One-step fabrication of in situ carbon-coated NiCo$_2$O$_4$@C bilayered hybrid nanostructural arrays as free-standing anode for high-performance lithium-ion batteries

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ABSTRACT

Rapid developments in revolutionary electric vehicles have led to an increase in the energy-density and cycling-life requirements for Li-ion batteries (LIBs). The binary transition metal oxide NiCo$_2$O$_4$ is attracting considerable attention due to its much larger specific capacity than graphite. However, NiCo$_2$O$_4$ suffers from poor cycling performance owing to a large volume change during cycling. To address this problem, we proposed an easy strategy to fabricate in situ carbon-coated NiCo$_2$O$_4$ bilayered hybrid nanostructural arrays supported on Ni foam (denoted as NiCo$_2$O$_4$@C BHNAs−NF) as free-standing anodes for LIBs through a sucrose-assisted hydrothermal method. The in situ-synthesized uniform carbon shell can simultaneously buffer the volume change during cycling and increase the conductivity. The micro/nano-structure also possessed outstanding structural advantages, such as large surface area and hierarchical porous characters, enabling NiCo$_2$O$_4$@C BHNAs−NF to have excellent electrochemical performance. Its capacity can reach 1298 mAh/g at a current density of 100 mA/g, and 86% of the initial capacity can be retained after 100 cycles. All these results revealed that NiCo$_2$O$_4$@C BHNAs−NF was a promising candidate anode for next-generation LIBs.

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1. Introduction

Given the excessive consumption of non-renewable energy resources, many problems, such as resource shortage and environmental pollution become increasingly serious around the world [1−4]. Nowadays, looking for energy storage devices with safety, low cost, high energy density, and long life is the priority in the development of new energy [5]. Lithium ion batteries (LIBs) have been considered as potential green energy storage systems due to their high energy density and power density, long cycle life, and high working voltage, which were widely used in electronic information and automobiles [6−8]. However, the current LIB technology has not met yet the ever increasing market demands, especially for electric vehicles (EVs), hybrid electric vehicles (HEVs), and portable electronic devices due to their limited specific capacity, energy density, power density, and safety. Thus, great efforts have been aimed at the progress of electrode materials and the optimized design of electrode structure [8−11].

Recently, various active materials have been studied for LIBs as anode materials, including carbon materials (graphene and carbon nanotube) [12,13] and transition metal compounds (oxides [14−18], sulfides [19], and nitrides [20]). Among these abovementioned active materials, carbon materials had a lower theoretical capacity of 372 mA h g^{-1} compared with other anode materials (for instance, transition metal compounds) [21]. These materials not only greatly restricted further improvement of energy density but also did not meet the stringent requirements of high capacity [22,23]. Transition metal oxides, especially Co$_3$O$_4$, had high theoretical capacity and important properties of semiconductors with extensive

applications in energy-storage device [24,25]. However, the high cost and toxicity of cobalt element severely restricted its wide application. Furthermore, the low conductivity of Co_3O_4 may adverse to electron behavior during charging and discharging [26]. Fortunately, binary metal oxide as an alternative promising anodic material for LIBs can obtain its superior structure by using cheaper metal to partly substitute expensive Co [27]. Among binary metal oxides, spinel nickel cobaltice ($NiCo_2O_4$) with a high theoretical capacity of ~890 mA h g^{-1} and low cost has aroused wide concern [28–30]. In addition, $NiCo_2O_4$ has much better electrical conductivity and electrochemical activity than mono-metal oxide, which is advantageous to the fast electron transfer and sufficient electrochemical reaction, respectively [31,32]. Nevertheless, $NiCo_2O_4$ also has the common drawbacks of many other binary and ternary metal oxides, such as huge irreversible capacity loss and inferior cycling stability, which may be caused by the large volume changes during repeated lithium insertion/extraction processes [33,34]. These disadvantages enabled the pristine $NiCo_2O_4$ to show poor cycling performance and rate performance [35].

In attempt to solve above problems, many projects have been reported, such as hierarchical porous flower-like structure [36], uniform $NiCo_2O_4$ hollow spheres [37], and 3-D porous $NiCo_2O_4$ nanocomposite [38]. These improvements not only obtained a large surface area contact with electrolyte to have a rapid electrochemical reaction but also a porous structure to release the stress produced by the volume change during cycling. To further ameliorate the electrode structure, a variety of free-standing electrodes consisting of $NiCo_2O_4$ and substrates (Ni foam [39,40], carbon cloth [28,41], and Ti foil [42]) was reported. For instance, Cheng et al. reported the synthesis of 3-D $NiCo_2O_4$@ $NiCo_2O_4$ nanocactus arrays grown directly on a Ni current collector using an easy solution method followed by electrodeposition [40]. Zhao and coworkers obtained the hierarchical structures of porous $NiCo_2O_4$ nanosheets directly grown on a conductive carbon cloth substrate [28]. These strategies improved the conductivity and suppleness of the electrode and optimized the design of electrode structure [43–46]. At the same time, free-standing electrode saves the electrode coating process without additionally introducing conductive agent and adhesive that may hinder the electronic movement. However, these porous structures have poor structure stability during long cycling because the large specific surface area also has high surface energy that introduces some unexpected side reactions [10,47,48]. To further improve the conductivity and structure stability of the electrode, another effective strategy is to create in situ synthesis carbon-coated porous hybrid nanostructure based on free-standing electrode [49]. The thin layer of carbon on the surface of metal oxides not only ensures the stability of the active material when volume changes but also as an over cloth to alleviate the agglomeration and pulverization of the active material [50]. In addition, most of the carbon coating process have time-consuming and multiple-step characteristics. Therefore, coating amorphous carbon on porous micro/nanostructures of metal oxides by in situ synthesis is an effective method to improve its rate performance and cycling stability.

