Research Article

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In-situ synthesis of Fe$_2$O$_3$/rGO using different hydrothermal methods as anode materials for lithium-ion batteries

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Abstract: This paper studies in-situ synthesis of Fe$_2$O$_3$/reduced graphene oxide (rGO) anode materials by different hydrothermal process. Scanning Electron Microscopy (SEM) analysis has found that different processes can control the morphology of graphene and Fe$_2$O$_3$. The morphologies of Fe$_2$O$_3$ prepared by the hydrothermal in-situ and oleic acid-assisted hydrothermal in-situ methods are mainly composed of fine spheres, while PVP assists The thermal in-situ law presents porous ellipsoids. Graphene exhibits typical folds and small lumps. X-ray diffraction analysis (XRD) analysis results show that Fe$_2$O$_3$/reduced graphene oxide (rGO) is generated in different ways. Also, the material has good crystallinity, and the crystal form of the iron oxide has not been changed after adding GO. It has been reduced, and a characteristic peak appears around 25°, indicating that a large amount of reduced graphene exists. The results of the electrochemical performance tests have found that the active materials prepared in different processes have different effects on the cycle performance of lithium ion batteries. By comprehensive comparison for these three processes, the electrochemical performance of the Fe$_2$O$_3$/rGO prepared by the oleic acid-assisted hydrothermal method is best.

Keywords: Hydrothermal in-situ method, anode material, morphology, particle size, crystallinity, electrochemical performance

1 Introduction

Poizot et al. [1] conducted extensive research on Fe$_2$O$_3$ anode materials in 2000 and believed that they had promising potential to replace commercial graphite anodes for lithium ion batteries. Iron oxide has advantages of non-toxicity and pollution-free, low cost, abundantly resourced, and high theoretical capacity, but they do exhibit problems, such as a large loss of reversible capacity after the first cycle and poor conductivity [2]. Today’s society is ushering in the rapid development of composite materials [3–5], especially composite materials used in electrochemistry have been widely manufactured in order to improve the conductivity of polymer composite materials [6]. Due to the special two-dimensional structure of graphene [7, 8], graphene-based composite materials with a "surface-to-surface" electrical contact mode are recognized as the mode that can maximize the advantages of graphene [9–11]. And the research of graphene for battery load is gradually increasing [12]. It was found that the lithium storage capacity of a high-performance battery prepared by the composite material of iron-based oxide and graphene is more than twice that of the current commercially available graphite anode [13–15], but the existing preparation methods generally require multi-step processing and must be prepared under an inert and high temperature environment [16–18]. Therefore, this simple and low cost synthetic method has become the focus of some scholars [19–21]. To solve these problems, this paper uses FeCl$_3$ as the raw material, adopts a one-step hydrothermal method (hydrothermal in-situ method, PVP-assisted hydrothermal in-situ method, or oleic acid-assisted hydrothermal in-situ method) to synthesize Fe$_2$O$_3$/rGO composite material for the performance improvement of iron-based oxide anode materials.

Liu et al. [22] used a one-step hydrothermal method, using water and glycerin as hydrothermal solvents, to construct in-situ a-Fe$_2$O$_3$ embedded in a graphene network to present a nanoplate structure with a size of 20-30 nm and a-Fe$_2$O$_3$ enclosed by a closely-connected, flexible con-
ductive graphene network. Using α-Fe₂O₃/rGO composite material as a negative electrode material for lithium ion batteries, a high discharge capacity over 200 cycles can be obtained at 5°C. In this paper, FeCl₃ is used as a raw material, and a one-step hydrothermal method (hydrothermal in-situ method, PVP-assisted hydrothermal in-situ method, or oleic acid-assisted hydrothermal in-situ method) is used to prepare the Fe₂O₃/rGO composite material, for use in a button battery assembly. Constant current charge and discharge, CV and AC impedance test methods were used to measure the electrochemical performance of the battery, which revealed the influence of morphology and grain size of composite material on electrochemical performance of the Fe₂O₃/rGO anode material. The iron oxide and graphene compound is able to avoid the phenomenon of iron oxide agglomeration due to the small particle sizes of the nanoparticles. The excellent graphene conductivity also provides a fast transmission channel for electron transmission and improves the overall conductivity of the composite material [23]. The deficiencies of iron oxide as a negative electrode material were also exposed. In the composite of iron oxide and graphene, the content of graphene not only affects the electrochemical performance of the composite, but also the dispersion and agglomeration of iron oxide on graphene also affects the performance of the composite. But there are few reports about how to improve the agglomeration of iron oxide nanoparticles on the graphene surface. Therefore, this paper attempts to use different hydrothermal methods to improve the agglomeration of iron oxide particles on graphene and change the morphology of iron oxide, and the electrochemical performance of Fe₂O₃/rGO anode material is carried out.

