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Extraction of Li and Co from industrially produced Li-ion battery waste – Using the reductive power of waste itself

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ABSTRACT

Industrially produced spent lithium-ion batteries (LIBs) waste contain not only strategic metals such as cobalt and lithium but also impurity elements like copper, aluminum and iron. The current work investigates the distribution of the metallic impurity elements in LIBs waste, and their influence on the acid dissolution of target active materials. The results demonstrate that the presence of these, naturally reductive, impurity elements (e.g. Cu, Al, and Fe) can substantially promote the dissolution of active materials. Through the addition of Cu and Al-rich larger size fractions, the extraction efficiencies of Co and Li increased up to over 99%, to leave a leach residue that is rich in graphite. By this method, the use of high cost reductants like hydrogen peroxide or ascorbic acid could be avoided. More importantly, additional Co and Li associated with the Cu and Al electrode materials could be also recovered. This novel approach contributes not only to improved reduction efficiency in LIBs waste leaching, but also to improved total recovery of Co and Li from LIBs waste, even from the larger particle size fractions, which are typically lost from circulation.

1. Introduction

Li-ion batteries (LIBs) are widely used in consumer electronics, electronic vehicles, energy-storage systems, etc., where high-energy density and lightweight are of prime importance. It is forecasted that the worldwide demand for LIBs will reach ca. 900 GWh by 2026 (Drabik and Rizos, 2018). Consequently, this also means there will be large quantities of waste LIBs being produced in the near future as the average lifespan of LIBs is only 2–3 years for consumer electronics and 8–10 years for automotive or energy storage systems (Richa et al., 2017). Moreover, these end-of-life LIBs contain heavy metals with known toxic effects and flammable electrolyte, which can pose a serious environmental risk if they are not disposed properly (Zhao and You, 2019). Furthermore, as this waste is a valuable secondary source of raw materials - it contains significant quantities of metals like cobalt (5–20%), nickel (5–10%), lithium (5–7%) and copper (6–12%) (Zeng et al., 2014) - the recycling of waste Li-ion batteries (LIBs) has recently garnered significant interest.

1.1. Spent LIBs management and policies

Generally, end-of-life LIBs are classified as either portable LIBs or LIB modules that are utilized in electric vehicles and energy storage systems. The large-size LIB modules can be easily collected and treated by recycling companies, whereas spent portable batteries are more commonly disposed to municipal waste streams, landfill or incineration depending on local legislation requirements (Terazono et al., 2015; King and Boxall, 2019). Consequently, significant traces of Co and Li can often be found in municipal waste incinerator bottom ashes (Allegrini et al., 2014; Alam et al., 2019). According to the Europe Commission, in 2014 (European Commission – DG Environment, 2014), the collection rates of portable LIBs was only 4.5%, whereas research in California has revealed that the costs associated with the collection of 1 ton of waste batteries from the municipal waste streams can be as high as 2700 US dollars (Turner and Nugent, 2016). In order to improve the management of spent batteries (not only LIBs), a policy of 'extended producer responsibility (EPR)' has been adopted in the EU, Canada, USA and elsewhere, with the aim to raise consumer awareness, expand waste collection infrastructure and shift the costs of battery collection/recycling from municipalities to stewardship organizations (Terazono et al., 2015). In the EU, the 2006 Battery Directive clearly established EPR requirements for all battery types (not only LIBs) and this also includes strict requirements

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that each member state set target collection rates (e.g. 45% in 2016) and the minimum recycling efficiencies of >50% (Council Directive, 2006). Similarly, the Corporation for Battery Recycling (CBR) in the USA proposed an act that requires battery producers to participate in a battery stewardship plan, which details the collection points, educational efforts and recycling process of each operator. In contrast, the latest battery recycling edict within China dictates that all the power batteries need to be encoded and a related tracking system is required that traces battery movement between designer, producers, downstream enterprises and recyclers (Xu et al., 2017). In terms of other batteries like portable LIBs however, the Chinese government has chosen to give a direct financial subsidy to recyclers based on their production capacities. Although numerous incentives and compulsory policies have been adopted in many countries, these strategies often lack any details about how waste batteries should be managed in an economic and environmentally sustainable way.

