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# Pillow-shaped porous CuO as anode material for lithium-ion batteries

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## A R T I C L E I N F O

## ABSTRACT

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Keywords: Porous cupric oxide Thermal decomposition CuC<sub>2</sub>O<sub>4</sub> precursor Electrochemical performance Pillow-shaped porous cupric oxide (CuO) was prepared by a template-free method. Highly crystallized  $CuC_2O_4$  precursor with micron-size in high dispersivity was prepared through a hydrothermal method first. Thermal treatment was carried out with the obtained precursor to produce porous cupric oxide. Thermogravimetry and differential thermal analysis (TG-DTA), X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and galvanostatic cell cycling were employed to characterize the structure and electrochemical performance of the porous cupric oxide. The porous CuO powder exhibited high average coulombic efficiency (98.3%) and capacity retention (83.3% of the discharge capacity of the second cycle after 50 cycles) at a current rate of 0.1 C.

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Lithium-ion batteries are currently the dominant power sources for portable appliances such as mobile phones and notebook computers. And they also have potential appliances in electric vehicles. Graphite is used as the main anode material of lithium-ion batteries currently in commercial. Thus, the graphite electrode has its theoretical capacity limit of 372 mAh g<sup>-1</sup>. In order to meet the increasing demands of lithium-ion batteries, the exploration of new electrode materials with superior capacity is an important issue in lithium-ion batteries development.

In recent years, transition-metal oxides have become promising candidates for anode materials of lithium-ion batteries due to their huge specific capacity [1–7]. Among these transition-metal oxides, copper oxide is of particular interest for its inexpensiveness and nontoxicity. The electrochemical process of the CuO electrode is expected that is evolved in the following reaction:  $CuO + 2Li^+ + 2e^- Cu + Li_2O$ . For the conversion reaction of CuO with two-electron transfer, the theoretical capacity can be calculated as  $(96,500 \text{ Cmol}^{-1} \times 2)/(80 \text{ g mol}^{-1}) = 2412.5 \text{ Cg}^{-1} = 670 \text{ mAh g}^{-1}$ .

Various researches prove that the morphology and the size of CuO have significant influences on its electrochemical performances [8–10]. Many efforts have been demonstrated to enable CuO and CuO-based composites with diverse morphologies, in order to improve the electrochemical capability of Li-ion batteries. For example, dendrite-shaped CuO [11] and nanoflower-like CuO/Ni film [12] have been fabricated via Kirkendall-effect-based approach and direct oxidation method, respectively. Morales et al. [13] have prepared nanostructured CuO thin films and found that the CuO electrodes could deliver a

reversible capacity as high as 625 mAh  $g^{-1}$ . Yang and his co-workers [14] have fabricated CuO nanotube film electrode which demonstrated a reversible capacity over 417 mAh  $g^{-1}$  after 30 cycles. Owning to the high surface area, porous materials have promising application in high-efficiency battery materials [15,16].

Herein, novel pillow-shaped porous CuO has been prepared through a template-free approach from copper oxalate precursor. Electrochemical reaction of lithium was under research taking this porous active material as the anode material. It is confirmed to be a promising method to prepare excellent porous electrode materials for Li-ion batteries.

All the reagents used were of analytical grade, and were used without further purification. In a typical synthesis process, 0.0125 M  $K_2C_2O_4$  solution and 0.0125 M  $CuSO_4$  solution were prepared first. Then 40 mL  $K_2C_2O_4$  solution was slowly added into  $CuSO_4$  solution with the equal volume under constant stirring at room temperature. The obtained blue solution was transferred into a 100 mL Teflon-lined autoclave and sealed. The autoclave was heated at 100 °C for 4 h and cooled down naturally to room temperature.

The blue precipitates were collected by centrifugation, washed with distilled water for several times and dried at 80 °C for 12 h. The obtained precursor was calcined at 350 °C for 4 h to obtain a final cupric oxide powder sample.

