Materials Chemistry and Physics 207 (2018) 58–66

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Leaf-like α-Fe_2O_3 micron-particle: Preparation and its usage as anode materials for lithium ion batteries

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HIGHLIGHTS

- Leaf-like micron particles of Fe_2O_3 were prepared by a pyrolysis method.
- Leaf-like particles of Fe_2O_3 delivered a discharge capacity of 317 mAh g^{-1} at 500 mA g^{-1} even after 10 cycles.
- NaOH-boiled MWCNTs and H_2SO_4-boiled MWCNTs had different influences on the morphology of the products.

ARTICLE INFO

Article history:

Keywords:
Nanostructures
Oxides
Electrochemical techniques

ABSTRACT

For the first time, the preparation of leaf-like α-Fe_2O_3 micron-particles via a pyrolysis method using potassium ferricyanide ($K_3[Fe(CN)_6]$) as the precursor was reported in this work. The characterizations of the synthesized samples were mainly conducted by using XRD, XPS and SEM. The existence of α-Fe_2O_3 in the final samples was effectively demonstrated by the XRD patterns and XPS spectra, and the SEM images indicated that the micron-particles with leaf-like crystal morphology as the main components were observed in sample b, and instead, more micron-particles with cubic crystal morphology were displayed in sample a. The electrochemical performances of the prepared samples as anode materials for lithium ion batteries (LIBs) were principally evaluated by using CV, galvanostatic charge-discharge tests and EIS. The results of electrochemical measurements demonstrated that at the current density of 100 mA g^{-1}, the initial specific capacity of sample b was about 741 mAh g^{-1}, much larger than that of sample a (564 mAh g^{-1}). More importantly, after 10 cycles, at the current density of 500 mA g^{-1}, the capacity of sample b was maintained as high as 317 mAh g^{-1}, significantly larger than that of sample a (244 mAh g^{-1}).

1. Introduction

Although graphite as one kind of carbon has been widely used as an anode material in the commercial LIBs, the disadvantages of using it were urgently claimed in recent years [1]. Among these disadvantages, relatively lower theoretical capacity (372 mAh g^{-1}) and safety issue are thought as the main problems which greatly impeded the further applications of graphite [2]. Thus, the pursuit of novel anode materials of LIBs has become an important topic in the LIBs-related research realm [3,4].

Recently, many kinds of metal oxides such as SnO_2 [5], Co_3O_4 [6] and NiO [7,8] have been developed as anode materials for LIBs. Among these developed metal oxides, iron oxide of Fe_2O_3 is regarded as the most promising anode material for LIBs since it can react with Li basing on a conversion-type reaction ($Fe_2O_3 + 6Li \rightarrow 2Fe + 3Li_2O$) [9,10] showing a higher theoretical capacity value of 1005 mAh g^{-1}. Also, except for the higher theoretical capacity value, the more abundance in nature, environmental friendliness and relatively lower cost are all the merits of Fe_2O_3 when compared to other metal oxides. However, due to the poor electronic and ionic

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https://doi.org/10.1016/j.matchemphys.2017.12.046

conductivity of iron oxides as well as the dramatic volume changes in cycling, the further commercialization of Fe_2O_3 is remarkably hampered by the fast capacity drop in cycling and the poor capacity retention [11]. Thus, many strategies have been proposed to promote the electrochemical performance of Fe_2O_3. Among these strategies, being mixed with carbon materials was reckoned as the simplest way to improve the electrochemical behavior of Fe_2O_3 [12]. Many kinds of carbon such as carbon nanotubes [13], carbon nanofibers [14] and graphene [15] have been mixed with Fe_2O_3, showing an improved electrochemical performance compared to the pure Fe_2O_3. For example, Chen's groups [16] reported the synthesis of Fe_2O_3 nanobelts/carbon nanotubes (CNTs) composites, and stated that the resultant composites could deliver an initial specific capacity of 847.5 mAh g^{-1} at 100 mA g^{-1}. However, to the best of our knowledge, the research work concerning the synthesis of the composite that contained NaOH-boiled (or H_2SO_4-boiled) carbon nanotubes and Fe_2O_3 has not yet been published so far.

It is well known that the morphology of an anode material is, also, a key parameter which can effectively influence the electrochemical performance of a battery cell. Very recently, many novel morphologies of Fe_2O_3 such as hollow spheres [17], nanotubes [18] and nanorods [19] have been created with an intention to enhance the electrochemical properties of Fe_2O_3. However, as far as we know, the work concerning the preparation of leaf-like micron particles of Fe_2O_3 in the presence of multi-walled carbon nanotubes (MWCNTs), not to mention the investigation work of leaf-like particles of Fe_2O_3 as anode materials for LIBs, was not reported till present.

