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Short communication

Lithium storage mechanism in superior high capacity copper nitrate hydrate anode material

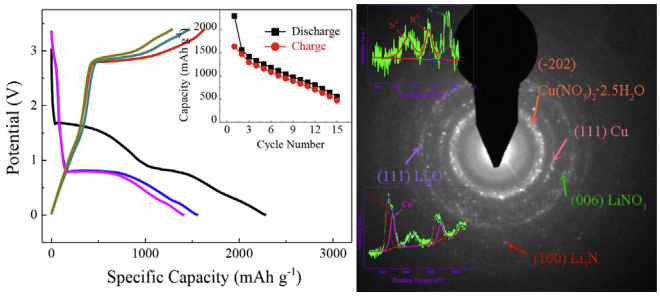
Xinxin Jiang, Kaiqiang Wu, Lianyi Shao, Miao Shui, Xiaoting Lin, Mengmeng Lao, Nengbing Long, Yuanlong Ren, Jie Shu*

Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, Zhejiang Province, People's Republic of China

HIGHLIGHTS

- Lithium storage process in $Cu(NO_3)_2\cdot 2.5H_2O$ is studied by various *ex-situ* techniques.
- $Cu(NO_3)_2\cdot 2.5H_2O$ reveals quasi-reversible conversion mechanism for lithium storage.
- $Cu(NO_3)_2\cdot 2.5H_2O$ shows a lithium storage capacity of 2285.0 mAh g^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

Copper nitrate hydrate ($Cu(NO_3)_2\cdot 2.5H_2O$) exhibits superior high lithium storage capacity (2285 mAh g^{-1}) as anode material for lithium-ion batteries. The structural transformation and lithium storage mechanism of $Cu(NO_3)_2\cdot 2.5H_2O$ are thoroughly studied by various advanced analytical techniques. It is found that the lithium storage process of $Cu(NO_3)_2\cdot 2.5H_2O$ is associated with a quasi-reversible electrochemical conversion reaction. During the discharge process, the electrochemical reaction of $Cu(NO_3)_2\cdot 2.5H_2O$ with lithium results in the formation of Cu, $LiNO_3$, Li_3N, Li_2O and H_2O. In the reverse charge process, $Cu(NO_3)_2$ can be generated by a conversion reaction. As a result, $Cu(NO_3)_2\cdot 2.5H_2O$ shows the reversible charge capacities of 1632.1 mAh g^{-1} in 0.0–3.4 V and 689.1 mAh g^{-1} in 1.0–3.4 V, respectively.

1. Introduction

Recently, energy storage batteries for transportation and communication have gradually become the main power sources owing to global energy issues. Among these rechargeable energy storage batteries, lithium-ion batteries are dominant in the electric vehicles and portable electronics market for their advanced characteristics, such as high energy density and long cycling life [1–4]. However, anode materials have been focused on the carbonaceous materials, such as graphite [5,6], carbon nanotube [7,8], since the lithium-ion batteries were developed in 1991. Nowadays, these carbonaceous materials cannot satisfy the demands of the market. Therefore, intensive worldwide attempts have been done to develop novel high capacity materials to take place of carbonaceous materials in the past two decades.

According to the previous studies, Cu-based metal oxides and nitrides, such as CuO [9–11] and Cu_3N [12], attract intensive

* Corresponding author. Tel.: +86 574 87600787; fax: +86 574 87609987.
E-mail addresses: shuimiao@nbu.edu.cn (M. Shui), shujie@nbu.edu.cn, sergio_shu@hotmail.com (J. Shu).

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attentions from researchers all over the world. CuO with high theoretical capacity (670 mAh g^{-1}), various structural patterns and inexpensive price has activated lots of attentions in recent years. Cu_3N, which exhibits high reversible capacity of 1280 mAh g^{-1}, good cycle life and excellent rate capability, is also examined as a candidate anode material for rechargeable lithium-ion batteries. Whether CuO, Cu_3N, CuF_2 or $CuCl_2$, their lithium storage mechanisms are based the reversible conversion reactions between Li_xM/Cu and Li/Cu_yM_z (M = O, N, Cl, F) [9–14].

In most recent, copper nitrate hydrate ($Cu(NO_3)_2{\cdot}xH_2O$) with high specific capacity has been investigated by our group as a novel anode material for lithium-ion batteries [15]. It is found that $Cu(NO_3)_2{\cdot}xH_2O$ can deliver an initial discharge capacity higher than 2200 mAh g^{-1}. This superior high lithium storage capacity is much higher than all the ever reported transition metal oxides and nitrides, which generally show the initial discharge capacities of 1000–1500 mAh g^{-1} as anode materials. After 30 cycles, a large reversible charge capacity of 597.6 mAh g^{-1} can be maintained for $Cu(NO_3)_2{\cdot}xH_2O$. As a result, $Cu(NO_3)_2{\cdot}xH_2O$ shows outstanding potential as high capacity anode material for lithium-ion batteries. However, the structural transformation and lithium storage mechanism of high-capacity $Cu(NO_3)_2{\cdot}xH_2O$ material during charge–discharge cycles were not investigated. To inspire the researchers to develop novel high capacity anode materials, it is necessary to discover the characteristics of superior high lithium storage capability.

In this paper, the structural transformation and lithium storage mechanism of high-capacity $Cu(NO_3)_2{\cdot}2.5H_2O$ materials are thoroughly studied by *ex-situ* X-ray photoelectron spectroscopy (XPS), *ex-situ* high-resolution transmission electron microscopy (HRTEM), *ex-situ* selected-area electron diffraction (SAED), *ex-situ* Fourier transform infrared spectroscopy (FTIR) techniques. A quasi-reversible conversion reaction mechanism between $Cu(NO_3)_2{\cdot}2.5H_2O$ with Li is discussed and proposed for the first time in this work.

