Facile Synthesis of Micro CuO Crystals for Li Ion Full Battery

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Research Article

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Abstract

One step facile synthesis of micro CuO crystals is carried out by hydrothermal method. The porous lithium foil/Li-graphite is used as the anode for CuO-Li ion full battery. The micro CuO crystals are characterized by scanning electron micro porousscopy, X-ray powder diffractometer, Fourier Transform infrared spectrometer, thermogravimeter and differential scanning calorimeter. The battery with porous lithium foil/graphite anode is tested by the galvanostatic current charge-discharge technology at higher current densities of 0.25–0.5 mA/cm². The porous lithium foil-graphite anode can effectively improve the discharge capacity of the CuO crystal battery.

1. Introduction

Metal oxides as a cathode, such as CuO [1], Fe₂O₃, Nb₂O₅ [2], MnO₂ [3], Bi₂O₃ [4], etc. have smaller molecular weight and higher electron gain and loss number, thus can obtain higher SC values. CuO as a kind of a p-type semiconductor material is environmentally friendly, cheap and rich in resources for the energy storage. Many researcher have focused on the CuO/Cu composite [5], CuO/Cu/TiO₂ NT/Ti [6], CuO nanoflake arrays [7], mesocarbon microbead/CuO/Cu [8] and their carbon or organic polymer composites such as C@SnO₂/Cu₂O nanosheet [9], Cu₂O/CuO/Cu/Carbon-polymer composite fibers [10], and polypyrrole coated Cu/Cu₂O [11]. However, the discharge capacity of most of CuO-Li half batteries decays rapidly due to the so-called dead lithium (formed solid electrolyte interphase (SEI) [12]), especially when the amount of CuO is large the Li pulverization is more serious, thus the anode lithium far from commercial battery requirements.

The full battery composed of graphite and LiFePO₄ can be recycled more than 2000 times [13], indicated graphite is stable in the charge/discharge progress. In our previous work the simple lithium-rich graphite anode /LiFePO₄ battery was successfully prepared by electrodeposition of lithium into graphite with a satisfactory full battery, the lithium-rich graphite anode was very stable [14].

In this paper, the micro CuO crystals were synthesized, and assembled a full cell with Li-graphite. The effect of high density current charge and discharge on the performance of the full cell was studied.

2. Experimental

2.1. Materials

Except for CuO crystals the materials used were the same as those in references [14]: Commercial acetylene black and natural graphite (purity, > 99.9 wt%, purity, >99.9 wt %, ~500 mesh) were obtained from Shenzhen Tuling Evolution Technology Co. Ltd. (Shenzhen ,China), 0.1 mm thick glass fiber filter, and other reagents were purchased from Shanghai Analytical Chemicals Company (Shanghai, China). 60% polytetrafluoroethylene (PDPE) water emulsion was provided by Shanghai San-Ai-Fu new material Ltd (Shanghai, China). All other chemicals were of analytical grade without further purification.

2.2. Synthesis of CuO crystal

The CuO crystal was synthesized as the method: The mixtures of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ of 10.0 g and 0.1 M HNO_3 of 50 ml in a crucible of 100 ml were stirred with glass rod for 20 min, and put the crucible in a oven of 90 °C for 18 h to evaporate the water. The obtained white precipitate in the crucible was put in a muffle furnace, and then the temperature of muffle furnace was raised to 400 °C at 10 °C/Min, then to 500 °C at 3 °C/ Min, kept at 500 °C for 240 min, and cooled to room temperature of 20 °C.

2.3. Material characterization

The thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed using a NETZSCH STA 449F3 simultaneous thermal analyzer (German). The Fourier Transform infrared (FT-IR) spectra were measured by a NICOLET NEXUS470 spectrometer (USA) in the frequency range 4000 $\sim$ 400 cm^{-1} . The images of the as-prepared products were examined by scanning electron microscope (SEM) (QUANTA FEG 450, USA) equipped with an EDAX OCTANE PRO energy dispersive spectrometer (EDS) (FEI, USA). X-Ray diffraction (XRD) analysis was performed on the as-prepared products with a Switzerland ARL X'TRA X-ray diffractometer rotating anode with Cu-K α radiation source ($\lambda = 0.1540562$ nm).

2.4. Electrochemical experimental

To reduce the limits of error in measurement the loading mass of CuO was 0.15 g. The CuO (graphite of 0.2000g), acetylene black and PVDF were taken in the weight ratios of 80: 20: 10. The glassy fiber was used as the separator due to its strong structure and good adsorption of electrolyte. 1 M LiPF_6 dissolved in the solution of dimethyl carbonate (DMC), ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with a 1:1:1 volume ratio, which was used as the electrolyte. The electroactive mixture was firstly formed to slurry by ethyl alcohol, then the CuO mixture was coated on the aluminum foil in diameter of 1.6 cm, and the graphite mixture was also coated on the copper foil in diameter 1.6 cm, finally dried in vacuum at 80°C for 24 h. The electrochemical performances of battery were investigated using a CR2025 coin-type cell. The full battery were constructed as the method [14] in the order of CuO cathode / battery separator/ porous lithium sheet/graphite. The lithium foil of 18 mg in diameter of 1.6 cm with 2 mm ϕ holes for the transmission of Li ions was prepared using a multi hole punch in an argon-filled glovebox. The amount of electrolyte injected into CR2025 battery was about 0.15 ml. The full battery was galvanostatically charged and discharged between 1.0 and 4.0 V vs. graphite on a Land-CT2001A battery analyzer (Wuhan, China). All electrochemical measurements were carried out at room temperature.

