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Selective reductive leaching of cobalt and lithium from industrially crushed

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waste Li-ion batteries in sulfuric acid system

Chao Peng¹, Joseph Hamuyuni¹, Benjamin P. Wilson¹, Mari Lundström^{1*}

⁴ ¹ Hydrometallurgy and Corrosion, Department of Chemical and Metallurgical Engineering (CMET),

5 School of Chemical Engineering, Aalto University, P.O. Box 16200, FI-00076 AALTO, Finland

6

*Corresponding author: <u>mari.lundstrom@aalto.fi</u>

7 Abstract

8 Recycling of valuable metals from secondary resources such as waste Li-ion batteries (LIBs) has 9 recently attracted significant attention due to the depletion of high-grade natural resources and 10 increasing interest in the circular economy of metals. In this article, the sulfuric acid leaching of 11 industrially produced waste LIBs scraps with 23.6% cobalt (Co), 3.6% lithium (Li) and 6.2% copper 12 (Cu) was investigated. The prior dissolution of Li to Co and the higher leaching efficiency of Li and Co 13 with industrially produced LIBs scraps compared to pure LiCoO₂ chemicals could be observed. In 14 addition, with the addition of ascorbic acid, copper shows opposite trends compared to Co and Li. Based 15 on this, we propose a new method for the selective leaching of battery metals Co and Li from industrially 16 crushed LIBs waste at high solid/liquid ratio (S/L) that leaves impurities like Cu in the solid residue. 17 Using ascorbic acid ($C_6H_8O_6$) as a reductant, the optimum conditions for LIBs leaching were found to be T = 80 °C, t = 90 min, $[H_2SO_4] = 2$ M, $[C_6H_8O_6] = 0.11$ M and S/L = 200 g/L. This resulted in 18 leaching efficiencies of 95.7% for Li and 93.8% for Co, whereas in contrast, Cu extraction was only 19 20 0.7%. Consequently, the proposed leaching method produces a pregnant leach solution (PLS) with high 21 Li (7.0 g/L) and Co (44.4 g/L) concentrations as well as a leach residue rich in Cu (up to 12 wt.%) that 22 is suitable as a feed fraction for primary or secondary copper production.

23 Keywords: waste Li-ion batteries, reductive leaching, LiCoO₂, ascorbic acid, copper

24 **1. Introduction**

25 Recycling of waste Li-ion batteries (LIBs) is becoming increasingly crucial in terms of saving both 26 resources and protecting the environment. Worldwide, the consumption of LIBs has increased

1 dramatically between 2010 - 2015 from 4.6 billion to 7.0 billion units (Li et al., 2011) and it has been 2 estimated that by 2020 the quantity of discarded LIBs will surpass 25 billion units with a combined 3 weight of 500 thousand tonnes (Zeng et al., 2014). These discarded batteries are rich in both valuable 4 metals and organic chemicals (e.g. EC/EMC electrolytes: ethylene carbonate and ethyl methyl 5 carbonate), with the approximate proportions ranging between 5-20% cobalt, 5-10% nickel, 5-7% 6 lithium, 6-12% copper, 15% organic chemicals and 7% plastics (Zeng and Li, 2014), (Gratz et al., 2014). 7 These valuable metals are of considerable economic value, especially as the availability of high-grade 8 ores are gradually depleting. Nevertheless, if these waste batteries cannot be collected and recycled 9 efficiently, the inherent toxicity of the heavy metals and organic chemicals within can cause serious 10 environmental and human-health problems (Kang et al., 2013).

11

12 A typical waste battery recycling process involves two steps: Firstly, the spent batteries are pre-treated 13 by physical techniques like mechanical crushing and sieving, thermal treatment or dissolution with 14 solvent (e.g. N-methylpyrrolidone, NMP) (Bernardes et al., 2004), (Pagnanelli et al., 2017a). By using 15 a thermal treatment or dissolution with NMP the cathode materials can be separated effectively from 16 other components (e.g. iron shell or current collectors) to obtain scraps with a higher content of Co and 17 Li (Meshram et al., 2016), (Chen et al., 2011). Currently these two methods are still at the lab scale 18 however, due to problems related to waste gases and plastic hardening during thermal treatment as well 19 as the vaporization of solvents, like NMP, from the dissolution process.

20

21 Compared to thermal treatment and dissolution process, mechanical separation is the modern industrial 22 approach, even though cathode materials cannot be separated effectively from other components by 23 traditional crushing and sieving. The subsequent recovery of the valuable components from the crushed 24 waste is achieved by either smelting or hydrometallurgical technologies like leaching followed by 25 precipitation, solvent extraction or electrochemical processes (Chen et al., 2015). One of the state-of-26 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-Mn alloy and slag (Sojka, 1998). The 27 28 alloy obtained is then dissolved to recover the cobalt, nickel and other base metals. 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 increase threefold within the next 10 years (Metalary, 2017). Development stage hydrometallurgical techniques - like acid leaching followed by a purification 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).

