Synthesis and characterization of carbon-coated Fe₃O₄ nanoflakes as anode material for lithium-ion batteries

Yun-hai Wan a, Xiao-qin Shi a, Hui Xia a,b,*, Jian Xie c,***

a School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China
b Herbert Gleiter Institute of Nanoscience, Nanjing University of Science and Technology, Nanjing 210094, China
c Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

A R T I C L E   I N F O

Article history:
Received 19 April 2013
Received in revised form 9 July 2013
Accepted 18 August 2013
Available online 25 August 2013

A B S T R A C T

The carbon-coated Fe₃O₄ nanoflakes were synthesized by partial reduction of monodispersed hematite (Fe₂O₃) nanoflakes with carbon coating. The carbon-coated Fe₃O₄ nanoflakes were characterized by X-ray diffraction, Raman spectroscopy, field emission scanning electron microscopy, transmission electron microscopy, and galvanostatic charge/discharge measurements. It has been demonstrated that Fe₃O₄ can be completely converted to Fe₂O₃ during the reduction process and carbon can be successfully coated on the surface of Fe₃O₄ nanoflakes, forming a conductive matrix. As anode material for lithium–ion batteries, the carbon-coated Fe₃O₄ nanoflakes exhibit a large reversible capacity up to 740 mAh g⁻¹ with significantly improved cycling stability and rate capability compared to the bare Fe₂O₃ nanoflakes. The superior electrochemical performance of the carbon-coated Fe₃O₄ nanoflakes can be attributed to the synthetic effects between small particle size and highly conductive carbon matrix.

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1. Introduction

Lithium-ion batteries (LIBs) are becoming not only the dominant power sources for portable electronic devices but also the potential power sources for electric vehicles and hybrid electric vehicles [1]. Their energy density and power density mainly depend on the physical and electrochemical properties of both cathode and anode materials [1,2]. For commercial LIBs, graphite is the most widely used anode material because of its low cost, high abundance, and outstanding electrochemical performance. But the fact that the theoretical specific capacity of graphite is only 372 mAh g⁻¹ (by forming intercalation compounds of LiC₁₀) limits the further development of LIBs [3]. To develop the next-generation high-performance LIBs, efforts have been devoted to searching new anode materials with larger specific capacity. Among those new candidates, Fe₃O₄ has been widely considered as one of the most promising anode materials for LIBs due to its large theoretical capacity (924 mAh g⁻¹), high electronic conductivity (2 x 10⁴ S m⁻¹), good safety, low cost, eco-benignity and natural abundance [4–10]. However, Fe₂O₃ based anodes suffer from the poor cycling stability caused by the drastic volume change during the repeated Li insertion/extraction based on the conversion mechanism [11].

It has been well demonstrated that the cycling stability of Fe₂O₃ could be significantly improved in nanostructured electrode materials due to their large surface-to-volume ratio and small dimensions, which can alleviate the mechanical stress associated with Li insertion/extraction. Various nanostructures of Fe₂O₃, including nanoparticles [12–16], nanoflakes [17], nanorods [8], and nanobelts [18], have been synthesized and tested in lithium-ion batteries. Recently, several groups reported the synthesis of various Fe₂O₃ nanostructures with differing aspect ratios by a simple hydrothermal processing of aqueous FeCl₃ solution [19,20]. The shape and size of the Fe₂O₃ nanoparticles can be easily tailored by changing the reaction temperature, time and NH₄H₂PO₄ concentration. This could be a facile method to synthesize various Fe₂O₃ nanostructures as Fe₂O₃ can be easily reduced to Fe₃O₄ without changing the morphology [20].

