



# The electrochemical performance of commercial ferric oxide anode with natural graphite adding and sodium alginate binder



Shibing Ni <sup>a,b,1</sup>, Jianjun Ma <sup>a</sup>, Jicheng Zhang <sup>a</sup>, Xuelin Yang <sup>a,b,\*</sup>, Lulu Zhang <sup>a,b</sup>

<sup>a</sup> College of Materials and Chemical Engineering, China Three Gorges University, 8 Daxue Road, Yichang, Hubei 443002, China

<sup>b</sup> Collaborative Innovation Center for Microgrid of New Energy, Hubei Province, China

## ARTICLE INFO

### Article history:

Received 25 October 2014

Received in revised form 12 November 2014

Accepted 30 November 2014

Available online 3 December 2014

### Keywords:

Ferric oxide

Natural graphite

Sodium alginate

Lithium ion battery

## ABSTRACT

A low cost and facile way was developed to prepare high performance Fe<sub>2</sub>O<sub>3</sub>/natural graphite electrode for lithium ion batteries. For the purpose of reducing the cost and improving the feasibility of large-scale fabrication, commercial ferric oxide and natural graphite were adopted as raw materials and mechanical milling was adopted as preparation method in material fabrication process, and water soluble sodium alginate was adopted as binder in electrode preparation procedure. The Fe<sub>2</sub>O<sub>3</sub>/natural graphite electrode delivers initial discharge and charge capacity of 943.8 and 691.4 mAh g<sup>-1</sup> at a specific current of 72 mA g<sup>-1</sup>, maintaining of 687.6 and 679.3 mAh g<sup>-1</sup> after 100 cycles. After 60 cycles at various specific currents from 104 to 3470 mA g<sup>-1</sup>, the discharge and charge capacity of the Fe<sub>2</sub>O<sub>3</sub>/natural graphite electrode can restore well when lowering the specific current to 104 mA g<sup>-1</sup>. A novel electrochemical reconstruction between Fe<sub>2</sub>O<sub>3</sub> and natural graphite was observed for the electrode after cycling, which results in the formation of an integrated architecture with good combination between Fe<sub>2</sub>O<sub>3</sub> and natural graphite, being responsible for the good electrochemical performance.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Transition metal oxides (TMOS) are becoming one kind of promising anode materials for lithium ion batteries owing to their high theoretical capacity (500~1000 mAh g<sup>-1</sup>) that based on a novel redox reaction mechanism [1]. However, the practical application of TMOS in lithium ion batteries was badly restricted owing to their low electronic conductivity and structure destruction in cycling. Much effect on improving the electrochemical performance of TMOS has been tried on designing various architectures and/or combing them with carbon materials [2–9], which has shown impressive results. As known, the practical application of TMOS in lithium ion batteries was determined not only by the electrochemical performance, but also by the cost, the feasibility and stability of the fabrication way. Aimed at this, we are devoted to explore a low cost and facile way to improve the electrochemical performance of TMOS.

Fe<sub>2</sub>O<sub>3</sub> is a typical TMOS with obvious advantages over other TMOS in terms of abundance in nature, facile synthesis, low cost and high theoretical capacity, which has been widely studied as anode for lithium ion batteries [10–15]. Natural graphite has the advantages over amorphous carbon materials in terms of abundance in nature, low cost, high electronic conductivity and better performance of lithium ion storage, thus can be used as an ideal carbon component in TMOS/carbon composites [16]. Meanwhile, it is demonstrated that binders have important effect on the electrochemical performance of Fe<sub>2</sub>O<sub>3</sub> electrode [17–20], and water-soluble binders show advantages in terms of low cost and environmental friendless, which are beneficial for large-scale fabrication. Here in this paper, we report the preparation of Fe<sub>2</sub>O<sub>3</sub>/natural graphite composite via a facile method, which shows good electrochemical performance as anode for lithium ion batteries with sodium alginate binder. In the fabrication procedure, commercial Fe<sub>2</sub>O<sub>3</sub> and natural graphite were adopted as raw materials and mechanical milling was adopted as preparation method, which are beneficial to reduce the cost and improve the feasibility of large-scale fabrication. The effects of natural graphite and sodium alginate on the electrochemical performance of the Fe<sub>2</sub>O<sub>3</sub> electrode are studied, which suggest that natural graphite can improve the electronic conductivity of the electrode and

\* Corresponding author. Fax: +86 717 6397559.

E-mail addresses: [shibingni07@126.com](mailto:shibingni07@126.com) (S. Ni), [xlyang@ctgu.edu.cn](mailto:xlyang@ctgu.edu.cn) (X. Yang).

<sup>1</sup> Fax: +86 717 6397505.

prevent the aggregation of  $\text{Fe}_2\text{O}_3$  in cycling, and sodium alginate is beneficial for the electrochemical reconstruction of the electrode.

