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Enhanced sodium storage property of copper nitrate hydrate by carbon nanotube

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ABSTRACT

In this work, novel nano/micro structure nitrates are reported for sodium storage for the first time. By using a facile solution route, carbon black (CB) and carbon nanotube (CNT) are introduced to incorporate with copper nitrate hydrate ($Cu(NO_3)_2 \cdot 2.5H_2O$) to form $Cu(NO_3)_2 \cdot 2.5H_2O$/CB and $Cu(NO_3)_2 \cdot 2.5H_2O$/CNT composites for high capacity sodium storage, respectively. Morphological and structural investigations show that CB or CNT coating does not obviously change the particle size and phase composition of $Cu(NO_3)_2 \cdot 2.5H_2O$, while, the electrochemical performance of $Cu(NO_3)_2 \cdot 2.5H_2O$ is significantly improved by introducing CB or CNT as a conductive network. Moreover, carbon matrix can also provide a buffer for suppressing particle pulverization during sodiation/desodiation process. Especially for CNT, it builds a three-dimensional conductive network for active particles. As a result, $Cu(NO_3)_2 \cdot 2.5H_2O$/CNT exhibits higher reversible specific capacity and better cycling stability than bare $Cu(NO_3)_2 \cdot 2.5H_2O$ and $Cu(NO_3)_2 \cdot 2.5H_2O$/CB. After 30 cycles, $Cu(NO_3)_2 \cdot 2.5H_2O$/CNT can deliver a reversible charge capacity of 140.7 mAh g^{-1} at a current density of 50 mA g^{-1}. This result demonstrates that CNT reinforced $Cu(NO_3)_2 \cdot 2.5H_2O$ composite could be a probable anode material for sodium-ion batteries. Besides, the probable sodium storage mechanism in $Cu(NO_3)_2 \cdot 2.5H_2O$ is also proposed by using various ex-situ analytical methods.

1. Introduction

Due to high natural abundance of sodium element, sodium ion batteries have recently attracted much scientific attention as alternatives to current lithium ion batteries [1–8]. Especially for the huge reserves of sodium element in sea, sodium ion batteries have been intensively considered as the key technologies in the past five years for meeting large-scale energy storage needs [9,10]. In lithium ion batteries, graphite has been used as anode material for thirty years. Unfortunately, conventional commercial graphite is not suitable as anode material for sodium ion batteries due to large ionic radii (0.102 nm for Na^+ versus 0.076 nm for Li^+) [11–13], which make sodium ions fail to intercalate into the inter-layer of graphite [12]. As a result, hard carbon has been proposed as one of promising carbonaceous anodes for sodium ion batteries [14–18]. However, for hard carbon there still remains some major issues such as low reversible capacity and poor rate property, which hinder its practical application in sodium ion batteries.

To find proper sodium storage materials, a great number of anode candidates such as $Na_2Ti_3O_7$, SnO_2, TiO_2, $NiCo_2O_4$ and $Na_{2/3}Ni_{1/3}Ti_{2/3}O_2$ have been examined for sodium ion batteries to replace the graphite anode [19–23]. However, the reported $Na_2Ti_3O_7$ and TiO_2, suffering from low specific capacity (175 mAh g^{-1} for $Na_2Ti_3O_7$ and 70 mAh g^{-1} for TiO_2) and rapid capacity fading, cannot satisfy the requirements of the practical application as anode candidates for sodium ion batteries [21,22]. For comparison, the sodium storage performance of $Na_2Ti_3O_7$, TiO_2 and $NaCrO_2$ can be significantly enhanced by carbon coating, as a result of increased electronic conductivity and reduced electrolyte decomposition [24–26]. It indicates that the carbon incorporation (coating or mixing) may be an effective method to enhance the sodium storage capability of titanates and other metal compounds. In the previous reports, Wu ever demonstrated that $Cu(NO_3)_2 \cdot 2.5H_2O$ was a probable anode material for lithium ion batteries with huge lithium storage capacity (>2500 mAh g^{-1}) [27]. In addition, CNT coating was also successively used to enhance the sodium/lithium storage capability of nitrates, such as $Pb(NO_3)_2$ [28,29]. Hence, it is expected that $Cu(NO_3)_2 \cdot 2.5H_2O$ or its carbon composite may be a high capacity anode material for sodium ion batteries.