3. Results And Discussion

3.1 SEM image of CuO crystals

Fig. 1 shows the SEM images of micro CuO crystals, the micro honeycomb-shaped CuO crystals were found in the sample, and the size of micro CuO crystals was $\sim 570 \times 560$ nm.

3.2 EDS spectra and element analysis of micro CuO crystals

The EDS spectra and element analysis of micro CuO crystals are shown in Fig. 2. Only O and Cu elements in the sample were found in Fig. 2(a), and the ratio of O : Cu was 1.15 : 1, which was close to the theoretical value of 1 : 1 in stoichiometry, revealing that the micro CuO crystals were pure.

3.3 XRD pattern of CuO crystals

The XRD pattern of micro CuO crystals shown in Fig. 3 could distinguish crystal types effectively. The diffraction peaks of micro CuO crystals matched well with the reported structure (PDF Card No. 89-5896), the peaks at 2θ values of 32.4, 35.4, 35.6, 38.7, 38.9, 46.5, 48.8, 51.3, 53.5, 57.0, 58.3, 61.7, 65.8, 66.4, 66.6, 67.8, 68.4, 72.4, 75.2, 80.2, 83.2 and 89.6 ° could assigned to the respective (110), (002), (-111), (111), (200), (-112), (-202), (112), (020), (021), (20 2), (-113), (022), (-311), (310), (113), (220), (311), (-222), (-204), (222) and (-131) planes .

3.4 FT-IR of micro CuO crystals

The FT-IR spectra of CuO crystal are shown in Fig.4. For micro CuO crystals, the typical peaks of deformation vibration of Cu-O were found at 503 and 586 cm^{-1} , and the peak sat 808 and 1086 cm^{-1} was attributed to Cu-O stretching vibrations [15]. The bond at 3437 and 1646 cm^{-1} were assigned to the O-H stretching, related with the adsorbed water in the sample.

3.5 TG and DSC curves of micro CuO crystals

The decomposition temperature of battery material has a great influence on the safety of battery. The TG and DSC curves of CuO crystals are shown in Fig.5. Within 816 °C, CuO crystals showed high stability. When the temperature raised to 1000 °C, the CuO crystals of 89.7 % remained, indicated that CuO crystals were a highly safe battery material. From DSC curves in Fig.5 the endothermic temperature were found at 142 and 919 °C, which were assigned to the volatilization of bound water and CuO, respectively.

3.6 Charging and discharging of full battery

The Charge-discharge curves of batteries are shown in Fig. 6 a&d. From the first discharge in Fig. 6a and 6b, when the voltage decreased from 3.45 to 0 V, the first discharge capacitance at 0.25 $\text{mA}\cdot\text{cm}^{-2}$ was 59.2 mAh (specific capacitance is 394.7 mAh/g), and a flat discharge curve at about 1.7 V was found. When the voltage was set between 4~1.0 V, the capacity decreases greatly due to the formation of SEM and the stored Li in the micro CuO crystals. The first charge capacities at 0.25 $\text{mA}\cdot\text{cm}^{-1}$ was 78.9 $\text{mAh}\cdot\text{g}^{-1}$, and the discharge capacity at 0.50 $\text{mA}\cdot\text{cm}^{-1}$ was 47.1 $\text{mAh}\cdot\text{g}^{-1}$, but the second charging/discharging capacities at 0.50 $\text{mA}\cdot\text{cm}^{-1}$ decays to 39.2 and 37.6 $\text{mAh}\cdot\text{g}^{-1}$, respectively, indicated that the fast charging led to the decrease of capacity due to the increase of polarization and the higher currents (i) ($E = i R$). Fig. 6c shows the charge/discharge curves at 0.5 $\text{mA}\cdot\text{cm}^{-2}$ in cycle number of 420~440, and the discharging capacities and efficiency (cycle number of 1~440) were shown in Fig 6 d. The discharge efficiency in cycle

number of 105 A increased with the continuous dissolution of lithium metal, while the discharge efficiency in cycle number of 3–420 fluctuated within $\pm 5\%$. The discharge capacities are listed in Table 1. From Fig 6d and Table 1 the discharge capacities decayed from 37.6 to about 9.9 mAh.g⁻¹ in the cycle 3 to 200.0 due to the continuous SEM formation, and then to from 9.9 to about 8.6 mAh.g⁻¹ in the cycle 200 to 420, indicating the discharge capacities of full battery was stable.

4. Conclusions

In this paper, synthesis of micro CuO crystals was carried out by hydrothermal method. The porous lithium foil/Li-graphite was used as the anode for CuO full battery. The performance of micro CuO crystal battery was studied. The porous lithium foil-graphite anode could effectively improve the discharge capacity of the CuO crystal battery.

Declarations

Acknowledgment

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Tables

Due to technical limitations, table 1 is not available for this version.

Figures

Figure 1

SEM images of micro CuO crystals

Figure 2

EDS spectrum of micro CuO crystals

Figure 3

XRD spectrum of micro CuO crystals

Figure 4

FT-IR of CuO crystals

Figure 5

TG and DSC curves of micro CuO crystals

Figure 6

Charge-discharge curves of lithium-rich (a, b, c), discharge capacity and efficiency (d) of micro CuO crystal-Li ion full battery at 0.5 mA/cm²