

Preparation and characterization of CoO used as anodic material of lithium battery

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Abstract

The characteristics of CoO prepared from the calcination of $\text{Co}(\text{OH})_2$ (precursor of CoO) in the N_2 atmosphere were analyzed, and the charge/discharge properties of CoO was also investigated in this paper. Increasing the calcination temperature from 200 to 900 °C the grain size of CoO increased from 6.59 to 31.5 nm, and the BET surface area decreased from 89.83 to 0.47 $\text{m}^2 \text{g}^{-1}$. For CoO calcinated at 200 °C the maximum charge capacity, the coulomb efficiency and the irreversible capacity at the first cycle of Li/CoO battery were found to be 1233.57 mAh g^{-1} , 98.46% and 305.87 mAh g^{-1} , respectively. The irreversible capacity in the first cycle could be recovered in the following charge/discharge cycles.

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1. Introduction

The commonly used anodic material in the lithium ion battery is a carbonaceous compound due to its low cost and high operational voltage. However, the theoretical capacity of the graphite or graphitizable carbons is limited to be 372 mAh g^{-1} due to the formation of LiC_6 [1]. The capacity has been much improved by the development of the highly disordered structure carbonaceous compounds prepared by the pyrolysis of organic compounds [2,3]. Recently, Co_3O_4 [4–8] and the various vanadates [9–12] have been used as the anodic materials in the lithium-ion batteries. The relative higher reversible specific capacities are obtained for Co_3O_4 and vanadates, however, the large irreversible capacity during the first cycle and the higher fading rate are found in the charge/discharge processes.

A new insertion–extraction mechanism different from the carbonaceous compounds or lithium-alloying processes is proposed by using, namely, nano-sized transition-metal oxides (MO, where M is Co, Ni, Cu or Fe) [4,6,13–21]. The reversible electrochemical reaction mechanism of the charge/discharge process for CoO was mentioned to be

the decomposition of CoO to Li_2O and Co by insertion of Li^+ [13,22]. The reversible capacity of CoO is obtained to be 600–800 mAh g^{-1} in the room temperature [4,13,16]. The commercial CoO powder with particle size about 1 μm is commonly used as the anodic material in the most of the investigations. However, the electrochemical and charge/discharge characteristics of CoO used as the electroactive material of anode in the lithium-ion battery would be affected by the particle size and crystallinity of CoO. It is of interest to prepare CoO powders with different properties and be used as the anodic materials of Li-ion batteries.

In the present paper, CoO is prepared by the calcination of the precursor of $\text{Co}(\text{OH})_2$ synthesized by the chemical precipitation under the various calcinated conditions. The characteristics of the CoO particle and the charge/discharge properties of CoO used as cathode of Li/CoO coin cell are investigated.

2. Experimental

2.1. Preparation and characterization of CoO

$\text{Co}(\text{OH})_2$ was precipitated by mixing 100 ml of 1.0 M cobalt nitrate solution (J.T. Baker, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, >99.1%)

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and 500 ml of 0.4 M sodium hydroxide solution (Merck, NaOH, >99%) in a flask and stirring for 8 h under 99.995% nitrogen atmosphere. The obtaining $\text{Co}(\text{OH})_2$ was dried in a vacuum oven at 50 °C for 24 h. Cobalt oxides were obtained by the calcination of $\text{Co}(\text{OH})_2$ in a oven with various conditions.

The crystallographic information, surface area, surface morphologies and particle size of the preparing CoO were analyzed by X-ray powder diffraction (XRD, Shimadzu XRD-6000), BET surface analyzer (Micromeritics 2375) and SEM (Joel JSM-5400), respectively.

2.2. Cells assembling and measurements

The cobalt oxide electrodes were made by scraping and pressing the paste, which was prepared by dispersing the suitable compositions of the carbon black, PVDF (poly(vinylidene fluoride)) and the preparing CoO powder with NMP (*N*-methyl-2-pyrrolidinone) as solvent, on the Cu foil. The thickness and the loading of CoO were measured to be 80–100 μm and 5.5–7.0 mg, respectively. The electrolyte, separator and counter electrode of the coin cell were 1.0 M LiPF_6 EC–DEC (ethylene carbonate–diethyl carbonate, provided by FERRO) (v/v 1:1), PP (polypropylene) film (Ashahi N910) and Li foil, respectively. The cells were assembled in an argon-filled glove-box (VAC MO-5). The coin cells were galvanostatically charged and discharged at a suitable C-rate, and the voltage behavior against the time was recorded over the potential range of 0.02–3.0 V (versus 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. Characteristics of $\text{Co}(\text{OH})_2$ and CoO

