



# Multi-walled carbon nanotube-reinforced porous iron oxide as a superior anode material for lithium ion battery



Xin-Jing Pang<sup>a</sup>, Juan Zhang<sup>a</sup>, Gong-Wei Qi<sup>a</sup>, Xiao-Hui Dai<sup>a</sup>, Jun-Ping Zhou<sup>a</sup>, Shu-Yong Zhang<sup>a,b,\*</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Shandong University, No. 27, Shanda Nan Rd., Jinan 250100, PR China

<sup>b</sup> National Key Lab of Crystal, Shandong University, No. 27, Shanda Nan Rd., Jinan 250100, PR China

## ARTICLE INFO

### Article history:

Received 24 January 2015

Received in revised form 1 March 2015

Accepted 24 March 2015

Available online 30 March 2015

### Keywords:

Lithium-ion battery

Anode

Iron oxide

Multi-walled carbon nanotubes

Porous copper substrate

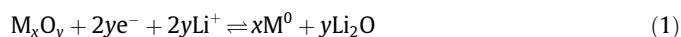
## ABSTRACT

Multi-walled carbon nanotube-reinforced porous iron oxide (Fe<sub>3</sub>O<sub>4</sub>/MWCNT) is synthesized by a two-step approach with porous Cu substrate serving as current collector. Porous Cu substrate is prepared through electroless deposition with hydrogen bubble serving as template. Fe<sub>3</sub>O<sub>4</sub>/MWCNT composites are prepared by the electrodeposition of Fe<sub>3</sub>O<sub>4</sub> in the presence of dispersed MWCNTs from a Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution with MWCNT suspension. Results showed that Fe<sub>3</sub>O<sub>4</sub> forms granular nanoparticles on the porous Cu substrate with several MWCNTs embedded in it. Adding MWCNTs changes the morphology of Fe<sub>3</sub>O<sub>4</sub>. Smooth Fe<sub>3</sub>O<sub>4</sub>, smooth Fe<sub>3</sub>O<sub>4</sub>/MWCNT, and porous Fe<sub>3</sub>O<sub>4</sub> composites are also prepared for comparison. When used as anode materials, porous Fe<sub>3</sub>O<sub>4</sub>/MWCNT composites have a reversible capacity of approximately 601 mA h g<sup>-1</sup> at the 60th cycle at a cycling rate of 100 mA g<sup>-1</sup>. This value is higher than that of the other materials. The reversible capacity at a cycling rate of 10,000 mA g<sup>-1</sup> is approximately 50% of that at 100 mA g<sup>-1</sup>. Therefore, the MWCNT-reinforced porous Fe<sub>3</sub>O<sub>4</sub> composite exhibits much better reversible capacity, capacity retention, and high-rate performance than the other samples. This finding can be ascribed to the porous structure of Fe<sub>3</sub>O<sub>4</sub>, better conductivity of porous Cu substrate and MWCNTs, and the morphology change of Fe<sub>3</sub>O<sub>4</sub> nanoparticles upon the addition of MWCNTs.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Lithium-ion batteries (LIBs) with carbonaceous materials serving as anodes were commercialized in 1990. After nearly 25 years, LIBs have been considered important rechargeable batteries because of their outstanding features, such as high energy density, small self-discharge, and minimal memory effect. However, the applications of carbonaceous anode materials are limited by their low reversible lithium intercalation capacity and mutual solvent intercalation. Over the past decades, other materials, such as metals, non-metals, and metal oxides have been studied as alternatives of carbonaceous anode. Among these new materials, SnO<sub>2</sub>, TiO<sub>2</sub>, and many other transition metal oxides like Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>, have attracted increasing attention because of their distinct lithium reaction mechanisms and electrochemical features [1–7]. The electrochemical reactions of most transition metal oxides can be generalized by the following equation [8,9]:



Among the transition metal oxides studied, iron oxides such as Fe<sub>2</sub>O<sub>3</sub> and FeO have attracted much attention because of their high reversible capacity, rich abundance, low cost, and eco-friendliness. In theory, one Fe<sub>3</sub>O<sub>4</sub> counters eight lithium ions and delivers a capacity as high as 926 mA h g<sup>-1</sup>. However, iron oxides also suffer from poor electronic conductivity, poor ion transport kinetics, and severe pulverization because of the pronounced volume expansion and reduction during cycling. Many approaches have been explored to overcome these shortcomings. The most common approaches include reducing the particle size to nanoscale [10,11] and turning iron oxides into special nanostructures such as nanoflakes [12], nanorods [13], and nanotubes [14]. Nanoporous iron oxides have been prepared by using porous current collectors, such as porous Ni, Cu, and C [15–21]. These methods have been proven effective for improving the cycle stability and reducing the pulverization. Another approach is adding conductive carbonaceous materials, such as carbon fibers [21], carbon nanotubes [22], carbon core [23,24], carbon sphere [23,24], carbon matrix [25,26], and graphene [27,28] into metal oxides. Such carbonaceous materials can increase the electronic conductivity, and buffer the volume change. Given their exceptional properties, such

\* Corresponding author at: School of Chemistry and Chemical Engineering, Shandong University, No. 27, Shanda Nan Rd., Jinan 250100, PR China. Tel.: +86 531 88361378; fax: +86 531 88364781.

