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Comprehensive evaluation on effective leaching of critical metals from spent lithium-ion batteries

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ABSTRACT

Recovery of metals from spent lithium-ion batteries (LIBs) has attracted worldwide attention because of issues from both environmental impacts and resource supply. Leaching, for instance using an acidic solution, is a critical step for effective recovery of metals from spent LIBs. To achieve both high leaching efficiency and selectivity of the targeted metals, improved understanding on the interactive features of the materials and leaching solutions is highly required. However, such understanding is still limited at least caused by the variation on physiochemical properties of different leaching solutions. In this research, a comprehensive investigation and evaluation on the leaching process using acidic solutions to recycle spent LIBs is carried out. Through analyzing two important parameters, *i.e.* leaching speed and recovery rate of the corresponding metals, the effects of hydrogen ion concentration, acid species and concentration on these two parameters were evaluated. It was found that a leachant with organic acids may leach Co and Li from the cathode scrap and leave Al foil as metallic form with high leaching selectivity, while that with inorganic acids typically leach all metals into the solution. Inconsistency between the leaching selectivity and efficiency during spent LIBs recycling is frequently noticed. In order to achieve an optimal status with both high leaching selectivity and efficiency (especially at high solid-to-liquid ratios), it is important to manipulate the average leaching speed and recovery rate of metals to optimize the leaching conditions. Subsequently, it is found that the leaching speed is significantly dependent on the hydrogen ion concentration and the capability of releasing hydrogen ions of the acidic leachant during leaching. With this research, it is expected to improve understanding on controlling the physiochemical properties of a leaching solution and to potentially design processes for spent LIBs recycling with high industrial viability.

1. Introduction

Lithium-ion batteries (LIBs) are currently used as electric power sources in portable electronic products such as mobile phones, laptops, cameras (He et al., 2017) and electric vehicles because of their high energy density, long cycling life and low self-discharge rate (Zeng et al., 2015a). According to the perspective of global vehicle market, the sales of the electric battery vehicle is expected to increase from 5 million in 2015 to about 180 million in 2045 (Li et al., 2017). With a relatively short life span of about 3–8 years, a large number of spent LIBs have already been generated for about 200 million tons in 2017 and it will be nearly 400 million tons in 2020 (Gu et al., 2017). Spent LIBs have caught much attention because of the possibility of recovering valuable resources such as lithium, nickel, cobalt and aluminum and they are also considered as potential environmental contaminants due to the content of heavy metals and fluoride-bearing electrolyte (Gao et al., 2017). Regulations (in Asia countries, European Union, North America or Channel Islands) have defined the requirements to reduce the contaminants during recycling of spent LIBs (Joulie et al., 2017). The recycling of spent LIBs is of great importance for the environment and ensuring the safe supply of corresponding resources.

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Hydrometallurgy, pyrometallurgy and biometallurgy are three typical recycling technologies for spent LIBs recycling. In a pyrometallurgy process, plastic housings, conductive agents, binders and organic electrolytes are burnt off to facilitate the subsequent recovery of valuable metals (Nayaka et al., 2015). However, the disadvantages, such as high capital cost, emission of hazardous gas (HF), dusts and consumption of intensive energy, limit the application of pyrometallurgy (Joulie et al., 2017). Biometallurgy is a very promising technology for its low cost and modest apparatus requirement, but the poor adaptability and rigorous leaching conditions reduce its applicability (Liu et al., 2013). Therefore, with effective metal recovery and relatively low energy consumption, hydrometallurgy has been paid significant attention. In a typical hydrometallurgical recycling process, the leaching process with acidic solution is essential to effectively recover metals from cathode scrap, which is considered as the most important fraction of a LIB (because of the content of cathode materials and high purity aluminum foil) (Gaines, 2014). Before 2005, $LiCoO_2$ was the main cathode material with 94% of the market share in 2015 (He et al., 2017). Although different cathode materials such as $LiMnO_2$, $LiFePO_4$, $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ are available in the market, their recovery are mainly focused on cobalt-containing spent LIBs (Gao et al., 2018; Lv et al., 2018) especially on $LiCoO_2$ (Table S2). Only a few reports are available for the recycling of $LiFePO_4$ using hydrometallurgy (Huang et al., 2016; Yang et al., 2017; Zheng et al., 2016). The leaching of cobalt-containing cathode materials often use inorganic acids (*e.g.*, H_2SO_4 (Sa et al., 2015; Zou et al., 2013), HCl (Guo et al., 2015; Shuva and Kurny, 2013) and HNO_3) or organic acids (*e.g.*, citric acid (Yao et al., 2015), DL-malic acid (Li et al., 2010; Yao et al., 2016) and oxalic acid (Sun and Qiu, 2012)) as leachant. To increase the leaching efficiency, reductants (*e.g.*, H_2O_2 (Gratz et al., 2014; Li et al., 2015), glucose (Chen et al., 2016) and $NaHSO_3$ (Meshram et al., 2015)) are often introduced to reduce the metal ions from high valances (*e.g.*, Co^{3+}, Mn^{4+}) to lower valence ions (*e.g.*, Co^{2+}, Mn^{2+}) which are more stable in the solution. Some natural substances can also act as leachant (*e.g.*, citrus fruit juice (Pant and Dolker, 2017)) or reductant (*e.g.*, phytolacca and tea waste (Chen et al., 2015)) to reduce environmental pollution and improve recycling efficiency.

