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Recovery of valuable metals from spent lithium-ion batteries by ultrasonic-assisted leaching process

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HIGHLIGHTS

- Ultrasonic-assisted leaching process is used to recover spent $LiCoO_2$ material.
- Citric acid works better than HCl and H_2SO_4 inorganic acids in the leaching process.
- The mechanism of ultrasonic cavitation on leaching process is explained.
- The recovery process is environmental-friendly, less costly and highly efficient.

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ABSTRACT

The anticipated significant use of lithium-ion batteries (LIBs) for energy storage applications in electric grid modernization and vehicle electrification shall generate a large quantity of solid waste that could become potential environmental hazards and waste natural resources. Recycling of the major components from spent LIBs is, therefore, considered desirable to prevent environmental pollution and to recycle valuable metals. This study reports on the application of ultrasonic-assisted technology to the leaching of cobalt and lithium from the cathode active materials of spent LIBs. Three acids were tested for the leaching process: two inorganic acids (H_2SO_4 and HCl) and one organic acid (citric acid, $C_6H_8O_7 \cdot H_2O$). The results show that the leaching of Co and Li is more efficient with citric acid than with the two inorganic acids. More than 96% Co and nearly 100% Li were recovered from spent LIBs. The optimal leaching conditions were 0.5 M citric acid with 0.55 M H_2O_2, a solid-to-liquid ratio of 25 g L^{-1}, a temperature of 60 °C, leaching time of 5 h, and ultrasonic power of 90 W. The high leaching efficiency is mainly ascribed to the unique cavitation action of the ultrasonic waves. This ultrasonic-assisted leaching process with organic acid is not only effective but also environmentally friendly.

1. Introduction

In the current modern economy, an enormous quantity of batteries has been used and disposed of due to the wide application of portable electronic devices such as mobile phones, laptops, and power tools [1]. This number is expected to dramatically increase with the transition to an electrified transportation system, which is already beginning with the advent of hybrid electric vehicles (HEVs) and will accelerate with the introduction of plug-in hybrid electric vehicles (PHEVs) and, ultimately, pure electric vehicles (EVs). Compared with nickel–cadmium (NiCd) or nickel–metal hydride (NiMH) batteries, rechargeable lithium-ion batteries (LIBs) are far more prevalent in consumer electronics [2,3] because of their high energy densities, lack of memory effect, small size, and light weight [4]. With the disposal of these spent electronic products, large quantities of LIB solid wastes are being generated every year. Furthermore, the spent LIBs will not only pollute the environment if they are not disposed of appropriately, but also waste valuable resources if not recycled and reused. Hence, it is imperative to recycle the valuable metals in spent LIBs [5–7].

The most frequently used LIB cathode material is $LiCoO_2$ because of its high energy density, high operating voltage, and good cycling

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performance [2,8]. However, it also has some drawbacks, such as high cost, limited cobalt resources, and toxicity [8–10]. In general, the contents of cobalt and lithium in spent LIBs are 5–20 wt. % and 5–7 wt. %, respectively [11,12]. It would be important to recycle the cobalt and lithium from spent LIBs from the viewpoint of resource conservation and environmental protection.

Currently, several approaches have been developed to recycle $LiCoO_2$ from the spent LIBs, including hydrometallurgical [4,13–15], electrochemical [3,6,16,17], and bioleaching [18–20] methods. The hydrometallurgical process is most widely used to recover various metals from spent LIBs by selective precipitation or solvent extraction. A recently proposed alternative involves leaching followed by a sequential selective precipitation, often a liquid–liquid extraction. High extraction of Co and Li has been achieved via leaching with inorganic acids, such as H_2SO_4 [4,11,15,21–23], HCl [14,24], and HNO_3 [25–27]. In our previous work, we investigated different organic acids as alternative leaching agents to avoid the secondary pollution introduced from strong inorganic acids. These organic acids include citric, malic, ascorbic, and aspartic acid [2,8,28,29]. However, the leaching efficiency for valuable metals, such as Co and Li, is low and still needs to be improved.

