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Improved electrochemical property of copper nitrate hydrate by multi-wall carbon nanotube

Xi Zheng, Kaiqiang Wu, Jinli Mao, Xinxin Jiang, Lianyi Shao, Xiaoting Lin, Peng Li, Miao Shui, Jie Shu *

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

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ABSTRACT

By using multi-wall carbon nanotube (MWCNT), a well-dispersed composite of $Cu(NO_3)_2 \cdot xH_2O$/MWCNT ($2.5<x<3.0$) is prepared by a simple solution route. Morphology and structure observations show that $Cu(NO_3)_2 \cdot xH_2O$/MWCNT is composed of $Cu(NO_3)_2 \cdot xH_2O$ particles with particle size of 50–400 nm embedded in the three-dimensional conductive network of MWCNT. The existence of MWCNT not only inhibits the agglomeration of primary $Cu(NO_3)_2 \cdot xH_2O$ blocks into bigger secondary particles but also improves the electronic conductivity of $Cu(NO_3)_2 \cdot xH_2O$. As a result, $Cu(NO_3)_2 \cdot xH_2O$/MWCNT reveals a stable and conductive structure for lithium storage. Charge/discharge results display that $Cu(NO_3)_2 \cdot xH_2O$/MWCNT delivers a lower initial discharge capacity of 2177.1 mAh g^{-1} at a current density of 50 mA g^{-1} than that of pure $Cu(NO_3)_2 \cdot xH_2O$ (2383.2 mAh g^{-1}.). However, $Cu(NO_3)_2 \cdot xH_2O$/MWCNT maintains a higher reversible lithium storage capacity of 980.2 mAh g^{-1} with a higher capacity retention of 83.6% after 30 cycles compared to pure $Cu(NO_3)_2 \cdot xH_2O$ (264.6 mAh g^{-1}, 47.1%). Contributed to the introduction of MWCNT, $Cu(NO_3)_2 \cdot xH_2O$/MWCNT also shows outstanding rate performance. It can provide the reversible lithium storage capacities of 943.4, 813.5, 702.9 and 642.0 mAh g^{-1} at 100, 150, 200 and 250 mA g^{-1}, respectively. Therefore, $Cu(NO_3)_2 \cdot xH_2O$/MWCNT may be a promising lithium storage material.

1. Introduction

Due to short of fossil energy, the development of new energy storage and conversion materials has become the top issue for most of governments all over the world in the past decades. Among all the rechargeable batteries, lithium-ion batteries with characteristics of large capacity, high power and no memory effect are the most promising power sources for portable electronic devices and electric vehicles. In the lithium-ion batteries, graphite has been used as the anode material for lithium-ion batteries for about 30 years. However, the low theoretical lithium storage capacity will make graphite lose its dominant market in the near future.

Metal oxides, such as Co_3O_4 [1–3], Cr_2O_3 [4,5], SnO_2 [6–8], CuO [9–11] and Fe_2O_3 [12–14], reveal the high capacity lithium storage properties as anode materials for lithium-ion batteries. For instance, multishelled Co_3O_4 hollow microspheres show a reversible lithium storage capacity of 1615.8 mAh g^{-1} at a current density of 50 mA g^{-1} after 30 cycles [15]. SnO_2 nanocrystals embedded in nitrogen-doped graphene sheets can deliver a reversible charge capacity as high as 1346 mAh g^{-1} after 500 cycles [16]. Fe_3O_4 submicron spheroids exhibit a stable and reversible capacity of over 900 mAh g^{-1} during up to 60 cycles [17]. However, the unsuccessful press of Sony's Nexelion battery suggests that the commercialization of metal oxides as anode materials is not ready for the practical lithium-ion batteries.

To explore novel high capacity electrode materials, metal nitrates and their derivatives have been proposed as new lithium storage materials in recent years [18–22]. Lead nitrate ($Pb(NO_3)_2$) was firstly developed as anode material with an initial discharge capacity of 938.5 mAh g^{-1}. While, it can only maintain a reversible specific charge capacity of 55.9 mAh g^{-1} with a poor capacity retention of 12.9% after 50 cycles [18]. For improving the cycling performance, carbon black, graphene and carbon nanotube were used to fabricate a composite with stable structure. Among these

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

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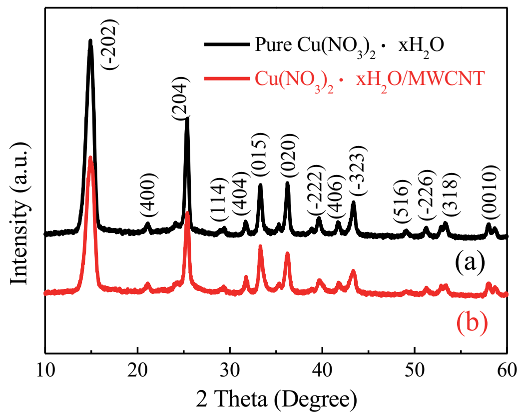

Fig. 1. XRD patterns of (a) pure $Cu(NO_3)_2 \cdot xH_2O$ (2.5<x<3.0) and (b) $Cu(NO_3)_2 \cdot xH_2O$/MWCNT powders.

