A promising approach for the recovery of high value-added metals from spent lithium-ion batteries

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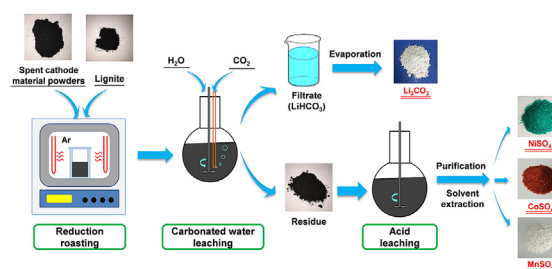
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HIGHLIGHTS

- A simple and efficient process is proposed for recovering spent LIBs.
- $LiNi_xCo_yMn_zO_2$ was transformed into Li_2CO_3, Ni, Co and MnO by reduction roasting.
- Carbonated water leaching was used to selectively recover Li from roasted products.
- Co, Ni and Mn were efficiently leached by H_2SO_4 solution without adding reductant.
- The products of Li_2CO_3, $NiSO_4$, $CoSO_4$ and $MnSO_4$ were obtained.

GRAPHICAL ABSTRACT

ABSTRACT

The aim of the paper is to present a promising approach for recycling high value-added metals from the cathode materials of spent LIBs. The synthesis process of NCM cathode material enlightened us to apply reduction roasting to break $LiNi_xCo_yMn_zO_2$ into simple compounds or metals. Accordingly, the effect of several factors such as temperature, carbon dosage and roasting time is assessed on the leaching efficiency of valuable metals. The roasted products are analyzed by XRD and SEM-EDS, and the results show that the cathode material after reduction roasting is primarily transformed into Li_2CO_3, Ni, Co and MnO. However, the solubility of Li_2CO_3 is relatively low, so carbonated water leaching is used to treat the roasted products. Then the filtrate is evaporated for the preparation of pure Li_2CO_3, and residue is leached to recycle other metals with H_2SO_4. The results indicate that, after roasted at 650 °C for 3 h with 19.9% carbon dosage, 84.7% Li is preferentially recovered via carbonated water leaching, and more than 99% Ni, Co and Mn are recycled via acid leaching without adding reductant. Finally, the products of Li_2CO_3, $NiSO_4$, $CoSO_4$ and $MnSO_4$ are obtained. The process have great potential for industrial-scale recycling from spent LIBs.

1. Introduction

Presently, lithium-ion batteries (LIBs) are widely used as electrochemical power sources in mobile phones, new energy vehicles and other fields due to the favorable characteristics of high energy density, long life cycles, low self-discharge and safe handling [1—3]. Navigant Consulting, Inc. has forecasted that global LIB demand for

vehicles is expected to total $221 billion from 2015 to 2024 [4]. Taking into account the overall world market evolution of LIB products and the average life expectancy of LIBs (the maximum life cycle of the most common cathode material $LiCoO_2$ is 1000 cycles [5]), it is expected that a large number of spent lithium-ion batteries will be produced in five years. These spent lithium-ion batteries contain a large quantity of heavy metals and organic chemicals which present a serious threat to the ecological system and human health [6]. Conversely, they have a high economic value because they contain valuable metals such as lithium, cobalt and nickel [7,8]. Therefore, the treatment and metal-recovery from spent lithium-ion batteries has become imperative and significant from the standpoint of both resource preservation and environmental protection.

Presently, the recycling of cathode active materials $LiNi_x Co_y Mn_z O_2$ attracts noteworthy attention due to the high content of Li, Co, and Ni which are significantly rare natural resources. The recovery methods of spent $LiNi_x Co_y Mn_z O_2$ materials can be divided into hydrometallurgy [9–19], pyrometallurgy [20–22] and combination methods [23–26]. Among them, hydrometallurgy is the most widely utilized method in both academic research and industrial application. Generally, this process includes the following main steps: (1) the cathode materials are separated and enriched from spent lithium-ion batteries by a series of pretreatment processes, such as discharging, dismantling, crushing, sieving, etc.; (2) valuable metals are leached from the cathode material using strong acid solutions as leaching agents, but generally, reducing agents such as H_2O_2 or Na_2SO_3 are required; (3) pure salt solutions of Co, Ni and Mn are obtained by purification and solvent extraction. However, the solutions generated from washing procedure in each stage of solvent extraction need to be merged into the raffinate, so a very low concentration of lithium ($0.5–3$ g L^{-1}), accompanied with sodium and ammonium of about 5 g L^{-1} is retained in the raffinate after extraction of Mn, Co and Ni [27], which is difficult and uneconomical to recover. Generally, the raffinate is directly discharged into the disposal system of waste water, leading to heavy losses of Li. Obviously, these processes are unreasonable based on the inability of current lithium production capacity to satisfy the rapidly growing global demand.