2.2 Methods of preparing Fe₂O₃/graphene by different processes

In this paper, the ratio of graphene was 1:0.2, where the molar number of ferric chloride was calculated by the law of conservation of elements, which was converted into the mass of ferric chloride, and the Fe₂O₃/graphene composite material was obtained by a one-step hydrothermal method.

2.2.1 Hydrothermal in-situ synthesis

Graphene and Fe₂O₃ were compounded by hydrothermal in-situ synthesis. The specific experimental process is shown in Figure 1. The sample preparation process is as follows:

1. Go (0.05 g) was dispersed into deionized water by ultrasonic stirring to form a graphene dispersion.
2. FeCl₃ · 6H₂O (0.87 g) was dissolved in deionized water and magnetically stirred, and then sodium hydroxide solution was added dropwise until a pH value greater than 10 was achieved. The solution was then placed in ultrasonic equipment for 1 h. Next, the resulting product was transferred into a polytetrafluoroethylene-lined high-pressure reaction kettle in a blast drying oven at 175°C, and the hydrothermal reaction was performed for 12 h.
3. The product obtained after the hydrothermal reaction was centrifuged and washed, and then placed in a vacuum drying oven to obtain a red powder. The dried sample was taken out, placed in a clean crucible, and calcined in a tube furnace vented with Ar gas at a calcination temperature of 300°C and a calcination time of 3 h to obtain an Fe₂O₃/rGO composite material.

2 Experiment

2.1 Experimental materials

The raw materials required for the preparation of the negative electrode material for lithium-ion battery during the experiment are as follows: ferric chloride hexahydrate, polyvinylpyrrolidone (PVP), oleic acid, sodium hydroxide, and absolute ethanol were provided by Sinopharm Group Chemical Reagent Co., Ltd. in China. Multilayer graphene oxide was provided by Suzhou Tanfeng Graphene Technology Co., Ltd. in China. The above materials belong to analytical grade.
2.2.2 PVP-assisted hydrothermal in-situ synthesis

Polyvinylpyrrolidone (PVP), a good surfactant and dispersant, can improve the dispersibility of metal oxides on the graphene surface and disperse graphene sheets to a certain extent [24]. This method can improve the uneven dispersion of iron oxide particles on graphene. PVP-assisted hydrothermal in-situ synthesis method was used to compound graphene and Fe$_2$O$_3$. The schematic diagram is shown in Figure 1. The sample preparation process is similar to the hydrothermal in-situ synthesis method, where the only difference is that 0.45 g polyvinylpyrrolidone (PVP) was added to the mixed solution in the second step.

2.2.3 Oleic acid-assisted hydrothermal in-situ synthesis

During the recombination of iron oxide and graphene, the assistance of oleic acid could avoid the agglomeration of iron oxide particles on graphene. Therefore, the method of adding oleic acid on the basis of hydrothermal method is adopted to improve the agglomeration of iron oxide particles. The schematic diagram is shown in Figure 2. The preparation process is basically the same as the hydrothermal in-situ synthesis method. The only difference is that the mixed solution in the second step is slowly added with 10 mL of oleic acid.

2.3 Preparation of negative electrode material and battery installation

Active substance, acetylene black, and polyvinylidene fluoride (PVDF) were weighed according to a mass ratio of 8:1:1. The PVDF binder and N-methyl-2-pyrrolidone (NMP) organic solvent were mixed together and stirred, and then mixed with other substances to obtain a uniform slurry. The slurry was spread evenly on the copper foil and placed in a vacuum drying oven for drying. Punching and pressing were performed to obtain electrode sheets.