8

9 Recently, a great deal of research has been devoted to the leaching process of waste Li-ion battery 10 scraps with different types of mineral acids like HCl (Guo et al., 2016), H₃PO₄ (Chen et al., 2017), 11 H₂SO₄ (Pagnanelli et al., 2016) and organic acids including citric acid (Zheng et al., 2016), malic acid 12 (Li et al., 2010) and lactic acid (Li et al., 2017). Moreover, the leaching efficiency of cobalt and lithium 13 has also been shown to increase with the use of additional reducing agents like H₂O₂ (Pagnanelli et al., 14 2017b), Na₂S₂O₅ (Vieceli et al., 2018), NaHSO₃ (Meshram et al., 2016), D-glucose (Granata et al., 2012) 15 as well as ascorbic acid (Li et al., 2012).

16

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

$C_{0}(%)$	Acids + Reducing agents	S/L	Concentra	ation (g/L)	Yields (%)			References
00 (70)	Actus + Reducing agents	ratio	Со	Li	Со	Li	Cu	. References
35.8 ^a	1 M H ₂ SO ₄	50	11.8	3.0	66	93	-	(Meshram et al., 2016)
35.8 <i>ª</i>	$1 \text{ M H}_2\text{SO}_4 + 5\% (v/v) \text{ H}_2\text{O}_2$	50	14.1	3.1	79	94	-	(Meshram et al., 2016)
44.2 <i>ª</i>	$4 \text{ M H}_2\text{SO}_4 + 10\% (v/v) \text{ H}_2\text{O}_2$	100	42.0	5.3	95	96	-	(Chen et al., 2011)
54.0 <i>ª</i>	$2~M~H_2SO_4 + 5\%~(v/v)~H_2O_2$	50	26.7	3.2	99	99	-	(Sun and Qiu, 2011a)
35.8 ^a	$1~\mathrm{M~H_2SO_4} + 7.5~\mathrm{M~NaHSO_3}$	50	15.2	3.0	85	93	-	(Meshram et al., 2016)
35.4 <i>ª</i>	$3 \text{ M} \text{ H}_2 \text{SO}_4 + 0.25 \text{ M} \text{ Na}_2 \text{S}_2 \text{O}_3$	66	23.1	2.4	99	99	50	(Wang et al., 2012)
41.5 <i>ª</i>	$0.34 \text{ M H}_3\text{PO}_4 + 2\% \text{ (v/v) H}_2\text{O}_2$	8	3.2	0.4	95	95	-	(Pinna et al., 2017)
54.0 <i>ª</i>	0.1 M Citric + 0.02 M ascorbic	2	0.9	0.1	80	100	-	(Nayaka et al., 2015)
54.0 <i>ª</i>	0.5 M glycine + 0.02 M ascorbic	2	1.0	0.1	95	95	-	(Nayaka et al., 2016a)
55.0 <i>ª</i>	1.25 M ascorbic acid	25	13.1	1.6	95	99	-	(Li et al., 2012)
-	$2 \text{ M H}_2 \text{SO}_4 + 4\% \text{ H}_2 \text{O}_2$	66	32.7	2.3	97	97	65	(Nayl et al., 2017)
52.0 <i>ª</i>	$1 \text{ M} \text{H}_2\text{SO}_4 + 0.02 \text{ M} \text{ glucose}$	35	16.0	1.5	88	92	-	(Pagnanelli et al., 2014)
25.0 ^{<i>b</i>}	$2 \text{ M} \text{H}_2 \text{SO}_4 + 0.03 \text{ M} \text{ glucose}$	100	24.3	3.4	97	98	98	(Granata et al., 2012)
25.0 ^{<i>b</i>}	4 M HCl	100	24.8	3.5	99	99	99	(Granata et al., 2012)

17 *N.B. *a*: Raw material from manual dismantling, *b*: Raw material from industrial process treatment

1 Table 1 summarizes the related literature about waste LIBs leaching processes, optimum leaching 2 conditions and metal yields. It is evident that most of the reported studies have focused on the use of 3 manually dismantled scraps, in which Co contents can be as high as 54%. A majority of these scraps 4 are produced by the manual deconstruction of LIBs waste, separation of anode and cathode materials, 5 followed by immersion in NMP or incineration to remove the binder materials (e.g. PVDF). Such 6 manually obtained cathodic materials are not representative of real battery waste compositions as these 7 typically include a higher variety of components like battery shells, current collectors (copper and 8 aluminum) and electrolytes. Table 1 also shows that little information is readily available on the 9 behavior of Cu, even though a majority of the monetary value of discarded LIBs depends on the Cu 10 content, which can be between 6-12% (Zeng and Li, 2014). In addition, most of the research has been 11 performed with low S/L ratios (2-100 g/L), which are not typical for industrial hydrometallurgical 12 processes. Notwithstanding, the Li concentration in most PLS produced in the research is below 3.5 g/L, which is much lower than the critical concentration of 20 g/L required for the effective recovery 13 14 of Li by precipitation with a saturated Na₂CO₃ solution (Jandova et al., 2012).

