Synthesis and Electrochemical Performances of Iron Oxalate-Multiwalled Carbon Nanotubes Composite Anode for Lithium-ion batteries

Yongjia Li¹, Geng Gao², Qianwen Wang², Keyu Zhang², * and Yaochun Yao²

¹Faculty of Metallurgy and Mining, Kunming Metallurgy College, Kunming, China
²Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming, China

*Corresponding author: 202000103@kust.edu.cn

Abstract. Iron oxalate, a widely used anode material in lithium-ion batteries for nearly 10 years, has been developed as promising candidates for anode materials owning to their higher electrochemical reactivity, outstanding cyclability, lower cost and environmental friendliness. In this paper, the iron oxalate-multiwalled carbon nanotubes (FeC₂O₄@C) composite was successfully synthesized by electrostatic self-assembly technique and the influence of special structure on lithium storage ability was also explored. The results show that the multiwalled carbon nanotubes are embedded inside the rod-like particles of FeC₂O₄ and also threaded on surface of the multilayer structure. Coupled with excellent structural stability and enhanced Li⁺ ion diffusion coefficient, FeC₂O₄@C exhibits suggests superior long-term stability (a reversible specific capacity of 970 mAh g⁻¹ after 50 cycles at 0.5 A g⁻¹) and satisfactory rate capability (824.06 mAh g⁻¹, 770.47 mAh g⁻¹ and 688.60 mAh g⁻¹ at 1, 2, 3 and 5 A g⁻¹, respectively).

Keywords: Iron oxalate, multiwalled carbon nanotubes, lithium-ion batteries.

1. Introduction

With the rapid development of new energy vehicles, energy storage systems and electronic equipment, new energy storage materials with high energy density, good rate performance, satisfied safety and stability have become a new direction for the development of lithium-ion batteries. Compared with other electrode materials, transition metal oxalate materials have great application potential in lithium/sodium ion battery, super capacitors, fuel cells and other fields because of their higher electrochemical capacity, excellent rate performance, and environmental friendlinesss [1-2]. But they still exist many of the key problems to be solved in its commercialization, such as the large irreversible capacity in first charge and discharge process, poor cycling performance and difficulties associated for obtaining 100% free of crystalline water materials [3-4]. Therefore, it is of great theoretical value and practical significance to further explore and study the preparation and lithium storage characteristics of transition metal oxalates.

In this paper, iron oxalate-multiwalled carbon nanotubes (FeC₂O₄@C) composite was prepared by electrostatic self-assembly technique. The characterization and electrochemical behavior of the FeC₂O₄ and FeC₂O₄@C composite were described. This unique nanostructure has a series of advantages, making it possible for lithium-ion batteries with high rate and stable cycle performance.
2. Experimental

Typically, 3.6 g hexadecyl trimethyl ammonium bromide was dissolved in 100 mL mixed solvent of alcohol and water to form a clear solution. 0.36 g multi-walled carbon nanotubes (MWCNTs) were added and the mixtures were ultrasonicated for 1 h to disperse them uniformly. A total of 2 mL Poly (diallyl dimethylammonium chloride, 20 ω%) solution and 15 mmol sodium oxalate were then added into this mixed solution under normal stirring for 6 h to form a dispersion solution. 5 mmol iron sulfate heptahydrate and 0.2 mmol ascorbic acid were dissolved in 30 mL deionized water. Afterwards, the above solution was slowly added to the dispersion solution with vigorous stirring for 1 h under reaction temperature of 60°C. The precipitate was separated by centrifuge, washed with deionized water and ethanol absolute for 3 times and then dried at 80°C for 12 h in a vacuum oven to get the FeC₂O₄ꞏ2H₂O and FeC₂O₄ꞏ2H₂O@C. Finally, the products were collected for characterization and electrochemical measurement after sintering in a tubular furnace at 300°C for 3 h under Ar protection.

