



Contents lists available at ScienceDirect

## Waste Management

journal homepage: [www.elsevier.com/locate/wasman](http://www.elsevier.com/locate/wasman)

# Thermal treatment and ammoniacal leaching for the recovery of valuable metals from spent lithium-ion batteries

Yongming Chen<sup>a</sup>, Nannan Liu<sup>a</sup>, Fang Hu<sup>b</sup>, Longgang Ye<sup>c</sup>, Yan Xi<sup>a</sup>, Shenghai Yang<sup>a,\*</sup>

<sup>a</sup> School of Metallurgy and Environment, Central South University, Changsha 410083, China

<sup>b</sup> College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China

<sup>c</sup> School of Metallurgy and Material Engineering, Hunan University of Technology, ZhuZhou 412007, China

## ARTICLE INFO

### Article history:

Received 16 November 2017

Revised 2 February 2018

Accepted 12 February 2018

Available online xxxx

### Keywords:

Spent Li-ion batteries

Cathode active powder

Thermal treatment

Ammoniacal leaching

Double salts

## ABSTRACT

The recycling of spent commercial lithium-ion batteries (LIBs) generates numerous environmental and economic benefits. In this research, a thermal treatment-ammoniacal leaching process is proposed to recover valuable metals from cathode active powder. Based on the thermal behavior by TG-DSC analysis, the cathode active powder is calcined at 300 °C and 550 °C in air atmosphere, and the crystalline phase characterization indicates that a new phase of  $\text{Co}_3\text{O}_4$  appears in the cathode active powder calcined at 550 °C, which signifies that the layer structure of  $\text{LiCoO}_2$  collapses. The valence of manganese increases to form  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  in spinel structure of  $\text{LiMn}_2\text{O}_4$ . Using calcined cathode powder as feed material, ammoniacal leaching is carried out in  $(\text{NH}_4)_2\text{SO}_4$ – $(\text{NH}_4)_2\text{SO}_3$  solution. Under the optimum conditions, Ni, Co, Mn and Li can be completely leached out with efficiencies of 98%, 81%, 92% and 98%, respectively. However, with the increase of ammonia concentration, the leaching efficiency of Mn decreases dramatically to 4% due to the formation of double salts. It is found that Co and Mn can be precipitated into residues in the form of  $(\text{NH}_4)_2\text{Co}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{Mn}(\text{SO}_3)_2 \cdot \text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{Mn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  under different leaching parameters. Based on the corresponding relationship between the leaching efficiency and phase evolution of object element, selective leaching can be achieved by controlling the formation of double salts.

© 2018 Published by Elsevier Ltd.

## 1. Introduction

Lithium-ion batteries (LIBs) have been widely used in portable electronic equipment, hybrid and electric-vehicles and energy storage field for their desirable characteristics such as small volume, light weight, high potential, high energy density, and no memory effect, etc. (Scrosati et al., 2011; Zhang et al., 2013). LIBs are the main power sources for today's portable devices while their application targets are moving from small-sized mobile devices in information technology to large-scale electric vehicles (xEVs) and energy storage systems (ESSs) (Kim et al., 2012). However, these batteries will eventually flow into waste stream after several years of service lifetime (about 1000 charging-discharging cycles) and a huge quantity of spent LIBs would be generated owing to their extensive applications (Chagnes and Pospiech, 2013; Contestabile et al., 2001). For instance in China, the quantity and weight of spent LIBs in 2020 can surpass 25 billion units and 500 thousand tons, respectively (Wang et al., 2016). In general, LIBs consist of heavy

metals, organic chemicals and plastics in the proportion of 5–20% cobalt, 5–10% nickel, 5–7% lithium, 15% organic chemicals, and 7% plastics, with slight variation in the composition for different manufacturers (Shin et al., 2005). As vital secondary sources, the potential reserves of cobalt, nickel and lithium in recyclable spent LIBs can be up to 100, 50, and 35 thousand tons. These sources have higher grades than those found in natural raw ores (Nayl et al., 2017), so that less energy consumption and lower treatment cost are needed to extract valuable metals from them. Furthermore, heavy metals and other toxic substances, such as  $\text{LiPF}_6/\text{LiBF}_4/\text{LiAsF}_6$  and PVDF binder, contained in spent LIBs would cause serious environment pollution without an appropriate treatment process (Chen et al., 2017).