Ultrasonic agitation has been intensively investigated for extraction of biological samples and plant tissues [30,31]. Swamy et al. [32] and Anjum et al. [33] reported that ultrasonic waves significantly enhance the efficiency of bioleaching of metals from minerals and shale. Marafi and Stanislaus [34] compared the efficiency of ultrasonic and conventional stirring methods for leaching metals from spent hydroprocessing catalysts. Balasubrahmanyam et al. [35] were also able to demonstrate that ultrasonic agitation could enhance the leaching rate of uranium in nitric acid media. However, the application of ultrasonic agitation in the extraction of the metals from spent LIBs has not been studied in detail yet.

In the present work, we applied ultrasonic agitation in the acidic leaching of Co and Li from spent LIBs. The effect of leaching conditions such as temperature, time, agents, and ultrasonic wave power on efficiency was determined. The mechanism of ultrasonic waves in the leaching process was also studied.

2. Experimental

2.1. Reagents, apparatus, and analytical methods

All reagents were of analytical grade and used as received without further purification. Sulfuric acid (H_2SO_4), hydrochloric acid (HCl) and citric acid ($C_6H_8O_7 \cdot H_2O$) were tested as the leaching agents. Hydrogen peroxide (H_2O_2) was used as additional reductant with sulfuric acid and citric acid. These acids were supplied by Beijing Chemical Works. Deionized water was used in the preparation of all solutions.

A chemical analysis of the cathodic active material before and after acid leaching was carried out with an X-ray diffractometer (Rigaku, Cu-Kα), and data were collected in the 2θ range of 10–90° at a scan rate of 8° min^{-1}. An FEI QUANTA 6000 scanning electron microscope (SEM) was used to analyze the morphology of the spent $LiCoO_2$ and the leaching residues.

An ultrasonic cleaning machine (KQ-3200 DE, frequency 40 kHz) was used to provide ultrasonic agitation. An inductively coupled plasma atomic emission spectrometer (ICP-AES) was used to determine the concentration of the metals.

2.2. Sample preparation

The spent LIBs were completely discharged to remove the remaining capacity and dismantled. The plastic and steel cases were removed from the cells, and the anodes and cathodes were extracted. The cathodic active materials were easily detached from the supports by immersing the electrode in N-methylpyrrolidone (NMP) for 1 h at 100 °C. After filtering and drying at 120 °C for 24 h, the materials were calcined in a 700 °C muffle for 3 h to eliminate carbon and polyvinylidene fluoride binder. Finally, the materials

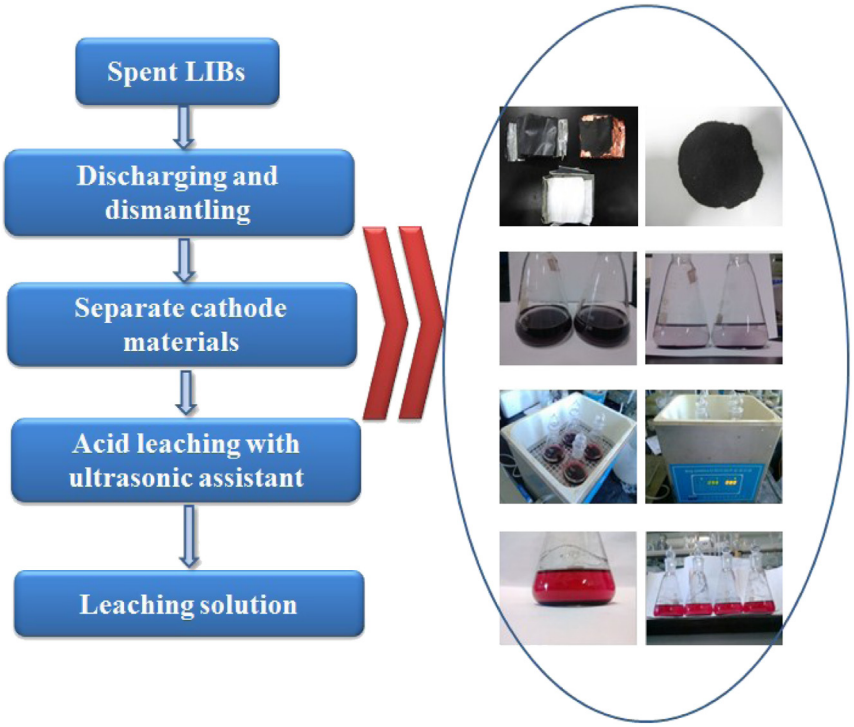

Fig. 1. Illustration of different steps in leaching process for spent $LiCoO_2$.