15

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 the leaching process using industrially produced waste LIBs scraps and pure LiCoO₂. In addition, we proposed a method for selectively dissolving 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.

22

23 1.1. Management of Li-ion battery waste

The management of waste LIBs generally involves three steps: collection, pretreatment of waste LIBs and recycling 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 either 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 comprises of an organic liquid with dissolved substances like LiClO₄, LiBF₄
 and LiPF₆ within the battery matrices (Xu et al., 2008).

6

7 Once collected, spent Li-ion batteries are discharged in order to release the residual charges and reduce 8 the risk of explosion, which can result from the mechanical shock of lithium metal produced by battery 9 overcharge (Lee and Rhee, 2002). After this, the waste LIBs are first crushed and then treated by 10 dissolution, ultrasonic cleaning, vacuum decomposition, or other mechanical methods, to the reduce 11 scrap volume, enrich valuable metals (Zhang et al., 2014, Sun and Qiu, 2011b, He et al., 2015). The 12 separated papers, iron (steel) shells, copper foils, or aluminum foils can be sold to a related industry, while the fractions rich in active materials will be recycled by hydrometallurgy, pyrometallurgy and/or 13 14 biometallurgy processes. The downside of pyrometallurgical processes is that they do not provide a 15 process route for recovery of lithium because lithium ends up in slag (waste stream) (Tirronen et al., 16 2017). However, hydrometallurgy, which is more selective, can provide a future process route for Li 17 recovery from LIB scrap. This creates a high driving force for the hydrometallurgical research of Li 18 and other battery metal recycling from real industrially treated battery scrap, having characteristics very 19 different from the pure active materials. Furthermore, sulfuric acid is the most abundant acid, which 20 can support the integration of spin-off hydrometallurgical LIB recycling production along the traditional 21 industrial base metal hydrometallurgical production.

22 **2. Experimental**

23 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 a modified flowsheet of the sample preparation, which is adapted from a patent (Pudas et al., 2011). According to this patented process, the collected waste LIBs are crushed into pieces via a two-step process without any pre-separation of anode and cathode materials. In order to minimize the risk of fire, the temperature of the first crushing process
is controlled at 40 - 50 °C. The resultant material are then subjected to magnetic separation followed
by a sieving process to obtain the underflow and overflow fractions. A very small portion of the binder
materials (PVDF) and plastics are present in the scraps, although this only has a minor impact on the
leaching phenomena, as these components are not dissolved in the sulfuric acid media investigated.





Fig.1 Modified schematics of the LIBs preparation process (Pudas et al., 2011) As observed in Fig.1 that underflow scraps are primarily composed of black powders, whereas overflow scraps mainly contains plastic-like, copper-colored and metallic fractions. The chemical analysis of these scraps were carried out by aqua regia digestion (HCl:HNO₃ = 3:1, v/v) followed by ICP analysis (ICP-OES, Perkin Elmer 7100 DV) and the results are displayed in Table 2.

12

Table 2. Chemical compositions of overflow and underflow scraps

Waste					Elements				
scraps	Li	Co	Cu	Ni	Al	Mn	Fe	Zn	Others
Overflow	1.40	8.42	11.9	0.80	16.1	0.59	0.18	0.01	60.6
Underflow	3.65	23.6	6.24	2.72	2.78	1.73	0.66	0.01	57.6

Results in Table 2 reveal that the underflow is rich in Li and Co - 3.6% Li and 23.6% Co - whereas, the Cu and Al scraps are mainly concentrated in the overflow (12% Cu, 16% Al). Nevertheless, due to the presence of binders in LIBs, cathode materials (e.g. LiCoO₂) cannot be effectively separated from other components (e.g. plastics, current collectors) by mechanical pretreatment methods. As a result , there are still appreciable quantities of Li (1.4 wt.%) and Co (8.4 wt.%) within the overflow material.





