



Electrochemical performance of CuO nanocrystal film fabricated by room temperature sputtering

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ABSTRACT

To develop high performance anode materials for thin film batteries, copper oxide (CuO) film is fabricated at room temperature by reactive radio frequency magnetron sputtering. Morphological characterization shows that the CuO film consists of compacted CuO columnar grains of 20 nm in diameter and 200 nm in thickness. The measurement of lithium storage capacity and cyclability of the CuO film show that the first charge capacity of the film is 585 mAh g⁻¹ with an efficiency of 68.3% at a current density of 200 mA g⁻¹. After the 50th cycle, the capacity retention remains as high as 97.4%. The nanostructured CuO film also shows a good rate capability even being cycled at 3000 mA g⁻¹ (5 C), demonstrating that the CuO film can be a promising material as an anode for high performance thin film batteries, especially for thin film battery with amorphous electrolyte.

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1. Introduction

All-solid-state thin film Li batteries are promising candidates as power sources for microelectronic and medical devices due to their compact dimensions, high energy densities, low self-discharge rate and long cycling life. A lot of efforts have been devoted to the development of all kinds of materials for high performance thin film batteries [1–4], among which anode materials using transition metal oxides (Co, Ni, Cu, Fe oxides, etc.) have attracted much attentions since first reported by Tarascon and co-workers [5]. The mechanism for Li storage using transition metals is different from the typical Li insertion/deinsertion process or Li-alloying process. The storage mechanism is through reversible formation and decomposition of Li₂O, accompanied by the reduction and oxidation of metal nanoparticles (in the range of 1–5 nm). This reversible process brings about the advantages of high capacity with 100% capacity retention for hundreds of cycles [6–9].

Among all the metal oxides, CuO is one of the promising anode materials not only due to its low cost, non-toxic and high theoretical capacity (674 mAh g⁻¹) [10–14], but also due to the fact that metallic Cu is an anode current collector [15–19]. The Li storage mechanism of CuO can be expressed by:



During charging, CuO is reduced by the formation of metallic Cu and Li₂O, while a reverse process takes place during discharging.

In all solid state thin film batteries, most of the electrolytes, such as lithium phosphorous oxynitride (LIPON), are amorphous compounds due to their high ionic conductivity. Deposition of anode on top of the electrolyte at elevated temperature may crystallize the amorphous electrolyte film and hence may deteriorate its ionic conductivity. It is therefore necessary to develop anode materials which can be deposited at low temperature for advanced thin film lithium batteries [1–4].

In this work, the synthesis of CuO nanocrystal film through reactive radio frequency (RF) magnetron sputtering at room temperature and the electrochemical performance of the nanostructured CuO are reported. The results show that the CuO synthesized at room temperature possesses good electrochemical performance and therefore can be used as a good anode material for all-solid-state thin film Li rechargeable batteries.

2. Experimental

2.1. Preparation of CuO nanocrystal film

CuO films were deposited on Si and stainless steel (SS) substrates by reactive RF sputtering (Denton, Germany) using a 2 in. Cu target (0.25 in. in thickness) with the substrate at ground potential. The distance between the target and the substrate was kept at 6 cm and the temperature of the substrate was uncontrolled throughout the deposition process. The base pressure in the plasma chamber was first of all pumped to 10⁻⁷ mTorr and then Ar

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(purity of 99.99%) and O₂ (purity of 99.99%), respectively, under flow rates of 10 sccm and 10 sccm was continuously supplied to keep the working pressure at 20 mTorr throughout the deposition process. After reaching 12 mTorr the target was pre-sputtered for 30 min to clean any surface impurities, after which CuO thin films were reactively sputtered at 150 W for 10 min to achieve a film thickness of about 150 nm.

2.2. Physical and electrochemical characterization

Structures of the thin film samples were measured using a Shimadzu XRD-7000 X-ray diffractometer with Cu K α radiation. Data were collected in the 2θ range of 10–50° at a scan rate of 2°/min. Surface morphology of the thin films was characterized using a Hitachi S-4100 field emission scanning electron microscope.