The main product of the precipitation by mixing the $\text{Co}(\text{NO}_3)_2$ and NaOH aqueous solutions with aging period greater than 1 h was the brucite-like compound with the formula $\text{Co}^{\text{II}}(\text{OH})_2 \cdot 0.03\text{H}_2\text{O}$ [23]. Comparing the XRD pattern of $\text{Co}(\text{OH})_2$ precipitate with the patterns in the literatures [23,24] revealed that the preparing $\text{Co}(\text{OH})_2$ was the brucite-like formula. A slice-like structure with the particle size of 200 nm was found in the SEM photograph of $\text{Co}(\text{OH})_2$, and the grain size of $\text{Co}(\text{OH})_2$ obtained from the XRD analysis was 22.9 nm (Table 1).

CoO can be obtained by the decomposition of $\text{Co}(\text{OH})_2$ in an elevated temperature. For the presence of a trace of oxygen in the furnace CoO can be further oxidized to Co_3O_4 . The pure phase of CoO was obtained for $\text{Co}(\text{OH})_2$ calcinated in a tubular furnace at 99.995% N_2 atmosphere (Fig. 1). The XRD patterns exhibited the characteristic peaks of CoO at 36.5°, 42.4°, 61.5°, 73.7° and 77.6°, and as the temperature increased, the intensities of peaks increased. The results

Table 1
Effect of calcination temperature on the grain size and the BET surface area of CoO

T (°C)	Grain size (nm)	BET surface area ($\text{m}^2 \text{g}^{-1}$)
– ^a	22.9	28.05
200	6.59	89.83
300	6.77	68.04
400	14.2	36.81
500	26.3	16.49
600	27.3	9.18
700	28.4	4.32
800	30.9	1.07
900	31.5	0.47

Calcination time = 1 h; 99.995% N_2 atmosphere.

^a Precursor of CoO.

indicated that the crystallinity of CoO increased with the calcination temperature. The average grain size was calculated based on the Sherrer equation [25] at $2\theta = 42.4^\circ$. Increasing the calcination temperature from 200 to 300 °C the grain size changed slightly from 6.59 to 6.77 nm, and the surface area was slightly decreased from 89.82 to 68.04 $\text{m}^2 \text{g}^{-1}$ as shown in Table 1. The grain size of CoO calcinated at 200 and 300 °C was significantly less than that of the precursor $\text{Co}(\text{OH})_2$, indicating that the $\text{Co}(\text{OH})_2$ crystallite was cracked at the calcination process due to the decomposition of $\text{Co}(\text{OH})_2$ to CoO and loss of H_2O . Furthermore the slice structure similar to the precursor $\text{Co}(\text{OH})_2$ was found for CoO prepared at 200 and 300 °C. The surface area of CoO prepared at 200 and 300 °C was hence greater than its precursor (Table 1).

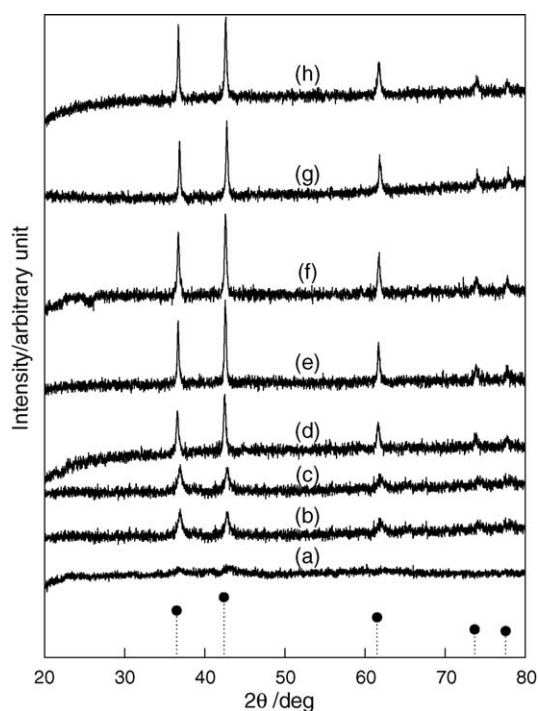


Fig. 1. XRD patterns of cobalt oxide calcinated in tubular furnace, $t = 1$ h, 99.995% N_2 atmosphere. Calcination temperatures: (a) 200 °C, (b) 300 °C, (c) 400 °C, (d) 500 °C, (e) 600 °C, (f) 700 °C, (g) 800 °C and (h) 900 °C.

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