



Characterization of cobalt monoxide thin film modified with silicon dioxide prepared by the cathodic deposition for lithium-ion battery



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ABSTRACT

The precursor (cobalt hydroxide, $\text{Co}(\text{OH})_2$) of cobalt oxide (CoO) is cathodically electrodeposited on copper foil in cobalt nitrate and sodium nitrated aqueous solution. CoO can be obtained by calcinating $\text{Co}(\text{OH})_2$ for the temperature greater than 500 °C in N_2 atmosphere. For the preparation of $\text{Co}(\text{OH})_2$ in the presence of silicon rubber as the sealant to define the electrodeposition area, some co-deposited components dissolved from silicon rubber are converted to SiO_2 in the calcination process. The charge/discharge performances of CoO thin film are enhanced by the presence of SiO_2 . When the TEOS (tetraethyl orthosilicate) is added into the solution for electrodepositing the precursor of CoO at pH 3.30–3.14, the grain size of CoO decreases from 33.47 to 8.85 nm by increasing the concentration of TEOS from 0 to 0.005 M. When 0.01 M TEOS is added to prepare the precursor of CoO, the irreversible discharge capacity at the first cycle can be completely recovered in the activation period with the activation rate of 16.50 mAh/g cycle, and the capacity fading fraction at 80th cycle is found to be 16.7%.

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1. Introduction

Lithium ion batteries have been widely applied as the power sources of 3C products. The potential applied fields of lithium ion batteries include the electric vehicles and the storage devices of the regenerative energies, such as the solar radiation, wind, and waves energies, which are variable in time. The commonly used and commercial anodic material in the lithium ion battery is a carbonaceous compound because of its low cost and high operational voltage. However, the specific capacities of the carbonaceous materials are still unsatisfied. Hence many anodic materials including SnO_x , Sn(II) salts (phosphates and oxalates), nanodispersed Si and Si compounds, metal pnictides, transition metal oxides and metal alloys have been developed for improving the performances of the lithium ion battery [1,2].

The high specific capacities of Sn, Si and intermetallic alloys are found for using as the anodic materials of lithium ion batteries [3]. However, a significantly irreversible capacity in the first charge/discharge cycle and the poor capacity retention are still needed to be overcome. The transition metal oxides (M_xO_y , $\text{M} = \text{Co}$, Ni, Cu, Fe, Ti, Sn, V) can be used as the anodic materials of lithium ion batteries due to the property of reversible redox reaction with lithium ion at low potential [4–13]. The reversible capacities of these tran-

sition metal oxides are significantly greater than those of graphite-based anodic materials. The reversible capacity of CoO is obtained to be 600–800 mAh/g at the room temperature [4,6,8]. The high charge/discharge rate of CoO porous nanowire arrays (CoO-NAWs) prepared by the complete pyrolysis of cobalt-hydroxide-carbonate (precursor) was studied [14]. The CoO nanoparticles encapsulated by graphitizable hollow carbon sphere (GHCS) containing 50 wt% CoO exhibits a reversible capacity of 584 mAh/g and remains a capacity retention of 95% after 50th cycle [15]. The reversible capacity of self-assembled porous hierarchical-like CoO@C nanoarchitectures was obtained to be 990 mAh/g at 30 cycle [16]. The electrochemical and charge/discharge properties of our homemade CoO powder are discussed [17], and the reversible capacity is found to be 1233.57 mAh/g [18].

Thin-film lithium batteries could potentially be applied to the microelectronic mechanical systems (MEMSs), implantable medical devices, integrated circuits with self-power sources, smart cards, zero-emission vehicles, portable electronic devices and aerospace and military industries [19–22]. Many kinds of anodic materials used in the lithium batteries can also be used for the thin film lithium batteries [22]. A large irreversible capacity in the first cycle and a higher fading of capacity are found for thin Co_3O_4 film used as the anodic material of lithium batteries [23]. Thin CoO film is synthesized by calcining $\text{Co}(\text{OH})_2$ thin film, which is electrodeposited on copper plate, and its maximum discharge capacity is obtained to be 1589.4 mAh/g [20]. The irreversible discharge capacity of the CoO thin film at the first cycle can be recovered in the following activation cycles [24].

