Materials Research Bulletin 79 (2016) 22–28

Contents lists available at ScienceDirect

Materials Research Bulletin

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

# Porous $CoFe_2O_4$ nanowire arrays on carbon cloth as binder-free anodes for flexible lithium-ion batteries

Saihua Zhao, Jinxin Guo, Fei Jiang, Qingmei Su, Gaohui Du*

*Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, China*

ARTICLE INFO

*Article history:*
Received 16 October 2015
Received in revised form 25 February 2016
Accepted 27 February 2016
Available online 2 March 2016

*Keywords:*
A. Nanostructures
A. Oxides
B. Chemical synthesis
C. Electron microscopy
D. Energy storage

ABSTRACT

A three-dimensional $CoFe_2O_4$ nanowire array on carbon cloth was fabricated with a hydrothermal method together with a post-annealing treatment. As a binder-free and flexible anode material for LIBs, it showed an improved electrochemical performance with high cycling stability and excellent rate capability. It exhibited an initial discharge capacity of 1615 mAh $g^{-1}$ and retained a reversible capacity of about 1204 mAh $g^{-1}$ after 200 cycles at a specific current of 500 mA $g^{-1}$. The high capacity, outstanding rate performance and cycling stability can be attributed to the special configuration of hierarchal porous $CoFe_2O_4$ nanowires on carbon cloth, which possess many advantages like short diffusion length, easy strain relaxation and fast electron transport. Moreover, the integrated $CoFe_2O_4$ nanowires/carbon cloth electrode shows high flexibility and high areal capacity (2.41 mAh $cm^{-2}$), which makes it suitable for use as a binder-free anode to build flexible LIBs.



## 1. Introduction

Flexible electronics is an emerging and promising technology for the next-generation optoelectronic devices, like rollup displays, smart electronics and wearable devices [1–4]. These devices demand batteries with high energy and power densities, which make flexible lithium-ion batteries (LIBs) suitable for utilization [5–7]. Flexible electrodes in LIBs are usually made from various functional organic and/or inorganic materials built on flexible conductive membrane substrates without conductive additives and binders. Recently, a lot of attention has been focused on the assembly of flexible LIBs and promising results have been reported [8–12]. The key challenge to realize flexible batteries is to design and fabricate reliable materials with high rate capability, cycling stability, and robust flexibility.

In order to meet the flexible performance of devices, various flexible electrode materials for LIBs have been prepared from carbonaceous and other membrane materials. For example, electrode materials based on CNTs [13–15], graphene [16,17], carbon cloth [18–20], conductive paper (cellulose) [21], textiles [1], and low-dimensional nanostructured materials [22] have been reported. Carbon cloth, as a new kind of substrate, possesses some advantageous properties over other materials, including low cost, high conductivity, high strength, excellent structural stability and good corrosion resistance, which make it commercially available and can be used as a lightweight, flexible current collector without any ancillary binders and conductive additives. These characteristics allow it to serve as a platform for the construction of flexible LIBs with improved properties and functionalities.

Recently, cobalt ferrite ($CoFe_2O_4$) has attracted great attention due to its high gravimetric specific capacity (916 mAh $g^{-1}$), safety, low cost, and environmental friendliness. However, like other transition metal oxides, $CoFe_2O_4$ suffers from the problems of poor electrical conductivity and electrode pulverization induced by huge volume changes during the charge–discharge processes, leading to poor cycling stability and rate capability. Thus, three-dimensional (3D) hierarchical architectures with large surface area, better permeability, and more active sites have been reported to solve the problems.

In this work, we report the fabrication of 3D $CoFe_2O_4$ nanowires on flexible carbon cloth via a simple hydrothermal method and subsequent annealing treatment. In this novel electrode design, $CoFe_2O_4$ nanowires of highly crystalline quality were directly grown on conductive carbon cloth to ensure quick electron transport. The 3D hierarchical architectures offer many advantages for flexible LIBs, such as large surface area and short Li-ion diffusion length. By using the hierarchal $CoFe_2O_4$ nanowires/carbon cloth as both a new class of binder-free anode and the current collector, the highly flexible LIBs demonstrate an improved electrochemical performance. To the best of our knowledge, the

* Corresponding author.
*E-mail addresses:* gaohuidu@zjnu.edu.cn, gaohuidu@gmail.com (G. Du).

http://dx.doi.org/10.1016/j.materresbull.2016.02.041
0025-5408/

porous 3D $CoFe_2O_4$ nanowires/carbon cloth flexible electrodes for LIBs have not yet been reported.

## 2. Experiment

### 2.1. Synthesis of materials

All chemicals (purchased from Sinopharm Chemical Reagent Co., Ltd.) were of analytical grade and used as starting materials without further purification. The carbon cloth (WOS1002, CeTech Co., Ltd.) was cleaned by sonication sequentially in acetone, deionized water and ethanol for 2 h each. Subsequently, the nitric acid was used to active the well-cleaned carbon cloth for 4 h. The $CoFe_2O_4$ nanowires/carbon cloth was synthesized via a two-step process. In a typical synthesis, 1 mmol cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$), 2 mmol ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), 2 mmol ammonium fluoride ($NH_4F$) and 5 mmol urea ($CO(NH_2)_2$) were added to 35 mL of distilled water and stirred for 30 min. The mixed solution was transferred into a Teflon-lined autoclave with a piece of round carbon cloth with a diameter of 14 mm and then heated to120 °C for 12 h. After being cooled to room temperature, the carbon cloth was collected, washed, and then calcined at 450 °C in Ar atmosphere for 2 h.

