0.25 V for the FeS2 electrode, which corresponds to Na+ intercalation and the formation of the Na+FeS2 (x < 2) phase, Fe and Na2S, and the formation of a solid-electrolyte interface (SEI) layer [13, 16, 32]. For the FeS2/rGO electrode, a large peak at ∼ 0.65 V and a small peak at ∼ 0.1 V are detected, which may be due to a...
similar electrochemical process with the FeS₂ electrode. The differences in the peaks of the two samples may be caused by the nanostructure and the introduction of rGO. During the subsequent anodic scan, the peaks observed at \( \sim 1.4 \) and \( \sim 1.8 \text{ V} \) can be attributed to be the desodiation process, with the formation of Na₂FeS₂ and Na₂₋ₓFeS₂ [19]. During the subsequent cycles, the CV curves are quite different from those in the initial cycle, which may be due to the irreversible formation of the SEI layer and the decomposition of the electrolyte [19, 33–35]. It can be observed that the FeS₂/rGO electrode shows much better repeatability and a larger closed curve area than those of the pure FeS₂ electrode, demonstrating its much better cycling stability and higher specific capacities.

Figure 5a presents the charge–discharge curves of FeS₂/rGO electrode at a current density of 100 mA g⁻¹. An initial discharge plateau at \( \sim 1.0 \text{ V} \) (vs. Na/Na⁺) and charge plateau at \( \sim 1.3 \text{ V} \) are observed, which are in good agreement with the CV curves. In the subsequent cycles, the charge–discharge curves do not change much, showing good electrochemical reversibility. The cycling performances of the two samples are further evaluated at 100 mA g⁻¹. As shown in Fig. 5b, both the electrodes have quite good cycling stability. However, the FeS₂/rGO electrode has obviously higher specific capacities than does the pure FeS₂ electrode, which may be due to the higher utilization of the active materials after the introduction of rGO. The FeS₂/rGO composite displays a high initial discharge capacity of 1263.2 mAh g⁻¹ and charge capacity of 759.4 mAh g⁻¹, showing a low coulombic efficiency of 60.1%, which is mainly caused by the irreversible formation of the SEI layer and electrolyte decomposition in the initial cycle. Moreover, the dissolution of sodium polysulfides into organic liquid electrolytes causes a parasitic redox shuttle, leading to unfavorable side reactions with sodium, reducing the charging efficiency and resulting in serious capacity decay [36–38]. In the following cycles, the coulombic efficiency increases over 95%. From the second cycle, the discharge and charge capacities are stable and remain at 609.5 and 581.7 mAh g⁻¹, respectively, after 100 cycles.

The rate capability of the two FeS₂ electrodes is evaluated using varying current densities from 0.1 to 10 A g⁻¹ and back to 0.1 A g⁻¹. As shown in Fig. 5c, the average specific capacities for FeS₂/rGO electrodes are 705, 672, 613, 555, 496, 426, and 344 mAh g⁻¹ at 0.1, 0.2, 0.5, 1, 2, 5, and 10 A g⁻¹, respectively, which are remarkably higher than those for pure FeS₂ electrode, demonstrating its superior rate performance. When the current density is altered back to 0.1 A g⁻¹, the reversible capacity remains at \( \sim 655 \text{ mAh g}^{-1} \) after 90 cycles, further confirming the excellent cycling stability of the FeS₂/rGO composite. We further investigate the electrode process kinetics of the two materials through EIS. As shown in Fig. 5d, both the Nyquist spectra are composed of a semicircle in the high-frequency region and an inclined line in the low-frequency region. The bigger semicircle for the FeS₂ electrode illustrates the poor electrical conductivity of the active...
Fig. 2  a XRD patterns of the as-prepared FeS$_2$ and FeS$_2$/rGO composite, b, c SEM images of FeS$_2$, d SEM image, e, f TEM images, g, h HRTEM images, and i SAED pattern of FeS$_2$/rGO composite

Fig. 3  a TG curves and b N$_2$ adsorption–desorption curves of FeS$_2$ and FeS$_2$/rGO composite
materials. According to the Z-view program in the Sai software set, $R_{ct}$ for FeS$_2$ and FeS$_2$/rGO electrodes is 1055.1 and 291.9 Ω, respectively, illustrating the better charge transfer kinetics of the FeS$_2$/rGO electrode.

The FeS$_2$/rGO composite displays much higher specific capacity and better rate capability than does the pure FeS$_2$ electrode. It is inferred that several features may contribute to the excellent electrochemical properties. First, the intimate contact of the FeS$_2$ nanoparticles with rGO and the integral conductive rGO networks provide a facile electron transport pathway, ensuring good rate performance [27, 30]. Second, the unique enwrapping structure can effectively improve the structural stability and buffer the volume change of FeS$_2$ during the charge–discharge process [26, 28]. To investigate the structural stability, the nanostructures of the freshly prepared FeS$_2$/rGO electrode and the FeS$_2$/rGO electrode after 100 cycles are investigated by SEM and TEM. From Fig. 6a, it can be seen that the morphology of the FeS$_2$/rGO composite does not change. After 100 sodiation–desodiation cycles, the nanoparticles are not very regular but are still enwrapped in the graphene networks (Fig. 6b, c). The high-resolution TEM test shows that the nanoparticles transform into smaller nanocrystals (Fig. 6d), which are still surrounded
by rGO. It is obvious that the graphene network can effectively prevent the collapse of the structure and the aggregation of FeS$_2$ nanoparticles, thus improving the cycling stability of the FeS$_2$/rGO composite. Moreover, the improvement of the BET surface area increases the contact area between the active material and the electrolyte, which helps improve the utilization of active materials, endowing the FeS$_2$/rGO composite with high specific capacitance.

4 Conclusions

In summary, an rGO-wrapped FeS$_2$ composite has been successfully synthesized via a hydrothermal method, followed by sulfuration, and used as an anode for SIBs. The well-dispersed rGO constructs 3D conductive networks and markedly increases the BET surface area and conductivity of the FeS$_2$ nanoparticles. Thus, the FeS$_2$/rGO composite displays an initial discharge capacity of 1263.2 mAh g$^{-1}$ at 100 mA g$^{-1}$ and a high discharge capacity of 344 mAh g$^{-1}$ at 10 A g$^{-1}$. Moreover, the enwrapping structure helps in preventing the aggregation of the FeS$_2$ nanoparticles during the electrochemical process, contributing to the excellent cycling stability. After 100 cycles, the discharge capacity is 609.5 mAh g$^{-1}$. We believe that our strategy could be extended to the fabrication of other high-performance metal sulfide/rGO composites for LIBs or SIBs.

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