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Environmentally-friendly oxygen-free roasting/wet magnetic separation technology for in situ recycling cobalt, lithium carbonate and graphite from spent $LiCoO_2$/graphite lithium batteries

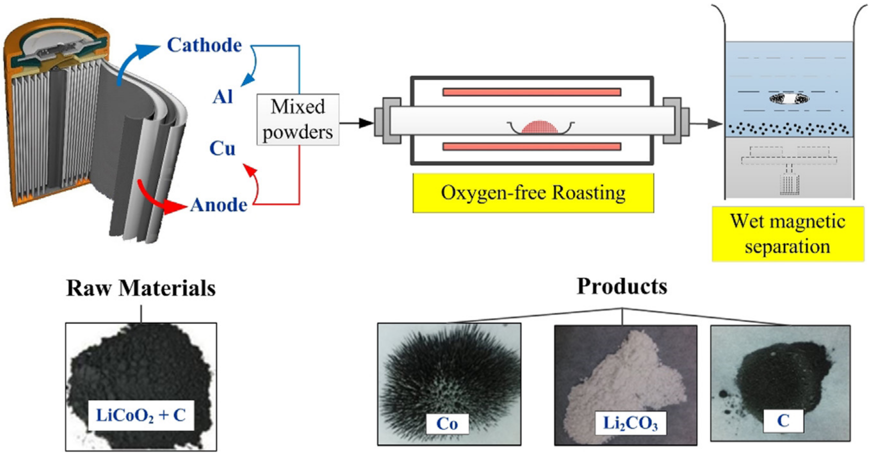
Jia Li, Guangxu Wang, Zhenming Xu*

School of Environmental Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China

HIGHLIGHTS

- The idea of “waste + waste → resources.” was used on this study.
- Based on thermodynamic analysis, the possible reaction between $LiCoO_2$ and graphite was obtained.
- The residues of oxygen-free roasting are cobalt, lithium carbonate and graphite.
- The recovery rate of Co and Li is 95.72% and 98.93% after wet magnetic separation.
- It provides the rationale for environmental-friendly recycling spent LIBs in industrial-scale.

GRAPHICAL ABSTRACT



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ABSTRACT

The definite aim of the present paper is to present some novel methods that use oxygen-free roasting and wet magnetic separation to in situ recycle of cobalt, Lithium Carbonate and Graphite from mixed electrode materials. The in situ recycling means to change waste into resources by its own components, which is an idea of “waste + waste → resources.” After mechanical scraping the mixed electrode materials enrich powders of $LiCoO_2$ and graphite. The possible reaction between $LiCoO_2$ and graphite was obtained by thermodynamic analysis. The feasibility of the reaction at high temperature was studied with the simultaneous thermogravimetry analysis under standard atmospheric pressure. Then the oxygen-free roasting/wet magnetic separation method was used to transfer the low added value mixed electrode materials to high added value products. The results indicated that, through the serious technologies of oxygen-free roasting and wet magnetic separation, mixture materials consist with $LiCoO_2$ and graphite powders are transferred to the individual products of cobalt, Lithium Carbonate and Graphite. Because there is not any chemical solution added in the process, the cost of treating secondary pollution can be saved. This study provides a theoretical basis for industrial-scale recycling resources from spent LIBs.

1. Introduction

Since 1992, the lithium ion batteries (LIBs) have been commercially used. They are one of the most popular types of rechargeable

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* Corresponding author. Fax: +86 21 54747495.
E-mail address: zmxu@sjtu.edu.cn (Z. Xu).

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batteries for portable electronics, with a high energy density, no memory effect, and only a slow loss of charge when not in use. LIBs are also used to swap traditional batteries in popularity for military, electric vehicle, medical equipment and aerospace applications. On average, battery performance is rarely specified over more than 500 cycles. This means that batteries of mobile phones, or other hand-held devices in daily use, are not expected to last longer than three years [1,2]. The phenomenon of electrode expansion happens in LIBs which leads to active material layer structure blocking and inactivation, then the cycle characteristics of LIB fall sharply. Spent LIBs contribute substantially to the increasing problem of electronic waste (e-waste), the fastest growing segment of the solid waste stream [3,4].

Lithium ion battery waste has significant resources [5], the intrinsic material value for 1 ton of LIBs is nearly \$7708 [6], nearly 36 ±9 wt.% of cobalt is contained in the battery cell after removing the plastic and metal casing [7]. However, a series of chemical reactions of hydrolysis, oxidation and decomposition, produces a negative carbon dust, alkali and heavy metal ions, may cause heavy metal pollution and dust pollution, when the electrode materials of spent LIBs go into the environment [8–10]. Thus, recycling spent LIBs with harmless technology has become more and more important.