Numerous physical and chemical processes have been reported to efficiently deal with spent LIBs. The primary chemical methods involved pyrometallurgy, hydrometallurgy and synthetic regeneration process (Chagnes and Pospiech, 2013; Meshram et al., 2014). At the Umicore Battery Recycling plant in Belgium, as an industrial scale pyrometallurgy process without any pre-treatment, battery modules were fed directly into an ultra high temperature (UHT) smelter. Battery production scrap and slag forming agents were

\* Corresponding author.

E-mail address: [yangsh@csu.edu.cn](mailto:yangsh@csu.edu.cn) (S. Yang).

simultaneously added to create three output fractions including Cu-Co-Ni-Mn-Fe alloy, slag fraction (containing Al, Li, Mn and REE) and gas emissions. Compared with pyrometallurgy process, hydrometallurgical treatment was widely adopted by most sizeable enterprise in China. It usually involved the following processes such as pre-treatment, leaching, chemical precipitation, solvent extraction (Yang et al., 2017) and electrodeposition (Garcia et al., 2008). As a crucial operation in hydrometallurgical process, the leaching systems mainly included inorganic acids such as HCl (Barik et al., 2017),  $\text{H}_2\text{SO}_4$  (He et al., 2017),  $\text{HNO}_3$  (Lee and Rhee, 2003),  $\text{H}_3\text{PO}_4$  (Meng et al., 2017) and organic acids (Golmohammadzadeh et al., 2017; Zeng et al., 2015). Because of popular prices and remarkable chemical reactivity,  $\text{H}_2\text{SO}_4$  was commonly used for the treatment of spent LIBs. However, other impurity metals such as Al, Cu and Fe, etc. were simultaneously leached into leachate, so that a series of separation and purification processes such as solvent extraction, selective precipitation and electrochemical method were subsequently performed, which might increase disposal costs and produce secondary pollution (Sun and Qiu, 2012).

Despite the fact that inorganic acid leaching technology was used in industrial scale recycling of spent LIBs, it had inherent drawbacks such as low leaching selectivity and difficult operating conditions. On the other hand, ammoniacal leaching has attracted attention due to their characteristics of selective leaching, which lied in the fact that valuable metals such as Ni, Co, Zn and Cu, etc could form stable metal ammine complexes. Hence, ammoniacal systems have been frequently used to treat low-grade oxidized ores (Meng and Han, 1996; Zuniga et al., 2010) and various other materials containing Cu, Ni, Co and Mn (Jana et al., 1999; Niinae et al., 1996). Recently, ammoniacal leaching processes have been also reported by several researchers to disposal different types of spent LIBs. The leaching behaviors of valuable metals in  $\text{NH}_3$ – $(\text{NH}_4)_2\text{CO}_3$ – $(\text{NH}_4)_2\text{SO}_3$  solution were investigated, and the results indicated that ammonium sulfite as a reductant was necessary to enhance leaching kinetics particularly in the ammoniacal leaching of Ni and Co (Ku et al., 2016). It was found that the leaching kinetics of valuable metals in  $\text{NH}_3$ – $(\text{NH}_4)_2\text{SO}_4$ – $\text{Na}_2\text{SO}_3$  solution fitted well to the shrinking-core model controlled by the chemical reactions (Zheng et al., 2017). In general, most studies reported in previous literature have focused on leaching behavior of valuable metals in ammoniacal medium, but the leaching mechanism rarely involved. However, the leaching behaviors of transition metal element in ammonia solution are rather complicated, and it is vital to find out the corresponding relationship between crystalline phase evolution of object element and its leaching behavior in ammonia medium.