Fig.2 XRD pattern (a) and BSE micrograph (b) of the underflow scraps

7

8 Further characterizations were performed on the underflow scraps by XRD (PANalytical X'Pert Pro 9 Powder, Almelo, Netherlands), SEM (A LEO 1450, Carl Zeiss Microscopy GmbH, Jena, Germany) 10 and EDS (Link Inca X-sight 7366, Oxfordshire, UK). Fig.2.a presents the results of the XRD analysis 11 of the used LIB raw material (underflow). The presence of crystalline LiCoO₂, LiCo_{0.25}Ni_{0.65}Mn_{0.1}O₂, 12 Cu and graphite phase were detected, however, the principal compounds related to Al and Fe could not 13 be accurately determined due to the presence of high backgrounds and their low intensity. In particular, 14 Al could not be identified clearly, even though aluminum was visually observed and its content was as 15 high as 2.7% (in Table 2). This is probably because the particle size of Al in scraps is somewhat larger 16 than the critical particle size of 75 µm necessary for XRD analysis.

17

Analysis by combined SEM-EDS (Fig.2.b) revealed that Cu in the scraps mainly exist in elementary form. Since element Li is too light to be detected by EDS, the quantity of LiCoO₂ particles could not 1 be determined by SEM-EDS, although the related compound CoO_x could be detected. When these 2 results are combined with those from XRD analysis, it is reasonable to suggest the existence of LiCoO2 3 within the underflow material. Moreover, Al containing compounds can also been detected, which 4 probably exist in both oxidized and elementary forms. Furthermore, there was often little or no 5 separation observed between the phases containing $LiCoO_2$ and Al, this is due to the binders used in 6 battery manufacture to attach the active cathode materials to the current collector. In turn, this also 7 indirectly explains the reason for the relatively high percentage of Co (8.4%) found in the sieve overflow 8 material.

9

10 2.2 Experimental procedure

In order to minimize the deviation from sampling, 4 kg of underflow scraps were divided into 80 parts with a rotary sample divider (Quantachrome Instruments SRR II). For each experiment, around 50 grams of sample was added into a cylindrical reactor (V = 1.2 L) fitted with a condenser and agitator (200 rpm), before being placed in a water bath (Thermo Haake®, DC10) in order to control the reaction temperature. Solution samples (1 mL) were taken as a function of time and analysed by ICP-OES. Additionally, the system redox potentials were measured using a platinum electrode with Ag/AgCl reference electrode (Inlab® Redox, Mettler Toledo) during sampling.

18

19 After leaching, the solids were filtrated and the resultant leaching residues were washed with hot 20 distilled water (70-80 °C) before being dried at 60 °C for 24 h. The filtrates, washing solutions as well 21 as the dried leaching residues were subsequently analyzed to calculate the leaching efficiency (η) as 22 follows:

23

24
$$\eta = (C_L \times V_L) / (x_0 \times m_0) \times 100\%$$
(1)

1	Where η is the leaching efficiency (%), C_L the concentration of target metal in leach solution (g/L), V_L
2	volume of the leach solution (L), x_0 the concentration of metal of interest - determined by ICP-OES -
3	within input scraps (as (%) and m_0 is the weight of the input materials (g).
4	
5	The factors and the parameters used in the leaching experiments are listed in Table 3.
6	

Table 3. Factors and its level of acid leaching experiments

Factors	Levels
Reducing agents	No reducing agents, $[C_6H_8O_6] = 0.06$ M
Temperatures (°C)	25, 60, 70, 80
$[H_2SO_4]$ (M)	1.5, 2.0, 3.0, 4.0
$\left[C_{6}H_{8}O_{6}\right](\mathbf{M})$	0, 0.03, 0.05, 0.06, 0.09, 0.11
S/L ratios (g/L)	100, 200, 300

8

9 **3. Results and discussion**

10 3.1 Investigation of leaching process in the absence reducing agents

Leaching experiments in the absence of separately added reducing agents were carried out with industrially produced waste LIBs and pure LiCoO₂ under the following conditions: 2 M H₂SO₄, S/L =100 g/L (waste LIBs) and 39.2 g/L (pure LiCoO₂) at T = 80 °C. The leaching behaviors of Co, Li and Cu over a period of 5 h are displayed in Fig.3. A cubic rate law (He et al., 2017) was utilized to determine the dissolution rates by the equation:

16
$$(1-f)^{1/3} = k \times t$$
 (2)

17 where f is the fraction dissolved at different intervals of time, t; k is the rate constant.