1.2. Acid leaching of spent LIBs

Acid leaching of spent LIBs is a critical step in the hydrometallurgical recycling of battery waste and this typically involves a reductive process as the target transition metals (e.g. Co, Ni, Mn) in active materials exist at higher valences, when compared to their aqueous solution equivalents. In the case of $LiCoO_2$, for example, the dissolution process occurs as follows (HSC Chemistry 9, $T = 353$ K):

$$LiCoO_2(s) + e^- + 4H^+ \rightarrow Li^+ + Co^{2+} + 2H_2O \quad E^\circ = 2.12\ \text{V (vs. SHE)} \tag{1}$$

Based on reaction (1), the dissolution process of $LiCoO_2$ can be enhanced by the addition of acids and reducing agents. As a result, recent research has been devoted to the investigation of different type of acids (Zhuang et al., 2019) and relatively costly reducing agents like H_2O_2, $NaHSO_3$, $Na_2S_2O_3$, as well as ascorbic acid and D-glucose (Chen et al., 2015; Gao et al., 2018). Despite this, the majority of the reported scientific research is primarily carried out with pure active materials from manually dismantled batteries (Chen et al., 2018; Fu et al., 2019) and therefore, does not represent the industrially crushed battery waste as a whole (Vezzini, 2014). In industry, the LIB scraps are usually processed through the following unit processes: discharging, mechanical crushing (or shredding), magnetic separation and sieving, resulting in waste composed of both active materials as well as some impurity metals (e.g. Cu, Fe, Al) (Tedjar and Foudraz, 2010; Pagnanelli et al., 2017). Furthermore, a small but appreciable amount of the active materials can also be found within the separated impurity metal fractions as a result of retention on the Cu/Al electrodes that segregate at larger particle sizes (Wang et al., 2016). In consequence, state-of-the-art pre-processing techniques do not provide a complete separation of active materials (Co, Ni, Mn, Li) from the impurity metals (Fe, Al, Cu) - in contrast to the hand dismantled battery materials often found in the literature - and therefore the effective treatment of both active materials and larger particle sizes is required. According to our previous research, the acid dissolution of Li and Co from industrially processed LIBs materials in the absence of external additives results in extraction of ~90% (Li) and ~80% (Co) (Peng et al., 2018). In contrast, findings from the leaching of manually dismantled 'pure' active materials under similar conditions show lower levels of ca. 60% for Co and 80% for Li (Vieceli et al., 2018; Li et al., 2017). These results suggest that the acid dissolution of industrial LIBs scraps is different from pure active materials and that the presence of metallic impurities within the mixed LIBs scrap might influence the acid dissolution behavior of active materials.

Consequently, this research investigates the distribution of impurity metals and active materials in industrially processed LIBs waste fractions with different particle size, as well as the influence of the existing impurity metals on the acid dissolution of active materials. Based upon this, we propose for the first time a method to utilize the existing Cu/Al rich overflow fractions of battery waste as reducing additives in order to promote the recovery of the desired valuable metals. The advantages of the current approach is that (i) very efficient reduction *i.e.* Co dissolution can be achieved during LIBs waste leaching, (ii) a high cost reducing agent (e.g. H_2O_2, ascorbic acid) is not needed, which contributes to the feasibility of the process and that (iii) the total Co and Li recovery can be increased as Co and Li present in the overflow fraction (*i.e.* Cu, Fe, Al rich fraction) that is normally lost, can also be recovered.

2. Experimental

2.1. Input LIBs scraps and the characterizations

The collected waste LIBs scraps were produced by a patented industrial-scale mechanical methodology that included two-step crushing, magnetic separation and sieving (Pudas et al., 2015). From this process, two distinct material streams were obtained, *i.e.* an underflow fraction (UF, <2 mm) rich in active materials (~21 wt% Co and 4 wt% Li) and an overflow fraction (OF, >2 mm) comprised primarily of aluminum/copper foils (~17 wt% Al and 12 wt% Cu) as well as active materials attached on the foils (~8 wt% Co and 1 wt% Li), Fig. 1. The former is typically used as the input material for the recovery of Li and Co, whereas OF is subjected to Cu smelting, resulting in the loss of Li and Co to the process slags (Tirronen et al., 2017). Fig. 1c and d show two examples of handpicked fractions of overflow, composed of Cu and Al flakes, which were washed with distilled water and then subjected to chemical analysis. It was found that in the copper colored fraction (Fig. 1c), Co content is <1 wt%, while in the aluminum colored flakes (Fig. 1d), the Co content can be as high as 11 wt%. This indicates that Co and Li in the overflow fraction (Fig. 1b) are not the result of entrainment, but that they are rather carried along with the binder material on the current collectors (Porvali et al., 2019).