In this preliminary work, a proper amount of MWCNTs, one kind of carbon nanotubes, were boiled in NaOH and H_2SO_4 solution, respectively, generating NaOH-boiled MWCNTs and H_2SO_4-boiled MWCNTs. And then, after filtration, the washed and dried MWCNTs were transferred into a potassium ferricyanide solution, and the formed suspension solution was heated at 200 °C for 2 h. Interestingly, micron particles with leaf-like morphology (sample b) were prepared in the presence of H_2SO_4-boiled MWCNTs, and cubic particles as the main components in the final samples (sample a) were displayed in the presence of NaOH-boiled MWCNTs. The results of electrochemical experiments revealed that at the current density of 100 mA g^{-1}, the initial discharge capacity of sample b was as high as 741 mAh g^{-1}, remarkably larger than that of sample a (564 mAh g^{-1}). Also, for sample b, the discharge capacity value could be retained at about 317 mAh g^{-1} at 500 mA g^{-1} even after 10 cycles. To my certain knowledge, this is the first report on the preparation of leaf-like α-Fe_2O_3 micron particles and its applications as anode materials for LIBs to date.

2. Experiment

2.1. Materials

MWCNTs (purity>95%) of 10–20 nm diameter were bought from Shenzhen nanotech port Co., Ltd. (China). All chemicals were purchased from Tianjin Chemical Reagent Co. Ltd. And all chemicals were utilized as received without any further purification. All electrodes employed were provided by Tianjin Aida Co., Ltd (China). All materials used in the battery testing experiments, such as the electrolyte of 1 M $LiClO_4$, acetylene black, polytetrafluoroethylene (PTFE) binder and the cell, were all supported by the Tianjin Lianghuo S&T Developing Co. Ltd (China). The aqueous solutions were produced by the doubly distilled water.

2.2. Preparation of samples

Prior to the preparation of the samples, the fabrications of NaOH-boiled MWCNTs and H_2SO_4-boiled MWCNTs were respectively conducted first. In brief, 5 mg MWCNTs were dissolved in 100 mL of 0.5 M NaOH solution, and then the resultant suspension solution was boiled for 2 h to complete the NaOH-boiling treatment. And then the filtered samples were washed with copious distilled water until the pH value of filtrate was equal to 7. The obtained samples were dried in air, leading to the formation of NaOH-boiled MWCNTs. Correspondingly, the H_2SO_4-boiled MWCNTs were synthesized using the same process, in which 3 M H_2SO_4 solution rather than 0.5 M NaOH solution was employed.

Subsequently, 0.15 g of the NaOH-boiled MWCNTs was dispersed in 5 mL of 0.1 M potassium ferricyanide solution forming a suspension solution. And soon afterwards, the resulting suspension solution was transferred into a well-sealed home-made autoclave (its volume was 50 mL), followed by a 200 °C heating treatment for 2 h in a muffle furnace, so as to finish the pyrolysis process. After naturally cooling down to the room temperature, the products were obtained, which was nominated as sample **a**. Similarly, sample **b** was produced using the same procedure, in which 0.15 g of the H_2SO_4-boiled MWCNTs instead of NaOH-boiled MWCNTs was used.

2.3. Characterization

The phase homogeneity of the prepared samples was studied by X-ray diffraction (Bruker AXS, D8 ADVANCE, Germany). The particle morphologies of the synthesized samples were examined by using scanning electron microscopy (HITACHI, SEM S-570) and transmission electron microscopy (HITACHI, TEM H-7650). The components of the as-prepared samples were analyzed by Energy dispersive spectrometer (EDS, INCA Energy 350, England). X-ray photoelectron spectroscopy (XPS, Kratos Analytical spectrometer, Al K_α radiation) was employed to analyze the chemical valence of the elements in the prepared samples.

Electrochemical measurements, namely, Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS), were performed on a personal computer-controlled CHI 660B electrochemical workstation (Shanghai Chenhua Apparatus, China). In the EIS measurements, the oscillation voltage was 5 mV, and the frequency range was from 100 kHz to 0.1 Hz. All the experiments were carried out at room temperature.

The working electrodes were prepared principally based on the following steps. First, the active material powders, acetylene black and polyvinylidene fluoride binder were well mingled together basing on a weight ratio of 80:10:10 to form a mixture. And then, several drops of N-methylpyrrolidone were added into above as-prepared mixture, and after the thorough stirring uniform slurries were produced. To prepare a working electrode, the resultant slurries were coated onto a copper (Cu) foil, followed by 6 h drying at 120 °C in a vacuum oven. The prepared working electrode, lithium metal foil and Celgard 2400 separator were assembled together in a high pure nitrogen-filled glove box to produce the two-electrode electrochemical cells. It should be emphasized that in all prepared cells, 1 M $LiClO_4$ was the electrolyte and the mixed solvent contained ethylene carbonate (EC) and diethyl carbonate (DEC) and dimethyl carbonate (DMC) at the volume ratio of 2:5:11. Apparently, metallic lithium foils were used as both the reference and counter electrodes. The galvanostatic charge-discharge tests were carried out on a battery testing system (CT-3008W-5V20 mA-S4, Shenzhen Neware Electronics Co., Ltd. China) under various current densities between 0.01 and 3 V at room temperature.

3. Results and discussion

3.1. XRD analysis

XRD patterns of sample **a** and **b** as well as the standard XRD