

Short communication

Cobalt oxide preparation from waste LiCoO_2 by electrochemical–hydrothermal method

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Received 28 May 2002; accepted 14 August 2002

Abstract

Cobalt ions, extracted from waste LiCoO_2 by using a nitric acid leaching solution, are potentiostatically transformed into cobalt hydroxide on a titanium electrode and cobalt oxide is then obtained via a dehydration procedure. In linear sweep voltammetry, distinct cathodic current peak is observed and indicates that hydroxide ions are formed near the electrode via the electroreduction of dissolved oxygen and nitrate ions give rise to an increase in the local surface pH of the titanium. Under appropriate pH conditions, island-shaped cobalt hydroxide is precipitated on the titanium substrate and heat treatment of the cobalt hydroxide results in the formation of cobalt oxide.

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Keywords: Cobalt hydroxide; Cobalt oxide; Dehydration; Waste LiCoO_2 ; Electrochemical–hydrothermal method

1. Introduction

The Li-ion battery is a most attractive energy source for portable electronic products, such as cellular phones and laptop computers, since it has a high voltage, a large charge capacity, and good cycleability compared with previous batteries. Spinel structure LiCoO_2 is commonly used as the cathode material for Li-ion batteries due to its good performance in terms of high specific energy density and durability [1].

Spent Li-ion batteries can give rise to the environmental poisoning, and thus, the proper post-treatment of waste Li-ion materials is required [2]. The economics of such a process should be also considered since the recovered cobalt and/or cobalt oxide could be re-used for the preparation of commercial-grade LiCoO_2 , as well as spinel Co_3O_4 which is considered to be a promising electrochromic compound [3–5].

It has been reported [3] that cobalt can be recovered by a selective solvent extraction method. The cobalt was selectively leached between pH 4 and 6, while Li was extracted at pH = 7, by using organic phosphoric acid. This method could not, however, properly control the solution pH and this induced a lower extraction rate of each metal.

In this work, cobalt oxide is prepared from Co(III) of waste LiCoO_2 cathodes by applying both electrochemical deposition and appropriate thermal treatment.

2. Experimental

LiCoO_2 powder was separated from waste Li-ion batteries and dissolved in hot nitric acid (HNO_3). In order to increase the solubility of LiCoO_2 in HNO_3 solution, it was necessary to heat the solution. During heating of the HNO_3 solution, most of water was evaporated. Thus, double-distilled water was continuously added to the leaching HNO_3 solution in order to maintain an appropriate pH value of 2.6. The concentration of elements from commercial (fresh) and waste LiCoO_2 in HNO_3 was analyzed with an inductively couple plasma-mass spectrometer (ICP-MS, Shimadzu, ICPS-1000IV).

The electrodeposition mechanism was investigated by analysis of linear sweep voltammetry (LSV), and by morphological studies of the surface of the titanium substrate with a scanning electron microscope (SEM, Hitachi S-4200). A potentiostat/galvanostat (EG&G PAR 273) was used for all LSV experiments and the data was transferred to an IBM compatible PC controlled by a GPIB interface. The composition of the deposited material was determined by means of energy-dispersive X-ray spectroscopy (EDS in the

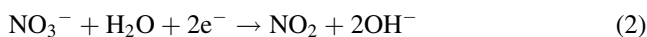
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SEM, Hitachi S-4200) analysis and X-ray diffraction (XRD, Philips DY616). The phase changes in the deposited material during heat treatment were investigated by means of thermogravimetric analysis, TGA (TA Instrument, Thermal Analyst 2000).

3. Results and discussion

The solubility of Li and Co from a waste LiCoO_2 cathode and commercial LiCoO_2 in HNO_3 leaching solution is shown in Table 1. Compared with fresh LiCoO_2 , waste LiCoO_2 produces a lower concentration of Li metal, but a higher concentration of Co. This may be due to the changed spinel structure of LiCoO_2 , that is, the irreversibility of charge–discharge of Li-ions in the operation of the Li-ion battery.

A linear sweep voltammogram of dissolved LiCoO_2 in HNO_3 solution for a Ti cathode is shown in Fig. 1. The curve indicates that a multi-step electroreduction occurs. A cathodic current peak appears at -0.8 V and becomes more pronounced with increasing concentration of LiCoO_2 . The detailed reaction mechanisms are considered to be:



As already reported in our previous studies [7–10], the reduction of dissolved O_2 and nitrate ion, i.e. reactions (1) and (2), could increase the local pH of the electrode. Thus, the precipitation of hydroxide films of $\text{Co}(\text{OH})_2$ (see Eq. (4)) under appropriate pH condition could be possible. The formation of hydroxide film retards the further reduction of active species due to its non-conducting (passive) property. The current peak at -0.8 V is attributed to the formation of a passive film. Comparison of curves (a) and (b) in Fig. 1 shows that the peak observed at -0.8 V increases with increasing concentration of Co^{2+} ions. This indicates that the rate of NO_3^- reduction and $\text{Co}(\text{OH})_2$ formation are strongly dependent on the concentration of Co^{2+} . Furthermore, the reduction of Co^{3+} to Co^{2+} (Eq. (3)) could also increase the cathodic current.