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In this study, the CoO thin film is prepared by calcining $\text{Co}(\text{OH})_2$ precursor, which is electrodeposited on the copper plate in the presence of silicon compounds, and used to fabricate the Li/CoO coin cell. The effect of the silicon compounds on the electrodeposition of $\text{Co}(\text{OH})_2$ and the charge/discharge properties of CoO thin film are also investigated.

2. Experimental

2.1. Preparation of $\text{Co}(\text{OH})_2$ and CoO thin films

A $4 \times 8 \text{ cm}^2$ copper foil folded in half was used as the working electrode for the electrodeposition of $\text{Co}(\text{OH})_2$ in 0.175 M $\text{Co}(\text{NO}_3)_2$ and 0.075 M NaNO_3 aqueous-ethyl alcohol (v/v ratio of 1) solution in the absence or presence of silicon compounds. The edges of the folded Cu foil were pasted up by the adhesive tape or the silicon rubber to ensure the $\text{Co}(\text{OH})_2$ to be deposited on one side of the $4 \times 8 \text{ cm}^2$ copper foil. Two Au plates with the dimension of $5 \times 6 \text{ cm}^2$ placed on both sides of the working electrode (folded copper foil) and the Ag/AgCl/3 M NaCl aqueous solution were used as the counter and reference electrodes, respectively. Using an electrochemical analyzer (CHI 604), the electrodepositing $\text{Co}(\text{OH})_2$ thin film was washed with ethyl alcohol and deionized (DI) water for several times, and then calcined in a tubular oven environed with 99.995% N_2 for preparing CoO thin film on copper plate [24].

2.2. Characterization of $\text{Co}(\text{OH})_2$ and CoO

The crystallographic information, grain size and surface morphologies of $\text{Co}(\text{OH})_2/\text{Cu}$ and CoO/Cu were analyzed by X-ray powder diffraction (XRD, Shimadzu XRD-6000) and SEM (Joel JSM-5400). When the precursor of CoO was electrodeposited on Cu foil in the presence of silicon rubber as sealant, the silicon compounds existed within CoO thin film was identified by SIMS (Secondary Ion Mass Spectrometry, Cameca IMS-4f).

2.3. Charge/discharge characteristics of CoO

The Li/CoO coin cells were fabricated in a glove-box (VAC MO-5) filled with argon environment described previously [17,18,24]. The coin cells were galvanostatically charged and discharged with a battery test system (Maccors 2300) at a suitable C-rate, and the voltage behavior against time was recorded over the potential range of 0.02–3.0 V (vs. Li/Li⁺). The coin cell was first discharged from the open circuit voltage (OCV) to 0.02 V, and then charged and discharged between 0.02 and 3.0 V in the following cycles. The charge/discharge capacities were calculated based on the total amount of CoO-SiO_2 thin film.

3. Results and discussion

3.1. Effect of the presence of silicon rubber for preparing $\text{Co}(\text{OH})_2$ on the charge/discharge properties of CoO thin film

When the copper foil was folded and then pasted up with the double-sided adhesive tape (main component was polyacrylate), the precursor of CoO ($\alpha\text{-Co}(\text{OH})_2$ [24]) was electrodeposited on the copper foil with the various pH, and then calcined to prepare CoO thin film. The nano-fibrillar structure of CoO thin film was demonstrated in Fig. 1. The anisotropic growth of the $\alpha\text{-Co}(\text{OH})_2$ deposit along with one crystal orientation resulted in the nano-fibrillar structure of the precursor of CoO. The nano-fibrillar structure of the precursor was retained in the calcination process for preparing CoO. The thicknesses of CoO thin film prepared at pH 3.30–3.14 and 2.82–2.71 are measured from the cross section of SEM images (Fig. 2) to be 2.5–3.0 and 1.8–2.2 μm , respectively.

