



Cobalt oxide thin film prepared by an electrochemical route for Li-ion battery

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ABSTRACT

Cobalt oxide (CoO) thin film was prepared by the calcination of its precursor (Co(OH)₂) electrodeposited in the Co(NO₃)₂ and NaNO₃ aqueous solution. The characteristics of Co(OH)₂ and CoO were analyzed by SEM, FTIR and XRD, respectively. The FTIR analysis revealed that the cobalt hydroxide was of the form α-Co(OH)₂, which could be converted to β-type by immersing in KOH solution. The pure CoO could be obtained by calcining α-Co(OH)₂ at a temperature greater than 500 °C in high purity N₂ atmosphere. Increasing the run number for electrodepositing α-Co(OH)₂ from 2 to 6, the weight of α-Co(OH)₂ and CoO decreased from 0.913 and 0.700 mg to 0.750 and 0.525 mg due to the decrease in the pH of the electrolyte with the run number. The grain size of CoO decreased from 12.88 to 6.98 nm by decreasing the pH for preparing α-type precursor from 3.30–3.14 to 2.82–2.71. The morphologies of CoO and α-type precursor found from the SEM images were to be nano-fibrillar structures. Using CoO synthesized by calcining α-Co(OH)₂ electrodeposited at pH 3.30–3.14 as the cathode, the maximum discharge capacity of Li/CoO coin cell was obtained to be 1589.4 mAh g⁻¹. The irreversible discharge capacity of the Li/CoO coin cells at the first cycle could be recovered in the following activation cycles.

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1. Introduction

Lithium-ion battery has been considered as a promising power source for modern electronics due to its highest energy density among commercial rechargeable batteries. The commonly used anodic material in the lithium-ion battery is a carbonaceous compound because of its low cost and high operational voltage. Though the capacity can be improved significantly by the development of highly disordered carbonaceous compounds [1,2], the capacity is still unsatisfied, especially for the thin-film Li-batteries. The high specific capacity is obtained upon using metal alloys [3–8] and metal oxides [9–12] as the anodic materials of lithium-ion battery. Using metal alloys as anodic materials, the decrease in the specific capacity with cycle number due to the pulverization problems associated with the large change of volume during the charge/discharge cycle is still a problem that needs to be solved [3,13]. Metal oxide, such as SnO₂, is developed to overcome the large volume change between the lithiated and lithium-free host. The reversible specific capacity of SnO₂ with good cycle stability is found to be 600 mAh g⁻¹ [9]. However, a large irreversible capacity in the first cycle due to the formation of Li₂O prevents the commercialization of tin oxides [13]. In recent years, Co₃O₄ [14–18] and various vanadates [19–22] are also used as the anodic materials in

lithium-ion batteries. The relative higher reversible specific capacities are found in these materials, however, the large irreversible capacity in the first cycle and fading rate are needed to be improved for further applications.

Using nano-sized transition metal oxides (MO, where M is Co, Ni, Cu or Fe) as anodes of Li batteries, an insertion-extraction mechanism different from that of carbonaceous compounds or lithium-alloying processes is proposed [14,16,23–27]. The reversible charge/discharge mechanism of CoO was mentioned to be the decomposition of CoO to Li₂O and Co by the insertion of Li⁺ [23,28]. The reversible capacity of CoO is obtained to be 600–800 mAh g⁻¹ at the room temperature [14,23,25]. Using the homemade CoO powder as the anodic material of lithium-ion battery, the electrochemical and charge/discharge properties of CoO, and the effect of calcination temperature were discussed in our previous papers [29,30].