Recently, the hydrometallurgical process was the main recycling way for waste lithium ion battery [11], because of the high recovery rate of valuable components. Hot topics are extraction rare, precious metals and process of deep chemical treatment. On the basis of inorganic acid leaching [12–15] and bioleaching [16,17], the technology of solvent extraction [18–21], chemical precipitation [22,23], electrochemistry [24,25], calcination [26] and mechanochemistry [27,28] are used to recycle resources of the Co, Li from cathode material [29]. The "large volume" of spending acid and alkali with high concentration will be generated in the process of cobalt leaching and relevant chemical treatment with hydrometallurgy [30]. The extra cost for environmental improvement of secondary pollutions is very high. Manual dismantling operation is not feasible for a huge amount of small LIBs (annual global production will reach 7 billion in 2015 [31]) in the economic perspective. Mechanical treatment is better than manual dismantling to deal with small LIBs. According to Zhang's study [32], after pretreatment of crushing, the diaphragm, aluminum foil, copper foil and plastics, etc., mainly existed in coarse particle, while the fine particles were mainly composed of electrode materials such as graphite and $LiCoO_2$. Generally, in the mixture of fine particles, graphite is regarded as an impurity and need to be removed before recycling $LiCoO_2$ or other resources [33,34]. Graphite is a crystalline form of carbon and is the most stable form of carbon under standard conditions. However, in oxygen containing atmospheres graphite readily oxidizes to form CO_2 at temperatures of 700 °C and above [35]. In industrial processes, the reduction of metal oxides is often affected by a carbothermic reaction, using carbon as a reducing agent. Under special conditions, if the graphite is regarded as a reducing agent, the electrode material of $LiCoO_2$ will be transferred to resources, such as cobalt or Lithium salt. Then the process will be the kinds of in situ recycle which means to change the spent LIBs into resources by its own electrode materials. Hence, the aim of this study is to explore the viability of utilizing the anode material of graphite reducing the cathode material of $LiCoO_2$ to get higher added value products, and to provide a theoretical basis for a full recovery technology for electrode materials from spent LIBs.

2. Thermodynamic analysis

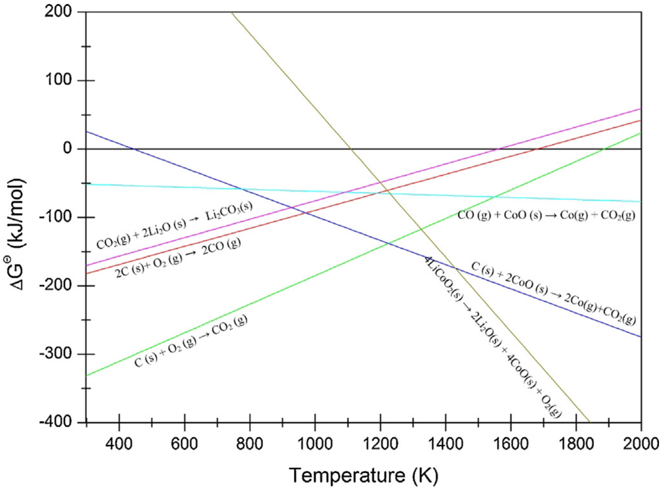

Fig. 1. The relationship between ΔG and temperature for different reactions.

The cathode material of $LiCoO_2$ is stable under 850 °C and it can be decomposed into Li_2O, Co_3O_4 and O_2 above 900 °C [36]. Because the bivalent cobalt ion is more stable than trivalent cobalt ion, the Co_3O_4 will be decomposed into CoO. Then the possible decomposition reaction of $LiCoO_2$ and the standard Gibbs free energy are listed below [37]:

$$4LiCoO_2 \rightarrow 2Li_2O + 4CoO + O_2(g) \tag{1}$$

$$\Delta_r G_T^{\theta} = 604.78 - 0.545\mathrm{T},\ kJ\,(298{\sim}2000\mathrm{K}) \tag{2}$$

The Gibbs free energy of Reaction (2) at a certain temperature is:

$$\Delta_r G = \Delta_r G_T^{\theta} + \mathrm{RTln}\left(p_{O_2}/p^{\theta}\right) \tag{3}$$

where R is the molar gas constant, T is the thermodynamic temperature, P_{O2} is the partial pressure of the gas product, $p^{\theta}$is the standard atmospheric pressure. When the decomposition reaction reacts under air atmosphere ($p_{O_2}/p^{\theta} = 0.21$), Eq. (3) changed to:

$$\Delta_r G_T = 604.78 - 0.557T,\ kJ\,(298{\sim}2000\mathrm{K}) \tag{4}$$

According to the Eq. (4), when $\Delta_\mathrm{r}G_\mathrm{T} = 0$, the theoretical temperature of decomposition is 1085 K (812.78 °C).

The anode material of graphite is the most stable form of carbon under standard conditions. In industrial processes, the reduction of metal oxides is often affected by a carbothermic reaction. When carbon is served as a reducing agent, the reduction of metals may be performed as a double redox reaction at relatively low temperature. The possible reactions between C and CoO as well as with O_2, and the corresponding Gibbs energies (calculated by HSC Chemistry 7.0) are listed below:

$$2C + O_2(g) \rightarrow 2CO(g) \tag{5}$$

$$\Delta_r G_T^{\theta} = -221.47 + 0.13184T,\ kJ\,(298{\sim}2000\mathrm{K}) \tag{6}$$

$$C + O_2(g) \rightarrow CO_2(g) \tag{7}$$

$$\Delta_r G_T^{\theta} = -393.98 + 0.20891T,\ kJ\,(298{\sim}2000\mathrm{K}) \tag{8}$$

$$C + 2CoO \rightarrow 2Co(g) + CO_2(g) \tag{9}$$

$$\Delta_r G_T^{\theta} = 78.52 - 0.17683T,\ kJ\,(298{\sim}2000\mathrm{K}) \tag{10}$$

$$CO(g) + CoO \rightarrow Co + CO_2(g) \tag{11}$$

$$\Delta_r G_T^{\theta} = -46.99 - 0.01488T,\ kJ\,(298{\sim}2000\mathrm{K}) \tag{12}$$

Fig. 1 shows the relationship between ΔG and temperature for different reactions (1–12). As shown in Fig. 1, the Reactions of (5), (7), (9) and (11) are spontaneously at high temperatures after the decomposition Reaction (1). Then the metal oxides of CoO can be reduced to metal of Co by C or CO under certain conditions. The