**Fe₃O₄/Graphene Aerogel as High-Performance Flexible Anode for Sodium-Ion Battery**

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**Abstract.** To overcome the volume expansion and poor electrical conductivity of metal oxides, graphene aerogel encapsulated Fe₃O₄ nanoparticles composite material was synthesized by hydrothermal self-assembled method. Fe₃O₄ was synthesized in situ during the self-assembled process, effectively relieving volume expansion and pulverization of metal oxides by the encapsulation of graphene aerogels (termed Fe₃O₄@rGA). Besides, the graphene aerogel enhances the conductivity of the composite material. The Fe₃O₄@rGA used as anode material for sodium ion batteries in this study displayed an excellent initial capacity of 220 mA h g⁻¹ at 100 mA g⁻¹, and even showed reversible capacity of 82 mA h g⁻¹ at 10 A g⁻¹.

1. **Introduction**

The excessive exploitation and utilization of fossil fuels have not only caused serious environmental pollution, but also brought about energy crisis [1]. Clean energy has attracted extensive attention in recent years, especially secondary batteries [2, 3]. Sodium ion batteries (SIBs) receive widespread attention because of low cost and rich resources [4]. Recently, extensive attention has been paid to exploring SIBs electrode materials [5]. Metal oxide receives extensive attention in electrochemical fields because of high theoretical capacity and low cost [6-8]. However, the serious problems of volume expansion and poor conductivity limit its further development. In order to overcome these shortcomings, composite with carbon materials is one of the most effective solutions [9, 10].

Here, three-dimensional (termed 3D) self-assembled graphene aerogel was synthesized by hydrothermal method, and Fe₃O₄ nanoparticles were encapsulated on the graphene sheets during self-assembled process. The composite electrode shows abundant porous and excellent mechanical strength. The self-assembled structure was formed by electrostatically attracted between metal cations and carboxyl functional groups at the edge of graphene sheets. The composite electrode was applied to sodium ion batteries anode, which significantly improved the electrochemical performance.

2. **Materials and Methods**

2.1. **Synthesis of Fe₃O₄@rGO and Fe₃O₄@rGA**

The mixture of Fe₃O₄ and graphene (termed Fe₃O₄@rGO) was synthesized via a simple mix and centrifugation process. 20 mg GO (Gaoxi Tech. Inc.) was dispersed into 6 mL deionized (DI) water and then stirred for 30 min. 100 mg Ferric nitrate was added to the GO solution and then stirred for 1 h. The solution was gathered by centrifugation, and then washed 4~5 times with ethanol and DI water. The sample was freeze-dried for 48 h and then heated in a tubular furnace at 800 °C for 2 h to obtain the final product.
The Fe₃O₄@rGA was synthesized via a simple self-assembled and thermal curing process. 20 mg GO (Gaoxi Tech. Inc.) was dispersed into 6 mL DI water and then stirred for 30 min. 100 mg Ferric nitrate was added to GO solution and then stirred for 1 h. The solution was transferred into a small petri dish, heated in a vacuum drying oven at 80°C for 6 h. After that, the hydrogel product was collected and washed 4-5 times with ethanol and DI water (1:15 v/v) mixture. The product was freeze-dried for 48 h to remove absorbed ethanol and water. Then the obtained cylindrical aerogel sample was heated in a tubular furnace at 800 °C for 2 h. The obtained Fe₃O₄@rGA sample was cut into small sequins to spare.

2.2. Materials Characterization
The microstructures and morphologies of the samples were characterized by Hitachi SU-70 field-emission scanning electron microscope (SEM). X-ray diffraction (XRD) was measured by D8 Advance diffractometer (XRD, Bruker AXS, WI, USA) over the range of 10-70°. Raman spectra was measured by JY Labram HR 800. Thermogravimetric analysis (TGA) was performed using TA Q5000IR and the heating rate is 20 °C min⁻¹ under flowing air.

2.3. Electrochemical Measurements
The compared electrodes were produced by mixing the Fe₃O₄@rGO (70%), conductive carbon black (20%) and polyvinylidene fluoride (PVDF; 10%) to form a slurry and then coated onto a copper foil. The electrochemical properties of Fe₃O₄@rGO and Fe₃O₄@rGA anodes were evaluated with CR2032 coin cells. Pure sodium foils were used as counter electrodes. The electrolyte of sodium coin cells was 1.0 M NaPF₆ in EC/DEC (1:1 v/v) with 5% FEC. Arbin BT2000 potentiostat was used to Galvanostatic cycling tests. Electrochemical impedance spectroscopy (EIS) was performed on a CHI 660e electrochemical workstation (ChenHua Instruments Co.) in the range of 100 kHz to 0.01 Hz.

3. Results and Discussion
A 3D Fe₃O₄@rGA with porous structure was produced by hydrothermal method at 80 °C for 6 h. Fig. 1(a) shows a picture of aerogel that self-assembled during hydrothermal treatment. The obtained aerogel was extremely light. As shown in Fig. 1(b), the sample was very flexible after it was deformed by pressure.

![Figure 1](image)

**Figure 1.** (a) Picture of the Fe₃O₄@rGA with ultra-light weight. (b) Picture of the Fe₃O₄@rGA with high flexibility.

In Fig. 2, the Fe₃O₄@rGA shows uniform porous structure, forming 3D conductive framework by connection between graphene sheets. The structure is beneficial for electron conduction between the whole 3D conductive framework. The Fe₃O₄ nanoparticles anchor uniformly on the graphene sheets. The graphene framework actions as a conductive channel, so that almost all Fe₃O₄ particles are electrochemically active. The anodes exhibit excellent mechanical properties, which preserves the structure integrity of the anodes and promotes the stability of the composites.
Figure 2. SEM images of the Fe₃O₄@rGA.