Morphology of the fabricated sample was characterized by fieldemission scanning electron microscopy (SEM, Hitachi S-4700) operated at an acceleration voltage of 5 kV. Powder X-ray diffraction (XRD, Philips X'Pert MPD diffractometer, Cu  $K_{\alpha}$  radiation) was used for phase identification. Scan rate of 4° min<sup>-1</sup> and step size of 0.04° were applied to record the pattern in the 2 $\theta$  range 10–80°. The operation voltage and current were 40 kV and 45 mA, respectively. TG-DTA curves were determined by a WCT-1 apparatus at a heating rate of 10 °C/min in air atmosphere.

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To evaluate the electrochemical discharge/charge properties of the porous pillow-shaped CuO as anode material for lithium ion batteries, a 2025-type half-cell was assembled. The CuO electrode was prepared by spreading the 1-methyl-2-pyrrolidone slurry onto a nickel foil, which containing 80 wt.% active material (the synthesized porous CuO), 10 wt. % polyvinylidene fluoride (PVDF) binder and 10 wt.% acetylene black. It was then dried in vacuum at 120 °C for 14 h. The active material loaded on the nickel foil with a surface area of 1.54 cm<sup>2</sup> was around 5 mg. The coin cell of CR2025 type containing electrode, separator, electrolyte and lithium foil as anode was assembled in an argon-filled glove box in which the moisture and the oxygen levels were less than 1 ppm. The electrolyte was a solution of 1 M LiPF<sub>6</sub> in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v).

The electrochemical test was carried out using Land battery test system (CT-2001A). The cell was aged for 12 h before measurement, and was cycled galvanostatically at a current rate of 0.1 C. All the electrochemical tests were performed at room temperature.

Fig. 1 shows the XRD patterns of the precursor and the as-prepared sample. The sharp diffraction peaks of the precursor (Fig. 1a) can be indexed as a pure monoclinic phase of copper oxalate and match well with the reported data (JCPDS No.21-0297). No characteristic peaks of other impurities were detected, indicating the high purity of the precursor. The crystalline structure of the copper oxalate is the Pnnm space group with the lattice parameters a = 5.403 Å, b = 5.571 Å and c = 2.546 Å (orthorhombic).

Fig. 1b is the XRD pattern of the as-prepared sample. The diffraction peaks can be indexed to the (110), (111), (020), (202), (220), (311) and (004) reflections of a monoclinic CuO phase correspondingly according to the standard card JCPDS No.72-0629.

The thermal behavior of the precursor  $CuC_2O_4$  crystal was illustrated in Fig. 2. The small amount of weight loss before 230  $^\circ C$ 



Fig. 1. XRD patterns of the precursor and as-prepared sample: (a) precursor; and (b) asprepared sample.



Fig. 2. TG-DTA curves of copper oxalate.

can be attributed to the emission of H<sub>2</sub>O in the existence of physical and chemical absorption. There is a large weight loss at 230 °C–300 °C accompanied with a sharp exothermic DTA peak at 300 °C. It could be attributed to the decomposition of the oxalate. The weight loss (47.02%) agrees approximately with the expected value (47.52%) for the following reaction,  $2CuC_2O_4 + O_2 \rightarrow 2CuO + 4CO_2$ .

The morphology of the precursor as well as the sample was detected by SEM measurement. SEM images are shown in Fig. 3. It can be seen that the precursor (Fig. 3a and b) exhibits square pillow-shaped morphology and imperfect round shape (similar to pillow shape), and the diameter is about  $3-4 \,\mu$ m. The obtained cupric oxide particles almost maintain the appearance morphology of the precursor after annealing treatment. Pillow-shaped architecture can be observed, as shown in Fig. 3c and d. It means that the framework of the precursor keeps well during calcinations process. Further observation shows that these CuO particles were porous and constructed by nanocrystals of about 30 nm.