2. Experimental

For being as active material, $Cu(NO_3)_2{\cdot}2.5H_2O$ powder (analytical grade, Aladdin Chemistry) was used as received and dried at 80 °C under vacuum before electrode preparation. The slurry for working electrode was composed of $Cu(NO_3)_2{\cdot}2.5H_2O$ powder as active material, carbon black as conductive additive, and polyvinylidene fluoride as a binder with a weight composition of 4:1:1 in N-methyl pyrrolidinone solvent. Then the slurry was coated on a Cu-foil current collector and dried at 80 °C under vacuum for 12 h. Discs with a diameter of 15 mm were cut and used as working electrodes.

The simulated $Cu(NO_3)_2{\cdot}2.5H_2O$/Li cells were assembled by using $Cu(NO_3)_2{\cdot}2.5H_2O$ disc as working electrode, metal lithium foil as counter electrode, Whatman glass fiber as separator and 1 mol L^{-1} $LiPF_6$ dissolved in ethylene carbonate-dimethyl carbonate (1:1 in volume) as electrolyte. All the $Cu(NO_3)_2{\cdot}2.5H_2O$/Li cells were assembled in an argon-filled glove box at room temperature.

The charge–discharge cycles were measured by a constant-current density (50 mA g^{-1}) on multi-channel Land battery test system. X-ray diffraction (XRD) pattern of $Cu(NO_3)_2{\cdot}2.5H_2O$ was collected by a Bruker D8 Focus powder X-ray diffraction instrument with Cu Kα radiation. SEM image was achieved by a Hitachi S3400 scanning electron microscopy. XPS investigation was measured by a focused and monochromatized Al Kα radiation with a Kratos Axis Ultra spectrometer. The structural evolution of $Cu(NO_3)_2{\cdot}2.5H_2O$ during charge–discharge cycles was directly imaged by a JEOL JEM-

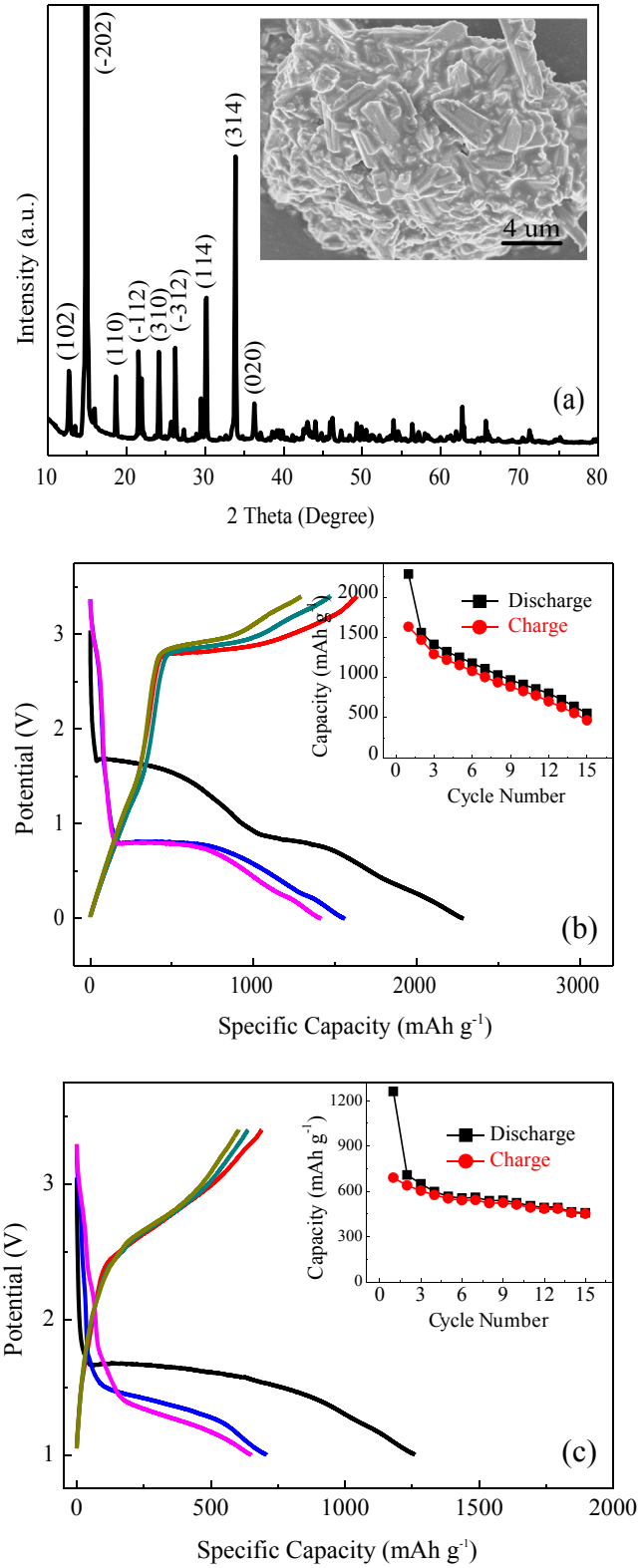

Fig. 1. (a) XRD pattern and corresponding SEM image of $Cu(NO_3)_2{\cdot}2.5H_2O$ powders, (b) charge–discharge curves and corresponding cyclic performance of $Cu(NO_3)_2{\cdot}2.5H_2O$ in 0.0–3.4 V and (c) charge–discharge curves and corresponding cyclic performance of $Cu(NO_3)_2{\cdot}2.5H_2O$ in 1.0–3.4 V.