Advanced Powder Technology 21 (2010) 175–179

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Preparation of cobalt oxide from concentrated cathode material of spent lithium ion batteries by hydrometallurgical method

Jingu Kang [a,b], Jeongsoo Sohn [b], Hankwon Chang [b], Gamini Senanayake [c], Shun Myung Shin [b,*]

[a] Department of Resource Recycling, Korea University of Science and Technology (UST), 52 Eoeun-dong, Yuseong-gu, Daejeon, Republic of Korea
[b] Metal Recovery Group, Mineral Resources Research Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), 92 Kwahak-no, Yuseong-gu, Daejeon, Republic of Korea
[c] Parker Centre, Faculty of Minerals and Energy, Murdoch University, Perth, WA 6150, Australia

ARTICLE INFO

Article history:
Received 6 October 2009
Received in revised form 28 October 2009
Accepted 29 October 2009

Keywords:
Spent Li-ion battery
Reductive leaching
Oxalate precipitation
Cobalt oxide

ABSTRACT

Cobalt oxide was prepared from spent lithium ion batteries (LIBs) by reductive leaching, copper sulfide precipitation, cobalt oxalate precipitation and thermal decomposition. The cobalt rich non-magnetic −16 mesh fraction obtained from spent LIBs by mechanical separation was leached using 2 M H_2SO_4, 6 vol% H_2O_2, reaction temperature 60 °C, agitation speed 300 rpm, pulp density 100 g/L, reaction time 1 h. The leaching efficiency of cobalt was more than 99% and its concentration was 27.4 g/L. Copper was removed (99.9%) as CuS by precipitating with Na_2S. The crystalline solid $CoC_2O_4{\cdot}2H_2O$ selectively precipitated by treating the copper-free liquor with oxalic acid was calcined to produce crystalline Co_3O_4, of which primary average particle size was 340 nm.

1. Introduction

The usage of lithium ion batteries (LIBs) has rapidly increased as they are widely used as electrochemical power sources in mobile telephones, personal computers, video cameras and other modern-life appliances [1,2]. Due to their characteristics of light weight, high energy and good performance, LIBs are increasingly substituting for other batteries [3,4]. They not only dominate the cellular phone and laptop computer markets at present, but also will be the first category of dynamic batteries to be chosen to provide power for electronic automobiles in the future.

The increasing public concern about the environment in the last decades has resulted in stricter regulations worldwide on the disposal of hazardous waste containing heavy metals, such as spent portable batteries. LIBs consist of organic chemicals (15%), plastics (7%), lithium (5–7%), cobalt (5–20%) and nickel (5–10%) with the composition varying slightly with different manufacturers [5]. Recycling practices are highly desirable at present and in the future from the viewpoints of environmental conservation, and the recovery of metal values from spent LIBs and their utilization as raw materials.

Despite the extensive research activities for recycling spent LIBs in many countries there is no commercialized recycling plant as yet [6]. The recycling processes under development stages are mainly composed of acid leaching, solvent extraction, precipitation and electro-winning. Zhang et al. [7] reported a hydrometallurgical process consisting of HCl leaching, solvent extraction of Co(II) with PC-88A, crystallization of $CoSO_4$ and precipitation of Li_2CO_3. Contestabile et al. [8] studied a recycling process of spent LIBs on a laboratory scale which comprised of the steps: (i) sorting, (ii) selective separation of $LiCoO_2$ powder using *N*-methylpyrrolidone, (iii) HCl leaching of $LiCoO_2$, (iv) cobalt hydroxide precipitation and thermal treatment to produce Co_3O_4, and (v) thermal treatment of Co_3O_4 with Li_2CO_3 to produce $LiCoO_2$ which was suitable for the production of new batteries. These studies, however, focused mainly synthetic solution or spent cathodic materials generated during the manufacturing process to investigate recycling processes. It is also required that the complex process to recover valuable metals as well as a high capital cost and the solvent cost to establish proper recycling processes. Comparing with previous studies, the present proposed method is a simple process to prepare cobalt compounds from spent LIBs using single leaching/two steps precipitation method.

In this study, laboratory tests were conducted for (i) the reductive leaching of LIBs with sulfuric acid and hydrogen peroxide, (ii) the removal of copper by sulfide precipitation with sodium sulfide, (iii) the selective precipitation of cobalt oxalate from the purified leach liquor, and (iv) the preparation of cobalt oxide by calcination.

2. Experimental procedure

The physical treatment of spent LIBs included discharging, dehydration, drying, and crushing. The square type spent LIBs were

---

[*] Corresponding author. Tel.: +82 42 868 3622; fax: +82 42 868 3415.
E-mail address: shin1016@kigam.re.kr (S.M. Shin).

0921-8831/$ - see front matter
doi:10.1016/j.apt.2009.10.015

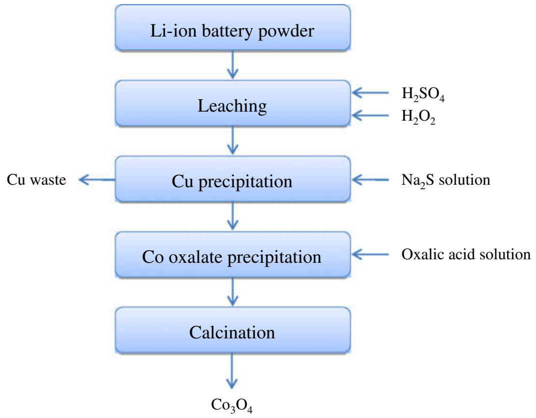

Fig. 1. Flow sheet of cobalt oxide production from Li-ion batteries (conditions in Table 2).