3. Results and discussion

Iron oxalate (FeC₂O₄ꞏH₂O) generally crystallizes into two allotropic forms: the space group of C2/C α with monoclinic form and the Cccm structure with β orthorhombic form [5]. As shown in Figure 2, the XRD peaks of the samples are consistent with the orthorhombic β-phase (ICDD PDF # 022-0635) and no impurity peak appears. After losing the crystal water, the dehydration products exhibit a small number of highly broadened reflections owing to the poor crystalline, which are in good agreement with the reported literature [6]. Obviously, due to the diversity of the interlayer structure, the diffraction peak intensity of FeC₂O₄ shows a slight of difference with FeC₂O₄ꞏH₂O@C composite. In addition, FeC₂O₄ꞏH₂O@C and FeC₂O₄ @C composites present an obviously diffraction peak at around 28.76°. This suggests that the active substances are efficiently deposited on the surface of MWCNTs.

![Figure 1. XRD spectra of iron oxalate.](image)

The TEM results confirm the marked changes in surface morphology and particle size of FeC₂O₄@C composites, as shown in Figure 2. It can be clearly seen that the nanostructured FeC₂O₄ exhibits irregular shape composed of nanometer-sized sheet with 500 ~ 800 nm length and 50 ~ 200 nm width. From HR-TEM micrographs (Figure 2b), FeC₂O₄ shows numerous pores on surface of the multilayer structure, which can be generated from the particles as a result of the release of crystallized water molecules during the dehydration process. As observed in Figure 2c and d, the MWCNTs is homogeneously dispersed...
among microrod-liked FeC$_2$O$_4$ particles which indicates that the excellent diffusion network for Li$^+$ ions. The HR-TEM micrographs (Figure 2d) provide the detail structure of the MWCNTs and FeC$_2$O$_4$. The nanotubes are embedded inside the rod-like particles and also threaded on surface of the multilayer structure, which can enhance the electrical conductivity.

**Figure 2.** TEM images of FeC$_2$O$_4$ (a-b) and FeC$_2$O$_4$@C (c-d).

**Figure 3.** (a) Rate performance of the obtained samples from 0.2 to 5 A g$^{-1}$ at 30°C. (b) Long-term cycling performance and coulombic efficiency for all electrodes at 0.5 A g$^{-1}$.

The respective rate property and cycling stability of FeC$_2$O$_4$ and FeC$_2$O$_4$@C electrodes were then tested in voltage range from 0.01 to 3 V by applying various current densities. As shown in Figure 3a, the FeC$_2$O$_4$ electrode exhibits an excellent discharge capacity (1047.18 mA h g$^{-1}$) in initial cycles at a rate of 0.2 C. However, the rate property of α@β-FeC$_2$O$_4$ is superior to FeC$_2$O$_4$ electrode. The specific discharge capacities of FeC$_2$O$_4$@C are 939.11 mA h g$^{-1}$, 896.42 mA h g$^{-1}$, 824.06 mA h g$^{-1}$, 770.47 mA h g$^{-1}$ and 688.60 mA h g$^{-1}$ at 0.5, 1, 2, 3 and 5 A g$^{-1}$, respectively. After these high-rate cycles, the capacity also can recover to 1032.33 mA h g$^{-1}$ at 0.2 A g$^{-1}$. It suggests that the high current charge/discharge process could not break down the integrity of the electrode, which can be ascribed to the efficient supporting role of MWCNTs. Then, the long-term cycling stability was tested at 0.5 A g$^{-1}$ over 50 cycles. As shown in Figure 3b, the initial discharge capacity is 1493.45 mA h g$^{-1}$ for FeC$_2$O$_4$@C, which is similar with that of FeC$_2$O$_4$ (1432.88 mA h g$^{-1}$). This indicates that the composite of MWCNTs has little influence on the lithium storage mechanism. After several dozen cycles of activation, its reversible
capacity is 970 mAh g\(^{-1}\), then keep stable in the subsequent cycle. In addition, the coulombic efficiency is lower than 100% at first five cycles, and then reaches almost 100% in subsequent cycling, which may be due to unstable electrochemical activity of complex nanocomposites and formation of solid electrolyte interface (SEI) films.

