Journal of Power Sources 286 (2015) 124–129

Contents lists available at ScienceDirect

Journal of Power Sources

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

Tetragonal hematite single crystals as anode materials for high performance lithium ion batteries

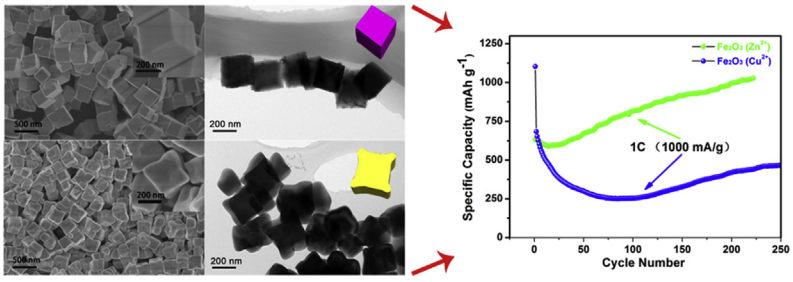
Shuanglei Yang [a, b, 1], Banghong Zhou [a, 1], Zhengping Ding [a], He Zheng [c], Lanping Huang [a], Jun Pan [a], Wei Wu [b, d, *], Hongbo Zhang [a, **]

[a] State Key Laboratory for Powder Metallurgy, Central South University, Changsha 410083, PR China
[b] Laboratory of Printable Functional Nanomaterials and Printing Electronics, School of Printing and Packaging, Wuhan University, Wuhan 430072, PR China
[c] School of Physics and Technology, Wuhan University, Wuhan 430072, PR China
[d] Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, PR China

HIGHLIGHTS

- Two different tetragonal α-Fe_2O_3 are synthesized via hydrothermal approach.
- Different metal ions induced different exposed facets and shapes for α-Fe_2O_3.
- Tetragonal α-Fe_2O_3 single crystals exhibit good cycling and rate performance.
- Cubic α-Fe_2O_3 products significantly improved Li-storage cycling performance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 January 2015
Received in revised form
7 March 2015
Accepted 25 March 2015
Available online 26 March 2015

Keywords:
Hematite
Shape-controllable synthesis
Single crystal
Electrochemical performance
Lithium ion batteries

ABSTRACT

Understanding the correlation between the desired morphology of nanostructures and its electrochemical properties is a prerequisite for widespread application of advanced energy materials. Herein, two types of tetragonal α-Fe_2O_3 single crystals with a mean size of ca. 200 nm, including cubic and thorhombic shapes, have been synthesized via a facile hydrothermal approach. The as-obtained shape of α-Fe_2O_3 nanocrystals depends on the addition of the metal ions precursor, the Zn^{2+} ions result in the cubic shape and the Cu^{2+} ions result in the thorhombic shape, respectively. These two different tetragonal α-Fe_2O_3 single crystals are used as anode materials for lithium ion batteries (LIBs), and the results reveal that cubic α-Fe_2O_3 single crystal exhibits a better performance than thorhombic α-Fe_2O_3 single crystal. The discharge capacity of cubic α-Fe_2O_3 single crystal is up to 1028 mAh/g, and the current density is up to 1000 mA/g (**1C**) after 222 cycles. Clearly, the α-Fe_2O_3 single crystal with controlled shapes would improve the electrochemical performance of LIBs as superior anode materials, and this approach could pave a way to develop high performance LIBs.

1. Introduction

Size- and shape-controllable synthesis of nanomaterials have attracted much interests due to their excellent physical and chemical performances [1]. As the most stable transition metal oxide under the natural conditions, hematite (α-Fe_2O_3) has many

* Corresponding author. Laboratory of Printable Functional Nanomaterials and Printing Electronics, School of Printing and Packaging, Wuhan University, Wuhan 430072, PR China.
** Corresponding author.
E-mail addresses: weiwu@whu.edu.cn (W. Wu), 13973183375@139.com (H. Zhang).
[1] the authors contributed equally to this work.

http://dx.doi.org/10.1016/j.jpowsour.2015.03.151
0378-7753/

advantages, such as easy to prepared, environment friendly and non-toxicity, and hence which it can be extensively applied in gas sensing, catalysts, energy storage, *etc*. Monodisperse single crystal of α-Fe_2O_3 with different exposed high-index facets would be a good model to reveal many fundamentals of facet-related properties and applications. And the high-index facets usually disappear during the early stage of growth of crystals due to the minimization of surface energy. Moreover, metal oxide crystals with particular exposed crystal planes such as high-index facets, could achieve improved chemical or physical performances, because high-index facets have high densities of atom steps, edges, kinks, and dangling bonds, which usually have high chemical activity [2–6].