The electrode pads were placed in a glove box filled with argon for CR2032 coin cell assembly, with 1 mol·L$^{-1}$ LiPF$_6$ / ethylene carbonate (EC) + dimethyl carbonate (DMC) (volume ratio 1:1). The mixed solution is the electrolyte, and it is assembled in the order of negative electrode case → spring sheet → lithium gasket sheet → diaphragm → electrode sheet → positive electrode case. The assembled half-cells were sealed, and the open circuit voltage was checked for normality. After 12 hours of standing, the electrochemical performance was tested.

2.4 Physical characterization of the anode material and the electrochemical performance of the battery

The surface morphology of the material was characterized by cold field emission scanning electron microscopy (FE-SEM). The phase composition of the material was characterized by XRD, and the microscopic crystal structure of the material was analyzed. The Xinwei battery test system was adapted to conduct constant current charge and
discharge testing on the simulated battery over a voltage range of 0.01-3.0 V. The specific discharge capacity of the material was calculated according to the quality of the prepared sample active material.

3 Results and analysis

3.1 Scanning electron microscopy (SEM) analysis

Figure 3 shows SEM morphology images of Fe₂O₃/rGO composite materials prepared by different hydrothermal in-situ methods. It can be seen from Figures 3(a) and 3(b) that the Fe₂O₃ in the Fe₂O₃/rGO composite prepared by the hydrothermal in-situ method was spherical with a par-

Figure 3: SEM morphology images of Fe₂O₃/rGO composites prepared by different hydrothermal in-situ methods (a-c) hydrothermal in-situ method; (d-e) PVP-assisted hydrothermal in-situ method; (f-g) oleic acid-assisted hydrothermal in-situ method
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Particle size of about 100 nm. Micro-aggregation was also observed. In Figure 3(c), it was found that graphene exhibits typical wrinkling characteristics. The presence of graphene wrinkles can significantly increase the specific surface area and provide active sites for electrochemical reactions, thereby improving the electrochemical performance of lithium battery anodes [25, 26].

It can be seen from Figures 3(d) and 3(e) that the Fe$_2$O$_3$/rGO composite prepared by PVP-assisted hydrothermal in-situ method has an elliptical spherical shape with a particle size of about 800 nm-1 µm. In a porous state, Fe$_2$O$_3$ particles were evenly dispersed on the graphene surface. The reason why the morphology of Fe$_2$O$_3$ is ellipsoidal is that PVP acts as a surfactant and reduces the surface active energy of Fe$_2$O$_3$. It can also be seen that the addition of PVP disperses the graphene sheets, and the PVP molecules were attached to the GO through hydrophobic interactions, alleviating agglomeration between graphene sheets, to provide more even Fe$_2$O$_3$ dispersion on the graphene. This shows that the addition of PVP decreases the agglomeration of Fe$_2$O$_3$ on the graphene surface and provides an even and consistent loading of Fe$_2$O$_3$.

As seen in Figures 3(f) and 3(g), the Fe$_2$O$_3$ in the Fe$_2$O$_3$ rGO composite prepared by the oleic acid-assisted hydrothermal in-situ method exhibits various morphologies, such as expanded graphene sheets, Fe$_2$O$_3$ particles located on the graphite on both sides of the ene sheet, and graphene in small pieces.

Comparing the morphology of Fe$_2$O$_3$/rGO composites prepared by oleic acid-assisted hydrothermal in-situ method and the morphology of Fe$_2$O$_3$ / rGO composites prepared by hydrothermal in-situ method, it can be found that: The Fe$_2$O$_3$ particles in the material are smaller, the specific surface area is larger, the active sites are more, and the lithium ion diffusion path is short, which is beneficial to rapid charge and discharge and stability.

Comparing the morphology of Fe$_2$O$_3$/rGO composite prepared by oleic acid-assisted hydrothermal in-situ method with the morphology of Fe$_2$O$_3$/rGO composite prepared by PVP-assisted hydrothermal in-situ method, it can be found that: Fe$_2$O$_3$/rGO composite prepared by oleic acid-assisted hydrothermal in-situ method The Fe$_2$O$_3$ in the rGO composite is coated with a carbon layer to build a more effective conductive network.