Despite their advantages, nanostructured electrodes also have some serious drawbacks, such as large irreversible capacity resulting from the decomposition of electrolyte on active materials, electrode pulverization during cycling, and nanoparticle agglomeration associated with low thermodynamic stability. In the efforts to solve these problems, strategies like carbon-coating [21,22] and making porous and hollow structures [23–26] have
been demonstrated to be very beneficial. Carbon-coating is one of the most widely used surface modification techniques. It has been applied for anode materials as it may serve as perfect barrier to protect inner active material and maintain its high capacity [11]. Recently, carbon coated Fe$_2$O$_3$ and Fe$_3$O$_4$ nanoparticles have been extensively studied as anode materials for LIBs. For example, carbon-coated single crystalline Fe$_3$O$_4$ nanowires [6], Fe$_3$O$_4$/carbon core–shell nanorods [27], and carbon-coated Fe$_3$O$_4$ nanospindles [4] have been prepared to improve the electrochemical performance of the pure Fe$_2$O$_3$ electrodes. The carbon coated Fe$_2$O$_3$ and Fe$_3$O$_4$ nanoparticles can deliver large reversible capacities in the range between 700 and 900 mAh g$^{-1}$ depending on the morphology and carbon content, and they usually exhibit better cycling performance and rate capability compared to the bare Fe$_2$O$_3$ and Fe$_3$O$_4$ nanoparticles. In this work, Fe$_3$O$_4$ nanoflakes were successfully synthesized by the hydrothermal treatment with the FeCl$_3$ solution. Carbon was coated on the Fe$_3$O$_4$ nanoflakes by another hydrothermal treatment using glucose. After that, the carbon-coated Fe$_3$O$_4$ nanoflakes were converted to carbon-coated Fe$_3$O$_4$ nanoflakes by thermal annealing in Ar atmosphere. It was found that the carbon-coated Fe$_3$O$_4$ nanoflakes exhibit significantly improved cycling stability and rate capability compared to the bare Fe$_2$O$_3$ nanoflakes. 

2. Experimental

2.1. Synthesis of Fe$_2$O$_3$ nanoflakes

The Fe$_2$O$_3$ nanoflakes were synthesized by a hydrothermal treatment. Briefly, 0.0066 g NH$_4$H$_2$PO$_4$ was first dissolved into 80 mL distilled water. Then, 0.432 g FeCl$_3$·6H$_2$O was gradually added into the above solution under continuous vigorous stirring. After stirring for 20 min, the solution was transferred into a Teflon-lined stainless-steel autoclave with a capacity of 100 mL. The autoclave was sealed and heated at 200 ℃ for 48 h in an electric oven. After the hydrothermal reaction, the autoclave was cooled down to room temperature naturally. The red precipitate was separated from the solvents by filtration and then washed with distilled water and absolute ethanol for several times. The samples obtained after drying at 80 ℃ for 24 h were Fe$_2$O$_3$ nanoflakes.

2.2. Synthesis of carbon-coated Fe$_2$O$_3$ nanoflakes

To synthesize the carbon-coated Fe$_2$O$_3$ nanoflakes, 0.1 g Fe$_2$O$_3$ nanoflakes were dispersed into 20 mL distilled water by ultrasonication for 1 h to form a suspension. After that, 0.31 g glucose and 5 mL ethanol were added in the above suspension with continuous gentle stirring. After stirring for 10 min, the solution was transferred into a Teflon-lined stainless-steel autoclave with a capacity of 30 mL. The autoclave was sealed and heated at 190 ℃ for 12 h in an electric oven. After cooling down to room temperature, the carbon precursor-coated Fe$_2$O$_3$ nanoflakes were harvested by centrifugation and washed with distilled water, then dried in an electric oven at 80 ℃ for 24 h. After that, the resulting samples were filled in an alumina crucible and heated at 600 ℃ for 6 h in an electric furnace under Ar atmosphere to carry out the carbon-thermal reduction. The finally obtained samples were carbon-coated Fe$_2$O$_3$ nanoflakes.

2.3. Structural and morphology characterization

The crystallographic information and composition of the synthesized carbon-coated Fe$_2$O$_3$ nanoflakes were characterized by X-ray diffractometer (XRD, Shimadzu X-ray diffractometer 6000) with Cu Kα radiation ($λ = 1.5418$ Å) and Raman spectroscopy (Jobin-Yvon T6400 Micro–Raman system). The morphology of the samples was investigated by field-emission scanning electron microscopy (FESEM, Hitachi S4300) and transmission electron microscope (TEM, JEOL, JEM-2010). The carbon content of the composite was quantified by thermogravimetric analysis (TGA, Shimadzu DTG-60H). The TGA measurement was carried out in air atmosphere with a heating rate of 5 ℃ min$^{-1}$ from ambient temperature to 750 ℃.