With the development of the society and scientific technology, LIBs have been considered as one of best solution for the energy crisis [7–9]. Owing to the theoretical capacity of tradition graphite anode material is only 370 mAh/g, which cannot meet the increasing requirements of higher power density of LIBs. As an alternative, α-Fe_2O_3 becomes as an ideal candidate to replace graphite for LIBs because of its high capacity (up to 1007 mAh/g) [10]. Recently, Poizot and co-workers discovered the nanosized transition metal oxides undergo conversion reaction with lithium ion according to the following equilibrium: [11]

$$MO + Li^+ + e^- \leftrightarrow M + Li_2O \quad (M = Fe, Co, Ni, Mn)$$

Therefore, the α-Fe_2O_3 can be reduced to metal Fe nanoparticles wrapped in Li_2O and gel-like polymer electrolyte matrix and then reversibly recovered to the oxidation condition. Obviously, the structure of transition metal oxide have natural advantages for their capacity [12,13]. As a result, size- and shape-controllable synthesis of α-Fe_2O_3 and application in LIBs has attracted much attention in recently [14]. For instance, Zhang and co-workers prepared the hierarchical hollow Fe_2O_3 spheres with a mean size of 500 nm and used as anode materials for LIBs, which exhibited a good cycling stability of 815 mAh/g at 0.5C and excellent rate performance which at current density of 2 A/g and 5 A/g, the capacity from 540 mAh/g to 330 mAh/g [15]. Gao and co-workers synthesized disk-like α-Fe_2O_3 particles by a facile hydrothermal method and used as anode materials for LIBs, which shown the reversible specific capacity of 632 mAh/g even at a high rate of 800 mA/g [16]. Yu and co-workers. synthesized the porous Fe_2O_3 microspheres by a lysine-assisted hydrothermal method, the as-obtained products show a stable and reversible capacity of 705 mAh/g [17]. Ogale and co-workers reported the synthesis and Li-cyclability of α-Fe_2O_3 nanospindles derived from Fe based metal organic frameworks (MOFs) show the higher reversible capacity of ~1024 mAh/g at 100 mA/g [18]. Lou and co-workers synthesized the α-Fe_2O_3 nanotubes which exhibited superior lithium storage capabilities, the capacity is 1377 mAh/g at 0.2C [19]. Mullins and co-workers synthesized single-crystalline α-Fe_2O_3 nano-rods which exhibited reversible capacity of 908 mAh/g at 0.2C [20]. Obviously, the shape of iron oxide are a key factor to the final performance of LIBs application. Understanding the correlation between the electrochemical properties and the morphology of nanostructures is a prerequisite for widespread applications of LIBs. The nanostructures with special exposed faces can facilitate both the electrons and Li^+ transport by reducing diffusion paths, improve the intercalation kinetics by providing a larger electrode/electrolyte contact area, and the Fe or O atom layers on the α-Fe_2O_3 with different exposed crystal faces maybe take the conversion reaction more easily, resulting in the higher capacity and a better cycling performance [21–27].

Herein, we report a facile ions-assisted hydrothermal methods for the synthesis of two different tetragonal α-Fe_2O_3 single crystal, including cubic and thorhombic shapes with different exposed facets, which are achieved by simple addition of Zn^{2+} and Cu^{2+}, respectively. The effect of the introduced ions on the shape of the α-Fe_2O_3 products are discussed. The as-obtained cubic and thorhombic α-Fe_2O_3 single crystal have uniform shapes with a mean size are *ca.* 250 nm. Subsequently, the two different tetragonal α-Fe_2O_3 single crystal have been applied as anode materials for LIBs, which exhibited a good cycling stability and excellent rate performance. Especially, the performance of the as-prepared cubic α-Fe_2O_3 single crystal is much better than the aforementioned literature [14,18,28,29]. The as-obtained cubic and thorhombic α-Fe_2O_3 single crystal can be served as promising candidates for the fabrication of high capacity, low cost, and environmentally safe anode materials for LIBs.

2. Experimental sections

2.1. Materials

$Fe(NO_3)_3 \cdot 9H_2O$ and $NH_3 \cdot H_2O$ (25%) were purchased from Sinopharm Chemical Reagent Co. Ltd., $Zn(CH_3COO)_2 \cdot 2H_2O$ and $Cu(CH_3COO)_2 \cdot H_2O$ were purchased from Shanghai Jingchun Chemical Reagent Co., Ltd. All the materials were analytical reagent and used as received without further purification. The deionized water was used throughout the experiments.

2.2. Synthesis of tetragonal α-Fe_2O_3 single crystal

Two different tetragonal α-Fe_2O_3 single crystals were synthesized by metal ions-assisted hydrothermal method, and the final shapes depends on the addition of zinc and cupric ions. Typically, 1 mmol zinc or cupric ions precursor were added into the $Fe(NO_3)_3$ solution (10 ml, 0.808 g) under stirring, after 10 min, 10 ml of $NH_3 \cdot H_2O$ was added into the above mixture and the solution color changed into the red-brown. Then, the mixtures were transferred into a 50 ml of Teflon-lined stainless steel autoclave for hydrothermal treatment at 160 °C for 16 h. The products was collected by centrifugation (5000 rpm, 5 min), washed with ethanol, and dried in air under the ambient conditions.

2.3. Electrochemical measurements

Briefly, coin cell assembly was implemented in a recirculating argon glove box. The test coin cells were composed of tetragonal α-Fe_2O_3 as an anode and metallic lithium as counter electrode, which were separated by microporous glass fiber separator. LiPF6 were used as the electrolyte solution. Electrochemical measurements were performed on a LAHE Battery Tester under different conditions.

2.4. Characterization

X-ray diffraction (XRD) were carried out by a D/ruanx2550PC (Japan) using Cu Ka radiation ($\lambda = 0.1542$ nm). X-Ray Photoelectron Spectrometer (XPS) was performed on a Thermo Fisher (ESCALAB 250Xi) photoelectron spectrometer. Scanning electron microscopy (SEM) was carried out using a Hitachi S4800 scanning electron microscopy, samples were dropped onto the silicon substrate. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on a JEOL JEM-2100F transmission electron microscopy at the accelerating voltage of 200 kV.

3. Results and discussion

The formation process of cubic and thorhombic single crystal α-