E-mail address: [syzhang@sdu.edu.cn](mailto:syzhang@sdu.edu.cn) (S.-Y. Zhang).

as good electronic conductivity and high mechanical strength, multi-walled carbon nanotubes (MWCNTs) have been proposed as the most suitable carbonaceous additive for this purpose [29,30].

In the present work, we combined a special nanoporous structure and MWCNTs to improve the capacity retention and rate performance of  $\text{Fe}_3\text{O}_4$  anode materials. Long MWCNT fibers were used not only to improve the electronic conductivity of  $\text{Fe}_3\text{O}_4$  but also to reinforce the electrode structure. A porous Cu substrate with a well-defined bi-continuous structure was fabricated by electroless deposition and used to increase the specific area and conductivity of the resultant  $\text{Fe}_3\text{O}_4$  materials. Results showed that the reversible capacity, capacity retention, and rate performance of  $\text{Fe}_3\text{O}_4$  were considerably improved.

## 2. Experimental procedures

### 2.1. Preparation of porous Cu substrate

A porous Cu substrate was prepared by the electroless deposition of porous Cu on one side of a piece of Cu foil (10  $\mu\text{m}$  thick). Prior to deposition, the Cu foil was washed with acetone and 0.1 M HCl to remove organic contaminants and oxide on the surface. The Cu foil was then immersed in acidic palladium chloride solution (0.5 mM  $\text{PdCl}_2$  in 20% HCl) for a few minutes to activate Cu by deposition of some Pd particles on Cu foil surface through replacement reaction. Finally, the activated Cu foil was placed in an electroless plating bath (Table 1). The electroless deposition was performed at pH 9 and  $80 \pm 0.2$  °C for 20 min. The resultant porous Cu substrate was removed from the bath, washed with deionized water and ethyl alcohol via ultrasonication, and then dried in air.

### 2.2. Preparation of $\text{Fe}_3\text{O}_4$ and $\text{Fe}_3\text{O}_4/\text{MWCNT}$ composite

$\text{Fe}_3\text{O}_4$  with/without MWCNTs was electrodeposited on one side of either a piece of Cu foil or porous Cu substrate in a bath (Table 2).

Tri-ethanol-amine (TEA) was used as a sequestering agent for  $\text{Fe}^{3+}$  in caustic solutions to prevent  $\text{Fe}^{3+}$  from precipitating as iron oxides or iron oxyhydroxides. As a surfactant, hexadecyl-trimethyl-ammonium bromide (CTAB) could effectively disperse MWCNTs in water. Good dispersion is necessary for the co-deposition of  $\text{Fe}_3\text{O}_4$  and MWCNTs [31].  $\text{Fe}_3\text{O}_4$  films were prepared by the electrochemical reduction of  $\text{Fe(III)}$ -TEA co-ordination compound [32,33]. Electrodeposition was conducted in a two-electrode home-made electrolytic cell, with the smooth Cu foil or porous Cu substrate as the cathode and a graphite sheet (20  $\text{cm}^2$ ) as the anode. The electrodeposition was performed at a constant current density of 13  $\text{mA cm}^{-2}$  for 4 min at  $70 \pm 0.2$  °C. The samples were removed, washed thrice with deionized water and absolute ethanol, and then dried in a vacuum oven at  $80 \pm 0.2$  °C for 24 h.

Four samples, i.e.,  $\text{Fe}_3\text{O}_4$  on the smooth Cu foil (S- $\text{Fe}_3\text{O}_4$ ), MWCNT-reinforced  $\text{Fe}_3\text{O}_4$  on the smooth Cu foil (S- $\text{Fe}_3\text{O}_4/\text{MWCNT}$ ),  $\text{Fe}_3\text{O}_4$  on the porous Cu substrate (P- $\text{Fe}_3\text{O}_4$ ), and MWCNT-reinforced  $\text{Fe}_3\text{O}_4$  on the porous Cu substrate (P- $\text{Fe}_3\text{O}_4/\text{MWCNT}$ ), were prepared. These samples were cut into discs of the same size and weighed on an analytical balance with the accuracy of 0.1 mg to obtain the mass

of the active material loaded on the Cu substrates. The area of all the electrodes are 1.2  $\text{cm}^2$ , and the mass of S- $\text{Fe}_3\text{O}_4$ , S- $\text{Fe}_3\text{O}_4/\text{MWCNT}$ , P- $\text{Fe}_3\text{O}_4$  and P- $\text{Fe}_3\text{O}_4/\text{MWCNT}$  are 0.24, 0.23, 1.80 and 1.70 mg, respectively.