Although the cubic rate law was originally derived for spherical particles, it has been also demonstrated to be applicable even for polydispersed particles (Manjanna and Venkateswaran, 2002). As shown in Fig.3.a and Fig.3.b, the leaching efficiency of Li is consistently 10 to 20% higher than Co, which can be attributed to the special structure of cathodic materials (e.g. LiCoO₂), in which, Li fractions lie between molecular octahedra formed by cobalt and oxygen atoms (Shao-Horn et al., 2003). It is
 therefore comparatively much easier for Li to be dissolved than Co. The dissolution of LiCoO₂ is
 highlighted by the following reactions:

$$LiCoO_2 + xH^+ \rightarrow xLi^+ + Li_{1-x}CoO_2 + xe^-$$
⁽²⁾

$$Li_{1-x}CoO_2 + 4H^+ + (1+x)e^- \to (1-x)Li^+ + Co^{2+} + 2H_2O$$
(3)

4

This hypothesis is supported by the XRD analysis of the leaching residue produced from acid leaching
with pure LiCoO₂, shown in Fig.4. The main phases in the residue was identified to be Li_{0.5}CoO₂, which
demonstrates the preferential leaching of Li when compared to Co.

8

9 In addition, results also show the different behavior of Co during the leaching process with LIBs scraps 10 and pure LiCoO₂, in the absence of externally added reducing agents. During the LIBs scrap leaching, 11 Co achieves equilibrium after around 45 minutes, whereas with the pure $LiCoO_2$ the leaching efficiency 12 of Co increase slowly from 40% to 62% over a 5-hour period. Additionally, the leaching efficiency of 13 Co and Li with industrial LIBs waste (Fig.3.a) was notably higher than that of pure LiCoO₂ (Fig.3.b). 14 This indicates that scraps that originate from an industrial mechanical processing can result in a higher 15 leaching efficiency for Co and Li when compared to the pure LiCoO₂. This finding most likely due to 16 the other metallic components present in industrially crushed scraps - like current collectors (copper 17 and aluminum foils) – that can promote LiCoO₂ leaching. This complex solution matrix can also explain 18 the high dissolution of the elementary Cu (61.5%) without externally added oxidizing agents, as 19 displayed in Fig.3.a. As has previously been demonstrated by Joulié et al. (2017), the leaching 20 efficiency of Co, Ni and Mn can be dramatically increased from 40% to around 90% with the addition 21 of sufficient current collectors (copper and aluminum foils). Nevertheless, the results of Joulié et al. 22 also show that the dissolution rates of the copper foils are generally quite slow, except for the initial 23 period at the beginning of the experiment - leaching efficiency of Cu reached 38% within 20 minutes 24 and then gradually increased by a further 20% over the next 25 hours of leaching. Similar behaviors of 1 Cu could be observed in our leaching experiments as Cu dissolution leveled off after approximately 90



2 minutes of reaction time and then maintained a level of around 60% (Fig.3.a).

4 Fig.3 Leaching kinetics and the cubic rate-law with (a, b) industrial LIBs scraps (S/L = 100 g/L) and

(c, d) pure LiCoO₂ (S/L = 39.2 g/L) with $[H_2SO_4] = 2 \text{ M}$, T = 80 °C).

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3



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7 8

Fig.4 XRD patterns of the leaching residue produced from leaching with pure $LiCoO_2$ (S/L =

$$39.2 \text{ g/L}, [H_2SO_4] = 2 \text{ M}, T = 80 \text{ °C}).$$

1 The kinetic studies using the cubic rate law (shown in Fig.3.c and Fig.3.d) reveal that the dissolution 2 process of Co and Li can be divided into two clear stages. The first-stage dissolution shows much faster 3 dissolution kinetics than the second-stage dissolution and has an exponentially higher dissolution rate 4 constant (k). The rate constants of the first-stage dissolution process in Fig.3.c (Industrial LIBs scraps) and Fig.3.b (Pure LiCoO₂) were between $0.7 - 2.1 \times 10^{-2}$ min, while the rate constants of the second 5 stage were significantly lower $(0.4 - 5.0 \times 10^{-4} \text{ min})$. In order to further study the limiting steps for both 6 7 Co and Li dissolution, different models were evaluated like shrinking core models based on the 8 chemical, diffusion and mixed control as well as an empirical model based on a logarithmic rate law. 9 Nonetheless, none of the models investigated provided a good correlation with the leaching kinetic data 10 from the industrial waste LIBs scraps. Previous research by Jha and co-workers (Jha et al. 2013) with 11 crushed LIBs scraps containing current collectors demonstrated that dissolution of Li followed a 12 chemical controlled reaction model, while the leaching kinetics of Co correlated well wait a model 13 based on 'ash diffusion control dense constant size - spherical particles'. In contrast, research by Pratima Meshram (Meshram et al., 2015) with mainly cathode active materials, revealed that dissolution of Li 14 15 and Co did not follow any shrinking core model based controls, but could be fitted with an empirical 16 model based on a logarithmic rate law. These different observations are probably the result of the 17 different pretreatment methods of waste LIBs as the obtained LIBs scraps are, in general, quite 18 heterogeneous and chemically complicated fraction, therefore either the electrode or active materials 19 are typically not present as dense particles.