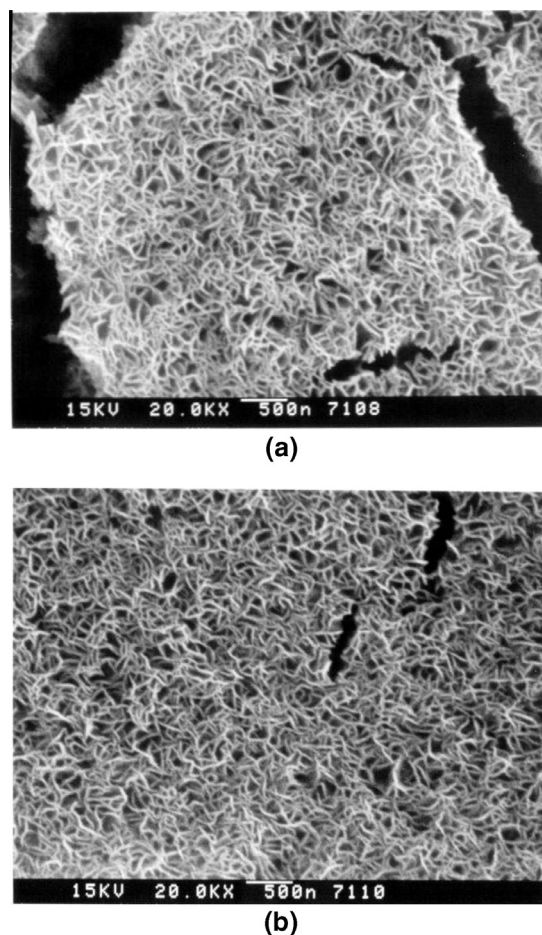


Fig. 1. SEM images of CoO/Cu prepared by calcining $\alpha\text{-Co}(\text{OH})_2$ electrodeposited without silicon compounds at pH of (a) 3.30–3.14 and (b) 2.82–2.71.

Using the as-prepared CoO thin film as the working electrode, the relationships of the charge/discharge capacity of Li/CoO and the cycle number were illustrated in Fig. 3. When the $\alpha\text{-Co}(\text{OH})_2$ precursor was prepared at pH 3.30–3.14 and 2.82–2.71, the activated periods (the period for charge/discharge capacities increased with the cycle number) were found for both cases, and the maximum capacities of CoO thin films were obtained to be 1334 and 1118 mAh/g at cycle number of 40 and 48, respectively. The capacity increasing rates in the activated period were obtained to be 9.42 and 8.34 mAh/g cycle for pH 3.30–3.14 and 2.82–2.71. After the activation period, the capacities of CoO thin films for their precursor prepared at pH 3.30–3.14 and 2.82–2.71 were decreased to 379 and 429 mAh/g when the cycle number was increased to 120. Both of the cases, the large capacity fading fractions based on the maximum capacities were found to be 71.6 and 61.6%.

When the precursor of CoO was prepared for the current collector substrate (copper foil) sealed with silicon rubber at pH 3.30–3.14 and 2.82–2.71, the charge/discharge capacities increased with cycle number in the activated period as shown in Fig. 4. The maximum discharge capacities of CoO thin film at cycle numbers of 70 and 141 were obtained to be 1583 and 1062 mAh/g for their precursor prepared at pH 3.30–3.14 and 2.82–2.71 in the presence silicon rubber. Further increasing the cycle number to 150 the discharge capacities were slightly decreased to 1450 and 1041 mAh/g, and the fading fractions of CoO were 3.8 and 4.5% for its precursor prepared at pH 3.30–3.14 and 2.82–2.71 (Fig. 4). Comparing with the precursor of CoO thin film prepared without silicon rubber the discharge capacity fading of CoO for its precursor prepared with silicon rubber as sealant was significantly suppressed.

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