The cathodic scans in acid and base solutions are shown in Fig. 2. A current peak is obtained at pH = 2.6, but not at the higher pH of 8.0. Curve (a) shows that the reduction current increase rapidly below -0.8 V, where the current peak is

Table 1
Compositional analysis of dissolved LiCoO_2 in HNO_3 solution

Sample	Li (ppm)	Co (ppm)
Commercial LiCoO_2	279.62	1387.54
Waste LiCoO_2	249.23	1449.90

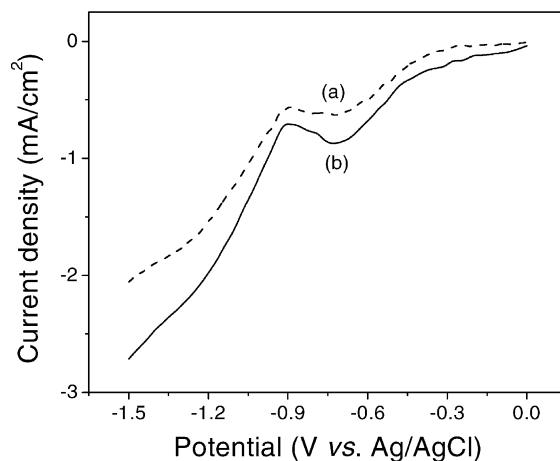


Fig. 1. Linear sweep voltammograms for different concentrations of waste LiCoO_2 in 0.1 M HNO_3 solution on a Ti electrode. (a) 10 mM LiCoO_2 ; (b) 100 mM LiCoO_2 . Scan rate = 10 mV s^{-1} . Bulk pH = 2.59.

obtained (see curve (b)). The decrease of cathodic current ranges from -0.7 to -1.0 V and could be due to the limitation of the mass transfer of reducing agent through the precipitated $\text{Co}(\text{OH})_2$ film, i.e. an N-shaped current–potential curve is obtained. The detail reaction mechanism has still to determined.

A potential of -1.0 V is applied for the formation of cobalt hydroxide. In order to characterize the cobalt hydroxide electrochemically formed on the titanium surface, the mass changes of the deposited material were measured by means of TGA. The results are given in Fig. 3. The mass decrease below 100 °C is due to the dehydration of physically-adsorbed water. Above 200 °C, about 18.7% of the initial mass is reduced, a value which is similar to the theoretical value of 19.5% according to following dehydration reaction (5):

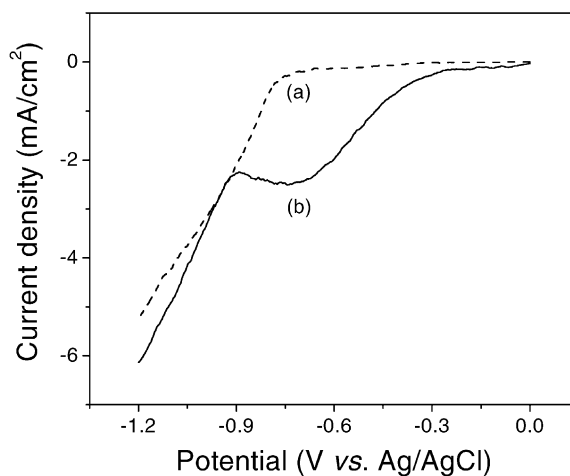
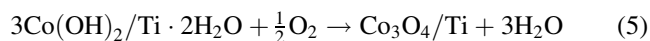


Fig. 2. Linear sweep voltammograms in acid and base solution. (a) pH = 8.0; (b) pH = 2.59. Scan rate = 5 mV s^{-1} .

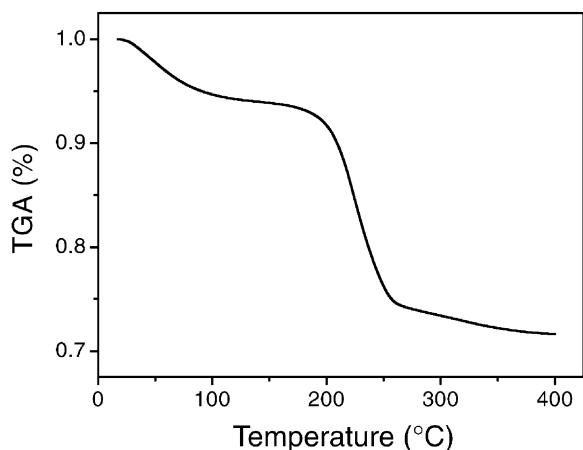


Fig. 3. TGA analysis of cobalt hydroxide prepared by electrodeposition.

