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Facile preparation and electrochemical properties of carbon coated Fe_3O_4 as anode material for lithium-ion batteries

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HIGHLIGHTS

- Nano-sized Fe_3O_4/C composite was prepared via a facile and productive route.
- Fe_3O_4/C composite is composed of Fe_3O_4 nanoparticles and carbon coating layer.
- Fe_3O_4/C electrode exhibits high specific capacity and stable cycling performance.
- Fe_3O_4/C electrode displays good rate-capability.

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ABSTRACT

Carbon coated Fe_3O_4 nanocomposite (Fe_3O_4/C) is synthesized via a simple sol–gel route and a subsequent carbon CVD process, with Fe_2O_3 xerogel as intermediate product. The nanoporous Fe_2O_3 xerogel is reduced to Fe_3O_4 during the CVD process. The prepared Fe_3O_4/C composite presents a well-distributed nanostructure composing of Fe_3O_4 nanoparticles coated with carbon layer. The electrode exhibits a stable reversible capacity of over 850 mAh g^{-1} at 0.1 A g^{-1}, excellent cycling performance and good rate capability. Both of the nano-scale particle size of Fe_3O_4 and the carbon layer contribute to the excellent electrochemical performance of Fe_3O_4/C. An increase in electrode capacity with cycling is observed for the prepared Fe_3O_4/C composite when cycled at 50 °C, which is similar to other reported transition metal oxides. The preparation process of Fe_3O_4/C composite is facile, mild and productive.

1. Introduction

As a kind of clean energy storage devices, lithium-ion batteries (LIBs) have been widely utilized in portable electronic devices, electric tools, and are beginning to be used in electric vehicles and hybrid electric vehicles [1]. For mobile application, a significant advance in energy storage density, power density and cycle life is required. Carbonaceous materials, especially graphite, are used as anodes in commercial LIBs because of their long cycle life, relative safety, low cost as well as a theoretical capacity of 372 mAh g^{-1} for LiC_6. To satisfy the increasing demands for high energy density batteries, various materials with higher specific capacity have been developed as new anode candidates, such as silicon-based materials [2–5], intermetallic alloys [6], and transition metal oxides [7–12].

Among the transition metal oxides (MO, M = Co, Mo, Ni, Cu, Fe, etc.), Fe_3O_4 as anode material is attracting much attention recently due to its high theoretical capacity of 926 mAh g^{-1}, environmental friendliness, low toxicity and natural abundance [13–15]. Additionally, Fe_3O_4 possesses higher electronic conductivity (2×10^4 S m^{-1}) than other transition metal oxides [15], which is desirable for electrode reaction. However, like other transition metal oxides, Fe_3O_4 also suffers from large volume change during lithiation/delithiation process, which leads to poor cycling stability with the active particle cracking or pulverization of electrodes.

In order to improve the electrochemical performance of Fe_3O_4 anode, many approaches have been employed, which can be mainly divided into two categories. One is the preparation of nanostructured materials such as nanospheres [16–18], hollow spheres [19,20], nanowires [21], nanorods [22] and nanospindle

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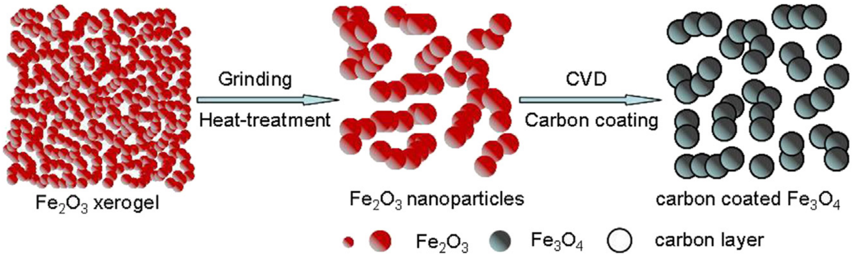

Scheme 1. Schematic illustration of the synthesis route of Fe_3O_4/C nano-composite.

[14]. Due to the large surface-to-volume ratio and small dimensions, the nanostructured electrode can partially alleviate the mechanical stress caused by large volume change, thus improve the cycling stability of Fe_3O_4 anode [23]. Chen et al. [20] produced porous hollow Fe_3O_4 beads by a solvothermal route, which exhibited a reversible capacity of 500 mAh g^{-1} at 100 mA g^{-1} for 50 cycles. Hierarchical hollow Fe_3O_4 micropheres were prepared by Xiong et al. [24], which presented a high specific capacity of 851 mAh g^{-1} at 1 C and a stable cycling performance for 50 cycles. The other effective strategy is fabricating Fe_3O_4-based composites by introducing a second component, which acts as a buffer to reduce the large volume change and prevent active nanoparticles from aggregation during electrochemical cycling, leading to an improved cycling stability. Carbon is frequently used as the buffer component to enhance the electrochemical performance of Fe_3O_4 because of its high tolerance to mechanical stress and good electronic conductivity [13]. Yuan et al. [25] prepared mesopores Fe_3O_4@C microcapsules by hydrothermal route, which demonstrated a high specific capacity of 1010 mAh g^{-1} for 50 cycles. Graphene anchored with Fe_3O_4 nanoparticles were prepared at very dilute and hydrothermal conditions, which exhibited a reversible capacity of 675 mAh g^{-1} after 50 cycles at 50 mA g^{-1} [26]. Zhou et al. produced graphene-wrapped Fe_3O_4 composite through *in situ* reduction of iron hydroxide existing between graphene nanosheets, which showed an excellent cycling stability and rate capability [27].