2.4. Electrochemical measurements

For making the electrodes, 80 wt% active material (Fe$_3$O$_4$ nanoflakes and carbon-coated Fe$_3$O$_4$ nanoflakes), 10 wt% acetylene black (Super-P), and 10 wt% polyvinylidene fluoride (PVDF) binder were mixed in 1-methyl-2-pyrrolidone (NMP) to form a slurry. The slurry was coated onto an etched Cu foil current collector using a doctor–blade and then dried at 120 ℃ for 2 h to remove the solvent. The dried electrodes were pressed and cut into small disks (10 mm in diameter) and the small disks were further dried at 80 ℃ in a vacuum oven for 12 h before battery tests. Half cells using Li foil as both counter and reference electrodes were assembled with Labmade Swagelok cells in a glove box. 1 M LiPF$_6$ in ethylene carbonate and diethyl carbonate (EC/DEC, v/v = 1:1) solution was employed as the electrolyte and Celgard 2400 was used as the separator. Galvanostatic charge and discharge measurements were carried out in the voltage range between 0.01 and 3 V at different current densities using LAND CT2001A battery testing system at room temperature.

3. Results and discussion

The phase purity and crystallinity of the resulting samples were examined by powder XRD and Raman spectroscopy. Fig. 1 shows the XRD patterns of the bare Fe$_2$O$_3$ nanoflakes and carbon-coated Fe$_3$O$_4$ nanoflakes. As shown in Fig. 1a, all of the diffraction peaks from the XRD pattern of the bare Fe$_2$O$_3$ nanoflakes can be exclusively indexed to the trigonal α-Fe$_2$O$_3$ (JCPDS no. 87-1165) with no impurity phases being observed. When the Fe$_3$O$_4$ nanoflakes were coated with carbon and heated in Ar atmosphere at 600 ℃, a phase transition took place in the iron oxide. Except for one small peak, all other diffraction peaks shown in Fig. 1b can be indexed to face-centered Fe$_3$O$_4$ (JCPDS no. 65-3107). The small diffraction peak at about 26 ℃ can be assigned to graphite (0 0 2), indicating graphitization of the coated carbon layers during the annealing process [28]. The Raman spectra of the bare Fe$_3$O$_3$
nanoflakes is shown in Fig. 2a, where six peaks can be observed in the range between 150 and 2000 cm\(^{-1}\). As hematite belongs to the \(D_4h\) crystal space group with two \(A_{1g}\) modes and five \(E_g\) modes [29–31], two peaks at 218 and 483 cm\(^{-1}\) are assigned to the \(A_{1g}\) modes and three peaks at 282, 392, and 587 cm\(^{-1}\) are assigned to \(E_g\) modes [20]. Another peak at 1283 cm\(^{-1}\) can be assigned to hematite two-magnon scattering [32]. Fig. 2b shows the Raman spectrum of the carbon-coated Fe\(_3\)O\(_4\) nanoflakes. The characteristic Raman scattering peaks for Fe\(_3\)O\(_4\) powders are observed at 301, 528, and 675 cm\(^{-1}\), corresponding to the \(E_g\) T\(_{2g}\) and A\(_{1g}\) vibration modes, respectively [29,33]. Another two peaks observed at about 1338 and 1596 cm\(^{-1}\) correspond to the D and G bands for graphite.

Fig. 3a and b shows the FESEM images of the as-prepared \(\alpha\)-Fe\(_2\)O\(_3\) nanoflakes with low and high magnifications, respectively. It can be seen that large-scale Fe\(_2\)O\(_3\) nanoparticles with similar size and flake morphology have been produced by the hydrothermal treatment. Fig. 3c and d shows the TEM images of the as-prepared \(\alpha\)-Fe\(_2\)O\(_3\) nanoflakes. As shown in Fig. 3c, the Fe\(_2\)O\(_3\) nanoflakes exhibit a similar round shape with an average diameter of about 100 nm and a thickness of about 50 nm. The magnified TEM image of a single Fe\(_2\)O\(_3\) flake in Fig. 3d shows that the flake has a mesoporous structure composed of interconnected Fe\(_2\)O\(_3\) nanocrystallines. The inset in Fig. 3d shows a high-resolution TEM image taken from the Fe\(_2\)O\(_3\) flake, where a lattice spacing of about 2.5 Å corresponding to the (1 1 0) plane of \(\alpha\)-Fe\(_2\)O\(_3\) can be clearly observed.