Apparently, copper oxalate can self-aggregate into pillow-shaped complex morphology in the absence of any specific additives or templates. It is known that crystal growth mainly occurs by two different mechanisms: classical model of crystallization and aggregation-mediated crystallization. Aggregation-mediated crystallization appears to be prominent for solids, such as copper oxalates [17] and copper oxides [18], which contains metal ions that readily undergo hydrolytic polymerization and cluster formation in aqueous solution. In our case, growth of copper oxalate may occur by aggregation mechanism. Aggregation-mediated crystallization produces particle assemblies, which can be ordered or disordered. Crystal growth by aggregation is explained by complex formation mechanisms [19-23]. According to the micro-mechanical mode developed by Hounslow et al. [21,23], the aggregation process is governed by the collision efficiency and rate, and low ionic strength in solution may facilitate the ordered assembly of building block. The ionic concentration in our reaction system is 0.0125 M, which may be low enough to result in regular assembly of the building blocks and cause the formation of the pillow shape.

Fig. 4a demonstrates the charge–discharge curves of the pillowshaped CuO electrode at a current rate of 0.1 C (C is defined as 2 Li<sup>+</sup> per hour; 670 mAh g<sup>-1</sup>). These voltage-capacity profiles of the porous CuO electrode are similar to those of CuO materials reported in literatures [13,24,25]. The first discharge and charge capacities were measured to be 770.3 and 374.2 mAh g<sup>-1</sup>, respectively. Unprospectively, the initial capacity of the porous CuO is higher than the theoretical specific capacity, which could be attributed to the formation of a solid electrolyte interphase (SEI) film during the discharge process [26]. However, the discharge capacity decreases greatly from 770 mAh g<sup>-1</sup> to around 400 mAh g<sup>-1</sup> during the second



Fig. 3. SEM images of the copper oxalate precursor and as-prepared CuO sample: (a-b) copper oxalate; and (c-d) cupric oxide.

charge/discharge cycle, which can be due to the irreversible insertion/ deinsertion of lithium into the pore structure during the cycle.

Fig. 4b shows the cycling behavior of the CuO/Li Teflon cell. The discharge capacity of the obtained porous CuO electrode maintains  $350 \text{ mAh g}^{-1}$  after 30 cycles and  $320 \text{ mAh g}^{-1}$  after 50 cycles, which



**Fig. 4.** (a) charge–discharge curves of the porous pillow-shaped CuO electrode; and (b) the cycling behavior of the pillow-shaped CuO electrode.

is better than that of spherical CuO nanoparticles reported by Zhang, 300 mAh g<sup>-1</sup> after 30 charge/discharge cycles [27]. The average coulombic efficiency is 98.3%. The coulombic efficiency is about 49% in the first cycle, while it increases to about 99.2% in the second cycle and maintains at this value for the rest cycles. After 50 cycles, the porous CuO can sustain 83.3% capacity of the second cycle at a current of 0.1 C. The reversible capacity of the CuO can be attributed to the porous pillow-shaped morphology, which provides large specific surface area for the intercalation of lithium ions and contains many structural defects to accommodate lithium ions [28].

In summary, pillow-shaped porous cupric oxide has been prepared by a template-free method. Micron-size  $CuC_2O_4$  crystal was first prepared by a simple hydrothermal chemical route. Porous cupric oxide was then obtained by the controlled thermal decomposition of the precursor  $CuC_2O_4$ . The CuO particles are porous and pillow-shaped (about 3.4 µm), which are constructed by nanocrystals with diameter about 30 nm. The fine and polycrystallized pillow-shaped CuO with porous structure was detected its electrochemical performance as anode material for lithium-ion batteries. It exhibits an initial discharge capacity of 770.3 mAh g<sup>-1</sup> with the average coulombic efficiency of 98.3% and 83.3% retention of the discharge capacity of the second cycle after 50 cycles.

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