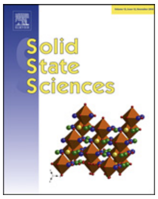
Solid State Sciences 12 (2010) 2024–2029

Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie



Fe_3O_4 dendrites reduced by carbon-coatings as high reversible capacity anodes for lithium ion batteries

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ARTICLE INFO

Article history:
Received 27 April 2010
Received in revised form
25 August 2010
Accepted 31 August 2010
Available online 19 September 2010

Keywords:
Magnetite
Carbon-coatings
Dendrite
Composite
Lithium ion batteries

ABSTRACT

Carbon-coated magnetite dendrites (CMDs) were prepared by partial reduction of hematite dendrites (HDs) with carbon-coatings. CMDs were characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction (XRD), and thermogravimetric analysis. The XRD results demonstrated the transformation of hematite to magnetite. As anode materials for lithium ion batteries, the CMDs showed much higher reversible capacity in the first cycle and better cycling performance compared with bare HDs. The improvement of the performance could be attributed to both the enhanced conductance and the increased structural stability coming from the carbon-coatings, which acted as elastic buffers to relieve the strains associated with the volume change during lithium insertion/extraction. Beside, the interspaces between CMDs were also propitious to relieve the strains. The results demonstrated that CMDs, with high reversible capacities and good cycling performance, were promising anode materials for lithium ion batteries.

Introduction

One of the major challenges in this century is the development of clear, inexpensive, safe and sustainable power sources. Alternative energy systems are crucial in order to deal with the environmental threat of global warming and the exhaustion of fossil fuels. A number of energy conversion and storage technologies, such as fuel cells [1], solar cells [2,3] and lithium ion batteries [4–15], are being developed to help cut carbon emissions.

Rechargeable lithium ion batteries have revolutionized portable electronic devices. They have become the dominant power source for cell phones, digital cameras, laptops, etc., because of their superior energy density and high voltage. Now, the worldwide market for rechargeable lithium ion batteries is valued at 10 billion dollars per annum and growing.

Lithium ion batteries are based on electrode reactions for which lithium are inserted (or extracted) from an open host structure with a concomitant addition (or removal) of electrons. Although they have high energy density available from existing rechargeable battery techniques, their performance still lie behind the demands of the consumers. New electrode materials with high specific capacities are necessary to meet these demands. In recent years, thanks to the works of Tarascon and other groups, nanometer-scale transition-mental oxides (TMOs) have become promising anode materials with high specific capacities [16–19]. Based on a new conversion mechanism, these materials have shown desirable properties, such as a high theoretical capacity (~500–1000 mA h/g, compared with ~372 mA h/g of commercial graphite). However, most of TMOs usually suffer from the problem of poor electronic conductance and inferior cycling performance, and hence need to be modified by adding electronically conductive phases or compositing with other anode materials of good cycling performance. There are very few TMOs with high electronic conductivities, including Fe_3O_4 and RuO_2 [16,20–23]. Since the iron has advantages over the ruthenium in terms of resourceful in the earth, inexpensive, environmentally friendly, many research works have focused on Fe_3O_4 recently.

The electrodes consisted of TMOs cannot maintain their integrity after several discharge/charge cycles. Hence their cycling performance is poor. It was well known that this problem can be partly solved in nanometer-scale electrode materials because of better accommodation of the strains of lithium insertion/extraction than in micrometer-scale materials [6,24–26]. For example, by reducing the diameter of α-Fe_2O_3 particles from 500 to 20 nm, the value of the maximum lithium uptake of α-Fe_2O_3 could be

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doi:10.1016/j.solidstatesciences.2010.08.021

reached as high as 1 and the cycling performance was improved [24]. However, the high specific surface area of nanometer-scale electrode materials increases the risk of secondary reactions including electrolyte decomposition between electrodes and electrolyte, which caused a high level of irreversibility and poor life cycle, and the formation of thick solid electrolyte interphase (SEI) films [23]. Besides, it was found in many nanostructured TMOs that thick SEI films formed during lithium uptake may disappear completely, catalyzed by transition-metal upon lithium extraction, which leaded to capacity fading and safe problems [6,27,28]. Hence, it is very necessary to modify the surface of nanometer-scale TMOs.

As a kind of commercial anode material for lithium ion batteries, carbon showed good cycling performance. Other anode materials modified by carbon-coatings showed better cycling performance compared with bare materials. For example, silicon nanoparticles coated with carbon materials resulted in the improvement of cycling performance [29]. Actually, carbon materials are very stable anode materials in lithium ion batteries due to a small volume change during lithium insertion/extraction [28,30]. So carbon-coatings can be used to modify nanostructured TMOs since they may serve as perfect barriers to protect the inner active materials and maintain their high capacities.