treated with a roll presser in order to short-circuit between the cathode and the anode. They directly fell into distilled water for discharging for 1 day. After dehydration and drying, discharged LIBs were subjected to crushing, magnetic separation, and screening to obtain three size fractions: +8 mesh, −8 + 16 mesh, and −16 mesh [9]. The −16 mesh fraction was selected for leaching. As shown in the flow sheet in Fig. 1, the leaching was conducted with 2 M sulfuric acid solution containing 6 vol% hydrogen peroxide. The addition of Na_2S at the molar ratios of Na_2S: Cu(II) in the ratio 3/1 to the leach liquor over a period of 30 min at 25 °C precipitated CuS. The residue was filtered and a solution of 1.5 M $H_2C_2O_4$ was added to the filtrate to precipitate $CoC_2O_4{\cdot}2H_2O$ over a period of 2 h. The composition of the precipitate was analyzed by AAS (Perkin Elmer, AAnalyst 400) and its crystal phases were analyzed by XRD (Rigaku, RU-200, Cu K-α). The oxalate product was heated for 2 h at 150–600 °C using an electric furnace to calcine to Co_3O_4 which was also analyzed by AAS and XRD. Morphology of the produced cobalt compounds was investigated by SEM (JEOL, JSM-6380LA). Brunauer–Emmett–Teller (BET; Quantachrome Instruments, Quadrasorb *SI*) analysis was performed to determine the specific surface area (m^2/g) and pore volume of the powders. The specific surface area (S_{BET}) was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P_0) range of 0.03–0.3. Desorption isotherm was used to determine the pore size distribution using the Barrett–Joyner–Halenda (BJH) method [10]. The Particle size of the produced powder was analyzed by a particle size analyzer (PAS; Malvern Instruments, Mastersizer 2000).

3. Results and discussion

3.1. Physical treatment and leaching of spent LIBs

The mass and metal composition of different size fractions of spent LIBs after the physical treatment is listed in Table 1 [9]. The optimum leaching conditions for the −16 mesh fraction have been reported in a previous study [5]: 60 min at 100 g L^{-1} pulp density, 2 M H_2SO_4, 6 vol% H_2O_2, 250 rpm, and 60 °C. The concentration of valuable metals in the leach liquor is shown in Table 2.

3.2. Removal of Cu(II) from the leach liquor

Copper(II) must be removed from the solution before oxalic acid precipitation for recovery of cobalt to avoid the co-precipitation of CuC_2O_4. Copper(II) can be selectively separated from other metal ions in a wide range of solution pH. The sulfide precipitation method is used more widely than hydroxide and carbonate precipitation because of the low solubility of CuS in acid solutions. This is demonstrated in Fig. 2 which represents the solubility diagram for Cu(II), Ni(II), and Co(II) at 25 °C and 1 atm H_2S based on reported thermodynamic data [11]. Lines for H^+ and Cu^{2+} in Fig. 2 represent the equilibrium for Eqs. (1a) and (1b), respectively. Although Na_2S was added as the precipitating agent in the present study, the solubility of metal ions as sulfides in acidic solutions is governed by the equilibrium in Eq. (1c) which represents the combined form of Eqs. (1a) and (1b):

$$H_2S = 2H^+ + S^{2-} \tag{1a}$$

$$CuS(s) = Cu^{2+} + S^{2-} \tag{1b}$$

$$Cu^{2+} + H_2S = CuS(s) + 2H^+ \tag{1c}$$

As predicted in Fig. 2 the free S^{2-} ion concentration at pH 1 is 10^{-17} M which corresponds to 10^{-15} M Cu(II) compared to the concentration of Co(II) and Ni(II) which are greater than 10^{-4} M. However, the application of such predictions for quantitative treatment

Table 1
Mass and metal composition in different fractions of spent LIBs.

Fraction	Mass%	Co%	Li%	Cu%	Fe%	Mn%	Ni%	Al%
Magnetic material	3.5	<0.01	<0.01	0.1	1.6	0.01	0.9	0.1
+8 mesh	49.4	9.3	1.1	7.4	0.1	0.1	0.4	7.8
−8 + 16 mesh	7.6	2.1	0.3	0.1	0.01	<0.01	0.01	0.09
−16 mesh	36.5	11.8	1.3	4.6	0.2	<0.01	0.1	5.1
Total	97[a]	23.3	2.7	12.2	1.8	0.11	1.41	13.1

[a] 3% lost in the process (Shin et al. [9]).

Table 2
Metal composition of starting material and other products in the flow sheet.

Metal	Co	Fe	Cu	Li	Mn	Ni	Al
Mass% in feed (−16 mesh)	11.8	1.3	4.6	0.2	<0.01	0.1	–
mg/L in leach liquor (pH 0.3)[a]	27,400	88.6	962.4	4870	15.7	71.1	1800
Mass% in Co-oxalate product[b]	35	0.03	0.01	0.1	0.3	0.2	0.1
Mass% in Co-oxide product[c]	79	0.1	0.01	0.08	0.6	0.4	0.2

[a] Leaching conditions for −16 mesh fraction: 60 min at 100 g L^{-1} pulp density, 2 M H_2SO_4, 6 vol% H_2O_2, 250 rpm, and 60 °C.
[b] $CoC_2O_4{\cdot}2H_2O$ obtained by adding oxalic acid to copper-free leach liquor.
[c] Co_3O_4 obtained by heating $CoC_2O_4{\cdot}2H_2O$ for 2 h at 150–600 °C using an electric furnace.