Before investigating the leaching process, the understanding on the interactive features between the materials and solutions is the foundation to achieve both high leaching efficiency and selectivity of the targeted metals. For example, besides acting as the leachant, oxalic acid can precipitate Co (Zeng et al., 2015b), citric acid can present as a chelating reagent to re-synthesis cathode materials (Yao et al., 2015), and formic acid can selectively recover Al foil and reduce the addition of reductants (Gao et al., 2017). However, variations on the physiochemical properties of different acidic solutions are readily bringing difficulties to design the best leachant for spent LIBs recycling. At the same time, in previous studies, it is always necessary to explore the optimal conditions such as acid concentration, solid to liquid (S/L) ratio, reductant content and reaction temperature to achieve high leaching efficiency. The analysis and evaluation of different acid leaching conditions for spent LIBs recovery are seldom carried out, and to achieve both high leaching efficiency and selectivity of the targeted metals has been difficult. Three aspects, *i.e.* the interactive features of materials and acidic solutions, the variation on physiochemical properties of leaching solutions and the affection of leaching parameters, are therefore critical to be considered to have a systematic and comprehensive evaluation on effective acid leaching process during metal recovery from spent LIBs.

In this study, a comprehensive investigation and evaluation on the leaching processes with acidic solutions for recovery of metals from spent LIBs ($LiCoO_2$ was used for simplification) was carried out. Among different leaching parameters (*e.g.*, acid species and concentrations, S/L ratios, reductant species and concentrations, leaching times, temperatures, leaching speed and recovery rate), the recovery rate is an important parameter to evaluate the viability of a leaching process, and the leaching speed is an important parameter to analyze the leaching kinetics or effectiveness of a leaching process. Through defining and analyzing these two parameters, the effects of hydrogen ion concentrations, acid species and concentrations on these two parameters were evaluated. In a typical leaching process, inconsistency between the leaching selectivity and efficiency was frequently noticed. Furthermore, the decisive factors of the leaching speed and recovery rate were identified by analyzing the leaching parameters. On one hand, 12 acidic solutions were used to understand the leaching behavior of cathode scrap from spent LIBs and to find out the correlation between the leaching speed and recovery rate of the corresponding metals. On the other hand, it is noticed that the conditions to ensure both high leaching efficiency and leaching selectivity can be achieved by optimized process design. Completion of these objectives will be expected to attain preliminary correlations to control the physiochemical properties of leaching solution and to potentially design process at both lab-scale and industrial levels.

2. Experimental

2.1. Materials and reagents

The cathode scrap, which are the cathodes used for manufacturing lithium-ion battery, was supplied by a local recycling company (Huayou Cobalt, China). Before leaching, the cathode scrap was cut into pieces with the size of 10 mm × 10 mm and dried at 60 °C for 24 h. To determine the composition, the cathode scrap was dissolved with aqua regia solution (HNO_3: HCl = 1:3, v/v) and sulfuric acid one after another. All chemical reagents were of analytical grade and all solutions were prepared with ultrapure water (Millipore Milli-Q). The leaching reagents are organic/inorganic acidic solutions (12 kinds of acids in Table S3) under certain concentrations, and the reductant is introduced to the reagents according to the leaching process.

2.2. Leaching process of cathode scrap

The cathode scrap was leached in a 50 mL sealed reactor which was placed in a temperature controlled shaking bath. The acidic solution was added to the reactor with a volume of 25 mL. The leaching conditions including acid species, acid concentration, reductant content and pH of the leaching solution were examined. Samples were taken out at leaching time of t ($t \le 5$ min) and identified by ICP-OES (ICP-OES, iCAP 6300, Radial, Thermo Scientific) to find the local leaching parameters for leaching speeds. After leaching, the residues (undissolved organic binder and conductive reagent) and Al foil were vacuum filtered immediately. The leachate was analyzed by ICP-OES to get the local leaching parameters of metals for recovery rate. The leaching speed and recovery rate are determined according to

$$g = \frac{C_1(\mathrm{M}) \times V}{m(\mathrm{M}) \times t} \times 100\% \qquad (1)$$

$$h = \frac{C_2(\mathrm{M}) \times V}{m(\mathrm{M})} \times 100\% \qquad (2)$$

where g (wt%/min) is the leaching speed of metal M (M = Co, Li, Al), h (wt%) is the recovery rate of metal M (M = Co, Li, Al), t (min, ≤ 5) is the leaching time, C_1 (M, g/L) is the concentration of metal M in the sample at t min, C_2 (M, g/L) is the concentration of metal M in the

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