The electrochemical behaviors of the CuO thin films on SS substrates were investigated by both galvanostatic charge–discharge and cyclic voltammetry (CV). A two terminal cell test system was used with the CuO thin film as cathode and Li metal foil as both anode and the reference voltage electrode. For a comparison, CuO electrode using commercial CuO powder was prepared by mixing CuO (99.99%, Sigma–Aldrich) powder with 10 wt% carbon black and 10 wt% polyvinylidene fluoride (PVDF, Sigma–Aldrich) binder in *N*-methyl-2-pyrrolidinone solvent to form a homogeneous slurry, which was then pasted onto a copper foil. Then the electrode was dried in a vacuum oven at 120 °C for 24 h. 1 M LiPF₆ in ethyl carbonate/dimethyl carbonate solution (EC/DEC, 1/1 vol.% Ozark Fluorine Specialties, Inc.) was employed as a liquid electrolyte. CV measurements were carried out between 0 and 3 V vs. Li/Li⁺ at a slow sweep rate of 0.5 mV s⁻¹ using Solatron 1287 station. Galvanostatic charge–discharge cycling test of CuO half cells was carried out in the potential range between 0 and 3 V using a constant current density of 200 mA g⁻¹. To test the AC impedance of the cell at different Li intercalation states, the cell was charged or discharged to a given potential at a current density of 200 mA g⁻¹, and then the potential was maintained for 2 h to fully reduce polarization before impedance testing in the range from 1 M Hz to 0.01 Hz.

3. Results and discussion

Fig. 1 shows the XRD spectra of the as-deposited thin film. The two diffraction peaks can be indexed as (0 0 2) and (1 1 1) diffraction of pure monoclinic CuO phase (JCPDS 48-1548) [20]. The strong (0 0 2) diffraction implies preferred orientation of CuO due to low surface energy of the (0 0 2) plane. This observation implies that CuO can be synthesized using very simple reactive sputtering.

Fig. 2 shows the field emission scanning electron microscope (FE-SEM) image of the surface morphology of the as-deposited CuO film on silicon substrate at (a) low and (b) high magnifications. It

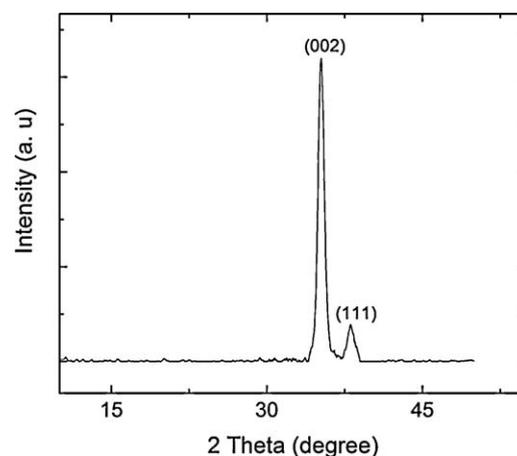


Fig. 1. X-ray diffraction spectrum of the CuO thin film grown on Si substrate.

can be seen that the film is composed of compacted CuO nanoparticles with a diameter of 20 nm without any pin holes. The nanostructure may facilitate diffusion of Li ions directly through surfaces as well as through grain boundaries since diffusivity along grain boundaries is much higher than that of lattice diffusion. Consequently, the reactivity between Li ions and CuO is increased with decrease in grain size [5,21].