To recover lithium efficiently, some researchers proposed combination methods to preferentially separate lithium from the spent cathode material before a leaching process. Georgi-Maschler [25] used the smelting process to treat spent lithium ion batteries. Fe, Co, Ni, and Mn were settled into the alloy after smelting, while lithium went into the smelting slag and flue dust. Then lithium could be extracted by sulphuric acid leaching. Also under the condition of high temperature, the direct vacuum evaporation and selective entraining gas evaporation method were applied by Träger [20] to evaporate lithium from spent Li-ion batteries. However, the relatively high reaction temperature (>1400 °C) in these two processes inevitably leads to a high energy consumption. Kondás [24], Li [28,29] reported similar methods in which the spent cathode materials were firstly roasted at lower temperature (<1000 °C), then water could be used to extract lithium from the roasted products. However, the concentration of Li is low in the resultant leachate, and the impure products need to be further refined. To leach lithium more efficiently, Koichi [30] applied the aqueous suspension containing $Ca(OH)_2$ or $Mg(OH)_2$ as leaching agent, then lithium in the roasted products could be leached as soluble LiOH.

In addition to the above combination methods, there are also some hydrometallurgical methods to preferentially extract lithium from spent LIBs. Higuchi [31] described a selective recovery process in which lithium could be successfully leached by using $Na_2S_2O_8$ as an oxidant, while Ni, Co and Mn were significantly suppressed.

However, the reaction time lasts up to 15 h, which is unfavorable for the industrial application. Sun [32] and Zeng [33] used oxalic acid as the leaching agent to treat the $LiCoO_2$ cathode material. $Li_2C_2O_4$ is soluble, while CoC_2O_4 is an insoluble precipitate. Hence, lithium could be separated preferentially via only leaching and filtering. However, CoC_2O_4 is difficult to leach even through the application of a strong acid, and thus the subsequent preparation for cobalt products is more complicated.

The separation of different elements depends on the difference of their physical and chemical properties. In an NCM cathode material, lithium is an alkali metal element, while cobalt, nickel, cobalt and manganese are transition elements. One apparent difference between Li and other metals is that lithium oxide can react with water to produce the water-soluble LiOH, while nickel oxide, cobalt oxide and manganese oxide are insoluble in water. It makes us associate the common process for preparation of NCM cathode material, in which the precipitate $NiCoMn(OH)_2$ is roasted with Li oxide in an oxidizing atmosphere [34]. Therefore, $LiNi_x Co_y Mn_z O_2$ is expected to convert into the simple compounds or metals of Li, Ni, Co and Mn through reduction roasting. Thereafter, lithium could be selectively leached using water as leaching agent, and other metals could be recovered by acid leaching (without reductant) and solvent extraction.

In this paper, we investigated the effects of reduction roasting conditions on the leaching efficiency of valuable metals. In particular, XRD and SEM/EDS were applied to research the phase transformation behavior before and after roasting. Finally, a new process was proposed to recover valuable metals from spent LIBs.

2. Experimental

2.1. Materials and reagents

The spent LIBs used in this study were provided by a local recycling center. Cathode material powders were obtained from spent LIBs after pretreatment, such as dismantling, sieving and grinding. The composition of the powder is presented in Table 1. Among them, the carbon content was measured by a carbon-sulfur analyzer (EMIA-820V, Horiba, Japan), while the contents of other elements were analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 7000 DV, Perkin Elmer instruments, US). Due to the low cost, lignite was employed as a reducing agent. The carbon content of lignite used in this study was measured at 62.20% according to Chinese national standards (GB/T 30733–2014).

2.2. Methods

In the reduction roasting experiments, the cathode powder with a certain amount of lignite was first mixed by a planetary ball mill (YXQM-1L, Mitr, China) for 1 h. Then, the uniformly mixed powder was heated for a candidate period of time in an argon atmosphere muffle furnace. When the roasting process was finished, the roasted product was immediately taken out from the furnace and quenched. Several factors that may influence the roasting process were investigated, including temperature (500–900 °C), carbon dosage (12.9–25.2 wt%) and roasting time (0.5–4 h). The structure of the roasting product was characterized by an X-ray

Table 1
Main components of waste cathode material powder.

Element	Ni	Mn	Co	Al	Li	Cu	C
wt.%	21.87	16.96	14.88	10.82	5.75	0.05	3.04