Electrochimica Acta 187 (2016) 234–242

Contents lists available at ScienceDirect

Electrochimica Acta

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

Nitrogen-doped porous carbon spheres anchored with Co_3O_4 nanoparticles as high-performance anode materials for lithium-ion batteries

Liangui Guo[a,c], Yu Ding[a,b], Caiqin Qin[a,c,*], Wei Li[a,c], Jun Du[a], Zhengbin Fu[a], Wulin Song[b], Feng Wang[a,**]

[a] College of Chemistry and Materials Science, Hubei Engineering University, Xiaogan 432000, China
[b] State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China
[c] Collaborative Innovation Center of Conversion and Utilization for Biomass Resources, Hubei Engineering University, Xiaogan 432000, China

ARTICLE INFO

Article history:
Received 3 July 2015
Received in revised form 10 November 2015
Accepted 12 November 2015
Available online 17 November 2015

Keywords:
Nitrogen-doped porous carbon spheres
Co_3O_4 nanoparticles
Hydrothermal
Lithium-ion battery
Anode material

ABSTRACT

In this work, Co_3O_4 nanoparticles were loaded on the nitrogen-doped porous carbon spheres (NPCS) by a facile hydrothermal method. The NPCS were derived from carboxymethyl chitosan as the carbon and nitrogen source. The as-prepared Co_3O_4/NPCS nanocomposites were used as anode materials for lithium-ion batteries. The electrochemical results showed that the materials possessed a high initial discharge capacity of 1245.5 mAh g^{-1} and still maintained a high reversible capacity of 983.9 mAh g^{-1} after 100 cycles at a current density of 100 mA g^{-1}. Even at a high current density of 5 A g^{-1}, it delivered a very stable reversible capacity of 659 mAh g^{-1}. The high electrochemical performance of the Co_3O_4/NPCS nanocomposites can be attributed to the synergistic effects of the nanoscale Co_3O_4 particles, the porous structure of the NPCS and the N functional groups on the NPCS.

1. Introduction

Lithium-ion batteries (LIBs) have been widely adopted in portable electronic devices due to their high energy density, long cycle life, and high operating voltage. LIBs are also considered as one of the most promising power batteries for pure electric vehicles (PEV) [1,2]. However, graphite as anode material for commercial LIBs cannot meet the ever-increasing demands for high-performance LIBs due to its low theoretical specific capacity (372 mAh g^{-1}) and limited rate capability [3].

Transition metal oxides have attracted attention as an anode material for LIBs, because they display higher theoretical capacity than conventional graphite [4–7]. Among them, Co_3O_4 is considered as a promising candidate anode material due to its high theoretical capacity (890 mAh g^{-1}) and excellent electrochemical reactivity [8]. But its practical application is limited due to low intrinsic electrical conductivity, large volume change, and severe particle aggregation during charge/discharge cycling, which will lead to electrode pulverization, capacity loss and poor cycling stability [9]. A few different strategies have been proposed to circumvent these intractable drawbacks. One is to fabricate various Co_3O_4 nanostructures, such as nanoparticles [10], nanowires [11,12], nanorods [13], nanotubes [14], nanobelts [15], nanosheets [16,17], nanocages [18], nanocubes [19] and nanoflowers [20,21]. The high surface area and small dimension of these nanostructured Co_3O_4 are beneficial to permitting high contact area with electrolyte and shortening diffusion distance of lithium ion in the solid phase [22,23]. However, the agglomeration of these nanostructured Co_3O_4 and the collapse of their crystal structures during the insertion and extraction of lithium ions still affect the preservation of high capacities [24]. Another promising strategy is to construct hybrid materials composed of nanostructured Co_3O_4 and carbonaceous matrix, such as porous carbon [25,26], onion-like carbon shell [27], graphene [28–31], carbon nanotubes [32], carbon nanowires [33,34], and carbon sheet [35]. The carbonaceous matrix will be expected to serve as both a stress buffer to release the volumetric stresses and a conductive path for fast lithium ion and electron transfer [33]. Although the above approaches have been proven more or less effective, there is still plenty room for improvement.

