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Selective reductive leaching of cobalt and lithium from industrially crushed waste Li-ion batteries in sulfuric acid system

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ABSTRACT

Recycling of valuable metals from secondary resources such as waste Li-ion batteries (LIBs) has recently attracted significant attention due to the depletion of high-grade natural resources and increasing interest in the circular economy of metals. In this article, the sulfuric acid leaching of industrially produced waste LIBs scraps with 23.6% cobalt (Co), 3.6% lithium (Li) and 6.2% copper (Cu) was investigated. The industrially produced LIBs scraps were shown to provide higher Li and Co leaching extractions compared to dissolution of corresponding amount of pure LiCoO₂. In addition, with the addition of ascorbic acid as reducing agent, copper extraction showed decrease, opposite to Co and Li. Based on this, we propose a new method for the selective leaching of battery metals Co and Li from the industrially crushed LIBs waste at high solid/liquid ratio (*S/L*) that leaves impurities like Cu in the solid residue. Using ascorbic acid (C₆H₈O₆) as reductant, the optimum conditions for LIBs leaching were found to be *T* = 80 °C, *t* = 90 min, [H₂SO₄] = 2 M, [C₆H₈O₆] = 0.11 M and *S/L* = 200 g/L. This resulted in leaching efficiencies of 95.7% for Li and 93.8% for Co, whereas in contrast, Cu extraction was only 0.7%. Consequently, the proposed leaching method produces a pregnant leach solution (PLS) with high Li (7.0 g/L) and Co (44.4 g/L) concentration as well as a leach residue rich in Cu (up to 12 wt%) that is suitable as a feed fraction for primary or secondary copper production.

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1. Introduction

Recycling of waste Li-ion batteries (LIBs) is becoming increasingly crucial in terms of saving both resources and protecting the environment. Worldwide, the consumption of LIBs has increased dramatically between 2010 and 2015 from 4.6 billion to 7.0 billion units (Li et al., 2011) and it has been estimated that by 2020 the quantity of discarded LIBs will surpass 25 billion units with a combined weight of 500 thousand tonnes (Zeng et al., 2014). These discarded batteries are rich in both valuable metals and organic chemicals (e.g. EC/EMC electrolytes: ethylene carbonate and ethyl methyl carbonate), with the approximate proportions ranging between 5 and 20% cobalt, 5–10% nickel, 5–7% lithium, 6–12% copper, 15% organic chemicals and 7% plastics (Zeng and Li, 2014; Gratz et al., 2014). These valuable metals are of considerable economic value, especially as the availability of high-grade ores are gradually depleting. Nevertheless, if these waste batteries cannot be collected and recycled efficiently, the inherent toxicity of the heavy metals and organic chemicals within can cause serious environmental and human-health problems (Kang et al., 2013).

1.1. Waste LIBs management and strategies

The recycling of waste LIBs generally involves three steps: collection, pretreatment of waste LIBs and recovery of the valuable metals. According to the Europe Commission, in 2014, the collection rates of LIBs was much lower than other batteries (e.g. Lead-acid batteries), especially in the case of portable LIBs, which only had a collection rate of 4.5% (European Commission – DG Environment, 2014). Consequently, a significant share of portable LIBs batteries (95.5%) end up in incineration plants or landfills for non-hazardous waste (if mixed with household waste). These improperly disposed LIBs pose serious threat to the environment due to the presence of heavy metals (e.g. Co, Ni, Mn) and toxic flammable electrolyte that compromise of an organic liquid with dissolved substances like LiClO₄, LiBF₄ and LiPF₆ within the battery matrices (Xu et al., 2008). Once collected, spent Li-ion batteries are discharged in order to release the residual charges and reduce the risk of explosion, which can result from the mechanical shock of lithium metal produced by battery overcharge (Lee and Rhee, 2002). After this, the waste LIBs are pretreated by mechanical methods (e.g. crushing and sieving), thermal treatment (e.g. vacuum decomposition) or dissolution with solvent (e.g. N-methylpyrrolidone, NMP) to reduce scrap volume, enrich valuable

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metals (Bernardes et al., 2004; Zhang et al., 2014; He et al., 2015). By using a thermal treatment or dissolution with NMP the cathode materials can be separated effectively from other components (e.g. iron shell or current collectors) to obtain scraps with a higher content of Co and Li (Meshram et al., 2016; Chen et al., 2011). Currently these two methods are still at the lab scale however, due to problems related to waste gases and plastic hardening during thermal treatment as well as the vaporization of solvents, like NMP, from the dissolution process. Compared to thermal treatment and dissolution process, mechanical separation is the modern industrial approach, even though cathode materials cannot be separated effectively from other components by traditional crushing and sieving.

The subsequent recovery of the valuable components from the pretreated waste LIBs is achieved by either smelting or hydrometallurgical technologies like leaching followed by precipitation, solvent extraction or electrochemical processes (Chen et al., 2015a, 2015b). One of the state-of-the-art technologies for dealing with LIBs and other battery types is smelting of the pre-treated scrap fractions, to produce metallic fractions rich in base metals like Co-Ni alloy (Sojka, 1998; Georgi-Maschler et al., 2012). The drawback of this methodology however is that the lithium ends up within the slag fraction and cannot currently be effectively recovered (Tirronen et al., 2017). Consequently, there has been increased interest towards alternative hydrometallurgical methods that allow for Li recovery, especially as the price of lithium is predicted to increase threefold within the next 10 years (Metalary, 2017). Development stage hydrometallurgical techniques - like acid leaching followed by purification and separation process - are promising alternatives for the sustainable recycling of fractions with higher quantities of valuable metals (e.g. Li, Co, Ni and Cu) (Hu et al., 2017; Horeh et al., 2016). After the primary removal of Al and Fe from PLS, the recovery of Cu, Co and Ni could be achieved by a combination of precipitation, solvent extraction and electrowinning process (Chen et al., 2015a, 2015b). In the case of Li, it can be recovered as Li_2CO_3 by carbonation with a saturated Na_2CO_3 solution. Noteworthy, a vaporization process has to be adopted to enrich Li because Li concentration in PLS is much lower than the critical 20 g/L for effective recovery of Li by carbonation (Jandova et al., 2012).