In this work, we report the synthesis, surface morphology, and sodium storage performance of $Cu(NO_3)_2 \cdot 2.5H_2O$ and its composites. All these samples are evaluated by various physical–chemical and electrochemical methods. Compared with the pristine $Cu(NO_3)_2 \cdot 2.5H_2O$ and $Cu(NO_3)_2 \cdot 2.5H_2O$/CB, it can be found that $Cu(NO_3)_2 \cdot 2.5H_2O$/CNT exhibits better sodium storage performance as anode material for sodium ion batteries.

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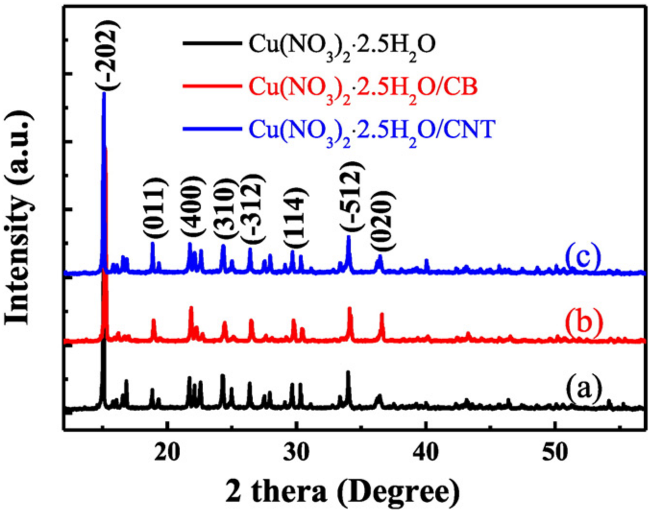

Fig. 1. XRD patterns of (a) $Cu(NO_3)_2{\cdot}2.5H_2O$, (b) $Cu(NO_3)_2{\cdot}2.5H_2O$/CB and (c) $Cu(NO_3)_2{\cdot}2.5H_2O$/CNT.

2. Experimental

All of the chemical reagents used in this study were of analytical grade and purchased from Aladdin Industrial Corporation. $Cu(NO_3)_2{\cdot}2.5H_2O$/CB and $Cu(NO_3)_2{\cdot}2.5H_2O$/CNT composites were prepared as follows. First of all, 1.0 g $Cu(NO_3)_2{\cdot}2.5H_2O$ powder was dissolved in 50 mL absolute ethanol. Then 0.2 g CB or CNT was added into the solution under magnetic stirring. After continuous stirring for 2 h, the suspension was transferred to a vacuum oven at 120 °C for 12 h to form the target composites. For comparison, new $Cu(NO_3)_2{\cdot}2.5H_2O$ powder was recrystallized from the above solution without CB or CNT additives. This recrystallized product was used as the carbon free pristine sample in the following sections.

The phase composition, crystal structure and surface morphology of the recrystallized $Cu(NO_3)_2{\cdot}2.5H_2O$, $Cu(NO_3)_2{\cdot}2.5H_2O$/CB and $Cu(NO_3)_2{\cdot}2.5H_2O$/CNT were detected by means of X-ray diffraction (XRD, Bruker AXS D8), scanning electron microscopy (SEM, Hitachi S3400), high resolution transmission electron microscopy (HRTEM, JEOL JEM-2100) and selected area electron diffraction (SAED, JEOL JEM-2100). Ex-situ Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu infrared spectrophotometer with the wavenumber range between 800 and 2000 cm^{-1}. The sodiated and desodiated $Cu(NO_3)_2{\cdot}2.5H_2O$ samples for ex-situ FTIR investigation were washed by dimethyl carbonate and vacuumed for 5 h before mixing with KBr.

The electrochemical tests of as-prepared samples were performed using CR2032 coin-type cells, which were assembled in an argon-filled dry glove-box. The working electrodes were prepared by a doctor blade technique. For $Cu(NO_3)_2{\cdot}2.5H_2O$/CB or $Cu(NO_3)_2{\cdot}2.5H_2O$/CNT, the electrode consisted of 90 wt.% active material and 10 wt.% polyvinylidene fluoride (PVDF) with nickel foil as current collector. For bare $Cu(NO_3)_2{\cdot}2.5H_2O$, the electrode composition was composed of re-crystallized active material, CB and PVDF with a weight ratio of 7.5:1.5:1.0.

