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Three-dimension hierarchical flower-like $Ni_{1.5}Co_{1.5}O_4$ nanostructures composed of two-dimension ultrathin nanosheets as an anode material for lithium ion batteries

Yuhong Jin [a], Li Wang [a,*], Yuming Shang [a], Jian Gao [a], Jianjun Li [a,c], Xiangming He [a,b,**]

[a] Institute of Nuclear and New Energy Technology, Beijing Key Lab of Fine Ceramics, Tsinghua University, Beijing 100084, PR China
[b] State Key Laboratory of Automotive Safety and Energy, Tsinghua University, Beijing 100084, PR China
[c] Huadong Institute of Lithium Ion Battery, Zhangjiagang, Jiangsu 215600, PR China

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ABSTRACT

Uniform three-dimension hierarchical flower-like $Ni_{1.5}Co_{1.5}O_4$ nanostructures were synthesized on a large scale by a simple, low-temperature hydrothermal method without any template, catalyst and surfactant, followed by a calcinating process. The obtained $Ni_{1.5}Co_{1.5}O_4$ products were composed of two-dimension ultrathin nanosheets with random attachment. Nitrogen sorption isotherm shows that this structure possesses a high specific surface area of 118.8 $m^2\,g^{-1}$ with an average pore diameter of 16.67 nm. When tested as an anode material, the as-prepared $Ni_{1.5}Co_{1.5}O_4$ nanostructures exhibit an initial discharge capacity of 1461.5 mAh g^{-1}. After 30 cycles at the current density of 100 mA g^{-1}, the discharge capacity still keeps 980.8 mAh g^{-1}. The obtained three-dimension hierarchical flower-like $Ni_{1.5}Co_{1.5}O_4$ nanostructures show a promising anode material for lithium ion batteries.

1. Introduction

Over the past decades, extensive research interest on lithium ion batteries (LIBs) has been widely stimulated due to their advantages of high energy density, long lifespan, no memory effect and environmental benignity, which holds great potential application in the areas of energy storage/conversion devices [1–6]. Numerous efforts have been devoted to developing novel and high performance electrode materials with the aim to realize LIBs with higher energy/power density [7–9]. Among the diverse materials that have been studied as potential anode materials for LIBs, $Ni_xCo_{3-x}O_4$ mixed oxides have been regarded as potential electrodes for the development of next generation LIBs due to their favorable performance inherited from Co-based metal oxides [10–12]. However, the $Ni_xCo_{3-x}O_4$ bulk as anode material shows the large irreversible capacity in the first cycle due to the low electronic conductivity. In order to solve this problem, synthesis of $Ni_xCo_{3-x}O_4$ with distinct nanostructure and morphology is an effective way to enhance the electrochemical performance for LIBs. Recently, Li and coworkers [10] prepared 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. The discharge capacity of the as-prepared sample can reach 1198 mAh g^{-1} after 30 discharge–charge cycles at a current density of 200 mA g^{-1}. Li and coworkers [11] demonstrated polyvinylpyrrolidone (PVP)-assisted method to prepare 3-dimensional (3D) hierarchical porous flower-like $NiCo_2O_4$. The investigated results show that PVP plays an important role in controlling the formation of the hierarchical flower-like structure. The as-prepared $NiCo_2O_4$ exhibits an enhanced lithium storage capacity and excellent cycling stability (939 mAh g^{-1} at 100 mA g^{-1} after 60 cycles). Zheng and coworkers [12] reported a novel and facile route for the large-scale fabrication of 2-dimensional porous $Ni_xCo_{3-x}O_4$ nanosheets, which exhibited improved lithium storage properties and good cycle performance.

Herein, we successfully developed a facile and scalable method without the help of surfactant to synthesis of three-dimension hierarchical $Ni_{1.5}Co_{1.5}O_4$ material. The high conductivity of $Ni_{1.5}Co_{1.5}O_4$ facilitates the electron transfer while three-dimension hierarchical flower-like structure ensures the large electro-active area and the ions diffusion-favored pathway. All these features make the as-fabricated $Ni_{1.5}Co_{1.5}O_4$ possess substantially enhanced rate capability and good cycling stability when used as the anode materials for LIBs.