The distribution of metallic components and active materials in the underflows was studied further by vibro-sieving the underflow (Retsch AS 300) into five fractions via a four-sieve combination (0.125 mm, 0.25 mm, 0.5 mm and 1 mm). Results, outlined in Table 1, show that the target elements (Li, Co, Ni, Mn) are distributed evenly amongst the different fractions, whereas the presence of Cu, Al, and Fe clearly increase with larger particle sizes. In the <0.125 mm fraction Cu, Al, Fe are all >0.6 wt%, whilst in the larger fractions (1.0–2.0 mm), their content increases substantially to approximately 20 wt% Cu, 13 wt% Al and 7 wt% Fe. XRD and SEM characterization of the fractions – shown in Figs. S1 and S2 - revealed that the active materials in the investigated battery waste mainly consist of $LiCoO_2$ and $LiCo_{0.25}Ni_{0.65}Mn_{0.1}O_2$, whereas copper is present in the elementary form and aluminum in both elementary and oxide forms.

2.2. Experimental procedures

2.2.1. Leaching of underflow fractions with different particle sizes

Acid leaching experiments for each particle size fractions were carried out at $T = 80$ °C, $[H_2SO_4] = 2.0$ mol/L, S/L (solid-to-liquid) = 100 g/L, $t = 1.5$ h, based on the operating parameters found in our previous research (Peng et al., 2018). Initially, a 40 g of sample and 400 mL of pre-heated H_2SO_4 (2.0 mol/L, 80 °C) were added into a cylindrical reactor ($V = 1.2$ L) fitted with a condenser and agitator (200 rpm), that was heated with a water bath (Thermo Haake®,

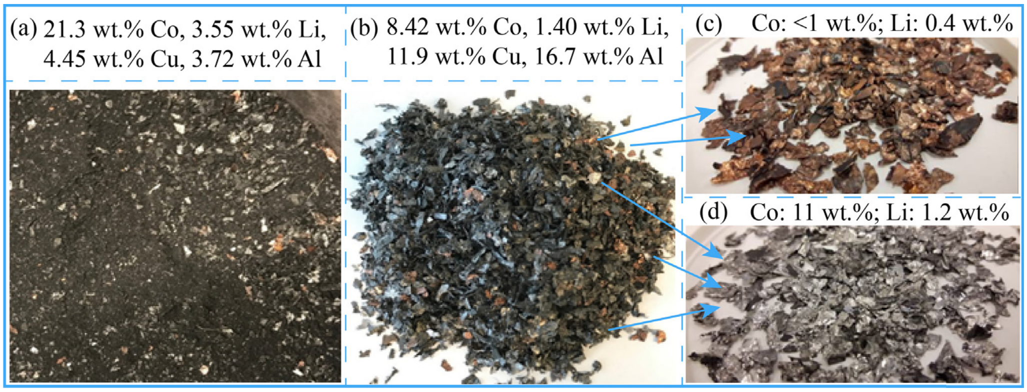

Fig. 1. Images and the metals predominating in crushed LIB waste fractions (a) underflow (<2 mm), (b) overflow (>2 mm) as well as (c) handpicked copper scraps and (d) aluminum scraps from overflow fraction (>2 mm).

Table 1
Weight percentages and chemical analysis of main metals in each particle size fraction of LIBs waste (raw material: underflow fraction <2.0 mm). *Rest denotes the residual material that is primarily a mixture of graphite and plastics.