## 2. Experimental details

$\text{Fe}_2\text{O}_3$  and sodium alginate were analytical grade and purchased from Sinopharm Chemical Reagent Corporation and Sigma-Aldrich commercial company, respectively. Natural graphite was obtained from Yichang Hengda graphite company (99.9%). For preparing of  $\text{Fe}_2\text{O}_3$ /natural graphite, natural graphite and  $\text{Fe}_2\text{O}_3$  with weight ratio of 1:1 ( $m_{\text{Fe}_2\text{O}_3} : m_{\text{natural graphite}} = 1:1$ ) were treated by mechanical milling at 400 rpm for 30 min.

The morphology and structure of the resulting products were characterized by field-emission scanning electron microscopy (FE-SEM JSM 7500 F, JEOL) and X-Ray powder diffraction (Rigaku Ultima IV, Cu  $K\alpha$  radiation  $\lambda = 1.5406 \text{ \AA}$ ).

For fabricating lithium ion batteries, a mixture of  $\text{Fe}_2\text{O}_3$ /natural graphite, acetylene black and sodium alginate (dissolved in deionized water,  $0.02 \text{ g mL}^{-1}$ ) with weight ratio of 8:1:1 were coated on copper foil and cut into disc electrode with a diameter of 14 mm using a punch. For preparing  $\text{Fe}_2\text{O}_3$ /natural graphite electrode with polyvinylidene fluoride (PVDF) binder, sodium alginate was replaced by PVDF with the same weight ratio (dissolved in N-methylpyrrolidone solution,  $0.02 \text{ g mL}^{-1}$ ). Coin-type cells (2025) of Li/1 M  $\text{LiPF}_6$  in ethylene carbonate, dimethyl carbonate and diethyl carbonate (EC/DMC/DEC, 1:1:1, v/v/v)/ $\text{Fe}_2\text{O}_3$ /natural graphite electrode were assembled in an argon-filled dry box ( $\text{H}_2\text{O} < 1.0 \text{ ppm}$ ,  $\text{O}_2 < 1.0 \text{ ppm}$ ). A Celgard 2400 microporous polypropylene was used as the separator membrane. The cells were tested in the voltage range between 0.02 and 3 V with a multichannel battery test system (LAND CT2001A). When calculating the specific capacity of the  $\text{Fe}_2\text{O}_3$ /natural graphite electrode, the mass of both  $\text{Fe}_2\text{O}_3$  and natural graphite was considered as the total mass of active material. The cyclic voltammetry (CV) measurement of the electrodes was carried out on a CHI660C electrochemical workstation at a scan rate of  $0.2 \text{ mV s}^{-1}$  between 0 and 3 V. Electrochemical impedance spectroscopy (EIS) measurements were performed on CHI660C electrochemical workstation under open circuit conditions over a frequency range of 0.01 Hz to 100 kHz by applying an AC signal of 5 mV in amplitude throughout the tests.

## 3. Results and discussion

XRD patterns of commercial  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ /natural graphite are shown in Fig. 1. As seen, the diffraction peaks located at  $24.3^\circ$ ,  $33.3^\circ$ ,  $35.7^\circ$ ,  $41.0^\circ$ ,  $49.6^\circ$ ,  $54.2^\circ$ ,  $57.7^\circ$ ,  $62.5^\circ$ ,  $64.1^\circ$ ,  $69.6^\circ$ ,  $72.1^\circ$ ,  $75.5^\circ$ ,  $80.8^\circ$ ,  $84.9^\circ$  and  $88.8^\circ$  can ascribe to the (0 1 2), (1 0 4), (1 1 0), (1 1 3),

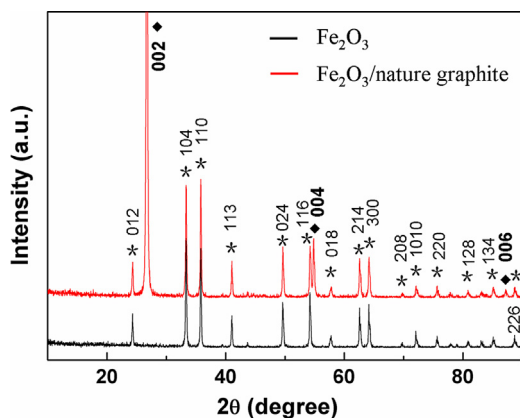


Fig. 1. XRD patterns of commercial  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ /natural graphite.

(0 2 4), (1 1 6), (0 1 8), (2 1 4), (3 0 0), (2 0 8), (1 0 1 0), (2 2 0), (1 2 8), (1 3 4) and (2 2 6) faces of hexagonal  $\text{Fe}_2\text{O}_3$  with lattice constant  $a = 5.031 \text{ \AA}$  and  $c = 13.73 \text{ \AA}$ , which is in good agreement with JCPDS, no. 134–0534. Three diffraction peaks located at  $26.5^\circ$ ,  $54.7^\circ$  and  $87.0^\circ$  are attributed to the (0 0 2), (0 0 4) and (0 0 6) faces of hexagonal graphite (JCPDS, no. 41-1487). The results indicate the structure of natural graphite was not destroyed in the fabrication process.