Thin-film batteries could potentially be applied to the micro-electronic mechanical systems (MEMSs), implantable medical devices, integrated circuits with self-power sources, smart cards, and portable electronic devices [31–33]. The charge/discharge properties of miniature Ni-MH batteries prepared by the microfabrication technologies based on the ceramic and polypropylene film substrates have been investigated in our previously works [34,35]. Recently, the lithium and lithium-ion micro-batteries fabricated with the thin-film technologies are also widely reported in the literatures [31–33,36–47]. However, thin-film lithium-ion batteries based on cobalt oxides as anode are seldom reported [47]. A large

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irreversible capacity in the first cycle and a higher fading of capacity are found by using thin-film Co_3O_4 as the anode of lithium-ion battery [47]. In our previous investigations [29,30], a relative lower irreversible discharge capacity is found based on the homemade CoO powder as the anodic material of Li-ion battery in the first cycle, and the irreversible discharge capacity can be recovered in the following charge/discharge cycles. Hence, it is of interest to prepare thin CoO film as the anode of thin-film Li-ion battery.

The CoO thin-film is prepared by the calcination of $\text{Co}(\text{OH})_2$ precursor synthesized by the electrolytic deposition. The factors affecting the properties of $\text{Co}(\text{OH})_2$, and the characteristics and the charge/discharge properties of CoO thin-film are investigated in this work.

2. Experimental

2.1. Electrodeposition of $\text{Co}(\text{OH})_2$ and preparation of CoO

A Cu $4 \times 8 \text{ cm}^2$ foil folded to $4 \times 4 \text{ cm}^2$ was placed 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 as the working electrode for the electrodeposition of $\text{Co}(\text{OH})_2$. The edges of the Cu foil were pasted up by some adhesives to obtain the $\text{Co}(\text{OH})_2$ deposit on one side of the $4 \times 8 \text{ cm}^2$ Cu foil. Two Au plates with the dimension of $5 \times 6 \text{ cm}^2$ placed on both sides of the working electrode (Cu foil) were used as the counter electrode, and the Ag/AgCl/3 M NaCl aqueous solution was used as the reference electrode. The $\text{Co}(\text{OH})_2$ electrodeposited on Cu foil with a constant current controlled by an electrochemical analyzer (CHI 604) was washed with ethyl alcohol and deionized (DI) water for several times, and then dried at 70°C in vacuum for 24 h. The obtained $\text{Co}(\text{OH})_2/\text{Cu}$ was cut into eight circular pieces with an area of 1.3 cm^2 and calcined in a tubular oven envired with 99.995% N_2 for 1 h to prepare CoO/Cu.

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

The bonding properties of $\text{Co}(\text{OH})_2$ were analyzed with a Fourier Transform Infrared (FTIR) Spectrometer (Shimadzu IR Prestige-21). 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).

2.3. Electrochemical and 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 [29,30]. The coin cells were galvanostatically charged and discharged 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.

3. Results and discussion

3.1. Preparation of $\text{Co}(\text{OH})_2/\text{Cu}$

Using Cu foil as the working electrode for the electrodeposition of $\text{Co}(\text{OH})_2$ at the current density (cd) of 0.5 mA cm^{-2} , the cathodic potential sharply increased from -1.1 V to -1.3 V in the initial stage of the first run, and then it decreased slowly to -1.1 V as shown in Fig. 1. The electrochemical reactions on the Cu foil were proposed to be the reduction of NO_3^- [48] and H_2O :

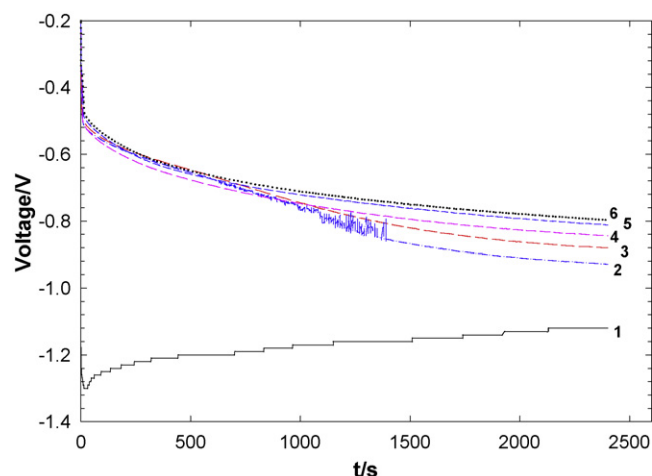
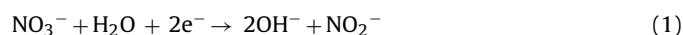


