Electrochimica Acta 193 (2016) 32–38

Contents lists available at ScienceDirect

Electrochimica Acta

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

Three-dimensional Fe_3O_4 Nanotube Array on Carbon Cloth Prepared from A Facile Route for Lithium ion Batteries

Weitao Qiu, Muhammad-Sadeeq Balogun, Yang Luo, Kaiqian Chen, Yikun Zhu, Xujing Xiao, Xihong Lu, Peng Liu*, Yexiang Tong*

KLGHEI of Environment and Energy Chemistry, MOE of the Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China

ARTICLE INFO

Article history:
Received 5 August 2015
Received in revised form 21 January 2016
Accepted 22 January 2016
Available online 24 January 2016

Keywords:
Fe_3O_4
three dimensional
nanotube arrays
ZnO templates
lithium-ion batteries
high rate performance

ABSTRACT

A facile templating method was used to fabricate a Magnetite (Fe3O4) nanotubes coated carbon cloth electrode as anode for lithium ion batteries in this work. In hope of achieving high-performance and stable electrode, ZnO nanorods were first electrodeposited and subsequently used as sacrificial templates for synthesis of Fe3O4 nanotubes arrays. According to structural analysis, this strategy led to a uniform nanotubes-like coating attached on interwoven carbon fiber of the three-dimensional (3D) carbon cloth. Unexpectedly, it was found that the nanotube structure was assembled from numerous nanoparticles that formed up a hierarchical structure with 3D arrangement inherited from carbon cloth substrate. The as-prepared electrode delivered excellent rate capability, giving a maximal specific capacity of ~930 mAh g^{-1} at 2 A g^{-1} but a relatively poor cycling retention of 73% after 200 cycles. This is attributed to the severe agglomeration of nanocrystalline Fe_3O_4 particles upon repeated cycling, revealing the fact that small particles accounting for high rate performance might in turn undermine the cycling stability.

1. Introduction

Lithium ion battery (LIB) is a popular research field in which tremendous efforts have been paid to increase the electrochemical properties of lithium storage materials [1,2]. In many works, physical properties such as electrical conductivity, ion diffusion efficiency and structural tolerance for volume expansion were modified to enhance the rate performance and the cycling stability of newly emergent materials [1,3]. Transition metal oxides (TMOs) demonstrate high theoretical capacity (500 to 1000 mAh g^{-1}) [4] and attract plenty of attention due to its prospect for high energy density battery in place of graphite-based one [2]. As members of TMOs, Fe-based metal oxides have been intensively studied due to its low-cost manufacturing potential [5–8]. Despite that, intrinsic nature of metal oxides results in their poor conductivity, large volume expansion and electrochemical process suffering from some irreversible conversion reactions [9]. Among the Fe-based metal oxides, magnetite immerged differently as a metal oxide with high electrical conductivity [10,11]. Therefore, more researches aiming at achieving low-cost and high-performance electrode with the use of magnetite (Fe_3O_4) appear in the field of metal oxide anode.

It is well-known that miniaturizing electrode material particles down to nanoscale is an effective route to shorten ion transfer distance and maximize the utilization of the whole electrode [2,12]. In light of that, different nano-sized Fe_3O_4 structures were studied previously [13–16]. On one hand, small particles with short radius require minimal diffusion length for lithium ion, which facilitates fast lithiation process [12]. On the other hand, nano-sized particles with reasonable arrangements allow effective contact with electrolyte and fast infiltration of solvent [17–20]. With all those virtues, one can expect such electrode with high rate capability. Moreover, 3D electrodes derived from carbon cloth were studied intensively in recent publications [21–23]. Due to the 3D layout of current collector and active materials that contains hierarchical structure usually involve with fast electrochemical response and deliver large capacity at high rate.

In pursuit of enhanced electrochemical performance, we demonstrated a facile templating preparation route of a carbon cloth electrode loaded with magnetite nanotube arrays (MNTAs) deriving from $Fe(OH)_3$ with the support of ZnO templates. A sacrificial templating method was used in this work to deposit Fe $(OH)_3$ layer onto the ZnO nanorods templates, while follow-up annealing helped to convert the layer into Fe_3O_4. By tuning deposition time from 10 to 30 minutes (designated as MNTA-10,

* Corresponding author. Tel.: +86 20 84110071; Fax: +86 20 84112245.
E-mail addresses: ceslp@mail.sysu.edu.cn (P. Liu), chedhx@mail.sysu.edu.cn (Y. Tong).

http://dx.doi.org/10.1016/j.electacta.2016.01.173
0013-4686/

MNTA-20 and MNTA-30, respectively), a controllable synthesis of Fe_3O_4 nanotube or Fe_3O_4/ZnO composites can be achieved. Interestingly, further characterization of the as-obtained electrode showed that the nanotubes consist of numerous nanoparticles with radius less than 100 nm, which might possibly contribute to enlarge lithium storage, ion diffusion capability and overall utilization of the electrode materials. The whole electrode shows a 3D configuration in which carbon cloth serves as a conducting backbone with tubular Fe_3O_4 coating assembled from nanoparticles. Thus, the resultant electrode was tentatively examined for potential LIB application, delivering an actual specific capacity ~930 mAh g^{-1} at a current density of 2 A g^{-1}, despite the contribution of carbon cloth. This carbon cloth electrode showed promising prospects for high-rate flexible LIB devices.

