FeS/Reduced Graphene Oxide Composite as Anode Material with Enhanced Performance for Lithium-ion Battery

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Abstract. FeS/Reduced graphene oxide (RGO) were synthesized successfully using a facile calcination method followed by a coprecipitation process. The structure and morphology were examined via X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR). Afterwards, the electrochemical performances were characterized by cyclic voltammetry, the electrochemical impedance (EIS), and charge/discharge techniques. The results reveal the following three points. First, compared with pure FeS, FeS/RGO composite material has a higher specific capacity. Second, the existence of RGO layers can enhance the electrochemical conductivity for overall electrodes. Third, the FeS/RGO composite showed outstanding coulombic efficiency and good cycling stability.

1. Introduction

Recently, lithium-ion batteries have garnered increasingly attention because of their high energy density and environmental friendly[1-3]. The performance of LIBs highly counts on the electrode material. Therefore, the selection of electrode materials with outstanding performance is exceedingly important. Graphite is the current commercially applied anode material, however, the theoretical capacity is low(372 mAh/g) [4,5]. For anode materials, transition metal oxides have been captured researchers' attention due to their higher theoretical specific capacity than the commercial graphite anode [6]. On the other hand, transition metal sulfides are abundant and their crystal structures can be stable. Furthermore, their electronic conductivity is superior to transition metal oxides [7-11].

Ferrous sulfide, as a transition metal sulfide, has been intensively exploited as anode materials for lithium ion batteries. Apart from the common advantages of transition metal sulfide, the electrode potential of transition metal sulfide is also higher than that of graphite, which can effectively limit the formation of SEI film[12,13]. However, iron sulfides as the anode is still far from the commercialization due to some problems. First, the product after discharge processes is an insulating polysulfide(Li₂Sₓ, 1<x<8), which could easily dissolve in a organic electrolyte. The dissolved polysulfides not only leads to lose active material, but also worsen the conductivity of the electrolyte and electrode [14]. Second, FeS often suffers from large volume expansion during cycles of lithium-ion battery, which is easy to cause powdering and deactivation of the material [15].

In our paper, in order to offset that shortcomings of related previous researches, we demonstrated a new method to synthesize FeS/RGO composite by using ferrous chloride, Sodium sulfide and graphene oxide(GO) as the reactant during the reaction process. By comparing with pure FeS, as expected, the as-prepared FeS/RGO composite presents superior electrochemical performance.
2. Experimental
The ferrous chloride solution (50 ml 0.2 mol/L) was prepared in a three-necked flask, and after that the GO powder was added. And the mixture was magnetically stirred for 1 hour and then sonicated for 1 hour. The sodium sulfide solution (16 ml 0.75 mol/L) was prepared in a constant pressure funnel. The ferrous chloride solution is slowly added to the sodium sulfide solution under nitrogen protection. A black precipitate was then formed, and stirring for 1 hour. Then, the precipitates in the solution were filtrated, washed several times with distilled water and ethanol, and then dried at 80°C for 12 hour. Finally, the obtained black solid were annealed in a tube furnace at 600°C for 1 hour in an argon atmosphere to obtain the final FeS/RGO composite. As comparison, pure FeS was also prepared by the identical procedures except for the addition of GO.

The crystal structure of the as-prepared FeS and FeS/RGO composite was characterized by X-ray powder diffraction (XRD; MiniFlex600, CuKa radiation), which the scanning range was 20°-80°. Their morphology were observed by field emission scanning electron microscope (FESEM), transmission electron microscopy (TEM; JEM-2100, 200 kV) and Fourier transfer infrared spectrooscope (FTIR; IRPrestige-21/FTIR-8400s).

The working electrode was prepared through the mixture of 70 wt.% active materials (FeS or FeS/RGO), 20 wt.% acetylene black, and 10 wt.% polyvinylidene fluoride (PVDF) binder in an N-methyle-2-pyrrolidone (NMP). Then the above slurries was coated on Cu foils, and drying in vacuum oven at 110 °C for 12 hour. The lithium foil was used as both the counter electrode and reference electrode. The coin-type cells (CR2032) were conducted in glove box. The cells were charged and discharged between 0.01 V and 3.0 V by the Land Battery Test System (CT2001A). The cyclic voltammetry (CV) and electrochemical impedance (EIS) were carried out on the electrochemical workstation (CHI660) [16].