### 2.3. Composition and morphological characterization

The composition and morphology of the samples were characterized using a JSM-7600F field emission scanning electron microscope (SEM; JEOL, Japan) at an accelerating voltage of 15 kV. A D8 Advance X-ray diffractometer (XRD; Bruker, Germany) was used to record the crystallographic information of the samples with Cu  $K\alpha$  radiation at a scan rate of  $0.5^\circ \text{ s}^{-1}$ .

### 2.4. Cell assembling

CR2025 coin test cells were assembled in a glove box filled with high-purity argon (Deyang Gas Co., Ltd., Jinan, China) at room temperature with the sample discs as the working electrode and a lithium sheet as the counter and reference electrodes.  $\text{LiPF}_6$  (1 M) was dissolved in an organic solvent mixture composed of ethylene carbonate, dimethyl carbonate, and diethyl carbonate (Beijing Institute of Chemical Reagents) with a ratio of 1:1:1 to serve as the electrolyte. A Celgard 2400 membrane was used to separate the working electrode and the counter electrode.

### 2.5. Electrochemical characterization

The test cells were galvanostatically cycled at a current density of 100  $\text{mA g}^{-1}$  on a CT2001C-001 Land battery test system (Jinnuo, Wuhan, China). The cut-off potential were between 0.01 and 3.0 V vs.  $\text{Li}^+/\text{Li}$ . The rate performance of the sample was studied by charging and discharging the test cells at 100, 500, 1000, 2000, 5000, and 10,000  $\text{mA g}^{-1}$ . Electrochemical impedance spectra were recorded using a CHI 604A electrochemical work station (CH Instrument, Shanghai, China) within the frequency range of 100 kHz to 10 mHz with a signal amplitude of 5 mV.

## 3. Results and discussion

### 3.1. Morphology and structure of the samples

As shown in the XRD patterns in Fig. 1, two strong diffraction peaks at  $2\theta = 43.3^\circ$  and  $50.5^\circ$  relevant to the Cu(111) and Cu(200) reflections originated from the Cu substrate. The weak reflection at  $2\theta = 44.0^\circ$  was assigned to the (400) of the magnetite  $\text{Fe}_3\text{O}_4$  phase (ICDD No. 26-1136). This result suggests that  $\text{Fe}_3\text{O}_4$  particles grew along a preferred orientation.

$\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  composites deposited on the smooth Cu foils were silvery white with bright surface, whereas porous  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  composites deposited on the porous Cu substrate were black. The SEM images of the porous Cu substrate and the four samples with different magnifications are shown in Fig. 2. The porous Cu substrate showed a bicontinuous 3D structure. For S- $\text{Fe}_3\text{O}_4$  and S- $\text{Fe}_3\text{O}_4/\text{MWCNT}$ , the surface of the  $\text{Fe}_3\text{O}_4$

**Table 1**

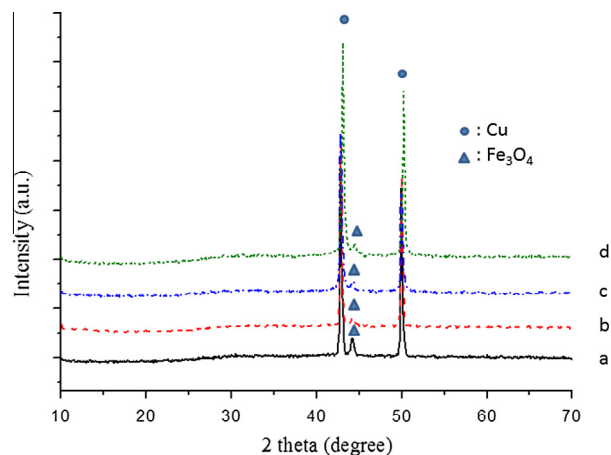
Bath composition for preparation of porous Cu collector.

Chemicals	Concentration ( $\text{g L}^{-1}$ )
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	5.0
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	1.5
$\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 4\text{H}_2\text{O}$	15.0
$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	30.0
$\text{H}_3\text{BO}_3$	30.0
$\text{C}_{14}\text{H}_{26}\text{O}_2$	0.8

**Table 2**

Bath composition for preparation of  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  composite.

Chemicals	Concentration ( $\text{g L}^{-1}$ )
NaOH	50.0
TEA	17.5
$\text{Fe}_2(\text{SO}_4)_3$	8.0
CTAB	4.0
MWCNT	5.0



**Fig. 1.** XRD patterns of S- $\text{Fe}_3\text{O}_4$  (a), S- $\text{Fe}_3\text{O}_4/\text{MWCNT}$  (b), P- $\text{Fe}_3\text{O}_4$  (c), and P- $\text{Fe}_3\text{O}_4/\text{MWCNT}$  (d).

Download English Version:

<https://daneshyari.com/en/article/1608930>

Download Persian Version:

<https://daneshyari.com/article/1608930>

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