1.2. Development of the acid leaching process

Recently, a great deal of research has been devoted to the leaching process of waste Li-ion battery scraps with different types of

mineral acids like HCl (Guo et al., 2016), H_3PO_4 (Chen et al., 2017), H_2SO_4 (Pagnanelli et al., 2016) and organic acids including citric acid (Zheng et al., 2016), malic acid (Li et al., 2010) and lactic acid (Li et al., 2017). Moreover, the leaching efficiency of cobalt and lithium has also been shown to increase with the use of additional reducing agents like H_2O_2 (Pagnanelli et al., 2017), $\text{Na}_2\text{S}_2\text{O}_5$ (Vieceli et al., 2018), NaHSO_3 (Meshram et al., 2016), D-glucose (Granata et al., 2012) as well as ascorbic acid (Li et al., 2012).

Table 1 summarizes the related literature about waste LIBs leaching processes, optimum leaching conditions and metal yields. It is evident that most of the reported studies have focused on the use of manually dismantled scraps, in which Co contents can be as high as 54%. A majority of these scraps are produced by the manual deconstruction of LIBs waste, separation of anode and cathode materials, followed by immersion in NMP or incineration to remove the binder materials (e.g. PVDF). Such manually obtained cathodic materials are not representative of real battery waste compositions as these typically include a higher variety of components like battery shells, current collectors (copper and aluminum) and electrolytes. Table 1 also shows that little information is readily available on the behavior of Cu even though a majority of the monetary value of discarded LIBs depends on the Cu content, which can be between 6 and 12% (Zeng and Li, 2014). In addition, most of the research has been performed with low S/L ratios (2–100 g/L), which are not typical for industrial hydrometallurgical processes.

In this study, we investigated the leaching behavior of Li, Co and Cu in a sulfuric acid system using industrially produced waste battery scraps at high S/L ratios (≥ 100 g/L). We compared the dissolution kinetics of Li and Co during leaching process using industrially produced waste LIBs scraps and pure LiCoO_2 . In addition, we proposed a method to selectively dissolve Co and Li from Cu with ascorbic acid as reducing agents in sulfuric acid system. The influence of time, temperature, acid concentration as well as S/L ratio were also studied in order to further optimize the leaching conditions.

2. Experimental

2.1. Preparation and characterization of raw material

Waste LIBs scraps were obtained from the underflow and overflow of industrially crushed and sieved portable LIBs from various consumer electronics. Fig. 1 shows the flowsheet of the sample preparation, which has already been patented (Pudas et al., 2011).

Table 1
Summary of the published acid leaching processes for waste LIBs.

Co (%)	Acids + Reducing agents	S/L ratio	Concentration (g/L)		Yields (%)			References
			Co	Li	Co	Li	Cu	
35.8 ^a	1 M H_2SO_4	50	11.8	3.0	66	93	–	Meshram et al. (2016)
35.8 ^a	1 M H_2SO_4 + 5% (v/v) H_2O_2	50	14.1	3.1	79	94	–	Meshram et al. (2016)
44.2 ^a	4 M H_2SO_4 + 10% (v/v) H_2O_2	100	42.0	5.3	95	96	–	Chen et al. (2011)
54.0 ^a	2 M H_2SO_4 + 5% (v/v) H_2O_2	50	26.7	3.2	99	99	–	Sun and Qiu (2011)
35.8 ^a	1 M H_2SO_4 + 7.5 M NaHSO_3	50	15.2	3.0	85	93	–	Meshram et al. (2016)
35.4 ^a	3 M H_2SO_4 + 0.25 M $\text{Na}_2\text{S}_2\text{O}_3$	66	23.1	2.4	99	99	50	Wang et al. (2012)
41.5 ^a	0.34 M H_3PO_4 + 2% (v/v) H_2O_2	8	3.2	0.4	95	95	–	Pinna et al. (2017)
54.0 ^a	0.1 M Citric + 0.02 M ascorbic	2	0.9	0.1	80	100	–	Nayaka et al. (2015)
54.0 ^a	0.5 M glycine + 0.02 M ascorbic	2	1.0	0.1	95	95	–	Nayaka et al. (2016a)
55.0 ^a	1.25 M ascorbic acid	25	13.1	1.6	95	99	–	Li et al. (2012)
–	2 M H_2SO_4 + 4% H_2O_2	66	32.7	2.3	97	97	65	Nayl et al. (2017)
52.0 ^a	1 M H_2SO_4 + 0.02 M glucose	35	16.0	1.5	88	92	–	Pagnanelli et al. (2014)
25.0 ^b	2 M H_2SO_4 + 0.03 M glucose	100	24.3	3.4	97	98	98	Granata et al. (2012)
25.0 ^b	4 M HCl	100	24.8	3.5	99	99	99	Granata et al. (2012)

^a Raw material from manual dismantling.

^b Raw material from industrial process treatment.

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