3. Results and Discussion

3.1 Structure and Morphology of Materials
The XRD spectra of FeS and FeS/RGO are shown in figure 1. All the diffraction peaks of the FeS in figure 1 matched well with FeS (JCPDS 37-0477), indicating the successful formation of FeS. And the peaks at 20=29.98°, 33.88°, 43.80°, and 53.12° correspond to the (110), (112), (114), and (300) planes of the troilite FeS, respectively. For the XRD patterns of FeS/RGO, the main peaks are in good agreement with the pure FeS. In addition, the peaks of are not observed, demonstrating the stacking of RGO layers in composite is largely disordered.

As shown in the figure 2, from the GO spectrum we can see that there is a broad absorption peak near 3404 cm⁻¹, which is due to the association of -OH with each other; The peaks at 1731 cm⁻¹ and at 1620 cm⁻¹ correspond to the C=O stretching vibration of the carboxyl group and the C=C double bond plane stretching vibration respectively [17]; The peaks at 1219 cm⁻¹ and 1047 cm⁻¹ are C-O absorption peaks [18]. Taking this as a comparison, let's look at the spectrum of FeS/RGO again. It is clear that the absorption peaks of C=O and C-O disappear. The absorption peak of -OH is narrowed, and the association phenomenon is weakened. This all shows that GO is well reduced after heat treatment. However, the absorption peak near 3404 cm⁻¹ still exists in the FeS/RGO spectrum, which may be due to the absorption peaks of FeS and graphene(G) at the same wavenumber, and the absorption peaks are superimposed. And more importantly, the absorption peak of C=C did not disappear in the FeS/RGO spectrum, which indicates that the single-double-bond alternating structure of graphene has not been destroyed in the synthesis of the composite material, which is beneficial to the material of conductivity.
Figure 1. XRD patterns of materials

Figure 2. FTIR spectra of materials.

Figure 3. FESEM images of FeS/RGO composite (c) and FeS (d); TEM image of the red circle in (a)(b)

The morphological features of the FeS/RGO composite and FeS were characterized through FESEM and TEM. FESEM images in figure 3(a) show the morphology of FeS/RGO over a large area. FeS is well compounded on both sides of the RGO sheet layer, which forms a unique sandwich structure. This structure is beneficial to alleviate the volume expansion of FeS during the cycle, thereby improving the electrochemical performance. In addition to this sandwich structure, as shown in figure 3(b), there are still a small number of FeS particles wrapped in the RGO sheet, which forms the pea pod structure. This structure has a stronger mitigating effect on the volume expansion of FeS. By comparing figure 3(c) and figure 3(d), we can see that FeS/RGO composites are more porous than FeS. This result may be caused by the large specific surface area of RGO, which makes the nucleation process of FeS more dispersed. The loose and porous morphology is more conducive to the diffusion
and transfer of lithium ions during the cycle, thereby improving the electrochemical performance of the battery.

### 3.2 Electrochemical Performance

![Figure 4](https://example.com/four.png)

**Figure 4.** Cyclic voltammetry of FeS(a) and FeS/RGO(b).

In order to explore the redox reactions, the cyclic voltammetry (CV) was investigated. The scanning rate voltage was set up from 0 to 3 V at a scan rate of 0.5 mV/s. For pure FeS, as shown in figure 4(a), the reduction peak of the first cycle is around 0.88 V, explained as follows [19]:

$$
\text{FeS} + 2\text{Li}^+ + 2e^- \rightarrow \text{Li}_2\text{S} + \text{Fe}
$$