Fig. 4a and b shows the FESEM images of the carbon-coated Fe\(_3\)O\(_4\) nanoflakes with low and high magnifications, respectively. It can be seen that the particles retained the flake morphology after the carbon-thermal reduction. TEM image in Fig. 4c shows that the flaky Fe\(_3\)O\(_4\) nanoparticles are embedded in a carbon matrix. The Fe\(_3\)O\(_4\) nanoflakes exhibit similar particle size as the Fe\(_2\)O\(_3\) nanoflakes. As shown in Fig. 4d, the surface of Fe\(_2\)O\(_3\) nanoflakes is covered with carbon layers although with different thickness. The outside carbon layers are interconnected, forming a conductive matrix for the embedded Fe\(_3\)O\(_4\) nanoflakes. The high-resolution TEM image (inset in Fig. 4d) taken from the carbon-coated Fe\(_2\)O\(_3\) nanoflake shows clear lattice fringes with a lattice spacing of 0.48 nm, corresponding to the (1 1 0) plane of Fe\(_2\)O\(_3\). The carbon content of the composite was evaluated by TGA. According to the weight loss between 200 and 600 °C (Fig. 5), the carbon content for the carbon-coated Fe\(_3\)O\(_4\) nanoflakes is estimated to be about 17 wt%.

To investigate the electrochemical performance, galvanostatic charge/discharge measurements were carried out on both the carbon-coated Fe\(_2\)O\(_3\) nanoflake electrode and the pure Fe\(_2\)O\(_3\) nanoflake electrode. Fig. 6a shows the charge/discharge curves of the Fe\(_2\)O\(_3\) nanoflake electrode at various cycle numbers at a
constant current density of 200 mA g\(^{-1}\) in the voltage range between 0.01 and 3.0 V (vs Li/Li\(^+\)). The first discharge and charge curves of the pure Fe\(_2\)O\(_3\) electrode show voltage plateaus at about 0.8 and 1.6 V, respectively, corresponding to the reduction/oxidation reactions during lithium insertion/extraction. The first discharge and charge capacities of the Fe\(_2\)O\(_3\) nanoflake electrode are 1393 and 889 mAh g\(^{-1}\), respectively, giving a coulombic efficiency of about 64%. After the first cycle, the charge and discharge are highly reversible with negligible irreversible capacity. The irreversible capacity loss of the Fe\(_2\)O\(_3\) nanoflake electrode for the first cycle is probably due to incomplete conversion reaction and the solid electrolyte interface (SEI) layer formation at the electrode/electrolyte interface caused by the reduction of electrolyte [34]. Although the initial reversible capacity of the Fe\(_2\)O\(_3\) nanoflake electrode is high, the capacity fading is quick with cycling. For the carbon-coated Fe\(_2\)O\(_3\) nanoflake electrode, the first discharge and charge curves show similar voltage plateaus as the Fe\(_2\)O\(_3\) nanoflake electrode (Fig. 6b), corresponding to the redox reactions during lithiation/delithiation processes. The first discharge and charge capacities of the carbon-coated Fe\(_2\)O\(_3\) nanoflake electrode are 1050 and 738 mAh g\(^{-1}\), respectively, with a coulombic efficiency of about 70%. The initial reversible capacity of the carbon-coated Fe\(_2\)O\(_3\) nanoflake electrode is smaller than that of the bare Fe\(_2\)O\(_3\) nanoflake electrode, which could be attributed to the high carbon content in the nanocomposite. The reversible capacity of the carbon-coated Fe\(_2\)O\(_3\) nanoflake electrode is similar to that of the previously reported carbon-coated Fe\(_2\)O\(_3\) nanosphindles [4]. It is clear to see that the carbon coating on Fe\(_2\)O\(_3\) nanoflakes can significantly enhance the initial reversibility of the electrode. As discussed by Zhang et al., carbon coating on the Fe\(_2\)O\(_3\) particles could not only suppress the formation of SEI films but also stabilize the formed SEI films, thus leading to an improved initial coulombic efficiency and better cycling stability [4].