2

Fig.5 Behaviors of Co, Li and Cu during the leaching process using PLS as lixiviant (S/L = 100 g/L,

 $[H_2SO_4] = 2 \text{ M}, T = 80 \text{ °C}).$

3

4 In order to determine the reason for the incomplete dissolution of Co and Li in Fig.3.a, further 5 experiments were conducted using pregnant leaching solution (PLS) - produced by the leaching process 6 with waste LIBs scraps – as the leaching medium/lixiviant with fresh waste LIBs scraps at 80 °C and 7 S/L = 100 g/L. As shown in Fig.5, the leaching efficiency of Li and Co when PLS was used as lixiviant 8 were still as high as around 80% and showed similar behaviors when compared with experiments using 9 only sulfuric acid (2M) as lixiviant in Fig.3.a. This means the PLS still bear a strong dissolution ability towards Co and Li. The first-stage rate constants were 1.1 x 10⁻²/min or Co and 1.5 x 10⁻²/min for Li 10 11 (shown in Fig.5.b), which were only slightly lower than that with only sulfuric acid in Fig.3.c. From the 12 results shown in Fig.3 and Fig.5, it can be concluded that the incomplete dissolution of Co and Li in Fig.3 was not as a result of the leaching solution properties like acidity or solubility. Rather, from the 13 14 properties of the leaching residue, where the presence of several metals – like Cu, Al, Fe - can act as 15 reducing agents that enhance Co and Li dissolution.

16 3.2 Investigation of leaching process in the presence reducing agents

Ascorbic acid is a well-known natural reducing agent that offers good reducing abilities in the leaching process of waste LIBs when used in conjunction with other organic acids like citric acid (Nayaka et al., 2015), glycine (Nayaka et al., 2016a) and tartaric acid (Nayaka et al., 2016b). In the experiments outlined here, the influence of ascorbic acid as additive on the leaching process was determined by performing measurements with ascorbic acid additions to the leachant at 0 (Fig.6.a) and after 60 min of leaching (Fig.6.b).

23

Fig.6.a shows leaching behaviors of Co, Li and Cu when ascorbic acid is added at the beginning of leaching process. It can be seen that the leaching efficiency of Li and Co rapidly attains 100% within only 30 minutes, whereas Cu dissolution increases slowly and maintains a low level of around 10%. A similar observation is shown in Fig.6.b, where the leaching efficiency of Li and Co increases to almost 1 100% after the addition of ascorbic acid, whilst Cu dissolution shows the opposite trend, decreasing 2 from 56% to 35%. This is because copper ions can be reduced to elementary copper by ascorbic acid, a 3 method that is widely utilized in the production of copper powders (Wu, 2007). As a mild reducing 4 agent ascorbic acid can provide two electrons and be doubly oxidized to the stable dehydroascorbic acid 5 $(C_6H_6O_6)$ (Li et al., 2012). Additionally, ascorbic acid can also potentially provide H⁺ for the leaching 6 process, although its acidity constants, pKa_1 and pKa_2 are 4.10 and 11.6, respectively, which indicates 7 that trace amounts of H^+ could be provided by 0.06 M ascorbic acid. The proposed reactions related to 8 ascorbic acid are as follows:

9

$$C_6H_8O_6 + 2LiCoO_2 + 6H^+ \to C_6H_6O_6 + 2Li^+ + 2Co^{2+} + 4H_2O$$
(3)

 $C_6H_8O_6 + Cu^{2+} \rightarrow C_6H_6O_6 + 2H^+ + Cu$

(4)

12

20

The different behaviors of Co (Li) and Cu demonstrate the possibility for selective leaching of Co and Li towards Cu, to leave a residue with a relatively high Cu concentration. This is particularly advantageous for the circular economy of battery metals perspective, as copper can be efficiently recovered from several types of complex solid residues in either primary or secondary copper smelters. As a result, in order to optimize the selective leaching process, a series of experiments were conducted to study the effect of factors like leaching temperature, time, and acid concentration, dosage of ascorbic acid as well as S/L ratios on battery metals extraction.



1 Fig.6 Behavior of Li, Co and Cu with the addition of ascorbic acid (a) at the beginning and (b) after

60 min of the leaching $(S/L = 100 \text{ g/L}, /H_2SO_4) = 2 \text{ M}, T = 80 \text{ °C})$

2

3 3.3 Influence of temperature and time on leaching process

4 Fig.7.a-d shows the influence of temperature (25 - 80 °C) and time (0 - 5 h) on the leaching efficiency 5 of Li, Co, Cu and the related redox potentials when using a 2 M H_2SO_4 - 0.06 M $C_6H_8O_6$ leaching 6 solution with a *S/L* ratio of 100 g/L.