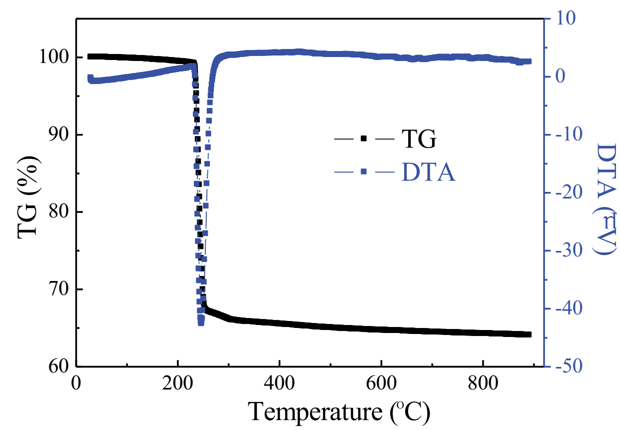

Fig. 2. TG-DTA curves of re-crystallized $Cu(NO_3)_2 \cdot xH_2O$.

composites, $Pb(NO_3)_2$/CNT shows the best cycling calendar life and the highest reversible capacity with a reversible charge capacity of 495.2 mAh g^{-1} after 45 cycles [19]. Furthermore, copper nitrate hydrate was also ever reported with a huge initial discharge capacity (2282.2 mAh g^{-1}) [20]. It exhibits the potential as super high capacity material for anode candidate. However, its poor cycling property fails to meet the requirement for long-term use.

In this work, copper nitrate hydrate is fabricated together with multi-wall carbon nanotube to form a three-dimensional structured composite by a simple solution route. Structural analysis displays that copper nitrate hydrate particles are well dispersed in the three-dimensional networks formed by multi-wall carbon nanotube. Electrochemical tests reveal that as-prepared copper nitrate hydrate/MWCNT composite is a promising candidate as high capacity lithium storage material.

2. Experimental

Commercial $Cu(NO_3)_2 \cdot 2.5H_2O$ (analytical grade, 99.0%) was purchased from Aladdin Industrial Corporation and used as received without further purification. Multi-wall carbon nanotubes (outside diameter: < 8 nm, length: 0.5–2 μm, purity: >95%) were purchased from XFNANO Materials Corporation and purified by HNO_3 reflux solution.

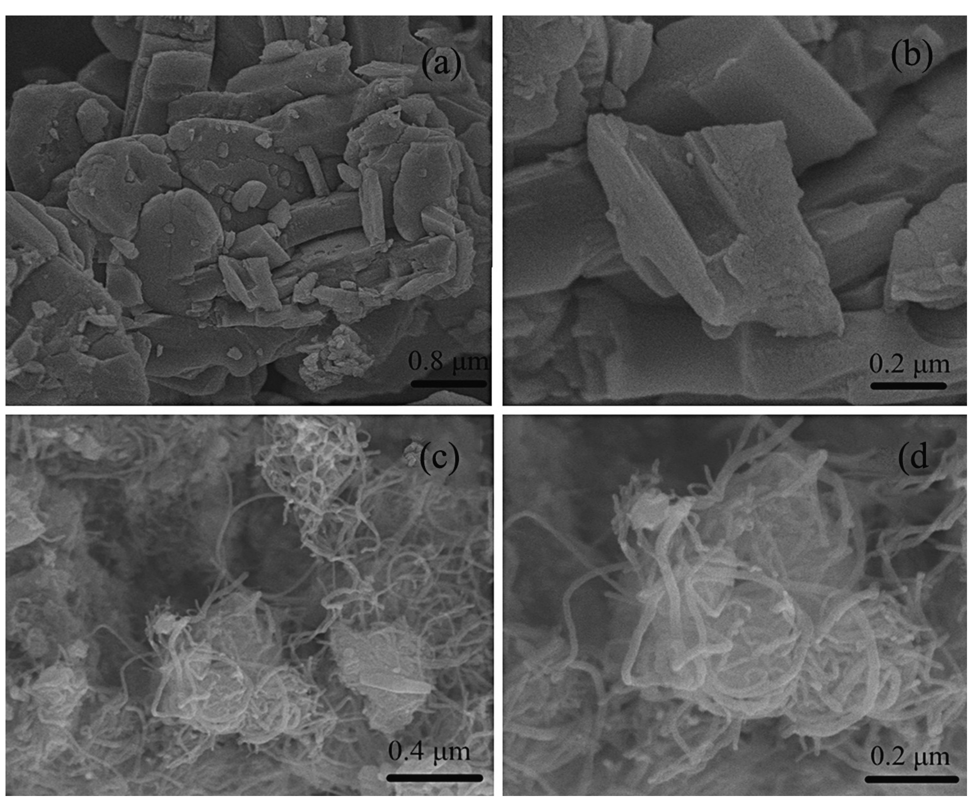

Fig. 3. SEM images of (a, b) pure $Cu(NO_3)_2 \cdot xH_2O$ and (c, d) $Cu(NO_3)_2 \cdot xH_2O$/MWCNT powders.