



Controllable synthesis of Cu-doped CoO hierarchical structure for high performance lithium-ion battery



Chengcheng Chen ^{a,1}, Yanan Huang ^{a,1}, Hao Zhang ^a, Xiaofeng Wang ^a, Yijing Wang ^{a,b,*}, Lifang Jiao ^a, Huatang Yuan ^a

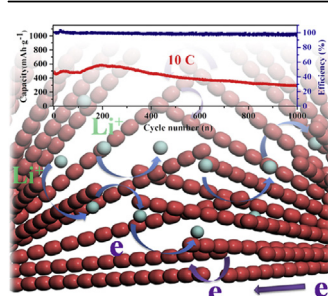
^a Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China

^b Collaborative Innovation Center of Chemical Science and Engineering, China

HIGHLIGHTS

- A series of Cu-doped CoO were successfully synthesized by solvothermal method.
- Cu-doped CoO shows the regular changes with an increase of Cu-doped amount.
- 0.05 M Cu-doped CoO shows straw-like bundle structure composed of nanoparticles.
- 0.05 M Cu-doped CoO shows the excellent high rate performance and long cycle life.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 27 October 2015

Received in revised form

25 January 2016

Accepted 26 February 2016

Available online 11 March 2016

Keywords:

CoO

Cu-doped

Controllable synthesis

Anode

Lithium-ion battery

ABSTRACT

We report on the strategy of Cu doping inducing the nanosize effect of CoO and their application as anode for lithium ion batteries. With an increase of Cu-doped amount, the structures and morphologies of CoO have special changes. The 0.05 mol Cu-doped CoO shows straw-like bundle structure assembled by nanorods, and the nanorods consist of ultra small nanoparticles (about 6–8 nm). Meanwhile, it shows an excellent rates performance and cycle life. The capacity of 800 mA h g^{-1} is obtained at 0.5 C after 80 cycles. The highest discharge capacity is 580 mA h g^{-1} at 10 C and the discharge capacities are relatively stable for 1000 cycles as an anode for Li-ion battery. Therefore, the controllable Cu-doped CoO composite could be deemed to be a potential candidate as an anode material.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Rechargeable lithium-ion batteries have become essential

power sources for portable electronic devices and increasing popular in today's world. These batteries have high capacity, long service life, light weight and facile manufacture [1,2]. Whereas, with the development of manufacturing industry, it is time to exploit the batteries with excellent rate property, outstanding cycle stability and high security, which can be applied to energy-guzzling devices [3–6]. Electrode materials as a part of Li-ion batteries (LIBs) play an important role in determining the performance of LIBs [7–9]. In order to meet the demand of high energy density, transition metal

* Corresponding author. Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China.

E-mail address: wangyj@nankai.edu.cn (Y. Wang).

¹ These authors contributed equally to this work.

oxides become the promising candidates for high theoretical capacity as anode material for LIBs [10,11]. In particular, CoO has aroused wide attentions due to its high gravimetric capacity of 715 mA h g^{-1} and good reversibility [12,13]. Nevertheless, CoO has suffered from poor ion/electron conductivity and drastic volume variation during the lithium insertion/extraction process, which seriously restrict its application [14,15].

To meet these challenges, nanosizing, high conductivity coating and heteroatom doping have been employed to improve the electrochemical property of CoO recently [16–18]. Among these promotion methods, adulteration has been extensively used owing to its good maneuverability and favorable effect [18,19]. Copper has an excellent electron conductivity and considerable electrochemical catalytic function. Park and his workmates using first-principles calculations and experiment demonstrated that the doping of Cu can change the orientation of crystal growth and significantly enhance the stability of CoO [18]. Our group also successfully synthesized Cu-doped dual phase $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-TiO}_2$ composite with great improvement in the electrochemical performance [19]. Therefore, facing the problem of poor electronic conductivity and drastic volume strain, an appropriate Cu doping could effectively control the hierarchical structure and enhance the electronic conductivity. It is believed that the designed Cu-doped CoO may have an excellent electrochemical performance as an anode material for LIBs.

Herein, we report on the successful synthesis of nanoscaled CoO by an appropriate amount of Cu doping and their application as high performance anode material for LIBs. With an increase of Cu doping amount, the CoO exhibits great distinction in structure and morphology. The original CoO shows a layered stack of nets, which tends to develop into two-dimensional (2D) structure. However, the CoO crystal particles are in favor of growing along one direction and forming 1D structure with the Cu-doped amount increase. Attractively, the 0.05 mol Cu-doped CoO with the straw-like bundle structure are composed of ultra-small nanoparticles (about 6–8 nm). Benefiting from the advantage of nanostructure and the electrocatalysis of Cu doping, the 0.05 mol Cu-doped CoO shows the excellent electrochemical property. The discharge capacity reaches 800 mA h g^{-1} at 0.5 C after 80 cycles. Even at high current density of 10 C, the highest capacity of 580 mA h g^{-1} is obtained and the capacity remains 300 mA h g^{-1} after 1000 cycles. It sufficiently evidences the great promotion of the capacity and stability of CoO after doping Cu as an anode for LIBs.