Recently, nitrogen-doping has attracted wide attention as an effective method to improve the electrochemical performance of

---

* Corresponding author. Tel.: +86 712 2345971; fax: +86 712 2345265.
** Corresponding author.
E-mail addresses: qincq@hbeu.cn (C. Qin), hbeukj@126.com (F. Wang).

http://dx.doi.org/10.1016/j.electacta.2015.11.065
0013-4686/© 2015 Elsevier Ltd. All rights reserved.

carbon materials [36]. Nitrogen-doping can induce plenty of defects and form a disordered carbon structure, which may offer more active sites for enhancing the lithium storage [37]. Moreover, nitrogen-doping can enhance the reactivity and electric conductivity of the carbon materials, which is of benefit for improving the rate capacity [38]. Porous carbon spheres have been demonstrated to be competent for using as anode materials for LIBs, because spherical materials enjoy a high packing density, a low surface to volume ratio, maximal structural stability and ease of preparing electrode films [39]. Furthermore, the porous structure can shorten the lithium ion transport length and facilitate the charge-transfer reaction on the electrode/electrolyte interface, which can provide extra high lithiation capability [38,40]. Thus one can expect that Co_3O_4 nanoparticles decorated NPCS should be a very promising high-performance anode material for LIBs.

Herein, we report a facile hydrothermal method for synthesizing Co_3O_4/NPCS nanocomposites. The NPCS were derived from carboxymethyl chitosan as the carbon and nitrogen source. Carboxymethyl chitosan containing amino group is a water soluble chitosan derivative prepared by carboxymethylation of chitosan. When used as anode materials for LIBs, the Co_3O_4/NPCS nanocomposites exhibit high lithiation capacity, good rate capability, and excellent cycle performance, which may be one of the most promising anode materials for LIBs.

2. Experimental

2.1. Materials preparations

The NPCS were obtained through a hard template method. In a typical procedure, 0.32 g cetyl trimethyl ammonium bromide (CTAB) was completely dissolved in mixed solvent of 106 mL deionized water and 56 mL ethanol under stirring, then 2 mL tetraethyl orthosilicate (TEOS) and 2 mL ammonium hydroxide were added under vigorously stirring for 8 h to form solution A. 1 g carboxymethyl chitosan (Viscosity: 10–80 mPaS; carboxymethylation degree > 80%) was completely dissolved in 50 mL of deionized water to form solution B. Subsequently, solution B was poured into the solution A under vigorously stirring for 12 h at room temperature. After the solvent of the white suspension mixture was evaporated in 100 °C water bath under stirring, the residuum was dried at 100 °C for 8 h and further carbonized at 800 °C for 4 h under N_2 atmosphere at the heating rate of 5 °C min^{-1} in a tube furnace. Finally, the NPCS were obtained after washing with 10 wt% HF solution and deionized water.

The Co_3O_4/NPCS nanocomposites were prepared by a facile hydrothermal method. In a typical procedure, 70 mg of the NPCS was added into 70 mL of ethanol, and then ultrasound dispersed for 30 min. Afterward, 0.36 g of cobaltous acetate, 2 mL of ammonium hydroxide and 4 mL of deionized water were added into above solution under stirring for 20 h at 80 °C. Then the mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave for hydrothermal reaction at 150 °C for 3 h. After cooled to room temperature naturally, the resulting product was collected by centrifugation, washed by deionized water and ethanol for three times, and dried at 80 °C for 12 h in the drying oven.

2.2. Materials characterizations

The structure and morphology of the nanocomposite were characterized by X-ray diffraction (XRD, Bruker D8 Advance using Cu Kα radiation in the 2θ range from 15 to 80°), field-emission scanning electron microscopy (FESEM, JEOL JSM-7100F), transmission electron microscopy (TEM, FEI Tecnai G2 F20) and nitrogen adsorption-desorption measurement (Micromeritics ASAP 2020). Thermogravimetric (TG) analysis was conducted on a STA 6000 instrument from room temperature to 800 °C at a heating rate of 10 °C min^{-1} in air. Raman spectroscopy was measured on a LabRAM HR Evolution equipped with 632 nm laser excitation wavelengths. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra DLD with a monochromatic Al Kα radiation source ($h\gamma = 1486.6$ eV).