Fig. 5. TGA curve of the carbon-coated Fe\(_2\)O\(_3\) nanoflakes.
higher reversible capacity after 50 cycles. The cycling stability of the carbon-coated Fe$_3$O$_4$ nanoflakes is even better than that of the carbon-coated nanospindles [4]. The superior cycling stability of the carbon-coated Fe$_3$O$_4$ nanoflake electrode can be attributed to the small particle size of Fe$_3$O$_4$ nanoflakes and the carbon coating. The coated carbon layer formed a shell that tightly attached to the Fe$_3$O$_4$ nanoflake, which not only improved the electrical conductivity of the electrode but also greatly enhanced the structural stability. The carbon shell can work as a buffer layer that can effectively suppress the volume change of Fe$_3$O$_4$ particles and reduce the loss of electrical contact of the pulverized Fe$_3$O$_4$ particles during the cycling, thus leading to greatly improved cycling stability.

In addition to reversible capacity and cycling stability, rate capability is also an important factor to evaluate the battery performance of the electrode material. The rate capabilities of the Fe$_3$O$_4$ nanoflake and the carbon-coated Fe$_3$O$_4$ nanoflake electrodes are compared in Fig. 7. To perform the rate capability measurements, the electrode was charged and discharged for 5 cycles at different current densities from 200 to 2000 mA g$^{-1}$. Fig. 7a shows the second charge/discharge curves of the carbon-coated Fe$_3$O$_4$ nanoflake electrode at different current densities. It can be seen that the cell polarization increases with decreasing reversible capacity as the current density increases. Fig. 7b compares the specific charge/discharge capacities of the Fe$_2$O$_3$ nanoflake and the carbon-coated Fe$_3$O$_4$ nanoflake electrodes as a function of cycle number at different current densities. The reversible capacity of carbon-coated Fe$_3$O$_4$ nanoflake electrode drops from 740 to 341 mAh g$^{-1}$ when the current density increases from 200 to 2000 mA g$^{-1}$. Even at a high current density of 2000 mA g$^{-1}$, the
carbon-coated Fe$_3$O$_4$ nanoflake electrode still can deliver a reversible capacity comparable to the theoretical capacity of graphite (372 mAh g$^{-1}$). When the current density was returned to its initial value of 200 mA g$^{-1}$ after deep cycling at 2000 mA g$^{-1}$, a constant capacity of about 700 mA h g$^{-1}$ was recovered for the carbon-coated Fe$_3$O$_4$ nanoflake electrode. By contrast, the reversible capacity of the Fe$_3$O$_4$ nanoflake electrode drops from 880 to 246 mA h g$^{-1}$ when the current density increases from 200 to 2000 mA g$^{-1}$. The superior rate capability of the carbon-coated Fe$_3$O$_4$ nanoflake electrode could be attributed to its small particle size and continuous carbon coating. On one hand, the Fe$_3$O$_4$ nanoflakes with thin thickness shorten the Li$^+$ ion diffusion paths. On the other hand, the conductive carbon network provides a three-dimensional electronic path for fast and stable charge transfer and lowers the internal electrode resistance.

4. Conclusions

Carbon-coated Fe$_3$O$_4$ nanoflakes were successfully prepared by partial reduction of monodispersed Fe$_3$O$_4$ nanoflakes with carbon coating. The carbon-coated Fe$_3$O$_4$ nanoflake electrode delivered a reversible capacity up to 738 mA h g$^{-1}$ with a high initial coulombic efficiency of 70%. Besides the high initial reversible capacity, the carbon-coated Fe$_3$O$_4$ nanoflake electrode also exhibited greatly improved initial coulombic efficiency, cycling stability, and rate capability compared to the Fe$_3$O$_4$ nanoflake electrode, making it promising as anode material for the next-generation high performance LIBs. The superior electrochemical performance of the carbon-coated Fe$_3$O$_4$ nanoflake electrode can be attributed to its small particle size and continuous carbon coating, which result in fast charge transport, improved structural stability, and suppressed SEI layer formation.

Acknowledgements

This work was supported by National Natural Science Foundation of China (No. 51102134) and Nanjing University of Science and Technology through NUST Research Funding (AB41385), Jiangsu Planned Projects for Postdoctoral Research Funds (No. 1202001B), and China Postdoctoral Science Foundation funded project (No. 2013M530258).

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