2. Experimental

2.1. Synthesis of magnetite nanotube array

All reagents used were of analytical grade and were used directly without any purification. ZnO nanorods were first electrodeposited on conductive carbon cloth, followed by an acidic $Fe(NO)_3$ solution etching process to form a layer of $Fe(OH)_3$ covering the ZnO nanorods. In this process, Fe (III) ion was deposited in form of $Fe(OH)_3$ through hydrolysis promoted by the dissolving of ZnO sacrificial templates, which was proposed by previous work [24,25]. Typically, a piece of carbon cloth (with geometric area of 3 cm *3 cm immersed in electrolyte) was used as working electrode and a carbon rod the counter electrofde. The deposition was carried out under galvanostatic condition in an electrolyte containing 0.01 M $Zn(NO)_3{\cdot}6H_2O$ + 0.01 M CH_3COONH_4 + 0.01 M $(CH_2)_6N_4$ at 70 °C, with a current density of 0.7 mA cm^{-2} maintained for 2 h. The resultant ZnO was cleansed with deionized (DI) water and immediately immersed into 0.025 M $Fe(NO)_3$ for 30 min. After washing with DI water again, the ZnO@$Fe(OH)_3$ composite was dried at 60 °C in an oven overnight. Subsequently, the ZnO@$Fe(OH)_3$ composite was transferred into a tube furnace and annealed in N_2 atmosphere at 600 °C for 60 min to produce Fe_3O_4 nanotubes array loaded on carbon cloth support. For samples with residual ZnO, shorter immersion time was applied to the ZnO templates and all the samples were denoted as MNTA-t, where t stands for immersion time in $Fe(NO_3)_3$ solution (in minutes).

2.2. Structural characterization

The morphologies of carbon cloth electrodes were observed by field emission scanning electron microscopy (FESEM, Quanta 400/INCA/HKL). Transmission electron microscopy (TEM, JEM-2010HR) was used to further study the tube-like morphologies in details, all samples for TEM observation were loaded on copper grids from a suspension prepared from ultrasonicating the carbon cloth electrodes in ethanol. Crystal structure was confirmed by X-ray diffraction (XRD), accompanied with Raman spectra which could provide vibration information of the samples to identify the existence of Fe_3O_4.

2.3. Electrochemical measurements

All MNTA electrodes were assembled into CR2032 coin cells for electrochemical measurements, using lithium foil as counter electrodes. To be specific, carbon cloth electrodes were prepared by cutting all samples into square pieces (8 mm*8 mm) and weighed in an analytical balance (Sartorius, max weight 5100 mg, d $^1/_4$ 0.001 mg) before coin cell assembling. Mass loading of active materials was simply calculated from the difference between

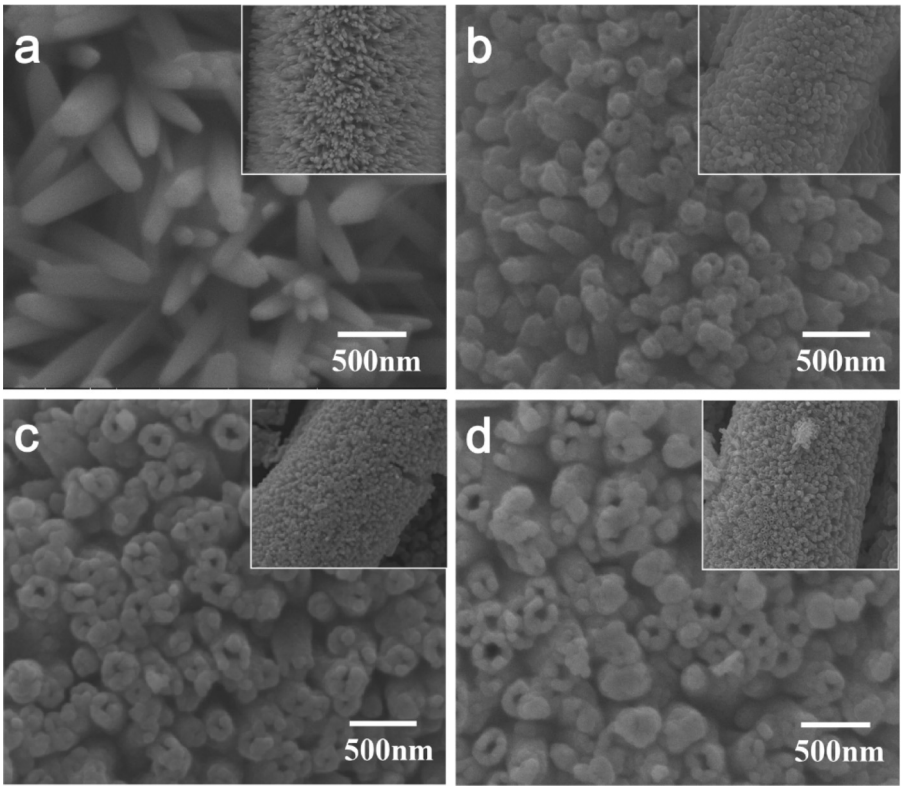

Fig. 1. FESEM images of pristine (a)ZnO; (b)MNTA-10; (c) MNTA-20; (d) MNTA-30. All samples (except for the ZnO templates) were annealed at 600 °C for 1 h. Insets are the corresponding images at a lower magnification.