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N-doped coaxial CNTs@α-Fe_2O_3@C nanofibers as anode material for high performance lithium ion battery

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ABSTRACT

N-doped coaxial CNTs@α-Fe_2O_3@C nanofibers have been successfully synthesized according to a facile solvothermal/hydrothermal method. The obtained CNTs@α-Fe_2O_3@C nanofibers composites exhibited special three-dimensional (3-D) network structure, which endows they promising candidate for anode materials of lithium ion battery. The coaxial property of CNTs@α-Fe_2O_3@C nanofibers could significantly improve the cycling and rate performance owing to the acceleration of charge/electron transfer, improvement of conductivity, maintaining of structural integrity and inhibiting the aggregation. The α-Fe_2O_3 nanoparticles with small size and high percentage of N-doped amount could further improve the electrochemical performance. As for the CNT@α-Fe_2O_3@C nanofibers, the capacity presented a high value of 1255.4 mAh/g at 0.1 C, and retained at 1213.4 mAh/g after 60 cycles. Even at high rate of 5 C, the capacity still exhibited as high as 319 mAh/g. The results indicated that the synthesized N-doped coaxial CNTs@α-Fe_2O_3@C nanofibers exhibited high cycling and rate performance.

1. Introduction

In the recent few years, tremendous efforts have been focusing on resolving the excessive energy consumption of fossil fuels due to the rapid economic development. Clean energy is becoming one of the promising candidates to satisfy the energy demand of human beings and reduce the fossil fuels consumption, greenhouse gas emission [1,2]. Rechargeable lithium ion batteries (LIBs) are increasingly developed as an energy storage device for portable electronics and electric vehicles owing to its promising potential as clean energy source, which attract great attention in the area of the electrode materials. As the key part of LIBs, anode materials, which are cheap, nontoxic, high capacity and stable, are the main requirements in the latest study [3–5]. However, the commercial anode material of LIBs, graphite, possesses a low practical capacity about 320 mAh/g [6]. Therefore, it is urgent to seek higher capacity anode materials to replace graphite. Recently, many various high capacity anode materials were developed, such as Co_3O_4 [7], Mn_3O_4 [8] and Si [9]. Among these materials, iron oxide, α-Fe_2O_3 [10,11], γ-Fe_2O_3 [5,12], and Fe_3O_4 [13], attracted great attention in the application as anode materials owning to their abundance, safety, high power density and high theoretic capacity. Specially, α-Fe_2O_3 becomes a prior selection among these promising candidates for its easy synthesis compared with γ-Fe_2O_3 and a theoretic capacity (1007 mAh/g) even higher than Fe_3O_4 (926 mAh/g).

However, a main problem of α-Fe_2O_3 is that the volume changes is huge (>200%%) during the cycling for the insertion/extraction of Li ions, especially at high current density. Besides, low conductivity, which exists in many metal oxide anode materials, is another serious problem of α-Fe_2O_3. The above-mentioned reasons could lead to poor cycle performance, capacity and rate performances [14–16]. One of effective strategies to solve the volume change of α-Fe_2O_3 is to design a special nanostructure material and introduce carbon materials, such as graphene oxide (GO), CNT and amorphous carbon. Great efforts have been done to synthesize special nanostructures, such as cubes [17,18], nanodisk [16,19], hollow structures [14,20,21], nanoflakes [22], spheres, [23] rods [24,25], nanotubes [10], spindles [26], raspberry [27] and foam [28] to improve the performance in a certain degree. Besides, many α-Fe_2O_3 composites, such as α-Fe_2O_3@GO

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[16,23], α-Fe_2O_3@CNT [1,23,29] and α-Fe_2O_3@carbon composite [30–32], have exhibited a relatively good electrochemical performance. Chai et al. [30] prepared carbon-coated Fe_2O_3 nanocrystals, which showed high capacity of 826 mAh/g after 20 cycles at 0.1 A/g. Ji et al. [1] prepared N-doped α-Fe_2O_3 nanoparticle loaded on carbon nanofiber, which maintained about 400 mAh/g at 0.1 A/g after 100 cycles. However, little attention has been focused on the coaxial CNTs@α-Fe_2O_3@C nanofibers, especially for N-doping nanofibers.

Our previous study showed that α-Fe_2O_3@CNT composite can improve the cycling and rate performance of LIBs, and the capacity can retain more than 700 mAh/g at 0.1 C after 30 cycles [2]. However, the capacity is still not very high. With the increasing demand of high energy storage devices, an anode material with high capacity, long cycling and high rate are needed. Herein, we reported a facile hydrothermal/solvothermal method to synthesize N-doped coaxial CNTs@α-Fe_2O_3@C nanofibers. The material was tested as anode materials for LIB, which showed high cycling and rate performance. N-doped coaxial CNTs@α-Fe_2O_3@C nanofibers can retain a high capacity about 1255.4 mAh/g in the first 10 cycles at 0.1 C and 319 mAh/g was obtained at a 5 C high rate. When the rate returned back to 0.1 C after 50 cycles, the capacity of coaxial CNTs@α-Fe_2O_3@C nanofibers is 1213.4 mAh/g. The main advantages of the synthesized N-doped coaxial CNTs@α-Fe_2O_3@C nanofibers have three aspects: (1) PVP, a kind of nonionic surfactant, not only act as a soft template to prepare small particles to enhance the effective capacity by increasing the surface area with lithium ion, but also used as N source for N-doped composites, which can offer more sites for lithium ions to enhance the capacity. (2) CNT can improve the conductivity of electrode by promoting charge transfer, relieving stress caused by the volume variation and inhibiting the aggregation during the synthesis process and cycling process. (3) The carbon layer could not only further enhance the conductivity, but also restrict the expansion of Fe_2O_3 to enhance the stability.

