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Fe_3O_4/C composite with hollow spheres in porous 3D-nanostructure as anode material for the lithium-ion batteries

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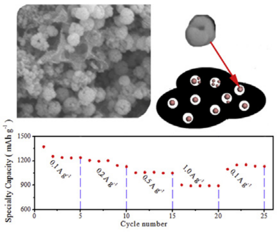
HIGHLIGHTS

- The composite with hollow spheres in porous 3D nanostructure was prepared.
- This structure endowed composite better volume buffer and electric conductivity.
- The Fe_3O_4/C composite exhibited excellent electrochemical properties.

GRAPHICAL ABSTRACT



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ABSTRACT

3d transition-metal oxides, especially Fe_3O_4, as anode materials for the lithium-ion batteries have been attracting intensive attentions in recent years due to their high energy capacity and low toxicity. A new Fe_3O_4/C composite with hollow spheres in porous three-dimensional (3D) nanostructure, which was synthesized by a facile solvothermal method using $FeCl_3 \cdot 6H_2O$ and porous spongy carbon as raw materials. The specific surface area and microstructures of composite were characterized by nitrogen adsorption-desorption isotherm method, FE-SEM and HR-TEM. A homogeneous distribution of hollow Fe_3O_4 spheres (diameter ranges from 120 nm to 150 nm) in the spongy carbon (pore size > 200 nm) conductive 3D-network significantly reduced the lithium-ion diffusion length and increased the electrochemical reaction area, and further more enhanced the lithium ion battery performance, such as discharge capacity and cycle life. As an anode material for the lithium-ion battery, the title composite exhibit excellent electrochemical properties. The Fe_3O_4/C composite electrode achieved a relatively high reversible specific capacity of 1450.1 mA h g^{-1} in the first cycle at 100 mA g^{-1}, and excellent rate capability (69% retention at 1000 mA g^{-1}) with good cycle stability (only 10% loss after 100 cycles).

1. Introduction

Recently, compared with the nickel-cadmium (Ni-Cd) batteries and nickel-metal hydride (Ni-MH) batteries, LIBs as potential power sources for pure electric vehicles (EVs), hybrid electric vehicles (HEVs) and plug in hybrid electric vehicles (PHEVs) have also been recognized due to their lighter weight, lower self-discharge property, higher energy density [1,2]. In order to meet the increasing demand intensified investigations are required to develop a new-generation Li-ion batteries with dramatically improved performances, including specific energy and volumetric energy density, cyclability, charging rate, stability, and safety [3,4]. Graphite as the commercial anode material for lithium-ion batteries, however, allows insertion-way of only one Li-ion within six carbon atoms, with

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a resulting low theoretical gravimetric capacity (372 mA h g^{-1}). This low theoretical capacity restricts the applications of LIBs [5–7]. High theoretical specific capacities (e.g. > 600 mA h g^{-1}) has been proposed for the transition metal oxides based on a novel conversion mechanism, including MnO_2 [8,9], Fe_3O_4 [10,11], Fe_2O_3 [12,13], CoO [14], Co_3O_4 [15,16], and NiO [17], and making these oxides promising anode materials for high performance LIBs. Among transition metal oxides, Fe_3O_4 exhibits high electrical conductivity ($2*10^4$ S m^{-1}), high theoretical capacity (924 mA h g^{-1}), and low conversion potential, making it one of the most promising anode candidate for LIBs [18,19]. However, a major challenge associated with Fe_3O_4 as anode material for LIBs is the large volume change (about 100%) during the processes of insertion and de-insertion of Li^+ [20,21]. Moreover, Fe_3O_4 suffers from the same problem as other transition metal oxides, such as surface instability and low initial reversibility for the pulverization of active materials, which are attributed to apparent phase and morphology changes accompanied by typical conversion reactions [22–24].

However, versatile controlled synthetic methods for low dimensional Fe_3O_4 nanostructures have been developed that may improve its unsatisfactory electrochemical performance. Investigations on nanocomposite reveal that carbon materials are beneficial to electrode material of transition metal oxides in two main ways [25–31]: Firstly by increasing the electrical conductivity, and secondly by reducing the volume change via accommodating the stresses, which are arose from volume increasing [32,33]. Such as Dong et al. [34] reported a preparation of hierarchical structures of carbon-coated Fe_3O_4 nanoparticles decorated on conductive multi-walled carbon nanotubes (CNTs) backbone (CNT@Fe_3O_4-C) with a reversible capacity of 1080 mA h g^{-1} at 500 mA g^{-1} after 700 cycles. Graphene-wrapped Fe_3O_4 hollow nanospheres [35] had been synthesized with a higher reversible capacity than CNT@Fe_3O_4-C. Fe_3O_4 nanoparticles & carbon composite of 1D-nanostructure demonstrated high reversible capacity at high current density and long cycling-life. Meanwhile, Fe_3O_4 composite of 3D-nanostructure with graphene (2D carbon material) exhibited excellent reversible capacity. Above all, the specific surface area and porosity are essential factors that affect electrochemical performances of carbon materials, 3D-nanostructure porous carbon materials exist potential application prospect in composite as anode material for LIBs [4].