CV is an additional effective method to determine the voltage that electrochemical reactions take place and to examine electrochemical reversibility. The first two CV curves of the CuO/Li half cell measured between 0 and 3 V at the rate of 0.5 mV s⁻¹ are shown in Fig. 3a. In the first cathodic scan, two peaks peaked at 1.1 V and 0.7 V are observed. The first peak is well known to be the reduction from CuO to Cu₂O while the second one is due to the further reduction from Cu₂O to Cu. Two corresponding oxidation peaks from Cu to Cu₂O and then from Cu₂O to CuO are observed, respectively, at 1.5 and 2.4 V with the formed Li₂O acting as oxygen reservoir [5]. The second cycle shows a similar profile as the first one but with much lower cathodic current. The large cathodic current in the first curve is due to the formation of SEI film on the CuO electrode [10–13,22–25]. From the CV curves it can therefore be concluded that CuO is capable of reversible Li storage. Fig. 3b shows the galvanostatic charge–discharge profiles of CuO/Li half cell between 0 and 3 V at a current density of 100 mA g⁻¹. During the first discharge, the cell voltage sharply drops from the open circuit potential (OCP) to 1.1 V. Then the voltage gradually decreases until 0 V. The first discharge capacity is 860 mAh g⁻¹ corresponding to 5.4 mol electron per mol of CuO. This value is higher than the theoretical 2 mol of electrons. The excess electron in the first cycle is caused by the consumption of the formation of SEI. The first charge curve between 1.2 and 2.6 V possesses a capacity of 585 mAh g⁻¹ with an irreversible capacity of

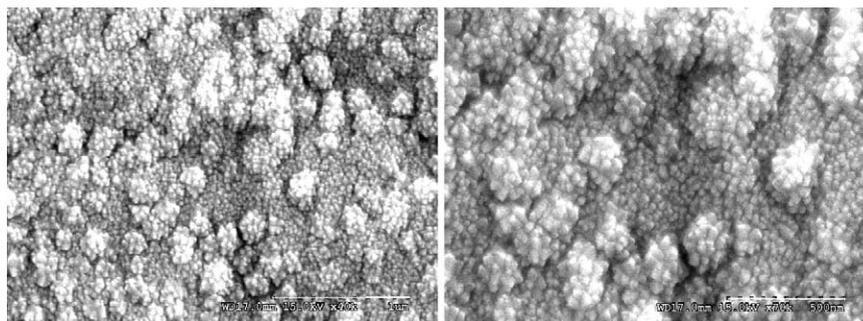


Fig. 2. Morphology of the CuO nanocrystal thin film deposited on Si substrate at (a) low and (b) high magnification.

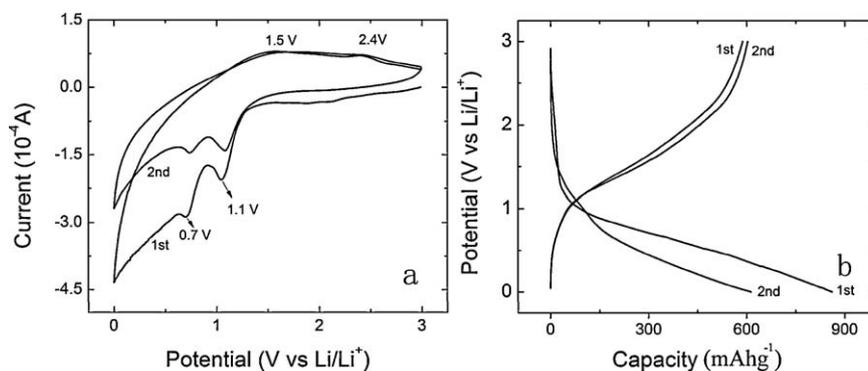


Fig. 3. (a) The first two cyclic voltammograms and (b) the first two galvanostatic charge–discharge curves of CuO/Li half cell.