2. Experimental

2.1. Materials

All the chemicals were commercially obtained with analytical grade without further purification. $FeCl_3 \bullet 6H_2O$ and anhydrous sodium acetate (NaOAc) were obtained from Sinopharm Chemical Reagent Co., Ltd. EG and anhydrous glucose was from Shanghai Ling Feng Chemical Reagent Co., Ltd. PVP was purchased from China Medicine Group Shanghai Chemical Reagent Co., Ltd. The surface area of the Flotube 9000 CNTs, purity of which is 97%%, is 240 m^2/g. Deionized water was used in the experiments.

2.2. Synthesis of oxdized carbon nanotube

Typically, a suspension liquid which was prepared by adding 1.0 g CNT into a mixed solution of 10 mL HNO_3 and 30 mL H_2SO_4 was stirred for 10.0 min. Then the suspension liquid was transferred to Teflon-lined autoclave and heated at 80 °C for 35 min. The products were filtered, washed by DI water three times after naturally cooling to room temperature and dispersed in 100 mL DI water to form suspension liquid [33].

2.3. Synthesis of CNTs@α-Fe_2O_3 nanofibers

The CNT@α-Fe_2O_3 composite was synthesized by a facile hydrothermal/solvothermal method. Typically, 0.8 g $FeCl_3 \bullet 6H_2O$ was added into 10 mL ethylene glycol (EG) with glass rod stirring to form a homogeneous solution. Then, 2 g polyvinylpyrrolidone (PVP) was added into aforementioned solution by ultrasound and stirring for 5 min, respectively, followed by 0.74 g. NaOAc was dissolved in the aforementioned solution with glass rod stirring for 5 min. Finally, 10 mL CNT suspension liquid (0.01 g/mL) was added into the solution to form final solution. The final solution was transferred into a 50 mL Teflon-lined autoclave and heated at 200 °C for 12 h. The products were obtained by centrifugation and repeatedly washed with anhydrous ethanol and DI water.

2.4. Synthesis of CNTs@α-Fe_2O_3@C nanofibers

The CNT@α-Fe_2O_3 products were dissolved in 10 mL water, followed by adding 30 mL DI water with 2 g glucose dissolving in it. Then, 20 mL anhydrous ethanol was added in the former solution to form final solution. The final solution was transferred in 100 mL Teflon-lined autoclave and heated at 190 °C for 12 h. The products were obtained by centrifugation and repeatedly washed with anhydrous ethanol and DI water and were dried in the stove at 80 °C for 12 h. The dried products were heated at 600 °C for 12 h in a tube furnace with N_2 atmosphere at 6 °C/min.

2.5. Characterization

The crystal structure was characterized by X-ray powder diffractometer (XRD/D8 ADVANCE Da Vinci). The structure and morphology were analyzed by field emission scanning electron microscope (FESEM/JEOL JSM-7800F Prime) and 120 kV Biology transmission electron microscope (TEM/Tecnai G2 Spirit Biotwin). X-ray photoelectron spectroscopy (XPS/AXIS Ultra DLD) was used to investigate the surface chemical species and states. Thermo Gravimetric Analyzer (TGA/Pyris 1 TGA) was conducted to measure the weight ratio under nitrogen atmosphere at a heating rate of 10 °C/min from 20 to 900 °C.

2.6. Electrochemical characterization

Lithium ion batteries were prepared by CR2032 coin cells. Typically, Fe_2O_3 nano-composite (80 wt%%), acetylene black (10 wt%%) and polyvinylidene fluoride (PVDF) (10 wt%%) binder in *N*-methylpyrrolidone (NMP) were mixed to fabricate working electrodes. Then the copper foil current collector coated by slurry was dried at 120 °C for 12 h in vacuum oven. The diameter of the copper foil is about 10 mm. Lithium disc was used as counter electrode. An argon-filled glove box was used to assemble coin cells. 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate/diethyl carbonate (EC/DMC/DEC, 1/1/1 by volume) was used as electrolyte. The amount of electrolyte in each cell is about 0.3−0.35 mL (6−7 drops). Galvanostatic tests by LAND battery testing system were measured between 0.01 and 3.00 V (versus Li^{++}/Li) at different C. To understand the reaction mechanism, cyclic voltammetry (CV) measurement was conducted on electrochemical workstation (Zahner IM6e) between 0.01 and 3.00 V at a scan rate of 0.3 mV/s. Electrochemical impedance spectroscopy (EIS) was carried out before cycle on the same instrument from 0.1 MHz to 0.1 Hz with an AC voltage amplitude of 5 mV.

3. Results and discussion

Fig. 1 shows the illustration of the synthesis process for N-doped CNTs@α-Fe_2O_3@C nanofibers, which included four steps. Firstly, the CNT was treated by concentrated nitric acid and sulfuric acid (1:3 by volume), which can modify the surface of CNT with many functional oxygen-containing groups, such as –OH or –OOH. Secondly, α-Fe_2O_3 was prepared according to solvothermal method with the mixture of oxdized CNT, precursor and PVP. Precursor attached on the surface of CNT by the functional groups

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