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ScienceDirect

Ceramics International 41 (2015) 7511–7518

CERAMICS INTERNATIONAL

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Core/shell-structured nickel cobaltite/onion-like carbon nanocapsules as improved anode material for lithium-ion batteries

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Received 30 January 2015; received in revised form 11 February 2015; accepted 12 February 2015
Available online 20 February 2015

Abstract

Core/shell-structured nanocapsules consisting of a nickel cobaltite ($NiCo_2O_4$) nanoparticle core encapsulated in an onion-like carbon (C) shell are synthesized by arc-discharge and air-annealing methods. Void spaces between $NiCo_2O_4$ core and the carbon shell are observed in the $NiCo_2O_4$/C nanocapsules. Lithium-ion batteries fabricated using the nanocapsules as the anode material exhibit enhanced initial coulombic efficiency of 82.3% and specific capacity of 1197.2 mA h/g after 300 cycles at 0.2 A g^{-1} current density. Varying the rate of charge/discharge current from 0.2 to 4 A/g does not show negative effects on the recycling stability of the nanocapsules and a recoverable specific capacity as high as 1270.4 mA h/g is obtained. The introduction of the onion-like C shell and the presence of the void spaces are found to increase the contact areas between the electrolyte and the nanocapsules for improved electrolyte diffusion, to enhance the electronic conductivity and ionic mobility of the $NiCo_2O_4$ nanoparticle cores, and to accommodate the change in volume during the lithium-ion insertion/extraction process.

Keywords: Core–shell nanocapsules; Onion-like Carbon shells; Nickel cobaltite; Anode; Lithium-ion batteries

1. Introduction

Development of rechargeable energy storage devices with high capacity, high rate capability, and long cycling life is the key to the developing sustainable and clean energy sources such as wind and solar energy sources [1]. Lithium ion batteries (LIBs) are considered as one of the most promising rechargeable energy storage devices because of their higher energy density and longer cycle life compared to conventional rechargeable batteries [1–5]. The low theoretical specific capacity (372 mA h/g) in graphite, the prevailing commercial anode material, is far from meeting the requirements for high energy/power density. Nanostructured transition metal oxides have been considered as a possible alternative anode material for LIBs due to their higher theoretical specific capacity (500–1000 mA h/g) and reversible conversion mechanism for lithium storage. The low electrical conductivity in conjunction with the pulverization problems induced by volume expansion/contraction during the lithium-ion insertion/extraction process significantly reduce the performance and lifetime of nanostructured transition metal oxide-based anodes.

In the past decade, extensive efforts have been made to replace single transition metal oxide anode with other inexpensive and environmentally friendly metal oxides [6–8]. As an abundant multiple oxidation state ternary metal oxide [6], nickel cobaltite ($NiCo_2O_4$) is considered as a very promising electrode material for supercapacitor owing to its high electronic conductivity, low diffusion resistance to protons/cations, and high electrolyte penetration [7]. In addition, $NiCo_2O_4$ is capable of delivering a theoretical specific capacity of 890 mA h g^{-1}. These features are favorable to develop high-performance electrode materials [6–9]. Today, there are only a few reports on the application of $NiCo_2O_4$ as an anode

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http://dx.doi.org/10.1016/j.ceramint.2015.02.073
0272-8842/

material for LIBs. These include: 1) the synthesis of three-dimensional (3D) hierarchical porous flower-like $NiCo_2O_4$ using a facile hydrothermal approach followed by calcination in air to give a reversible specific capacity of 939 mA h g^{-1} at 100 mA g^{-1} and to preserve the high capacity after 60 cycles [10]; 2) the growth of mesoporous $NiCo_2O_4$ nanowires on carbon textiles substrates to exhibit a reversible capacity of ~1012 mA h g^{-1} at a 0.5 A g^{-1} and a capability of 854 mA h g^{-1} after 100 cycles [11]; 3) the preparation of monodisperse $NiCo_2O_4$ mesoporous microspheres by a facile solvothermal method followed by pyrolysis of the $Ni_{0.33}Co_{0.67}CO_3$ precursor to increase capacitance and cycling stability [12]; and 4) the fabrication of highly porous $NiCo_2O_4$ nanoflakes and nanobelts by a hydrothermal technique followed by calcination of the $NiCo_2O_4$ precursors to exhibit high specific capacities of 1033 and 1056 mA h g^{-1}, good cycling stability, and high rate capability [8].In all these works, lithiation-induced volume expansion results in the fracture and aggregation of anode materials.

