Electrochimica Acta 247 (2017) 125–131

Contents lists available at ScienceDirect

Electrochimica Acta

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

Graphene enhanced anchoring of nanosized Co_3O_4 particles on carbon fiber cloth as free-standing anode for lithium-ion batteries with superior cycling stability

Qinxing Xie[a,*], Yufeng Zhang[a], Yating Zhu[a], Weigui Fu[a], Xu Zhang[a], Peng Zhao[b], Shihua Wu[b]

[a] Tianjin Key Laboratory of Advanced Fibers and Energy Storage, School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, China
[b] Department of Chemistry, Nankai University, Tianjin 300017, China

ARTICLE INFO

Article history:
Received 30 January 2017
Received in revised form 3 June 2017
Accepted 28 June 2017
Available online 29 June 2017

Keywords:
Cobalt oxide
Free-standing anode
Lithium ion battery
Graphene
Composite

ABSTRACT

The graphene-coated carbon fiber cloth (CC@Gr) anchored with nanosized Co_3O_4 particles was successfully fabricated. According to the results of structural characterization, it was observed that the graphene-coated carbon fibers are able to anchor much higher amount of Co_3O_4 nanoparticles than graphene-free carbon fibers. The composite was applied as free-standing anode for lithium ion batteries, and it exhibits enhanced energy storage capability. A high reversible specific capacity of nearly 400 mAh g^{-1} at a current density of 100 mA g^{-1} can be achieved based on the total mass of Co_3O_4 and CC@Gr fibers (mass ratio = 16:84). In addition, the composite demonstrates excellent rate performance and superior cycling stability.

1. Introduction

Lithium ion batteries (LIBs) have been considered as one of the most applicable energy storage systems for portable devices and electric vehicles because of a number of advantages including high energy density, high safety and long cycle-life [1–4]. Most commercial LIBs utilize graphite as anodes, however, graphite suffers from a low theoretical capacity of 372 mAh g^{-1}. Transition metal oxides (TMOs) including Fe_3O_4, CuO, Co_3O_4, MnO_2 and etc. have become more and more attractive as promising anode candidates for LIBs in recent years because of their high theoretical reversible capacity [5–7]. However, the practical application of TMOs are limited due to their large irreversible capacity loss and poor cycling stability owing to the large volume change and severe particle pulverization during lithium ion insertion/extraction process [6,8].

Generally, the morphology and particle size of TMOs have strong influence on their electrochemical properties. Therefore, nanosized TMOs with various morphologies including nanotubes, nanorods, nanowires/nanofibers, hollow spheres and nanosheets have been successfully fabricated and applied as anodes for LIBs [6,8,9–13]. The reduced dimension scale from micrometer to nanometer is able to shorten the diffusion path of electrolyte ions. The more applicable strategy to address the above mentioned shortcomings is to fabricate the composite anodes that are composed of nanosized active metal oxides and carbon substrates such as carbon nanotubes (CNTs), porous carbon, carbon nanofibers (CNFs) and graphene [11,14–19]. The substrates can not only buffer the volume change of metal oxides, but also improve the conductivity accounting for enhanced rate capability.

Graphene is a new kind of carbon material of two-dimensional cellular structure, it dominates superior benefits as anodes of LIBs including high electrical and thermal conductivity, large theoretical specific surface area, and excellent mechanical property [20,21]. Additionally, the electrochemical performance of TMOs can be significantly enhanced through a strategic combination with graphene. It was reported that the oxygenated graphene is able to construct strong bindings with TMOs through C-O-M bridges, which facilitates fast electron hopping from graphene to TMOs, hence accounting for dramatically enhanced reversible capacity and excellent rate performance [22]. Among these composites, cobalt oxides (CoO, Co_3O_4) anchored on graphene have attracted increasing interests as LIBs anodes due to their high

* Corresponding author.
E-mail address: qxxie@yahoo.com (Q. Xie).

http://dx.doi.org/10.1016/j.electacta.2017.06.167

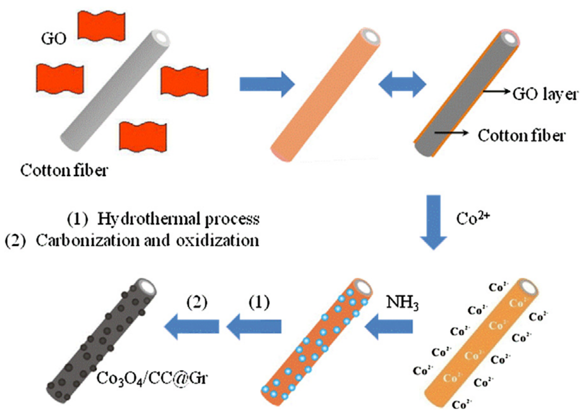

Fig. 1. Schematic illustration of the fabrication of Co_3O_4/CC@Gr composite.

