A facile fabrication of Fe₂O₃/C composite as anode for lithium ion batteries

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Abstract. The anode material Fe₂O₃/C composite is prepared by a solid phase method. The as-obtained Fe₂O₃/C composite was investigated by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical measurements. XRD results indicate the presence of hematite. SEM observations shows nano particles of Fe₂O₃/C composite and illustrate the good combination of Fe₂O₃ and carbon, Fe₂O₃ was well enwrapped by carbon. The electrochemical performance of the composite is good. In the potential range of 3.00–0.01 V, it delivers initial charge capacity of 314.6 mAh g⁻¹ at 100 mA g⁻¹, and 83.8% of initial capacity is retained even after 20 cycles. Meanwhile, the role of carbon was also discussed. The results indicate that it could be used as a promising anode material for Li-ion batteries.

Introduction

Lithium-ion batteries (LIBs) are one of the dominant power sources for portable electronics because of their high-energy density, long cycle life, high-power sources and ambient temperature operation [1–3]. Transitional metal oxides are attractive as a new type of anodes for LIBs due to their higher specific capacity, better rate performance and lower cost [4, 5].

Recently, Fe₂O₃ have been regarded as a promising negative electrode for its higher theoretical specific capacity (1005 mAh g⁻¹ compared to commercial graphite), non-toxicity and low cost [6]. However, the huge volume change during the charge/discharge process and the low electronic conductivity severely hindered the development of its practical use [7, 8]. Many efforts have been adopted to restrain the huge volume expansion and shrinkage and improve the electronic conductivity of Fe₂O₃-based materials, such as structure control and compound with other material to improve their electrochemical performance [9–11].

In this paper, we propose a facile, simple and rapid process to synthesize Fe₂O₃/C as an anode material for lithium-ion batteries.

Experimental

Fe₂O₃/C sample was synthesized as follows: FeCl₃·6H₂O was dissolved into a 100 mL deionized water in the 250 ml beaker. After stirring for 5min, sodium hydroxide solution was added to the solution drop by drop to maintain iron hydroxide. Then the slurry was filtrated to obtain iron hydroxide precipitate and washed 3 times with deionized water and absolute ethyl alcohol. Finally, the precipitate as dried at 120 °C for more than 8 h and calcined at 500 °C in air to obtain Fe₂O₃ particles. Further, the Fe₂O₃ particles and glucose were mix uniformly by solid-phase method and pyrolyzed at at 800 °C for 2 h in a tube furnace with a flowing argon atmosphere to yield Fe₂O₃/C sample.

The SEM images of the particles were observed with scanning electron microscopy (SEM, FEI, Quanta 200F). The powder X-ray diffraction (XRD, Rint-2000, Rigaku) using Cu K α radiation was employed to identify the crystalline phase of the materials. The electrochemical performance was carried out using a two-electrode coin type cell (CR2025) of Li | LiPF₆ (EC:EMC:DMC=1:1:1 in volume) | Fe₂O₃/C. The working anode was composed of 80 wt.% Fe₂O₃/C powders, 10 wt.% acetylene black as conducting agent, and 10 wt.% poly (vinylidene fluoride) as binder, and with

N-methyl pyrrolidinone as the solvent. The slurry was spread uniformly on a thin copper foil and dried in vacuum oven for 12 h at 120 °C. Electrodes were punched in the form of 12mm diameter disks. A polypropylene micro-porous film was used as the separator. The assembly of the cells was carried out in a dry argon-filled glove box. The cells were charged and discharged over a voltage range of 3.00–0.01 V versus Li/Li⁺ electrode at room temperature.

Results and discussion

Fig. 1 shows the XRD pattern of the as-prepared Fe₂O₃/C. According to Fig. 1, the diffraction peaks at $2\theta = 33.2^\circ$, 35.7° , 40.9° , 49.5° , 54.1° , 62.5° and 64.1° correspond well with (104), (110), (113), (024), (116), (214) and (300) reflections of hematite (JCPDS No. 33-0664). And the amorphous glucose-pyrolyzed carbon shows no obvious diffraction peak. As shown, no other impurity elements are absent in the as-prepared Fe₂O₃/C, but the crystallization of Fe₂O₃/C is not very complete, which need to be improved during the follow-up work.

Fig. 1 XRD pattern of Fe₂O₃/C

Fig. 2 SEM images of the as-prepared Fe₂O₃ (a) and Fe₂O₃/C particles (b)

In order to characterize the morphology of the materials, SEM was employed. Fig. 2 shows the SEM images of the Fe₂O₃ and Fe₂O₃/C particles. From Fig. 2 (a), it can be seen that spherical-like particles with an average particle size of 100–200 nm and smooth surface are observed obviously, and the nano particles are dispersed uniformly in amorphous glucose-pyrolyzed carbon (Fig. 2 (b)) which helps to reduce the formation of unstable SEI films and restrain the volume change during the charge-discharge process.

Fig. 3 (a) shows the initial potential-capacity profiles of Fe₂O₃ and Fe₂O₃/C electrode at the charge/discharge current density of 100 mA g⁻¹. In the first cycle, the discharge curve of Fe₂O₃ and Fe₂O₃/C both show similar plateaus at 1.6 V and 0.8 V, corresponding separately to lithium insertion into crystalline structure of Fe₂O₃ and reduction of Fe³⁺ to Fe⁰ by metallic Li [5]. But the plateau of Fe₂O₃/C is more distinct than Fe₂O₃, which may owing to the amorphous glucose-pyrolyzed carbon. The first discharge and charge capacities of Fe₂O₃/C are observed to be 817 and 314.6 mA h g⁻¹, respectively, while the initial discharge and charge capacities of Fe₂O₃ are observed to be 882.3 and 187.3 mA h g⁻¹, respectively. Compared with Fe₂O₃, the higher initial charge capacity and columbic efficiency are observed for Fe₂O₃/C composite, which could be attributable to good attachments between amorphous glucose-pyrolyzed carbon and Fe₂O₃ as presented in SEM images. The irreversible capacity loss in the first cycle could be resulted from uncomplete reverse conversion reaction and the formation of solid electrolyte interface film [5], and the existence of amorphous glucose-pyrolyzed carbon can ascribed to a shorter diffusion length for both the electron and Li⁺, and a larger electrode/electrolyte contact area of Fe₂O₃/C which facilitate the insertion and extraction of Li⁺.

Fig. 3 (b) illustrates the cycle profiles of Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{C}$ electrode at the charge/discharge current density of 100 mA g^{-1} . It can be seen that bare Fe_2O_3 fades rapidly at the first three cycles and its specific charge capacity decreases to only 45.9 mAh g^{-1} after 20 cycles. However, the $\text{Fe}_2\text{O}_3/\text{C}$ electrode exhibits a slower fade of the charge capacity, with a value of 263.7 mAh g^{-1} after 20 cycles, thus retaining 83.8% of the initial capacity. These results prove that the coating of an amorphous glucose-pyrolyzed carbon layer can restrain the structure damage of Fe_2O_3 .

Fig. 3 Initial charge–discharge (a) and cycling profiles (b) of Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{C}$

Conclusion

In summary, the $\text{Fe}_2\text{O}_3/\text{C}$ sample was synthesized by a simple, inexpensive and novel method. Owing to the stable structure and the good attachment between Fe_2O_3 and Carbon, $\text{Fe}_2\text{O}_3/\text{C}$ shows better electrochemical performance compared to bare Fe_2O_3 . The primary results illustrate that the as-prepared $\text{Fe}_2\text{O}_3/\text{C}$ could be improved and can be a promising anode material for lithium-ion batteries.

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