As suggested by Yoshino and Baba [6] cobalt oxide can be prepared by heat treatment of cobalt oxide films which consist mainly of cobalt hydroxide formed by electrochemical deposition. We have applied a dehydration temperature of 400 °C in order to obtain cobalt oxide (Co₃O₄) for use in electrochromic applications.

After applying the heat treatment in air, cobalt hydroxide can be changed into cobalt oxide (Co₃O₄). The EDS data of deposited materials on a Ti electrode before and after annealing are shown in Fig. 4(a) and (b), respectively.

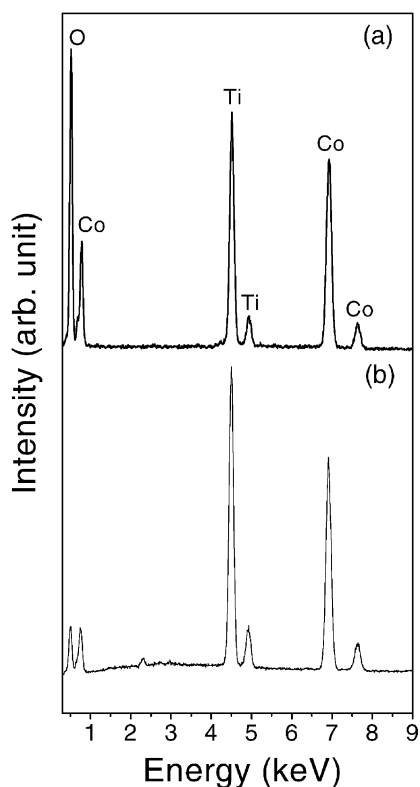


Fig. 4. EDS analysis of cobalt oxide deposited on a Ti electrode by electrochemical preparation and thermal treatment. Experimental conditions as in Fig. 3 ((a) before and (b) after heat treatment at 400 °C for 3 h).

Table 2
Atomic composition analysis of deposited material on Ti substrate

Sample	Co (%)	O (%)
Before annealing	17.0	73.0
After annealing	34.3	40.2

In addition to peaks for the substrate species oxygen and cobalt peaks are clearly detected, which can be assigned to cobalt hydroxide and cobalt oxide. The atomic ratios of cobalt and oxygen are given in Table 2. Interestingly, comparison of the atomic ratio between cobalt hydroxide and cobalt oxide strongly supports reaction (5) as the dehydration reaction. Before heat treatment, the O:Co composition of the