In the CR2032 coin-type cells, the counter electrode was made of sodium metal, the electrolyte was composed of 1 mol L^{-1} $NaClO_4$ dissolved in a mixture of ethylene carbonate and propylene carbonate (1:1 by volume) and Whatman glass fiber was used as separator. The electrochemical performance was evaluated by galvanostatic charge/discharge cycling on a LAND CT2001A multi-channel battery testing system at room temperature in the potential range between 0.0 and 3.0 V versus Na^+/Na. Electrochemical impedance spectroscopy (EIS) analysis was carried out by a CHI 660D electrochemical workstation with a frequency range of 10^{-2}–10^5 Hz.

3. Results and discussion

Fig. 1 shows the XRD patterns of the recrystallized $Cu(NO_3)_2{\cdot}2.5H_2O$, $Cu(NO_3)_2{\cdot}2.5H_2O$/CB and $Cu(NO_3)_2{\cdot}2.5H_2O$/CNT composites. Eight sharp diffraction peaks in Fig. 1 centered at 14.97, 18.74, 21.63, 24.25, 26.28, 29.57, 34.05 and 36.33° are indicative of the presence of $Cu(NO_3)_2{\cdot}2.5H_2O$ phase in the as-prepared samples, which are in good agreement with the (−202), (011), (400), (310), (−312), (−512), (020) and (222) lines in the monoclinic phase of $Cu(NO_3)_2{\cdot}2.5H_2O$ (JCPDS No. 75–1493), respectively. No diffraction peaks attributed to impurity phases can be observed, indicating that single-phase $Cu(NO_3)_2{\cdot}2.5H_2O$ is formed after recrystallization and the coating of CB and CNT does not change the basic structure of $Cu(NO_3)_2{\cdot}2.5H_2O$.

The surface morphologies of the recrystallized $Cu(NO_3)_2{\cdot}2.5H_2O$, $Cu(NO_3)_2{\cdot}2.5H_2O$/CB and $Cu(NO_3)_2{\cdot}2.5H_2O$/CNT are investigated by SEM analysis as shown in Fig. 2. It is clear that bare $Cu(NO_3)_2{\cdot}2.5H_2O$

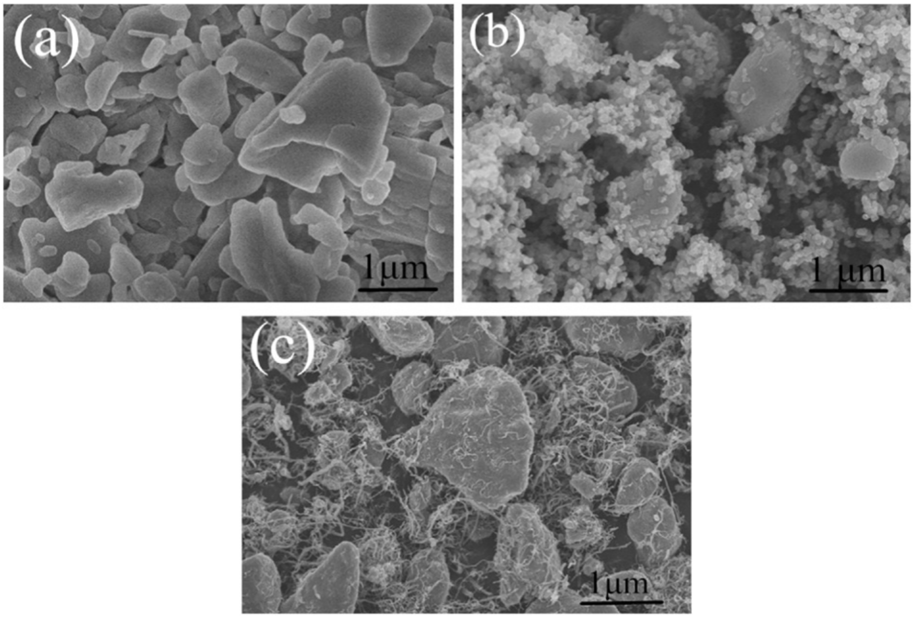

Fig. 2. SEM images of (a) $Cu(NO_3)_2{\cdot}2.5H_2O$, (b) $Cu(NO_3)_2{\cdot}2.5H_2O$/CB and (c) $Cu(NO_3)_2{\cdot}2.5H_2O$/CNT.