* Corresponding author.
** Corresponding author at: Institute of Nuclear and New Energy Technology, Beijing Key Lab of Fine Ceramics, Tsinghua University, Beijing 100084, PR China. Tel.: +86 10 62794226; fax: +86 10 89796031.
E-mail addresses: wang-l@tsinghua.edu.cn (L. Wang), hexm@tsinghua.edu.cn (X. He).

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2. Experimental sections

1 mmol of $Ni(NO_3)_2 \cdot 6H_2O$, 2 mmol of $Co(NO_3)_2 \cdot 6H_2O$ and 6 mmol of hexamethylenetetramine (HTMA) are dissolved into the mixed solvent (ethanol/water=20:40, volume ratio) to form a transparent pink solution under stirred for 10 min at room temperature. Then, the homogeneous solution was transferred into a Teflon-lined stainless steel autoclave. The steel autoclave was sealed and kept in an oven at 90 °C for 4 h. The HTMA is mainly used as the precipitator to produce OH^- in this reaction process. After cooling down to room temperature, the hydroxide precipitate was collected by centrifugation and washed with deionized water and ethanol for several times, the green $Ni_{1.5}Co_{1.5}O_4$ precursor was obtained by drying at 60 °C for 24 h. the $Ni_{1.5}Co_{1.5}O_4$ sample was obtained by annealing the precursor at 350 °C for 3 h in air with the heating rate of 1 °C min^{-1} to obtain black $Ni_{1.5}Co_{1.5}O_4$ power. It should be noted that the mole ratio of Co/Ni in the as-prepared product (1:1) is in disagreement with the feeding proportion of the initial reactants (2:1). This is mainly attributed to the fact that Co^{2+} can coordinate with NH_3 generated from the decomposition of HTMA more easily than the Ni^{2+}, and this immobilized the precipitation of the Co ion.

Crystal structure of the as-prepared product was characterized by X-ray diffraction (XRD) using D8 ADVANCE (3 kW). The morphology was investigated by the field emission scanning electron microscope (FESEM, JSM-7001F) with energy dispersive X-ray (EDX) spectroscopy. Nitrogen adsorption and desorption isotherms were performed at 77 K on a Quantachrome NOVA4200E (USA) volumetric adsorption system. The chemical composition of the products was measured by Inductive Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Varian 700).

The electrochemical performance of as-prepared $Ni_{1.5}Co_{1.5}O_4$ sample was evaluated using the CR2032-type coin cells. As-prepared $Ni_{1.5}Co_{1.5}O_4$ as active material was mixed with acetylene black as conductive agent and polytetrafluoroethylene as binder at a weight ratio of 50:30:20 to fabricate electrode. The cyclic voltammogram (CV) was performed on an electrochemical workstation (CHI 660E). The discharge/charge tests were conducted on LAND batteries test system (Wuhan, China).

3. Results and discussion

As observed in Fig. 1a, the diffraction peaks are similar to the standard patterns of $NiCo_2O_4$ (JCPDS No. 20-0781), suggesting that the as-prepared $Ni_{1.5}Co_{1.5}O_4$ structures also are the spinel structure with similar lattice constants [13]. As shown in Fig. 1b, according to the results, the specific surface area calculated by the Brunauer–Emmett–Teller (BET) method and the pore volume are 118.8 $m^2\ g^{-1}$ and 0.495 $cm^3\ g^{-1}$. The inset in the Fig. 1b shows the Barrett–Joyner–Halenda (BJH) pore size distribution indicates a narrow pore size distribution (10–20 nm) centered at around 16.67 nm. Fig. 2a demonstrates the FESEM image for the $Ni_{1.5}Co_{1.5}O_4$. Obviously, uniform three-dimension hierarchical flower-like $Ni_{1.5}Co_{1.5}O_4$ nanostructures are constructed with two-dimension nanosheets with random attachment. Fig. 2b–e shows the corresponding EDX mapping for Co, Ni and O elements, respectively. It is obvious that the distribution of all elements in the as-prepared sample is homogeneous. The representative EDX analysis (Fig. 2f) reveals that the content of Ni and Co is 3.26 and 3.19 mol%, respectively, close to the stoichimetric molar ratio of 1:1 in the spinel. The Co/Ni atomic ratio is further confirmed by ICP-AES.