Hematite dendrites (α-Fe_2O_3) (HDs) have been served as anode materials of lithium ion batteries [31]. But the cycling performance was not famous. In order to prepare anode materials with low cost, high reversible capacity and good cycling performance, we focus on the carbon-coated magnetite dendrites (Fe_3O_4/C) (CMDs). The HDs were synthesized by a hydrothermal method. The CMDs were also prepared by a hydrothermal method using glucose as a carbon source and following heat-treatment. The CMDs exhibited higher reversible capacity and significantly improved cycling performance compared with bare HDs [31]. This structure allows the CMDs to be excellent anode materials for high performance lithium ion batteries in the future.

Experimental section

Materials and reagents

$K_3[Fe(CN)_6]$ and glucose were purchased from Shanghai Chemical Reagent Co. All the chemicals were of analytical grade and used as received without further purification process. The water used in this study was Millipore Milli-Q grade with a resistivity better than 18 MΩ cm^{-1}.

Synthesis of the HDs

The HDs were synthesized by a hydrothermal method, which were similar to the literature [32]. In a typical procedure, 1 mmol $K_3[Fe(CN)_6]$ was dissolved in 100 ml of distilled water to form a clear solution. Then the solution was transferred into a 130 ml teflonlined autoclave, which was maintained at 413 K for 2 days. After the mixture cooled naturally to room temperature, the red product was collected by centrifugation, repeatedly washed with distilled water and absolute ethanol to remove impurities. Finally, the product was dried at 343 K for 12 h.

Synthesis of the CMDs

A 0.08 g HDs powder was dispersed in 10 ml water with the help of ultrasonication to form a suspension. Some glucose was dissolved in 10 ml water to form a solution of 0.5 M. After mixing the suspension of the HDs and the solution of the glucose, 10 ml ethanol was added to the above mixture. Then the final mixture was placed in a 40 ml teflonlined autoclave and maintained at 433 K for 10 h. The sample was centrifugally separated and repeatedly washed with absolute ethanol and water. At last, the sample was dried at 363 K for 12 h. The resulting sample was heated in a quartz tube at a rate of 10 K min^{-1} to 873 K in argon atmosphere. The temperature of the tube was kept at 873 K for 6 h before it began to drop. When a sample was heated for 3 h, the transformation of the hematite to the magnetite was incomplete. This product was marketed as α-Fe_2O_3–Fe_3O_4/C (CHMDs).

Characterization

The as-prepared products were characterized by a powder X-ray diffraction (XRD) on SIEMENS D5000 X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm). A JEM-3010 transmission electron microscope operating at 200 kV accelerating voltage was used for transmission electron microscopy (TEM) analysis. Scanning electron microscopy (SEM) was performed by JSM-6700 F and S4800 scanning electron microscopes. To analyze the elements of CMDs, energy dispersive X-ray (EDX) analysis was also carried out on scanning electron microscope (S4800). Magnetic measurement was performed on a vibrating sample magnetometer. Thermogravimetric analysis (TGA) data were achieved on a TGA-50.

Electrochemical properties of products were measured using CR2016-type coin cells. In a process of fabricating the lithium ion batteries, electrodes were prepared by compressing a mixture of active materials (including the HDs, CHMDs, or CMDs) (80wt%), carbon black (10wt%) and polyvinylidene fluoride (PVDF, 10wt%) on pure copper foils. The weight of active materials on each electrode was between 1.2 and 2 mg. A Celgard 2400 microporous polypropylene membrane was used as a separator. The electrolyte consists of a solution of 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1, in wt%). Pure lithium foil was used as a counter electrode. These cells were assembled in an argon-filled glovebox with water and oxygen contents less than 1 ppm. The discharge and charge measurements were carried on an Arbin BT2000 system with the cut off potentials being 0 V for discharge and 3 V for charge.

Results and discussion

Fig. 1 displays typical SEM images of the HDs and CMDs. The morphologies of the CHMDs were similar to the morphologies of the CMDs, so their figures were not shown here. The overall morphologies of the HDs were shown in Fig. 1a. It can be observed that the HDs consist almost entirely of dendritic structures with a length of 2.5–6 μm along the trunk, indicating that a good uniformity have achieved. The high magnification image in Fig. 1b shows the morphology of a single dendrite. It displays exquisite fractal feature, which morphologically resembles a leaf of pine tree. The branches at one side of the trunk are parallel to each other and keep the uniform angle of about 60° with the trunk. The low magnification image in Fig. 1c displays the morphologies of the CMDs which are similar to that of the HDs. It can be confirmed by the high magnification image (Fig. 1d). However, comparing the image of the HDs with the image of the CMDs, it could be found that the morphologies of the samples changed from HDs to nanorod-branched dendrites. Because HDs synthesized at 433K were nanorod-branched dendrites [32]. Fig. 1e presents the EDX elemental analyses of CMDs. Besides the Si signal from the wafer, Fe, O, and C were detected. Although the C signal was lower than that of Fe and O, the results of EDX confirmed the presence of C in CMDs.

TEM images of a single CMD are displayed in Fig. 2. The low magnification TEM image of a single CMD is shown in Fig. 2a. It reveals a clear and typical dendritic fractal structure with