Electrochemical impedance spectroscopy (EIS) was performed with FeC\(_2\)O\(_4\) and FeC\(_2\)O\(_4\)@C as reference samples to ascertain the excellent Li\(^+\) ions diffusion channels. As shown in Figure 4a, it can be noted that FeC\(_2\)O\(_4\)@C has the lowest R\(_{\text{st+ct}}\) values at 49.77 Ω suggesting excellent interaction with the electrolyte and separator. Because of homogeneous distributed pore structure and active function of MWCNTs, the value of Z\(_w\) (181.3 Ω) is far less than that of FeC\(_2\)O\(_4\) (364.3 Ω). To further calculate the Li\(^+\) ion diffusion coefficient (D\(_{Li^+}\)), Warburg impedance can be fitted according to the proportional relationship between Z’ (Z\(_{\text{re}}\)) and \(\omega^{-0.5}\) and the following equations [7-8]:

\[
Z_{\text{re}} = R_s + R_{\text{st+ct}} + \sigma\omega^{-0.5} \\
D_{Li^+} = \frac{(R^2T^2)}{(2A^2F^4\sigma^2C^2)}
\]

As shown in Figure 4b and Table 1, the calculated D\(_{Li^+}\) of FeC\(_2\)O\(_4\)@C (2.74×10\(^{-14}\) cm\(^2\) s\(^{-1}\)) is nearly higher third over than that of FeC\(_2\)O\(_4\) (8.17×10\(^{-15}\) cm\(^2\) s\(^{-1}\)) in fresh cells. This phenomenon illustrates that the special structure combined with MWCNTs could provide stable diffusion channels for Li\(^+\) ions.

![Figure 4](image_url)

**Figure 4.** (a) Nyquist plots of all FeC\(_2\)O\(_4\) electrodes. (b) Relationship between Z\(_{\text{re}}\) and \(\omega^{-0.5}\) at low frequencies.

**Table 1.** Fitting parameters of the cell with FeC\(_2\)O\(_4\) and FeC\(_2\)O\(_4\)@C electrodes.

| Electrodes   | R\(_s\) (Ω) | R\(_{\text{st+ct}}\) (Ω) | CPE\(_{\text{sf+dl}}\) (µF) | \(\alpha_1\) | Z\(_w\) (Ω) | C\(_{\text{int}}\) (mF) | D\(_{Li^+}\) (cm\(^2\) s\(^{-1}\)) |
|-------------|-------------|--------------------------|-----------------------------|-------------|------------|----------------|-------------------|
| FeC\(_2\)O\(_4\) | 3.45        | 79.06                    | 14.12                       | 0.83        | 364.3      | 2.52           | 8.17×10\(^{-15}\)   |
| FeC\(_2\)O\(_4\)@C | 3.62        | 49.77                    | 19.67                       | 0.81        | 181.3      | 1.68           | 2.74×10\(^{-14}\)   |

4. Conclusion

In this study, iron oxalate-multiwalled carbon nanotubes composite was successfully synthesized by electrostatic self-assembly technique. Due to the homogeneous distributed pore on surface of FeC\(_2\)O\(_4\) and embedded structure of MWCNTs, FeC\(_2\)O\(_4\)@C composite exhibits higher Li\(^+\) ion diffusion coefficient of 2.74×10\(^{-14}\) cm\(^2\) s\(^{-1}\) and better electrochemical performance with a reversible capacity of 970 mAh g\(^{-1}\) at 0.5 A g\(^{-1}\) after 50 cycles. These findings demonstrate that the composite of carbon-based materials for oxalate-based anode materials is an efficiency way to modify poor cycling performance.
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