2. Experimental section

2.1. Materials preparation

All the chemicals were analytical grade without further purification. CoO was synthesized by a facial hydrothermal method and followed thermal treatment. 2 mmol cobalt nitrate, 15 mmol urea and 1 g cetyltrimethyl ammonium bromide (CTAB) dissolved in 35 mL deionized water forming the pink solution, stirred for 2 h. Then, the pink solution was transferred into a 50 mL Teflon-lined stainless steel autoclave after mixed evenly. Then, they heated gradually to 70°C for 24 h, and further heated to 120°C for 12 h. After cooling to room temperature, the dark grey precipitate at the bottom of the autoclave was collected, washed with distilled water and ethanol for six times to ensure the CTAB is clear and dried at 60°C overnight. At last, the precursor was calcined at 600°C in Ar for 2 h to obtained CoO. Similarly, the different amount Cu-doped CoO was prepared according to mole ratio of $\text{Co}_{1-x}\text{Cu}_x\text{O}$ ($x = 0.02, 0.05, 0.08$). The desired amount of copper nitrate was added to the above pink solution during stirring process. After above same processes, Cu-doped CoO samples was obtained. The $\text{Co}_{1-x}\text{Cu}_x\text{O}$ ($x = 0.02, 0.05, 0.08$) samples was named $\text{Co}_{0.98}\text{Cu}_{0.02}\text{O}$,

$\text{Co}_{0.95}\text{Cu}_{0.05}\text{O}$, $\text{Co}_{0.92}\text{Cu}_{0.08}\text{O}$ based on the rate of charge, respectively.

2.2. Materials characterization

The crystal structure and surface configuration of samples were characterized by powder X-ray diffraction (XRD, Rigaku D/Max-250, Cu K α radiation), scanning electron microscope (SEM, JEOL JSM-6700F Field Emission), transmission electron microscope (TEM) and high-resolution transmission electron microscope (HR-TEM) on a JEOL JEM-2100 TEM. The actual amount of copper in the samples was measured by using an ICP-9000 (N+M) USA Thermo Jarrell-Ash Corp instrument. FTIR spectra were collected at room temperature by using an FTIR-650 spectrometer (Tianjin Gangdong) at a resolution of 4 cm^{-1} . Raman spectra were recorded using a confocal Raman microscope (DXR, Thermo-Fisher Scientific). The electronic states of the samples were investigated by X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa Probe).

2.3. Electrochemical measurements

The electrochemical measurement was carried out on a LAND (CT2001A) multi-channel battery test system by using a CR2032 coin-type cell. Electrodes were fabricated by mixing active materials, acetylene black, and polyvinylidene fluoride (PVDF) in a weight ratio of 70: 20: 10 in *N*-methyl-2-pyrrolidinone (NMP). The obtained slurry was coated onto Cu foils and dried at 60°C in a vacuum overnight to remove the possible solvent. The cells were assembled in an Ar-filled glove box with the electrodes and pure lithium foil as counter electrode. 1 M solution of LiPF_6 in which at the weight ratio of ethylene carbon (EC)/diethyl carbonate (DEC) was 1: 1 and contained 2% vitamin C was electrolyte. Galvanostatic discharge/charge measurements of the cells were performed in a potential range of 0.01–3.00 V at room temperature. CV and EIS were measured with a CHI660E electrochemical work station.

3. Result and discussion

3.1. Structural and morphological characterization

The structure of x mole Cu-doped CoO ($x = 0, 0.02, 0.05, 0.08$ named as $\text{Co}_{1-x}\text{Cu}_x\text{O}$) were initially examined through X-ray powder diffraction (XRD). Fig. 1a displays the XRD patterns of $\text{Co}_{1-x}\text{Cu}_x\text{O}$ ($x = 0, 0.02, 0.05, 0.08$), respectively. The diffraction peaks at 36.5° (111), 42.4° (200), 61.5° (220), 73.7° (311), 77.5° (222) match well with cubic CoO (JCPDS card No.48-1719). It's worth noting that all the samples were pure phase except $\text{Co}_{0.92}\text{Cu}_{0.08}\text{O}$, which occurs copper elemental phase may due to the excess addition amount. Furthermore, with an increase of Cu doping amount, the main peaks located at about 42.4° shift to the low angle direction shown in Fig. 1b. And If the Cu doping amount increases to 0.05, it has the maximum shift. It indicates that interplanar spacing of CoO gradually enlarges with the Cu doping amount and $\text{Co}_{0.95}\text{Cu}_{0.05}\text{O}$ has the largest interplanar spacing according to the Bragg's law. The Fourier Transform Infrared Spectroscopy (FTIR) spectra in Fig. S1 show that the precursors are cleaned by distilled water and ethanol without any residual CTAB. In addition, from the Raman spectrum displays in Fig. S2, the characteristic CoO peaks at about 468, 515, 605, 676 cm^{-1} band can be observed clearly, implying the existence of pure CoO. And no peaks can be found at around $1300\text{--}1600 \text{ cm}^{-1}$ demonstrating no carbon in final products, which is corresponding to the analysis of FTIR [20]. Meanwhile, the actual amount of copper in $\text{Co}_{0.98}\text{Cu}_{0.02}\text{O}$, $\text{Co}_{0.95}\text{Cu}_{0.05}\text{O}$ and $\text{Co}_{0.92}\text{Cu}_{0.08}\text{O}$ is 1.34, 3.16, 4.41 wt % determined by inductively coupled plasma (ICP), respectively. The values

Download English Version:

<https://daneshyari.com/en/article/1285361>

Download Persian Version:

<https://daneshyari.com/article/1285361>

[Daneshyari.com](https://daneshyari.com)