### 3.2 XRD analysis

Figure 4 shows the XRD patterns of Fe$_2$O$_3$/rGO prepared by three different processes. It is observed that the phase composition of these three samples is composed of α-Fe$_2$O$_3$ and a graphene phase, which shows that Fe$_2$O$_3$/rGO composites were successfully synthesized. The diffraction peaks are sharp, indicating higher crystallinity. For Fe$_2$O$_3$/rGO, the positions and relative intensities of the α-Fe$_2$O$_3$ diffraction peaks in the three samples fully coincide with the XRD standard spectrum of α-Fe$_2$O$_3$, confirming that ferric ion is completely transformed into α-Fe$_2$O$_3$ phase. The crystal form of iron oxide was unchanged after adding GO. All peaks of Fe$_2$O$_3$ were based on or-

![Figure 4: XRD pattern of Fe$_2$O$_3$/rGO composites prepared by three hydrothermal processes](image)
3.3 Cyclic stability analysis

Figure 5 shows cycle curves of Fe$_2$O$_3$/rGO anode materials prepared by three hydrothermal processes. From the figure, it can be clearly observed that at a current density of 100 mA g$^{-1}$, the first discharge cycle capacity of Fe$_2$O$_3$/rGO prepared by the hydrothermal in-situ method was 1425 mAh g$^{-1}$, the first 15 cycles rapidly decayed to about 600 mAh g$^{-1}$, and after 50 cycles, the reversible capacity of the cycle remained at 435 mAh g$^{-1}$.

The Fe$_2$O$_3$/rGO prepared by the PVP-assisted hydrothermal in-situ method showed a first discharge cycle capacity of 1398 mAh g$^{-1}$, and after 8 cycles, it decayed to 400 mAh g$^{-1}$. After 50 cycles, the reversible capacity was close to 225 mAh g$^{-1}$.

The discharge capacity of Fe$_2$O$_3$/rGO prepared by the oleic acid-assisted hydrothermal in-situ method was 1431 mAh g$^{-1}$ for the first cycle, and it decayed to 600 mAh g$^{-1}$ after 30 cycles. The capacity remained at 478 mAh g$^{-1}$. Through the cycle performance analysis, it can be found that the active materials prepared by different processes had various effects on the cycle performance of lithium ion batteries. Comparing the three processes, the electrochemical performance of Fe$_2$O$_3$/rGO prepared by the oleic acid-assisted hydrothermal method was best.

The first and 50th discharge capacities of Fe$_2$O$_3$/rGO anode materials prepared by three hydrothermal processes are listed in Table 1.

It can be seen from Table 1 that the Fe$_2$O$_3$/rGO prepared by the hydrothermal method showed excellent electrochemical performance, which was primarily related to the uniform dispersion of prepared nano-Fe$_2$O$_3$ on the corrugated graphene. The ultra-high conductivity of graphene can provide an ultra-fast electron transmission network for electrons, and graphene folds can also provide more lithium storage sites [29, 30]. The fine particles had a larger specific surface area, which provides more contact with the electrolyte and generates more reactive sites [31, 32]. To a certain extent, the diffusion path of lithium ions was shortened, and the performance of the electrode material under high current charge and discharge could be improved [33, 34]. At the same time, the small particle iron oxide material could also better relieve the stress concentration caused by the volume effects of the iron oxide material and prevent the material from quickly pulverizing [35, 36].

Fe$_2$O$_3$/rGO prepared by the oleic acid hydrothermal in-situ method showed the best electrochemical performance, which was mainly due to the ultra-small particles of Fe$_2$O$_3$ distributed on both sides of the graphene sheet. Due to the reaction in the two-phase system, the oil shell of the oleate chain was formed outside the composite material. The oil shell helps to avoid aggregation of growing crystals, thereby alleviating the volume expansion problems of Fe$_2$O$_3$ during charge and discharge [37, 38]. The excellent electrochemical performance is related to the unique structure of graphene and the synergistic effect of nano-Fe$_2$O$_3$. Graphene provides a volume buffer for nano-Fe$_2$O$_3$ and the shortest fast diffusion channel for electron and lithium ion transport [39]. The ultra-thin graphene sheet can greatly shorten the diffusion distance of lithium ions during the insertion and removal of lithium ions, thereby increasing the contact between the electrode and the electrolyte and maintaining the structural integrity and cycle stability of the electrode [40].