Based on above-mentioned background, thermal treatment and ammoniacal leaching were carried out in present study for the treatment of cathode active powder from spent LIBs. The phase transformation and leaching behavior of object element was investigated in detail under different operation parameters. The possible explanation of selective ammoniacal leaching mechanism from structure evidence aspects was proposed. Based on above results, a reasonable strategy for utilizing the spent LIBs was briefly proposed.

## 2. Waste management and strategies

Because of the potential pollution from spent LIBs, government organizations around the world begin to concern waste management measures. United States legislators have attempted to take the initiative to meet the challenge by instituting the mercury-containing and rechargeable battery management act in 1996 (US Public Law 104-142), aimed at minimizing the environmental impact of these batteries. The European Union has instituted and

revised a series of policies such as Battery Directive 91/157/EEC, Waste Electrical Electronic Equipment (WEEE) Directive 2002/96/EC and Battery Directive 2006/66/EC, which prescribed several goals about collecting and recycling in the next years. In particular, the minimum collection rate of spent LIBs must be 25% by 2012 and 45% by 2016. Moreover, the directive also stipulated that the minimum recycling efficiency of batteries must reach 50% by average weight (Granata et al., 2012; Wang et al., 2016). In China, the government is actively exploring and developing relevant policies and recycling models for e-waste covering batteries, especially with the vigorous development of new energy vehicles. The State Council has issued China's extended producer responsibility (EPR) plan in 2017 to achieve waste management throughout the life cycles of the products. The plan stipulated manufacturer's responsibility for the establishment of power battery recovery system and required battery production enterprises to adopt product coding, aiming to establish a life-cycle traceability system. Meanwhile, the plan also prescribed several goals for collecting and recycling of target product. In particular, the waste recycling rate should reach 40% by 2020 and 50% by 2025 on average. Furthermore, the proportion of renewable raw materials for key products should reached 20% by 2025.

With an objective of resource recovery and recycling, the present study was devote to discover a short-cut recovery process of valuable metals from the cathode active powder in  $(\text{NH}_4)_2\text{SO}_4$ – $(\text{NH}_4)_2\text{SO}_3$  system and provided explanation of ammoniacal leaching mechanism through detailed phase characterization of the leaching residues.

## 3. Experimental

### 3.1. Materials

The spent LIBs in this study were provided by a mobile phone batteries collection center. To avoid self-ignition and short-circuiting, the batteries were discharged in the electrolyte solution (10 wt% NaCl) for 36 h and then manually dismantled into cathodes, anodes, plastic separators and metal cases. The active cathode powder was separated from Al foil by heating at 300 °C in air atmosphere for 1 h (in Fig. 1). Afterwards, the separated powder was dissolved in aqua regia solution to determine the chemical composition by inductive coupled plasma atomic emission spectrometer (ICP-AES) and carbon-sulfur analyzer. The detailed results were listed in Table 1.

The main metals identified in the cathode active powder were Co, Ni, Mn, and Li along with trace amounts of Al, Fe, and Zn. All the other reagents used in this work were analytical grade and all solutions were prepared using distilled water.

### 3.2. Thermal treatment

A thermal pretreatment was necessary to eliminate acetylene black and polyvinylidene fluoride (PVDF) in the cathode active powder. The cathode collectors were first heated in a muffle furnace at 300 °C for 1 h to dissolve binder. After crushing and sieving, the cathode active powder was separated from Al foil, and further calcined at 550 °C in muffle furnace for 0.5 h. The particle size of the cathode powder was determined using a laser particle size analyzer (Malvern MS2000, UK), the average particle size was found to be 10.24  $\mu\text{m}$ .

### 3.3. Ammoniacal leaching

All the leaching experiments were carried out in a 2 L autoclave equipped with heating device, mechanical agitation and other

Download English Version:

<https://daneshyari.com/en/article/8869869>

Download Persian Version:

<https://daneshyari.com/article/8869869>

[Daneshyari.com](https://daneshyari.com)