 $100 \text{ g/L}, [H_2SO_4] = 2 \text{ M}, [C_6H_8O_6] = 0.06 \text{ M})$

10

9

From the results, it is evident that the leaching efficiency of Co and Li increases with increased leaching time and higher temperatures. The leaching efficiency of Co and Li increases dramatically for $t \le 75$ min before it gradually levels off after $t \ge 90$ min. Generally, the leaching efficiency of Li is observed

1 to be slightly higher and reaches equilibrium faster than Co; the maximum Co extraction was 81.5% at T = 25 °C and 98.3% at T = 80 °C, whereas the corresponding extractions for Li were 87.3% and 99.7%, 2 3 respectively. In the case of Cu, the leaching efficiency increases gradually with increasing time and 4 almost reaches equilibrium after 5 hours. The maximum leaching efficiency of Cu is seen to decrease 5 with increasing temperature, for example, when the temperature is increased from 25 °C to 80 °C the 6 leaching efficiency of Cu at 300 min decreased from 37.5% to 16.5%. Nevertheless, at times of less 7 than 180 min, Cu leaching efficiency at 25 °C is observed to slowly increase in a linear manner because 8 of the lower reaction kinetics at lower temperatures. Furthermore, Fig.7.d reveals that there is a clear 9 reduction in the measured system redox potentials for the $H_2SO_4 - C_6H_8O_6$ system when the temperature 10 changes from 25 °C to 80 °C. The system potentials also reach equilibria faster at higher temperatures due to the higher kinetics at higher temperatures and the recorded potential changes are consistent with 11 12 the Cu extraction behavior seen over the same temperature range.

13

14 3.4 Influence of sulfuric acid concentration

Fig.8 summarizes the influence of acid concentration on LIBs dissolution (T = 80 °C, t = 90 min and a 15 C₆H₈O₆ dosage of 0.06 M). Experiments were carried out over an acid concentration range of 1.5 - 4.0 16 17 M H₂SO₄ with a S/L = 100 g/L. Co and Li extraction into the solution was shown to increase from 88.6% 18 and 85.2% to 98.26% and 99.7% respectively, as sulfuric acid concentration was increased from 1.5 M 19 to 2.0 M (S/L = 100 g/L). With further acid concentration increases - from 2 to 4 M - the leaching 20 efficiency of Co and Li remained at ca. 99%, however, under the same conditions the dissolution of Cu 21 was enhanced from 10.5% (1.5 M H₂SO₄) to 38.6% (4 M H₂SO₄). Consequently, in order to achieve 22 the selective leaching of Co and Li from Cu, the optimum sulfuric acid concentration was determined 23 as 2 mol/L.



Fig.8 Influence of acid concentration on the leaching of waste LIBs scraps (T = 80 °C, t = 90 min, $[C_6H_8O_6] = 0.06 \text{ M}, S/L = 100 \text{ g/L} [H_2SO_4] = 1.5, 2.0, 3.0, 4.0 \text{ M})$

2 3.5 Influence of C₆H₈O₆ dosage

3 In order to study the influence of C₆H₈O₆ concentration on leaching behavior, experiments were carried 4 out in 2 M H₂SO₄ with different molarities of C₆H₈O₆ (0 to 0.11 M). The test used a S/L ratio of 100 5 g/L and a temperature of 80 °C for 90 min and the results, shown in Fig.9, demonstrate that leaching 6 efficiency of both Co and Li increases with the increased dosage of C₆H₈O₆. Interestingly, the addition 7 of C₆H₈O₆ had a more significant impact on the leaching of Co, as efficiency increased by nearly 15%-8 units, from 83.5% (0 M C₆H₈O₆) to 98.26% (0.06 M C₆H₈O₆). In comparison, the leaching efficiency 9 of Cu showed the opposite behavior, as yields were observed to reduce from 55% to 13% with an 10 increase of C₆H₈O₆ concentration from 0 to 0.06 M. Further increases in C₆H₈O₆ from 0.06 to 0.11 M, 11 caused the Cu yields to further decrease to 3%. This trend was matched by the recorded system redox 12 potentials, which showed an analogous decrease from 770 mV to 60 mV (vs. Ag/AgCl).