Compared with the other two methods, the PVP-assisted hydrothermal in-situ method showed the worst electrochemical performance, mainly because the size of the elliptical particles was too large, and the surface was not porous enough to buffer the volume expansion problems during charge and discharge.
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Table 1: Comparison of cycle stability of Fe$_2$O$_3$/rGO anode materials prepared by three hydrothermal processes

| Serial number | Preparation Method                                      | First discharge specific capacity (Ah g$^{-1}$) | Specific discharge capacity after 50 cycles (mAh g$^{-1}$) |
|---------------|--------------------------------------------------------|-----------------------------------------------|----------------------------------------------------------|
| 1             | Hydrothermal in-situ method                            | 1425                                         | 435                                                      |
| 2             | PVP-assisted hydrothermal in-situ method               | 1398                                         | 225                                                      |
| 3             | Oleic acid-assisted hydrothermal in-situ method        | 1431                                         | 478                                                      |

Table 2: Fe$_2$O$_3$/graphene material specific capacity

| Preparation method                         | First discharge specific capacity (mAh g$^{-1}$) | Specific discharge capacity after 50 cycles (mAh g$^{-1}$) | References |
|--------------------------------------------|--------------------------------------------------|-----------------------------------------------------------|------------|
| Hydrothermal                               | 1023.6 (Current density 40 mA g$^{-1}$)          | 406.6 (Current density 40 mA g$^{-1}$)                   | [41]       |
| Hydrothermal                               | 1062 (Current density 100 mA g$^{-1}$)           | -                                                         | [42]       |
| Oleic acid assisted hydrothermal in situ   | 1431 (Current density 100 mA g$^{-1}$)           | 478 (Current density 100 mA g$^{-1}$)                    | This work  |

Table 2 shows the specific capacity of Fe$_2$O$_3$/graphene material. Compared with the specific capacitance reported in the existing literature, the results of this study are higher than other Fe$_2$O$_3$/graphene materials.

Figure 6 shows the voltammetric curves of Fe$_2$O$_3$/rGO prepared by three different processes. From Figure 6(a), during the first discharge, two reduction peaks appeared near 0.37 V and 1.65 V, corresponding to the two-step lithiation reaction (Eqs. (1)).

$$\text{Fe}_2\text{O}_3 \rightarrow \text{Li}_x\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_0 + \text{Li}_2\text{O} \quad (1)$$

The reaction decomposes to form the SEI film [43]. During the first charge, a broad oxidation peak appeared at 1.92 V, corresponding to the reaction (Eqs. (2)).

$$\text{Fe}_0 \rightarrow \text{Fe}^{3+} \quad (2)$$

During the second and third discharges, the reduction peak shifted and the peak intensity weakened, because some irreversible reactions occurred and the interfacial SEI film was formed [44, 45]. This could be observed from the intensities of the second and third cycle peaks becoming smaller and closely coinciding, indicating that the structure changed little and had excellent cycle stability in the subsequent cycle process.

It can be seen from Figure 6(b) that during the first discharge, a high-intensity reduction peak appeared near 0.42 V, and a small reduction peak vaguely appeared near 1.5 V, indicating that the formation of $\alpha$-Fe$_2$O$_3$ and lithium occurred in two steps. The lithiation reaction was shown to be Fe$_2$O$_3$ $\rightarrow$ Li$_x$Fe$_2$O$_3$ $\rightarrow$ Fe$^0$ + Li$_2$O, which decomposed with the electrolyte reaction to form the SEI film. During the first charging process, a broad oxidation peak appeared at 1.73 V, which corresponds to Fe$^0$ $\rightarrow$ Fe$^{3+}$ and released electrons. During the second and third discharges, the 1.5 V peak disappeared, the reduction peak of 0.42 V positively shifted and widened, and the peak intensity weakened. This is due to irreversible reactions and the formation of SEI film at the interface. However, during the second and third charging, the oxidation peak position did not change, and the intensity weakened. The intensity of the reduction and oxidation peaks weakened and the current lessened, indicating that the capacity decreased during the cycle.