TGA measurement was carried out in the air to measure the chemical composition of Fe₃O₄@rGA. In Fig. 3, the TGA curve showed a significant weight loss at approximately 450 °C and a constant weight above 840 °C. The miniscule weight loss (~6%) that appeared below 300 °C was most attributed to evaporation of water molecules. The weight loss from 450 °C to 800 °C indicated the combustion of graphene aerogel (~23%). The content of Fe₃O₄ in Fe₃O₄@rGA was calculated to be 71%.

Figure 3. TGA curves for the Fe₃O₄@rGA in the air.

As shown in Fig. 4(a), XRD measurement displayed the crystal structure of the final products. GO showed a significant peak at 12°, but the peak disappeared after graphene reduction process, demonstrating the reduction of GO after hydrothermal. All the peaks in the upper profile in Fig. 4(a) can be assigned to Fe₃O₄ (JCPDS No. 26-1136), which proved the existence of Fe₃O₄. Raman spectra of GO, GA and Fe₃O₄@rGA were provided in Fig. 4(b). They all produced strong D bands (~1330 cm⁻¹) and G bands (1600 cm⁻¹). The D/G bands intensity ratio of GO and rGA was 0.92 and 1.02, while the ratio of Fe₃O₄@rGA increased to 1.15. The D/G ratio can be used as the test standard for the comparison of the order degree of crystal structure and the size of sp² region. These results showed that the number of sp² is increase in rGA and Fe₃O₄@rGA, proving that the GO was restored.
Figure 4. (a) XRD patterns of the Fe₃O₄@rGA, rGA and GO. (b) Raman spectra of the Fe₃O₄@rGA, rGA and GO.

Fig. 5 displayed the rate performance of Fe₃O₄@rGA at different current densities for SIBs. The Fe₃O₄@rGA electrode demonstrated stable capacity of approximately 220, 155, 112, 92, 81 and 91, 101 mA h g⁻¹ at 100, 500, 1000, 2000, 5000, 10000 and back to 5000, 2000 mA g⁻¹. Respectively, when it recovered from 10 A g⁻¹ to 5 A g⁻¹ and 2 A g⁻¹, the capacity showed no significant decay, indicating that the Fe₃O₄@rGA composite sample showed excellent structure stability. The Fe₃O₄@rGA electrode showed a high initial discharge capacity and remarkable capacity retention.

In order to further verify the capacity retention rate under high current density, Fig. 6 showed the galvanostatic charge-discharge curves of Fe₃O₄@rGA and Fe₃O₄@rGO at 10 A g⁻¹. The Fe₃O₄@rGA electrode produced a high specific capacity and exceptional cycling retention. The Fe₃O₄@rGA electrode showed excellent electrochemical cycling stability, with a discharge capacity of 82 mA h g⁻¹ after 100 cycles. After 500 cycles, the discharge capacities of the electrode showed no significant decay (78 mA h g⁻¹ at 10 A g⁻¹ after 500 cycles). Even after 800 cycles, the capacity still remained at 73 mA h g⁻¹, which showed exceptional cycling retention. For comparison, the discharge capacity of the Fe₃O₄@rGO electrode was only 71 and 69 mA h g⁻¹ after 500 and 800 cycles. It indicated that the Fe₃O₄@rGA effectively alleviated the low coulomb efficiency and poor electrical conductivity caused by the volume expansion of metal oxides in the electrochemical cycling.
Figure 6. Galvanostatic charge/discharge curves of (a) Fe$_3$O$_4$@rGA and (b) Fe$_3$O$_4$@rGO electrode for SIBs cycled for the 10th, 100th, 500th, 800th at 10 A g$^{-1}$.

Figure 7 presented the EIS spectra of the Fe$_3$O$_4$@rGO and Fe$_3$O$_4$@rGA. In the Nyquist plots, the charge transfer resistance and SEI at sodium surface correspond to the high frequency semicircle. As shown in the Nyquist plots, the semicircle diameter of Fe$_3$O$_4$@rGA was extremely smaller than that of Fe$_3$O$_4$@rGO in high-medium frequency region, stating that the charge-transfer resistance of Fe$_3$O$_4$@rGA (151 Ω) was lower than that of Fe$_3$O$_4$@rGO (552 Ω). The Fe$_3$O$_4$@rGA improved the conductivity of the electrode, at the same time, it also improved the electrochemical activity during the cycle.

Figure 7. The Nyquist plots of Fe$_3$O$_4$@rGO and Fe$_3$O$_4$@rGA electrodes for the 3th cycle, the inset is the equivalent circuit.

4. Conclusions

In summary, graphene aerogel encapsulated Fe$_3$O$_4$ composite material was synthesized by hydrothermal method, forming 3D porous structure with homogeneous distribution of Fe$_3$O$_4$ nanoparticles after thermal curing process. The porous self-assembled structure enhances electrical conductivity. Graphene coating by electrostatic adsorption can efficiently suppress particles aggregation during cycling, and prevent direct contact between electrolyte and Fe$_3$O$_4$ nanoparticles. Electrochemical tests showed that the composite electrode showed stable cycling performance in SIBs, maintaining a capacity of 240 mA h g$^{-1}$ at 100 mA g$^{-1}$. Compared with the method of directly mixing graphene and iron oxide particles, this work effectively alleviates volume expansion and material pulverization. More importantly, the architecture features and synthetic method facilitate other graphene-based metal oxides as high-performance anodes for SIBs.
5. Acknowledgments
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6. References
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