2.3. Electrochemical measurements

The electrochemical properties of the Co_3O_4/NPCS nanocomposites were evaluated using CR2016-type coin cells. The working electrodes were prepared by mixing 80 wt% Co_3O_4/NPCS active materials and 10 wt% acetylene black conducting additive and 10 wt% polyvinylidene fluorides (PVDF) binder in *N*-methyl-2-pyrrolidone (NMP) solvent to form a slurry. The mixed slurry was pasted on a copper foil and dried in a vacuum oven at 80 °C for 12 h. The obtained electrodes were cut into disks with the mass of about 2.0 mg and the diameter of 10 mm. The cells were assembled in an Ar-filled glove box using lithium foil as the counter electrode, Celgard 2400 membrane as the separator, and a solution of 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC)-dimethyl carbonate (DMC)-diethyl carbonate (DEC) (1:1:1 by volume) as the electrolyte. The galvanostatic charge and discharge measurements were performed on a battery testing system (LAND-CT2001A) with a voltage of 0.01–3.0 V (vs. Li^+/Li). The cyclic voltammetry (CV) measurement and electrochemical impendence spectroscopy (EIS) measurement was performed on CHI660E electrochemical workstation with a voltage range from 3.0 to 0.01 V at a scanning rate of 0.1 mV s^{-1} and a frequency range from 100 KHz to 100 mHz respectively.

3. Results and discussion

The XRD patterns of the NPCS and the Co_3O_4/NPCS nanocomposites are shown in Fig. 1a. For the NPCS, two broad peaks appear at about 24° and 43°, corresponding to (002) and (100) diffraction mode of graphitic structure, which is characteristic of amorphous carbon material [41]. The diffraction peaks of the Co_3O_4/NPCS nanocomposites at $2\theta = 19.0$, 31.3, 36.9, 38.5, 44.8, 55.7, 59.4, and 65.2 belonged to the (111), (220), (311), (222), (400), (422), (511), and (440) planes, which can be indexed as the face-centered cubic phase Co_3O_4 (JCPDS No. 42-1467) [42]. The broadening of these peaks indicates very small crystals for Co_3O_4. No obvious diffraction peaks of the NPCS are observed in the XRD patterns of the Co_3O_4/NPCS nanocomposites, which can be attributed to the well-crystallized structure of the Co_3O_4 nanoparticles and the amorphous nature of the NPCS [25,26,34,43–46].

The Raman spectra of the NPCS and the Co_3O_4/NPCS nanocomposites are shown in Fig. 1b. For the NPCS and the Co_3O_4/NPCS nanocomposites, two peaks positioned at about 1350 cm^{-1} and 1594 cm^{-1} correspond to the D band (disordered induced phonon mode) and G band (graphite band) of carbon materials, respectively [25,42]. The intensity ratio (I_D/I_G) of the two bands is about 0.95, indicating the low graphitization degree of the NPCS, which is in good agreement with the XRD pattern of the NPCS. However, the peaks at 190 cm^{-1}, 471 cm^{-1}, 517 cm^{-1}, 612 cm^{-1}, and 679 cm^{-1} in the Co_3O_4/NPCS nanocomposites are observed, which can be assigned to the characteristic Raman peaks of crystalline Co_3O_4 [26,31,42,46–48]. The Raman results of the Co_3O_4/NPCS nanocomposites confirm the coexistence of crystalline Co_3O_4 and amorphous carbon.

The content of the NPCS in the Co_3O_4/NPCS nanocomposites was investigated by TG. The TG curves of the NPCS and the Co_3O_4/NPCS nanocomposites are shown in Fig. 1c. Below 100 °C, the occurrence of a weight loss of about 1.8 wt% can be ascribed to the release of the absorbed gases or moisture on the surface of the two