It could be seen from Figure 6(c) that during the first cycle, a high-intensity reduction peak appears at 0.44 V during discharge, and a small reduction peak appears at 1.46 V. $\alpha$-Fe$_2$O$_3$ and lithium Two-step lithiation reaction; during charging, a broad oxidation peak appeared at 1.75 V, corresponding to Fe$^0$ $\rightarrow$ Fe$^{3+}$ and releases electrons. During the second and third cycles, the reduction peak shifted and the peak intensity weakened because of irreversible reactions and the formation of an interfacial SEI film. It could also be seen from the figure that the Fe$_2$O$_3$/rGO composite materials prepared by different processes had similar charge-discharge curves on the IV curve and are typical of an IV curve of a typical conversion metal oxide anode material [46, 47].
Figure 6: Cyclic voltammetry curves of Fe₂O₃/rGO anode materials prepared by three hydrothermal processes (a) Hydrothermal in situ method; (b) PVP-assisted hydrothermal in situ method; (c) Oleic acid-assisted hydrothermal in situ method

Figure 7: EIS curves of Fe₂O₃/rGO anode materials prepared by three different processes

3.4 AC impedance analysis

Figure 7 shows the AC impedance graph of Fe₂O₃/rGO composites prepared by three different processes. The AC impedance diagram of the material electrode is divided into two parts: a high frequency region and a low frequency region. The intercept value of the semicircle in the high frequency region and the horizontal axis is equal to the ohmic impedance value, and the value corresponding to the diameter of the high frequency/medium frequency semicircle represents the charge transfer impedance. The order of the internal resistance of the composite material is: R (oleic acid-assisted hydrothermal in-situ method) < R (hydrothermal in-situ method) < R (PVP-assisted hydrothermal in-situ method), indicating that the observed results are generally consistent with the cycle performance. The charge transfer impedance of the oleic acid-assisted hydrothermal in-situ method is smaller than that of the other two methods and showed better electrochemical performance [48, 49].

4 Conclusions

In conclusion, three hydrothermal methods are adopted to prepare Fe₂O₃/rGO anode materials using FeCl₃ and graphene oxide as a raw material in this paper, and it is found that the morphologies of graphene and Fe₂O₃ are controllable by different hydrothermal methods, thus affecting electrochemical performance of anode materials. The experiment results are as follows:

1. SEM results indicates that the morphology of Fe₂O₃ prepared by hydrothermal in-situ method and oleic acid-assisted hydrothermal in-situ method is mainly composed of fine spheres, while this morphology also presents porous ellipsoids by PVP-assisted hydrothermal in-situ method. Graphene exhibits typical folds and small lumps by these synthesis processes.

2. XRD analysis results show that the material has good crystallinity, and the crystal type of iron oxide has not been changed after adding GO. And a characteristic peak appears around 25°, indicating that a large amount of reduced graphene oxide exists.

3. The results of electrochemical performance tests show that the active materials prepared by different hydrothermal processes have various effects on the cycle performance of lithium ion batteries. By comprehensive comparison for these three processes, the electrochemical performance of Fe₂O₃/rGO prepared by oleic acid assisted hydrothermal method is best. The first cycle discharge capacity of Fe₂O₃/rGO prepared by oleic acid-assisted hydrothermal in-situ method is 1431 mAh·g⁻¹ at a current density of 100 mA·g⁻¹, and the discharge capacity is decayed
to 600 mAh·g⁻¹ after 30 cycles. The cycle reversible capacity remains at 478 mAh·g⁻¹ after 50 cycles.

Graphene had a conductive network that could significantly increase conductivity and electrolyte transport. The steric hindrance of graphene could limit the crystal growth of iron oxide, increase or decrease its active site and shorten the transmission path of lithium ions in the crystal. Graphene could additionally provide some negative electrode capacity.

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