Fig. 2(a) is a low magnification SEM image of the  $\text{Fe}_2\text{O}_3$ /natural graphite, which shows the coexistence of particle-like  $\text{Fe}_2\text{O}_3$  and flake-like natural graphite. A high magnification SEM image of the  $\text{Fe}_2\text{O}_3$ /natural graphite is shown in Fig. 2(b), which suggests these  $\text{Fe}_2\text{O}_3$  particles are of smooth surface with mean size about 300 nm, and the natural graphite flakes show mean thickness about 100 nm with diameter ranges from 500 nm to  $4 \mu\text{m}$ . SEM images of the  $\text{Fe}_2\text{O}_3$ /natural graphite electrode were provided for studying the effect of electrode preparation on the morphology and structure of  $\text{Fe}_2\text{O}_3$  and natural graphite. Fig. 2(c) is a low magnification SEM image of the electrode, which suggests the general distribution of  $\text{Fe}_2\text{O}_3$  particles and natural graphite flakes is uniform. A high magnification SEM image of the electrode is shown in Fig. 2(d). A large number of nanoparticles with mean size about 50 nm between  $\text{Fe}_2\text{O}_3$  and natural graphite can be seen, which correspond to acetylene black that introduced in the electrode preparation process. The results indicate that the morphology and size of  $\text{Fe}_2\text{O}_3$  and natural graphite were not destroyed in the electrode preparation process.

Fig. 3(a) shows the initial three and the 100th discharge and charge curves for the  $\text{Fe}_2\text{O}_3$ /natural graphite electrode at a specific current of  $72 \text{ mA g}^{-1}$ . The initial discharge curve differs from the others, showing two plateaus near 0.84 and 0.1 V. The plateau near 0.84 V is attributed to the formation of solid electrolyte interface (SEI) and the reduction of  $\text{Fe}_2\text{O}_3$ , and the plateau near 0.1 V is due to the insertion of lithium ions into natural graphite [16,21,22]. In the subsequent discharge curves, the plateau corresponds to the reduction of  $\text{Fe}_2\text{O}_3$  shifts to high potential region owing to the activation of the electrode, which is similar to that of NiO and  $\text{Cu}_x\text{O}$  ( $x = 1, 2$ ) [3,5,23]. The charge curves show similar profile with two sloping potential regions (0.02~0.25 and 1.0~3.0 V), which correspond to the extraction of lithium ions from natural graphite and the oxidation of Fe into  $\text{Fe}_2\text{O}_3$  [16,21,24]. The capacity versus cycle number plots for the  $\text{Fe}_2\text{O}_3$ /natural graphite electrode and pure natural graphite are shown in Fig. 3(b). As seen, the initial discharge and charge capacity of the electrode are 943.8 and  $691.4 \text{ mAh g}^{-1}$ , which maintain of 687.6 and  $679.3 \text{ mAh g}^{-1}$  after 100 cycles, showing good cycle stability. The natural graphite electrode shows initial discharge and charge capacity of 392 and  $298 \text{ mAh g}^{-1}$ , maintaining of 304 and  $302 \text{ mAh g}^{-1}$  after 100 cycles. Despite the low cost and facility of fabrication way, the electrochemical performance of the  $\text{Fe}_2\text{O}_3$ /natural graphite is comparable and even better than  $\text{Fe}_2\text{O}_3$ /activated carbon,  $\text{CNT@Fe}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ @carbon,  $\text{Fe}_2\text{O}_3$ /graphene and  $\text{Fe}_2\text{O}_3$ @MWCNTs [25–29], which endows it with practical application in lithium ion batteries. Fig. 3(c) shows the coulombic efficiency of the  $\text{Fe}_2\text{O}_3$ /natural graphite. It delivers coulombic efficiency of 73.3% in the initial cycle, which increases gradually along with cycling number in the first few cycles and then gradually reaches stable value, showing an average value of 99.5% in 100 cycles. Fig. 3(d) shows the cyclic voltammetric (CV) curves of the  $\text{Fe}_2\text{O}_3$ /natural graphite electrode between 0 and 3.0 V. In the first cathodic scan, a strong reduction peak near 0.61 V and a weak reduction peak near 0.14 V are observed, corresponding to the reduction of  $\text{Fe}_2\text{O}_3$  into Fe, the formation of amorphous  $\text{Li}_2\text{O}$  and SEI, as well as the insertion of lithium ions into natural graphite [2,16,21,22]. The locations of the reduction peaks are lower than the initial discharge plateaus in Fig. 3(a), which can be ascribed to polarization. The smaller the

Download English Version:

<https://daneshyari.com/en/article/184790>

Download Persian Version:

<https://daneshyari.com/article/184790>

[Daneshyari.com](https://daneshyari.com)