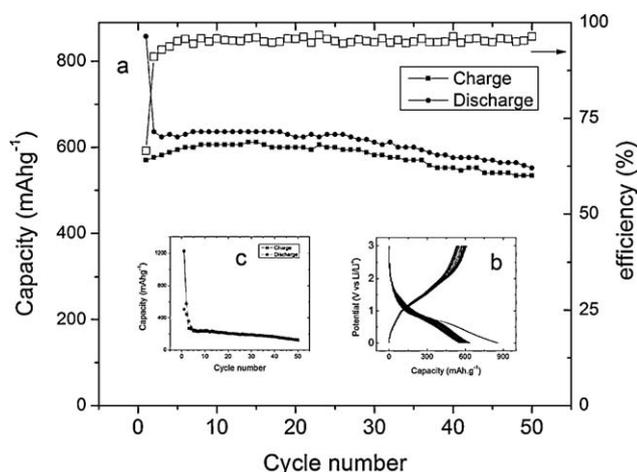


Fig. 4. (a) Capacity vs. cycle number and (b) charge–discharge curves of the first 50 cycles of CuO film electrode at current density of 200 mA g⁻¹. (c) Charge–discharge curves of the first 50 cycles of common CuO electrode at current density of 200 mA g⁻¹.

275 mAh g⁻¹. The second cycle curve shows a similar shape with increased efficiency, indicating a reversible electrode reaction.

Fig. 4 shows the cycling performance and charge–discharge profile of the first 50 cycles of the CuO/Li cell at a current density of 200 mA g⁻¹ between 0 and 3 V. It can be seen that at the beginning of the cycles, there is a slight increase in the capacity from 585 mAh g⁻¹ to 610 mAh g⁻¹, followed by very slow decrease to 570 mAh g⁻¹ after 50 cycles with a 97% capacity retention. The slow capacity decrease in the following cycles is due to the formation of dendritic lithium metal, which has been verified by Tarascon and co-workers [5]. The efficiency is 75% for the first cycle due to the formation of the SEI films [10–23] and as nearly 100% after the first cycle. For comparison, the electrochemical properties of common size CuO were tested, as shown in Fig. 4(c). Although the electrode shows a first charge capacity of 516 mAh g⁻¹, the capacity reduces to about 125 mAh g⁻¹ after 50th cycles. The better and improved capacity retention in the present work is due to the nanostructured CuO film, which buffers the volume changes during the reaction with lithium [5–10].

The rate capability of the CuO film was investigated at different current density. The charge/discharge rate was first increased from 1/3 C where 1 C is assumed to be 600 mA g⁻¹ to 5 C and was then reduced to 1/3 C. At each step, 5 charge/discharge cycles were performed. As shown in Fig. 5, the capacity can be seen to be stable at each rate step. The capacity changes from 600 mAh g⁻¹ to 400 mAh g⁻¹ when the current density is increased from 1/3 C to

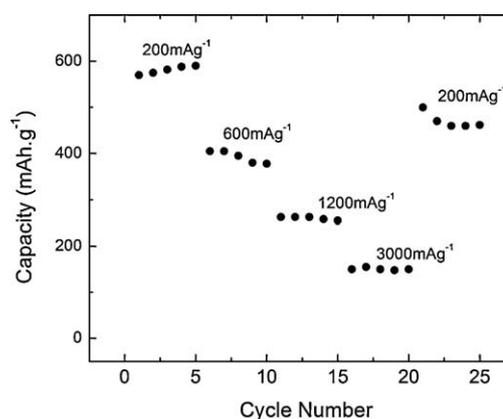


Fig. 5. The charge capacity of CuO/Li cell under different charge–discharge rate.

1 C, respectively. When the current density is further increased to 5 C, the capacity decreases to about 170 mAh g⁻¹. The decrease in capacity may be caused by low electronic conductivity since CuO is a semiconductor [5–10]. By decreasing the rate from 5 C to 1/3 C, the reversible capacity increases to 500 mAh g⁻¹, suggesting that the CuO film electrode possesses acceptable rate ability.

Morphological changes of the electrode may greatly influence its electrochemical property. The CuO film after 50 cycles was taken out and washed with tetrahydrofuran, then fully dried in a vacuum at room temperature before subjecting to FESEM characterization. The result is shown in Fig. 6. It can be seen that the morphology of the CuO electrode is greatly changed. The nanocrystal features have vanished into compact films composed of some fine particles of about 5–10 nm, which is believed to be caused by volume change. This observation is similar to that reported by Tarascon and co-workers [5]. During discharge, Cu is reduced from CuO leading to volume change. At the same time, newly produced Li₂O forms Li₂O and Cu composite. The continuous change in structure and volume gradually leads to partial loss in contact between active materials with the current collector. However, the nanosized grains may buffer the volume change and reduce the capacity fade [5,26].