In this study, we designed and synthesized a special 3D-nanostructure with a hollow Fe_3O_4 spheres into spongy carbon matrix, by a facile and disposable solvothermal method. The hollow spheres in porous unique architecture with 3-dimensional void can relieve the huge volume variation of Fe_3O_4 during cycling processes, and prevent the aggregation of hollow Fe_3O_4 spheres from aggregation. Furthermore, nano-porous spongy carbon could offer electronic conductivity. Herein, the title composite was found to exhibit a highly reversible capacity and excellent cycle performance as anode material for LIBs.

2. Experimental

2.1. Synthesis

The schematic synthesis process pattern of title composite was illustrated in Fig. 1. The composite was prepared in two steps. The spongy carbon was obtained, and then the hollow Fe_3O_4 spheres were decorated on the spongy carbon by solvothermal reaction. The mixture of $CaCO_3$ and phenolic resin was carbonization at 800 °C in Ar atmosphere for 2 h. After the treatment of acid (0.1 mol L^{-1} HCl) corroding, the solution was dried at 80 °C for 10 h and the spongy carbon was obtained. The spongy carbon, $FeCl_3 \cdot 6H_2O$, PVP, and carbamide were dissolved in 45 mL of $C_2O_2H_6$ solution. The Fe_3O_4/C composite was synthesized by the solvothermal method at 200 °C for 24 h.

2.2. Characterization

Phase analysis was conducted using powder X-ray diffraction (XRD, D/MAX2500PC) with Cu *Ka* radiation. The particle

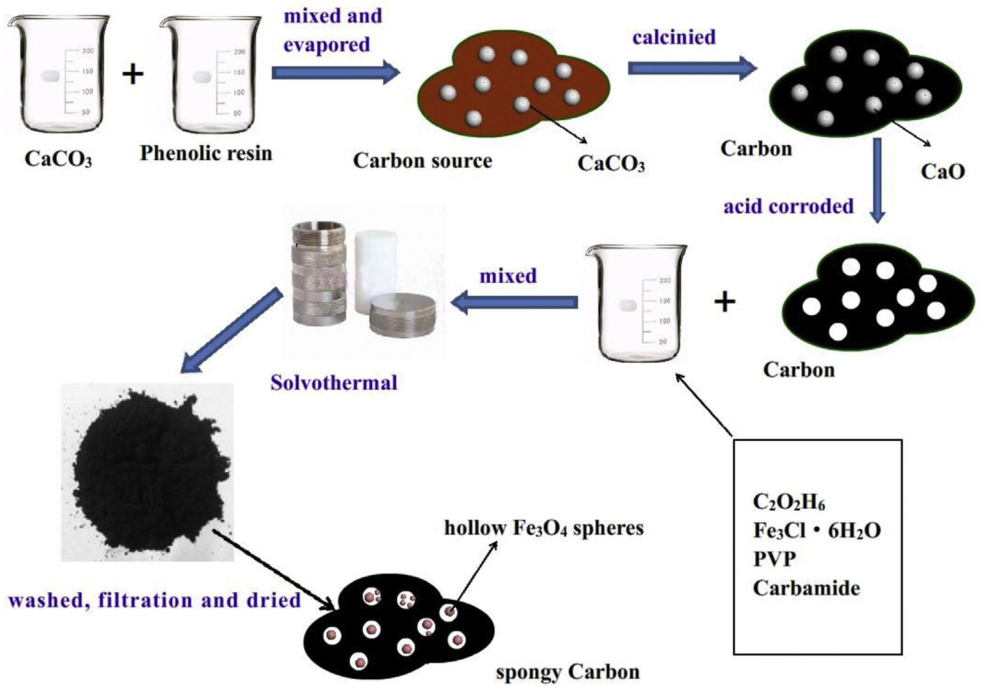

Fig. 1. Schematic illustration of Fe_3O_4/C composite preparation.