### 2.2. Characterization

The products were characterized using X-ray powder diffraction (XRD) on a philips PW3040/60 X-ray diffractometer with Cu Kα (λ = 1.5418 Å) radiation for phase identification. The morphologies were examined using scanning electron microscopy (SEM) on a Hitachi S4800 microscope, and the microstructures were investigated using transmission electron microscopy (TEM) and selected area electron diffraction (SAED) performed on a JEOL 2100F instrument.

### 2.3. Electrochemical test

The $CoFe_2O_4$ nanowires/carbon cloth composite was directly used as working electrode in coin-type half cells (CR2025), which were assembled in an argon-filled glove box with metallic lithium foil (China Energy Lithium Co., Ltd) as the counter electrode and Celgard 2400 membranes as separator. The electrolyte was 1 M $LiPF_6$ in ethylene carbonate and diethyl carbonate (1:1 by volume) (China Energy Lithium Co., Ltd). Coin-type half-cells were cycled at various specific current in the voltage range of 0.005–3.0 V (vs. $Li/Li^+$) at room temperature with a multichannel battery measurement system (Neware, China). Cyclic voltammetry (CV) was conducted on an Autolab work station. The CV was carried out in the range of 0.02–3.00 V (vs. $Li/Li^+$) at a scan rate of 0.1 mV $s^{-1}$.

## 3. Results and discussion

Fig. 1 shows the XRD pattern of the resultant $CoFe_2O_4$ nanowires on carbon cloth. All the diffraction peaks in this pattern can be readily indexed as spinel $CoFe_2O_4$ (JCPDS Card No. 22–1086). The peaks around 26° and 43° are also observed and can be assigned to the carbon cloth substrate. Furthermore, the diffraction peaks are sharp and intense, implying the successful synthesis of highly crystalline $CoFe_2O_4$.

The structure of $CoFe_2O_4$ nanowires/carbon cloth was characterized using SEM technique as shown in Fig. 2. The SEM image of the pure carbon cloth is shown in Fig. 2(a), which exhibits ordered texture structure, and each carbon fiber has a smooth surface and a uniform diameter of around 9 μm. Fig. 2(b) clearly reveals that the final product still remains the ordered woven structure of the carbon cloth substrate. High-magnification SEM images shown in Fig. 2(c–e) provide clear information about the $CoFe_2O_4$ nanowires. Obviously, the nanowires are densely grown on the whole surface of carbon fibers, and the nanowires are well aligned, forming an array with a highly open structure on large scale. Fig. 2(f) shows a photo of the integrated $CoFe_2O_4$ nanowires/carbon cloth electrode, which can be readily rolled up with tweezers (Fig. 2g). It can be clearly observed that the electrodes exhibit excellent flexibility, which makes them possible for application in flexible devices. The $CoFe_2O_4$ nanowires with high density have been successfully grown on the carbon cloth by using a facile hydrothermal method. The exact mass of the nanowires was determined by weighing the carbon cloth before/after the nanowire growth. The loading density of the $CoFe_2O_4$ active material is calculated to be 1.7–2.0 mg $cm^{-2}$.

The microstructure of the $CoFe_2O_4$ nanowires was analyzed by means of TEM and SAED. Fig. 3(a) reveals that the diameters of $CoFe_2O_4$ nanowires are about 50–100 nm. These $CoFe_2O_4$ nanowires are found to be porous (Fig. 3b), which was induced by dehydration and pyrolysis during the calcination process. The porous feature of the nanowires is beneficial for electrode materials due to the large surface area and the short Li ion diffusion pathways. The HRTEM image shown in Fig. 3(c) reveals two sets of lattice fringes with spacing of 0.25 nm and 0.19 nm, respectively, corresponding to the (3 1 1) and (3 3 1) planes of spinel $CoFe_2O_4$ phase. The corresponding SAED pattern shown in Fig. 3(d) indicates the polycrystalline nature of $CoFe_2O_4$ nanowires. The

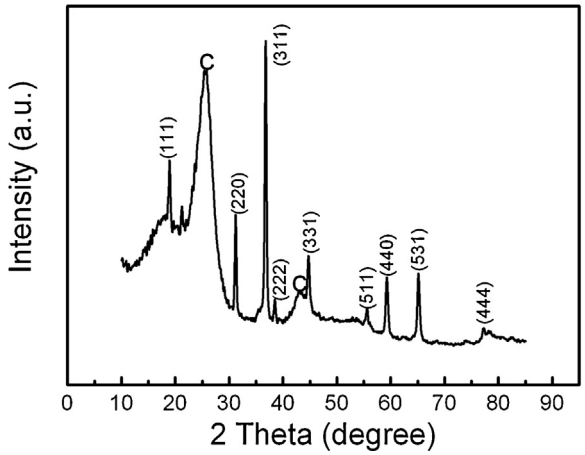


**Fig. 1.** XRD pattern of $CoFe_2O_4$ nanowires/carbon cloth composite.