Electrochemical impedance spectroscopy (EIS) studies were carried out using the CuO/Li half cell to study the kinetics of Li reaction with CuO. In the EIS study, CuO electrode was used as a working electrode with Li foil as an anode and a reference electrode. The cells were charged or discharged to a given potential at 100 mA g⁻¹ and then balanced at the potential for 2 h before impedance data were collected [27,28]. The results are typically shown as Nyquist plots as shown in Fig. 7 for the 1st and 50th charge cycle. Impedance data consisting of two semicircles and a

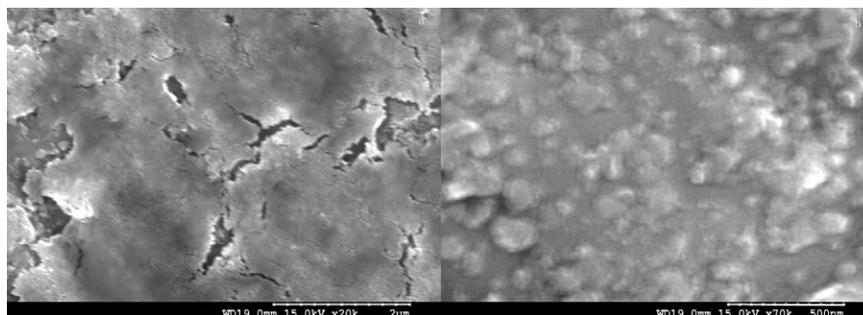


Fig. 6. Morphology of CuO film after 50 cycles at low (a) and high (b) magnifications.

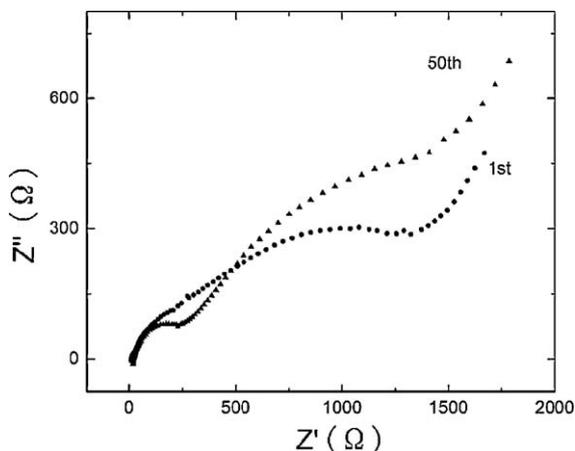


Fig. 7. Nyquist plots of CuO/Li cell at different cycles. (●) First cycle charged to 3 V and (▲) after 50 cycles charged to 3 V.

straight line correspond to the resistance of the Li ion transfer through the solid electrolyte interphase (SEI) layers (R_{SEI}) in high frequency range, resistance (R_{ct}) for charge transfer at the electrode/electrolyte interface in medium frequency range and the Li ion Warburg diffusion resistance in the solid electrode material in low frequency range (R_d) [27,28]. Through a comparison of the two plots, it can be seen that the SEI film is formed during the first cycle and the R_{SEI} is almost the same after 50 cycles, further confirming the stability of the SEI film formed at the first cycle. However, the charge transfer resistance shows an increase due to the aggregation of Cu nanoparticles leading to an isolation of them from the Li_2O matrix so that charge transfer resistance increases.

4. Conclusions

Nanostructured CuO film has been synthesized using reactive sputtering at room temperature. Electrochemical characterization shows that the CuO film possesses a capacity of 580 mAh g^{-1} with efficiency of 68% at the first charge. The capacity retention of the CuO/Li half cell is 97.4% after 50 cycles at a moderate current density. The good cycle ability may be attributed to the nanostructured thin film which may buffer the volume change during charge/discharge.

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