In this work, we use Fe_2O_3 xerogel as precursor for the first time to prepare Fe_3O_4/C nanocomposite used as anode material for lithium-ion batteries. The nano-porous feature of Fe_2O_3 xerogel can make the preparation of nanosized Fe_2O_3 particles much easier with a simple grinding process. The sol–gel process was employed for the preparation of Fe_2O_3 xerogel, which allows a high productivity. With chemical vapor deposition (CVD) of carbon, the Fe_2O_3 can be reduced to Fe_3O_4 and at the same time carbon coated nanosized Fe_3O_4 (Fe_3O_4/C) was *in situ* produced. The preparation of Fe_3O_4/C nano-composite is facile, mild and mass-productive. The structure characteristics and the electrochemical properties of Fe_3O_4/C were investigated.

2. Experimental

2.1. Preparation of carbon coated Fe_3O_4 nano-composite

The preparation of the nano-sized Fe_3O_4/C can be briefly described by the following process. The schematic illustration is shown in Scheme 1. The Fe_2O_3 xerogel precursor was prepared via a sol–gel route and a subsequent ambient drying process. In a typical experiment, 2.43 g of $FeCl_3$ (0.015 mol) was dissolved in 100 ml of ethanol under magnetic agitation to form a clear red–orange solution, in which 2.7 ml of distilled water (0.15 mol) was then added. After stirring for 15 min, 10.48 ml of propylene oxide (0.15 mol) as basic catalyst was introduced, which made the solution rapidly change to an intense dark red–brown color, accompanying by a significant heat generation. Gel formation occurred within several minutes. The resulted gel was aged in ethanol for 48 h under ambient conditions. Then fresh ethanol was used to replace the aging solution and this step was repeated every 12 h for 3 times to remove the unreacted chemicals and ensure a complete solution exchange. After solvent exchange, the wet gel was dried at room temperature for 24 h and then oven-dried at 80 °C for 48 h to obtain Fe_2O_3 xerogel. After grinding, the Fe_2O_3 xerogel was heated at 600 °C in air for 3 h to prepare Fe_2O_3 powders, which were transferred into a reaction tube for carbon coating by a chemical vapor deposition process. A toluene vapor carried by argon gas was flowed through the reaction tube at a rate of 0.1 L min^{-1}. The reaction temperature was maintained at 800 °C for 30 min to obtain Fe_3O_4/C composite.

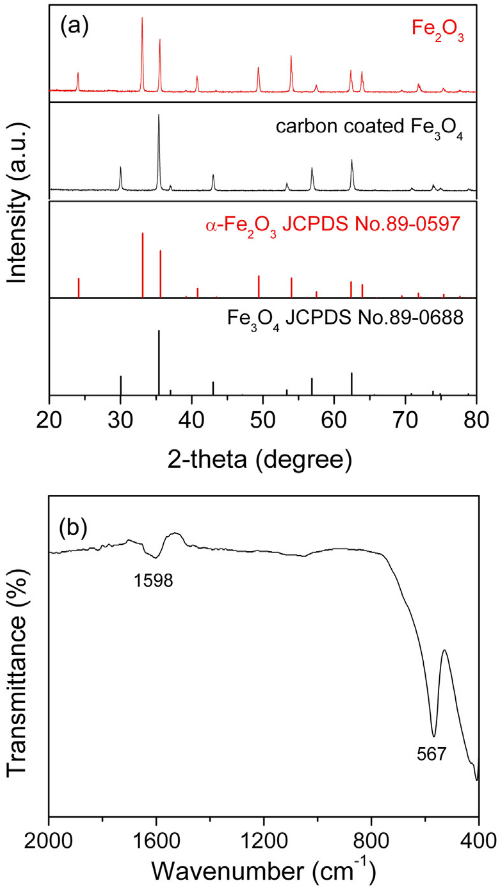

Fig. 1. (a) XRD patterns of Fe_2O_3 and Fe_3O_4/C samples. Also shown are JCPDS patterns for α-Fe_2O_3 (no. 89-0597) and Fe_3O_4 (no. 89-0688). (b) FTIR spectrum of Fe_3O_4/C sample.