The peak at 0.5 V is attributed to the formation of the SEI. The broad peak at 2.12 V is due to the oxidation reaction from Fe to Li$_{2-x}$FeS$_2$ [19, 20]. In addition, the peaks appearing are obviously different after the first cycle. In the second and third cycles, two reduction peaks at 1.88 and 1.25 V are related to the step-by-step formation of Li$_2$FeS$_2$ from the Li$_{2-x}$FeS$_2$ phase [21]. And the oxidation peak moved to 2.2 V after the first cycle, which indicated the beginning of the delithiation process (Li$_2$FeS$_2$ to Li$_{2-x}$FeS$_2$) [19, 22].

$$
\text{Li}_2\text{FeS}_2 + x\text{e}^- = \text{Li}_{2-x}\text{FeS}_2^{2-} + x\text{Li}
$$

Notably, FeS shows an decrease of both anodic and cathodic peaks. However, the FeS/RGO composite, as shown in figure 4(b), after the first cycle, reveals considerably small changes in the CV curves, suggesting the promising structure stability and the reversibility of the electrochemical reactions.

Electrochemical impedance spectroscopies of FeS and FeS/RGO composite are tested to analyze their electrochemical processes. As shown in figure 5, the Nyquist plots are composed of a semicircle and the straight line (Warburg line) in the low-frequency region, which is attributed to the charge-transfer resistance at the electrode interface and Li$^+$ diffusion in the electrolyte to the electrode interface, respectively. And the semicircle of FeS/RGO is smaller than FeS, which reveals the electrochemical resistance of FeS/RGO is lower. This fact indicates that the existence of RGO thin layers can improve the electrochemical conductivity.

Figure 6(a) shows the discharge/charge profile of FeS/RGO for the 1st, 2nd, 10th, 50th, and 100th cycles at the current density of 100 mA/g. The FeS/RGO composite delivers higher initial discharge capacity of 1170.1 mAh/g. The initial charge capacity is only 879.1 mAh/g, showing the irreversible capacity loss of 291.0 mAh/g, around 24.8% of the first discharge capacity, which can be explained the formation of SEI[22]. In contrast, as seen in figure 6(b) the initial discharge capacity of the pure FeS is only 740.1 mAh/g. The reason for this result may be attributed to the capacity contribution of the RGO thin layers can intercalate and de-intercalate lithium ion.
Figure 5. Nyquist plots for FeS and FeS/RGO composite.

Figure 6. The charge/discharge curves of FeS/RGO composite (a) and FeS (b); Cycle performances of FeS/RGO composite and FeS at the current density of 100 mA/g (c); A rate capabilities of FeS/RGO composite.

The cycle performance of FeS/RGO composite and FeS at the current density of 100 mA/g is showed in figure 6(c). Obviously, after a slow decline, the specific capacity of FeS/RGO becomes basically stable after the 65th cycle. In addition, the Coulombic efficiency of FeS/RGO composite is close to 100% for all the 100 cycles. It is noteworthy that the curve of FeS/RGO is always above the curve of FeS, which shows that the specific capacity of the materials has been greatly improved. The
rate performance of FeS/RGO at different current densities is showed in figure 6(d). The specific capacities are decreased along with increasing the current density: 100, 200, 400, 800, and 1000 mA/g. The tenth-cycle discharge capacities remain at 438.8, 283.4, 166.1, 82.3, and 51.3 mAh/g, respectively. Moreover, when the current density was changed back to 100 mA/g, the specific capacity rebounded to 404.1 mAh/g. These results show that FeS/RGO composite has good rate performance as the anode electrode for LIBs.

4. Conclusions
The FeS/RGO composite was successfully synthesized via a facile calcination method followed by a coprecipitation process. Compared with pure FeS, FeS/RGO composite material has a higher charge/discharge specific capacity. Moreover, the existence of RGO can enhance the electrochemical conductivity. More importantly, the FeS/RGO composite showed perfect coulombic efficiency and outstanding cycling stability. The FeS/RGO composites also has excellent rate performance as the negative electrode for lithium-ion battery.

5. Acknowledgments
This work is supported by the National Natural Science Foundation of China (No. 21571132).

6. References
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