Various composite materials with oxides, Si and C, including core/shell structures and nanocomposites, are employed to prevent nanoparticles from pulverization and to improve the electrochemical performance [13–15]. In particular, C has been extensively studied because it is a cheap, abundant, and low-toxic source to enhance the conductivity and stability of anode materials [16]. The core/shell-type nanostructure, named by nanocapsules, is identified as a good way to markedly improve the cycling behavior and kinetics of lithium intercalation and de-intercalation in composites [17]. For example, onion-like C-coated NiO, Co_3O_4 and CuO nanocapsules demonstrate superior electrochemical performances [18–20]. The onion-like C shell acts as a barrier to prevent aggregation of transition metal oxides and provides a void space for volume changes. Therefore, the development of core/shell-structured nanocapsules with $NiCo_2O_4$ nanoparticles as the core and onion-like C as the shell is imperative to new generation anode materials in high-performance LIBs. In this paper, core/shell-structured $NiCo_2O_4$/onion-like C nanocapsules have been prepared by a modified arc-discharge method followed by an annealing process at 100 °C for 2 h in air. The electrochemical performance of $NiCo_2O_4$/onion-like carbon nanocapsules as an anode for LIBs is investigated.

2. Experiments

2.1. Synthesis of $NiCo_2O_4$/onion-like C nanocapsules

A modified arc-discharge process and an air-annealing process, which have been described in details elsewhere, were used to prepare $NiCo_2O_4$/onion-like C nanocapsules [18–21]. Metallic powders of Ni and Co of 99.9% purity with an average size of 10 μm were mixed thoughtfully for the preparation of targets in which the molar ratio of Ni/Co was set to 1:2 in accordance with the Ni–Co binary phase diagram and their evaporation pressures. Elemental powders were compacted into a cylinder shape with a diameter of 20 mm under a pressure of about 20 MPa. In the modified arc-discharge process, the compressed Ni–Co powder placed on a water-cooled carbon crucible was employed as the anode, while the cathode was a carbon needle. After the arc-discharge chamber was evacuated, 1.6×10^4 Pa pure argon, 0.4×10^4 Pa hydrogen, and 40 ml liquid ethanol were introduced into the chamber. The arc-discharge current was maintained at 80 A for 0.5 h. The partial pressure of ethanol was found to increase with the time, and the pressure of the chamber could reach 1 atm at 0.5 h because the decomposition of ethanol and the expansion of the gas both increased with increasing temperature. The products were collected from the depositions formed on the top of the chamber after passivation for 8 h in argon. To prepare the $NiCo_2O_4$/onion-like C nanocapsules and $NiCo_2O_4$ nanoparticles, the products prepared by the modified arc-discharge process were put on an Al_2O_3 crucible and were annealed at 100 and 300 °C for 2 h in a tubular furnace in still air, respectively.

2.2. Characterization of $NiCo_2O_4$/onion-like C nanocapsules

The composition and phase purity of the products were analyzed by an X-ray diffraction (XRD) technique at a voltage of 40 kV and a current of 50 mA with Cu K_α radiation (λ=1.5418 Å). The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained using a JEOL JEM-2010 transmission electron microscope at an acceleration voltage of 200 kV. The oxidation behavior was investigated by thermal gravimetric analysis (TGA) in air atmosphere at a heating rate of 5 °C min^{-1} from 50 to 400 °C. Raman spectroscopy was used to estimate the bond structure of the graphite shells.

2.3. Electrochemical measurements of $NiCo_2O_4$/onion-like C nanocapsules

The electrochemical measurements were performed under ambient temperature using standard R2032-type coin cells with lithium as both the counter electrode and the reference electrode. The working electrodes were prepared by mixing the $NiCo_2O_4$/onion-like C nanocapsules, conductivity agent (acetylene black), and poly(vinyl difluoride) (PVDF) at a weight ratio of 50:30:20 and by pasting with pure Cu foil. 1 M $LiPF_6$ in ethylene carbonate (EC)–diethyl carbonate (DEC) (1:1 in volume) was employed as the electrolyte. The cells were assembled in an argon-filled glove box with both the moisture and the oxygen content below 1 ppm. Galvanostatic charge–discharge was carried out using a LAND battery program-control test system (Wuhan, China) in the potential range of 0.01–3.0 V at a setting current rate. The cyclic voltammetry (CV) test was implemented using an electrochemical workstation (Model 2273, Princeton Applied Research, USA). Electrochemical impedance spectroscopy (EIS) measurements were performed on this apparatus over a frequency range of 0.01 Hz–0.1 MHz at different charge–discharge stages.

3. Results and discussion

The phase purity and crystalline structure of the sample were detected by XRD. As shown in Fig. 1, all of these diffraction peaks can be assigned to (111), (220), (311), (222), (400), (422), (511), (440), and (531) crystal planes and indexed as the spinel crystalline structured $NiCo_2O_4$ (JCPDS no. 73-1702). It should be noted that