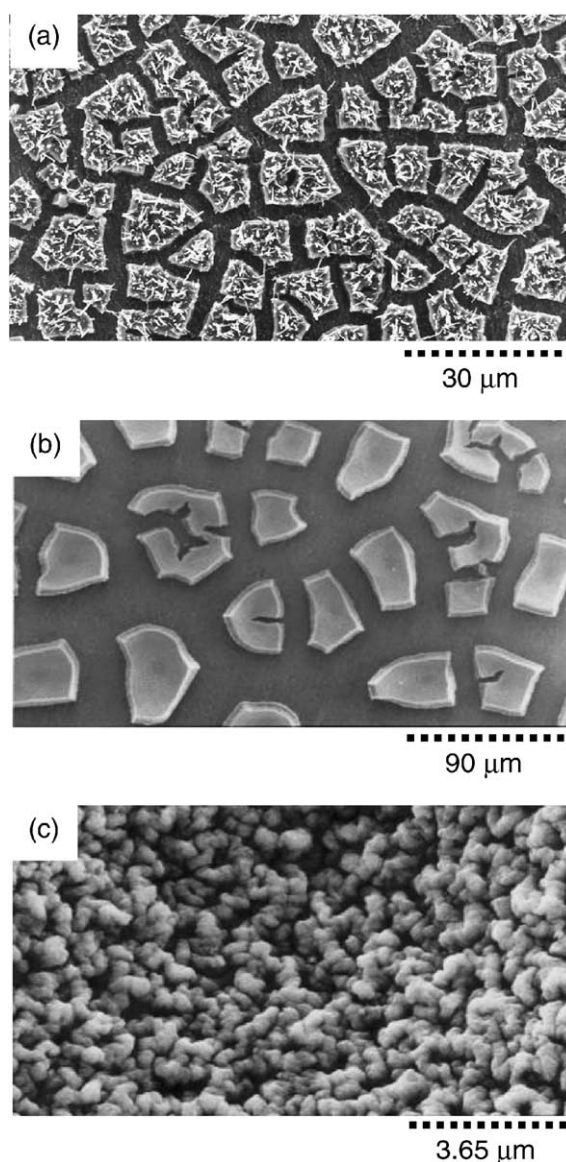


Fig. 5. Electron micrograph of cobalt (hydro)oxide formed on a Ti surface at -1.0 V before and after heat treatment at 400 °C for 3 h. (a) Electrodeposited Co(OH)₂ (600×); (b) after heat treatment (200×); (c) after heat treatment (5000×).

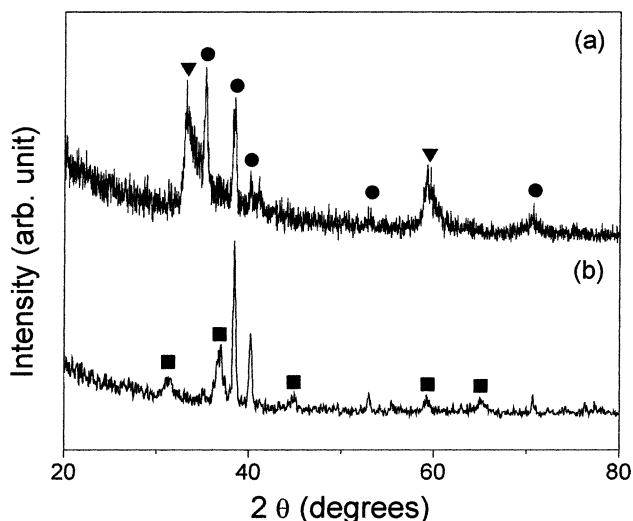


Fig. 6. XRD data of cobalt (hydro)oxide formed on a Ti surface at -1.0 V (a) before and (b) after heat treatment at 400 °C for 3 h. Reversed triangle, closed square, and circle indicate peaks for $\text{Co}(\text{OH})_2$, Co_3O_4 , and Ti, respectively.

deposited material is approximately 4.36:1, as determined by EDS, which equals to cobalt hydroxide hydrate ($\text{Co}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$). Since the dehydration occurs during the annealing, a relatively lower amount of oxygen compared with cobalt is observed. The oxygen:cobalt atomic ratio is about 1.17 and is assigned to Co_3O_4 (for the details of the reaction mechanism see Fig. 6 below).

To obtain a better understanding of the different structural and morphological features of cobalt hydroxide before annealing and cobalt oxide formed on the titanium substrate by annealing, ex situ SEM and XRD analyses were performed.

The morphology of deposited cobalt hydroxide/oxide on titanium before and after heat treatment is shown in Fig. 5. The as-deposited $\text{Co}(\text{OH})_2$ shows an island-type deposition of $\text{Co}(\text{OH})_2$ (Fig. 5(a)), but thermal treatment causes dehydration and structural transformation into cobalt oxides, as shown in Fig. 5(b) and the average size of the islands is reduced significantly. A magnified image of a region inside the island deposit is shown in Fig. 5(c). It can be seen that the randomly grown precipitates are agglomerated and the deposits do not have strong adhesion strength.

XRD data for the deposited material on titanium in LiCoO_2 solution before and after heat treatment, are presented in Fig. 6(a) and (b), respectively. Before heat treatment,

several broad phases are formed on the Ti substrate, especially at 32.412 and 59.56° , and are assigned to $\text{Co}(\text{OH})_2$. Unlike the amorphous $\text{Co}(\text{OH})_2$ formed by electrodeposition, the XRD peaks of Co_3O_4 prepared by heat treatment are quite sharp. This indicates that annealing results in the formation of crystalline Co_3O_4 .

4. Conclusions

From analysis of linear sweep voltammogram, it is found that a non-conducting material, i.e. cobalt hydroxide, can be formed on a titanium substrate. On the other hand, cobalt oxide is not obtained by applying a constant cathodic potential. When a constant potential of -1.0 V is applied, a peculiar island-like structure of deposited material is deposited on the titanium electrode. By analyzing EDX and XRD data, the deposited material was assigned to $\text{Co}(\text{OH})_2$. The cobalt hydroxide changes to cobalt oxide by applying appropriate heat treatment. Different morphological and structural features are observed and are due to the dehydration of cobalt hydroxide. The electrochemical-hydrothermal technique offers a possible means for the mass production of cobalt oxide from waste LiCoO_2 .

Acknowledgements

This work was supported by KOSEF through the Research Center for Energy Conversion and Storage.

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