Herein, we developed an easy method to controllably in situ synthesize carbon-coated $NiCo_2O_4$ bilayered hybrid nanostructural arrays supported on Ni foam ($NiCo_2O_4$@C BHNAs–NF) through a sucrose-assisted hydrothermal method, and the sucrose acted as carbon sources. Ultimately, the as-prepared porous $NiCo_2O_4$@C BHNAs–NF as a free-standing electrode exhibited excellent performance of lithium-ion storage, such as high reversible capacity, long-term cycling stability, and excellent rate capability. This novel nanocomposite and electrode structure has potential applications in energy and power storage.

2. Experimental procedure

2.1. Preparation of $NiCo_2O_4$ BHNAs–NF

All chemicals were analytical grade and used without further purification. In a typical process, 0.582 g of $Co(NO_3)_2 \cdot 6H_2O$ and 2.0 g sucrose were dissolved in 40 mL of deionized water at room temperature to form a homogeneous pink solution, added with 6 mmol NH_4F and 12 mmol urea separately, and then stirred for 10 min. The next key step was the control of the solution to become a weak acid with a pH of approximately 5. Furthermore, one piece of NF (1 cm × 4 cm) was carefully cleaned with 3 M HCl solution in an ultrasonic bath for 25 min to remove any surface oxide layer. Subsequently, the foam was cleaned with deionized water and with absolute ethanol several times and then dried in a vacuum oven at 80 °C. Afterward, the as prepared aqueous solution and the pretreated NF were transferred into a 70 mL Teflon-lined stainless steel autoclave, which was sealed and maintained at 100 °C for 5 h. After the autoclave cooled down to room temperature, the NF covered with NiCo precursor was carefully rinsed several times with deionized water and absolute ethanol and then dried in an oven at 80 °C overnight. The $NiCo_2O_4$@C BHNAs–NF was obtained through a thermal treatment at 300 °C for 2 h at a heating rate of 2 °C/min under air atmosphere. To compare the electrochemical performance, another group of the same experiment was also carried out but had no added sucrose and obtained $NiCo_2O_4$ HNAs–NF.

2.2. Material characterization

The crystal structure and phase purity of the resultant samples were determined by a powder X-ray diffractometer (XRD; Bruker D8 Advance, Germany) by using Cu Kα radiation ($\lambda = 0.15418$ nm) radiation at 40 kV and 40 mA ranging from 10° to 80° at room temperature. The morphologies and microstructures of the products were observed using field emission scanning electron microscope (HITACHI S-4800, Japan) and transmission electron microscope (TEM; Tecnai G2 F30 S-Twin TEM, FEI, USA). The specific Brunauer–Emmett–Teller (BET) surface area was characterized using a Coulter SA 3100 surface area analyzer, and pore size distribution curve was derived from the Barrett–Joyner–Halenda (BJH) method based on the adsorption branch. Raman spectroscopy was employed using a WITec CRM200 Raman system with a 532 nm laser source.

2.3. Electrochemical measurement

Free-standing $NiCo_2O_4$@C BHNAs–NF directly acted as a working electrode without involving any auxiliary process. Electrode cuttings were only needed to be placed into rounded wafers with a diameter of 12 mm. Cells (2032) were assembled in an argon-filled glove box with O_2 and H_2O concentrations of less than 1 ppm. A lithium metal foil was used as a counter electrode, and Celgard2400 was used as a separator. The solution consisting of 1.0 M $LiPF_6$ in Ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 vol/vol) was used as electrolyte. The high loading (7 mg cm^{-2}) of $NiCo_2O_4$@C BHNAs–NF was measured by an easy method [51,52]. The battery was installed 1 day before to ensure good contact between the electrode and the electrolyte, and the electrochemical test was performed. Galvanostatic charge/discharge measurement was performed on a multichannel battery testing system (LAND CT2001A) within a voltage window of 0.01–3.0 V. Cyclic voltammogram (CV) test was performed on an electrochemical workstation (PARSTAT 4000) at a scan rate of 0.1 mV s^{-1}. In addition, electrochemical impedance spectroscopy (EIS) was conducted