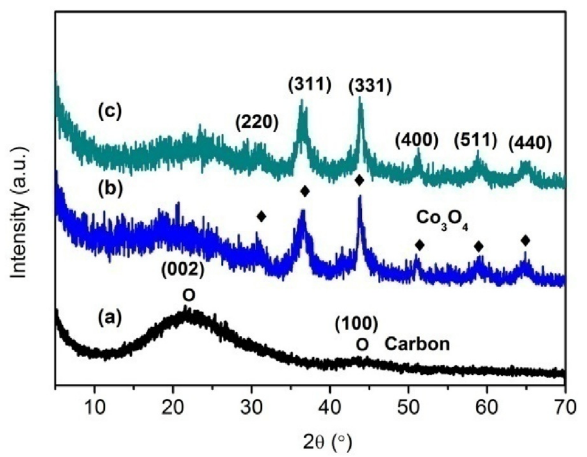

Fig. 2. XRD patterns of (a) CC@Gr, (b) Co_3O_4/CC and (c) Co_3O_4/CC@Gr.

theoretical specific capacity, i.e. 750 and 890 mAh g^{-1} for CoO and Co_3O_4, respectively [19,23,24].

In this work, nanosized Co_3O_4 particles anchored on flexible carbon fiber cloth were successfully fabricated. To facilitate the anchoring, the cotton fibers, i.e. the precursor of the carbon cloth were pre-coated with a thin layer of graphene that contains adequate oxygen-containing functional groups. The functional groups are able to form strong interactions with cobalt cations through Co-O coordination bonds, therefore homogeneous and stable anchoring of Co_3O_4 on carbon fibers can be achieved after carbonization process, and the particle aggregation problem can be effectively hindered. Additionally, the interwoven framework of graphene-coated carbon fibers provides an efficient conductive network. The composite cloth was applied as free-standing anode for LIBs, which exhibits excellent rate performance and superior cycling performance.

2. Experimental

All chemicals for the experiments are analytical grade and used as received. Graphite oxide was prepared by a modified Hummers method [25–27]. The cotton cloth with a thickness of ca. 1 mm was washed with distilled water and ethanol in turn for several times, and cut into small pieces of 18 mm in diameter prior to the experiment. 0.1 wt.% aqueous solution of graphene oxide (GO) was used as the coating agent, which was prepared by ultrasonically dispersing 100 mg of graphite oxide in 100 mL distilled water.

2.1. Materials preparation

The cotton cloth was coated with 0.1 wt.% aqueous solution of GO using a simple dip-coating method, and dried at 150 °C for 5 h. The coating amount of GO can be determined according to the mass difference of the cotton cloth before and after coating, it was about 0.08 wt.% relative to the cotton cloth. The GO-coated cotton cloth was then dipped into 0.1 mol L^{-1} aqueous solution of cobalt

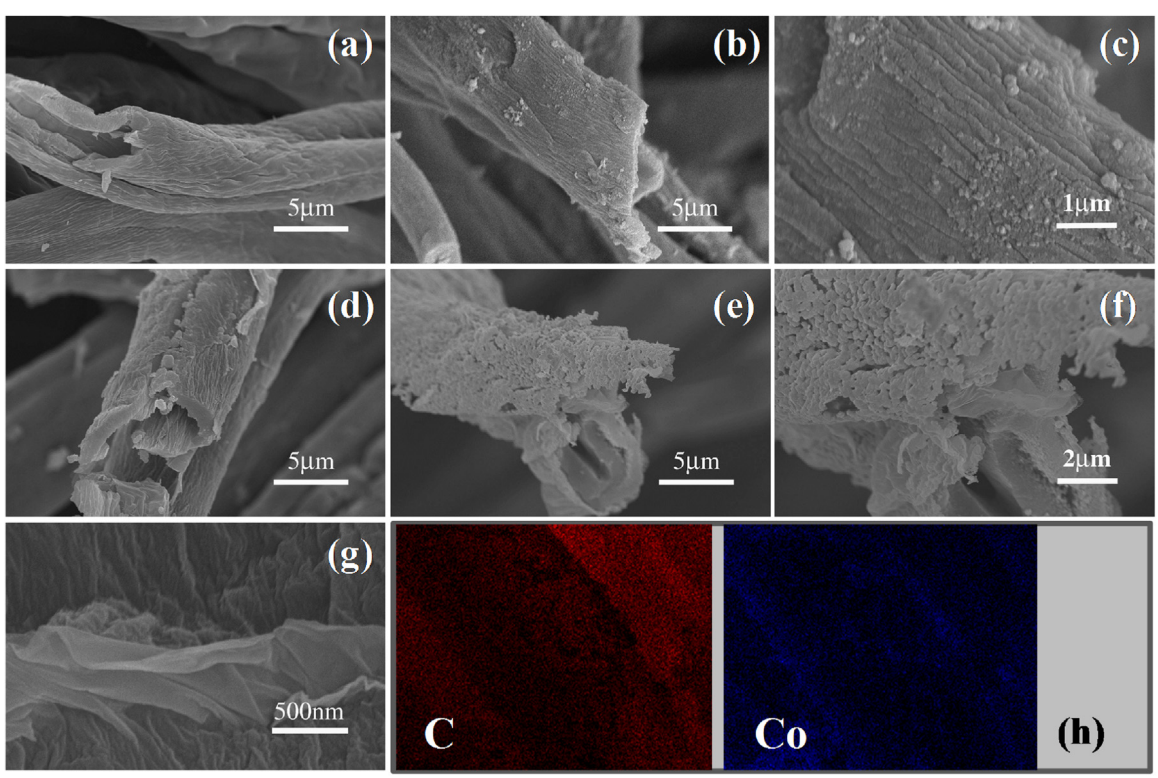

Fig. 3. SEM images of (a) CC, (b-c) Co_3O_4/CC, (d) CC@Gr and (e-f) Co_3O_4/CC@Gr.