Fig. 1. Effect of electrolysis time on the voltage for electrodeposition of $\text{Co}(\text{OH})_2$. Working electrode: Cu foil ($4 \times 4 \text{ cm}^2$); counter electrode: Au plate ($5 \times 5 \text{ cm}^2$) \times 2; reference electrode: Ag/AgCl/3 M NaCl aqueous solution; cd = 0.5 mA cm^{-2} ; $T = 5^\circ\text{C}$; electrolyte: 0.175 M $\text{Co}(\text{NO}_3)_2$, 0.075 M NaNO_3 aqueous and ethyl alcohol solution (v/v = 1); volume of electrolyte = 250 ml.



Hence the significant increase in the cathodic potential from -1.1 to -1.3 V was mainly caused by establishing the diffusion boundary layer on the cathodic surface. The hydroxide ion (OH^-) produced in Eqs. (1) and (2) was deposited with Co^{2+} in the solution onto the Cu foil. At the same time, the increase in the concentration of H^+ in the solution was due to the anodic oxidation of H_2O on the anode, resulting in a decrease in the solution pH from 5.40 to 3.30 in the first run of electrodeposition (Table 1). The increase in the concentration of H^+ induced the cathodic reduction of H^+ on the cathode, resulting in a decrease in the cathodic potential from -1.3 to -1.1 V (Fig. 1).



In the first run of the electrodeposition of $\text{Co}(\text{OH})_2$, a non-uniform film was obtained due to the higher $\text{Co}(\text{OH})_2$ deposition rate caused by the fast OH^- generation rate based on Eqs. (1) and (2).

The cathodic reaction of H_2O to produce OH^- (Eq. (2)) was generally replaced by the evolution of H_2 (Eq. (3)) for the run number greater than 2 due to the decrease in pH of the solution (Table 1). For the run number greater than 2, the uniform $\text{Co}(\text{OH})_2$ deposits

Table 1
Effect of the run number on the preparation of $\text{Co}(\text{OH})_2$.

Run no.	pH	Residual Co^{2+} ^a (%)	Weight ^b (mg)	
			α - $\text{Co}(\text{OH})_2$	CoO
1	5.40–3.30	99.5	–	–
2	3.30–3.14	99.0	0.913	0.700
3	3.14–2.94	98.5	0.888	0.675
4	2.94–2.82	98.0	0.800	0.575
5	2.82–2.71	97.5	0.763	0.538
6	2.71–2.66	97.0	0.750	0.525

Working electrode: Cu foil ($4 \times 4 \text{ cm}^2$); counter electrode: Au plate ($5 \times 5 \text{ cm}^2$) \times 2; reference electrode: Ag/AgCl/3 M NaCl aqueous solution; cd = 0.5 mA cm^{-2} ; $T = 5^\circ\text{C}$; electrolysis time = 40 min; electrolyte: 0.175 M $\text{Co}(\text{NO}_3)_2$; 0.075 M NaNO_3 aqueous and ethyl alcohol solution (v/v = 1); volume of electrolyte = 250 ml.

^a Residual Co^{2+} in the solution (%) = $([\text{Co}^{2+}]_t / [\text{Co}^{2+}]_i) \times 100\%$, where $[\text{Co}^{2+}]_t$ and $[\text{Co}^{2+}]_i$ were the concentration of Co^{2+} in the present time and the initial state, respectively.

^b The average weights were measured based on the eight pieces of the samples with area of 1.327 cm^2 .

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