Fig.9 Influence of C₆H₈O₁₂ dosage on the leaching of waste LIBs scraps (T = 80 °C, t = 90 min, S/L = 100 g/L, $[H_2SO_4] = 2 \text{ M}$, $[C_6H_8O_6] = 0$, 0.03, 0.05, 0.06, 0.09, 0.11 M)

5

6 3.6 Influence of S/L ratios

7 The study of the effect of S/L ratios was performed under the following conditions: T = 80 °C, t = 90min, $[H_2SO_4] = 2$ M, $[C_6H_8O_6] = 0.06$ or 0.11 M and S/L = 100, 200 and 300 g/L. The results in Fig.10 8 9 show that the leaching efficiencies of Li, Co and Cu all decrease as the S/L ratios are increased, 10 especially at the S/L ratio = 300 g/L, the leaching efficiency of both Li and Co had decreased by 15-11 20% (Fig.10.a). As C₆H₈O₆ concentration increased from 0.06 M to 0.11 M, the leaching efficiency of 12 Li and Co increased slightly, however the Cu leaching efficiency was shown to markedly decrease from 13 7.5 - 13.3% to a low of 0.2 - 3.2%. Under the optimal conditions of S/L = 200 g/L and $[C_6H_8O_6] = 0.11$ M, only 0.7% of Cu was dissolved, whereas the leaching percentages of Co and Li were 93.8% and 14 15 95.7%, respectively. This result clearly demonstrates the highly selectivity of this leaching system for 16 the battery metals (Co and Li) cf. Cu.



2 3

5 3.7 Pregnant liquid solution (PLS) and copper rich residue

6 Table 4 summarizes the products of the optimized LIBs leaching process $(/H_2SO_4) = 2 \text{ M}, /C_6H_8O_6) =$ 7 0.11 M, T = 80 °C t = 90 min, S/L = 200 g/L). It can be see that the PLS of the reductive LIBs leaching 8 process had [Co] = 44.1 g/L, [Li] = 7.0 g/L and [Cu] = 0.1 g/L, with the mass ratio of Co/Cu in the 9 PLS being ca. 400, and for Li/Cu ca. 70. This suggests that reductive leaching with these optimized 10 parameters results in a PLS that is rich in Co with good selectivity towards Cu. The content of Cu in 11 the leaching residue was determined to be around 12% and XRD analysis suggests that the Cu is present 12 in the elementary form (see Fig.11). Furthermore, the PLS produced also has attractive concentrations 13 of Co, Li, Ni and Mn for subsequent hydrometallurgical recovery processes.

- 14
- 15

Table 4. The product (PLS and Cu rich leach residue) analysis after optimized reductive leaching of

16

LIBs $([H_2SO_4] = 2 \text{ M}, [C_6H_8O_6] = 0.11 \text{ M}, T = 80 \text{ °C}, t = 90 \text{ min}, S/L = 200 \text{ g/L}).$

Optimum results		Со	Li	Cu	Fe	Ni	Al	Mn
PLS	g/L	44.14	6.98	0.11	1.29	4.96	5.59	3.20
Leaching residue	%	0.52	0.06	~12	0.03	0.61	0.05	0.12
Leaching efficiency	%	93.8	95.7	0.7	> 99	91.5	> 99	92.7

Fig. 11 XRD pattern of the leaching residue after the optimized reductive LIBs leaching experiment ($[H_2SO_4] = 2$ M, $[C_6H_8O_6] = 0.11$ M, T = 80 °C t = 90 min, S/L = 200 g/L)

1 4. Conclusions

2 Currently, the copper present in battery waste is a suitable feed material for either primary or secondary 3 copper smelter. However, at the same time some valuable elements like Li are lost to the slag. In this 4 paper, a reductive sulfuric acid leaching process is outlined for industrially crushed LIBs waste scraps 5 that utilizes industrially attractive S/L ratios of 100 g/L and 200 g/L, directly to produce a concentrated 6 Co rich PLS. It has been shown scraps that originate from an industrial mechanical processing can result 7 in higher leaching efficiency for Co and Li compared to pure LiCoO₂ chemical, and leaching efficiency 8 of copper decrease as the addition of reducing agents, which is opposite to the behaviors of Co and Li. 9 On basis of this, selective leaching of Co and Li vs. Cu was proposed and achieved at 80 °C with a 10 leaching time of 90 min in a sulfuric acid system (2 M) with C₆H₈O₆ (0.11 M) added at the beginning 11 of leaching process. The levels of metal extraction achieved by this selective process were 95.7% for 12 Li, 93.8% for Co and 0.7% for Cu (S/L ratio of 200 g/L), which resulted in a PLS with a Co/Cu ratio of 13 400 (44.1 g/L Co and 0.1 g/L Cu). XRD analysis of the Cu-rich leach residue confirmed that the copper 14 in the residue exists in the elementary form, which is attractive for further processing. The procedure 15 presented allows for the improved circular economy of metals as battery materials like Co, Li (and Ni) 16 can be recovered by hydrometallurgical methods resulting in a residue that is suitable as a feed material 17 for primary or secondary copper smelters.

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