The first three CV curves were investigated at the scanning rate of 0.1 mV s^{-1} in the potential range of 0.01–3.00 V (vs. Li^+/Li) (Fig. 3a). At the first cycle, the intense reduction peak at 0.81 V can be ascribed to the reduction of Ni^{2+} and Co^{3+} to metallic Co and Ni, and the formation of Li_2O and solid electrolyte interface (SEI) layer. The following two anodic peaks at ~1.7 V and ~2.2 V can be attributed to the oxidation of metallic Ni and Co to nickel and cobalt oxides [7,9]. In the second cycle, the main reduction peak shift to ~1.0 V due to the pulverization of the $Ni_{1.5}Co_{1.5}O_4$ [9]. However, from the second cycle, the CV curves overlap very well, which indicates the good reversibility of the electrochemical reactions. A high rate capability is investigated as shown in Fig. 3b. Even at high rate of 1000 mA g^{-1}, a capacity of ~320 mAh g^{-1} can still be kept. Moreover, when the current density is reduced back to 100 mA g^{-1}, an average discharge capacity of ~988 mAh g^{-1} can be recovered. Representative discharge–charge curves of the as-prepared $Ni_{1.5}Co_{1.5}O_4$ microflower electrode at a current density of 100 mA g^{-1} as shown in Fig. 3c. The initial discharge and charge capacities are 1461.5 and 1098.5 mAh g^{-1}, respectively. The initial capacity loss during the first cycle can be attributed to the formation of a SEI film and some undecomposed Li_2O phase [9,14]. Fig. 3d shows the corresponding discharge–charge cycling performance of $Ni_{1.5}Co_{1.5}O_4$/Li cell. It has a high initial discharge capacity followed with fast decay. However, it keeps a stable capacity of 980.8 mAh g^{-1} from second to 30th cycle.

Based on the above results, $Ni_{1.5}Co_{1.5}O_4$ electrode possesses a large initial discharge capacity and good cycle stability, which can be attributed to unique three-dimension hierarchical flower-like structure. This structure can increase the $Ni_{1.5}Co_{1.5}O_4$/electrolyte

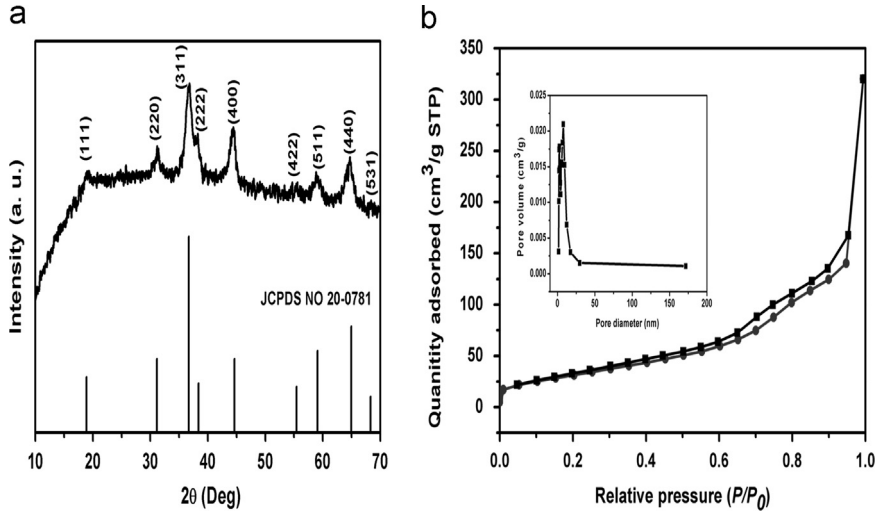

Fig. 1. (a) XRD pattern and (b) N_2 adoption and desorption isotherms (inset: BJH pore size distributions) of the as-prepared $Ni_{1.5}Co_{1.5}O_4$ sample.