Fractions (mm)	Weight percentages (%)	Chemical composition of elements (%)							
		Li	Co	Mn	Ni	Cu	Al	Fe	Rest*
<0.125	41.25	3.34	18.79	1.87	2.99	0.40	0.54	0.37	71.70
0.125–0.25	19.72	4.66	25.02	2.86	4.45	1.44	1.61	0.34	59.62
0.25–0.5	18.39	4.02	25.32	3.05	4.44	5.27	5.37	0.52	52.01
0.5–1.0	18.13	3.29	19.30	2.31	3.65	14.00	10.20	2.41	44.84
1.0–2.0	2.51	2.55	17.20	1.83	3.01	19.50	12.80	7.22	35.89

DC10). The fractions investigated were <0.125 mm, 0.125–0.25 mm, 0.25–0.5 mm, 0.5–1.0 mm and 1.0–2.0 mm. In order to study the behavior of elements as a function of time, intermittent solution samples were taken at pre-determined time intervals and the yields of the elements were calculated following Eq. (2). In order to ensure the accuracy of the results, the leaching residue were also analyzed to verify the results.

$$\gamma_i = (C_i \times V_i)/(m_i \times w_i) \times 100\% \quad (2)$$

where $m_i(g)$and $w_i(\%)$ are the mass of the input materials and the compositions of element (i), respectively; C_i (g/L) and V_i (L) are the concentration of elements (i) and the volume of leach solution.

2.2.2. Leaching of underflow battery wastes in the presence of additives

The possibility to use the Cu and Al rich overflow fraction (>2.0 mm, Fig. 1b) as an additive for the recovery of Li and Co from underflow fractions was investigated with the following parameters: $T = 80$ °C, $[H_2SO_4] = 1.5$, 2.0, 2.5 mol/L, $S/L = 100$ g/L, overflow/underflow (OF/UF) = 1/10, 1/20 (mass/mass). Overflow was added at t = 1 h and the leaching was allowed to proceed for a further 1 h. Leaching efficiencies of Co and Li were calculated via Eq. (2). As a comparison, acid leaching of the underflow wastes in the presence of H_2O_2 (5%, v/v) reducing agent was also conducted with 2.0 mol/L H_2SO_4, $S/L = 100$ g/L at 75 °C and the results are outlined in the supplementary materials (Fig. S3).

2.2.3. Leaching with pure substances

In order to define the effect of metallic components on the dissolution of active materials, initial acid leaching experiments with pure $LiCoO_2$ powders in the presence and absence of Cu, Al and Fe were conducted (Table 2). Similar amounts of metal ($LiCoO_2$: 19.6 g, Cu: 3.2 g, Al: 1.35 g, Fe: 0.33 g) to that of the investigated underflow battery waste material chemical composition (21.3 wt% Co, 4.6 wt% Cu, 3.7 wt% Al, 0.6 wt% Fe) were used. Experiments were conducted with $T = 80$ °C, $[H_2SO_4] = 2$ mol/L, S/L ≈ 40 g/L) and the solution samples were taken at pre-defined times and analyzed by ICP-OES. Yields were calculated based on the analysis of the solution samples via Eq. (2) in order to allow ease of comparison.

3. Results and discussion

3.1. Investigation of acid leaching of underflow fractions (<2 mm) in the absence of external reducing agents

In order to study the influence of metallic impurities on the acid dissolution of active materials, experiments with LIBs fractions that contained different amount of impurities were conducted

Table 2
Acid leaching experiments with pure substances ($LiCoO_2$: 19.6 g, Cu: 3.2 g, Al: 1.35 g, Fe: 0.33 g).

No.	Input materials				Temperature (°C)	S/L (g/L)	H_2SO_4 (mol/L)
	$LiCoO_2$	Cu	Al	Fe			
E1	√				80	40	2.0
E2	√	√			80	40	2.0
E3	√	√		√	80	40	2.0
E4	√		√		80	40	2.0
E5	√		√	√	80	40	2.0

Table 3
Yields of Co and Li when different LIBs particle size fractions are leached (T = 80 °C, t = 2.5 h, *S/L* = 100 g/L, $[H_2SO_4]$ = 2 mol/L).

Fractions (mm)	Yields (%)	
	Co	Li
<0.125	55.0	88.2
0.125–0.25	56.4	87.7
0.25–0.5	88.6	96.1
0.5–1.0	96.7	98.5
1.0–2.0	95.1	98.7

(T = 80 °C, t = 2.5 h, *S/L* = 100 g/L, $[H_2SO_4]$ = 2 mol/L). Results in Table 3 show that the leaching efficiencies of both Co and Li increase with laregr fraction particle sizes. For fractions <0.125 mm composed of ca. 0.5 wt% Al, 0.4 wt% Cu and 0.4 wt% Fe, the leaching efficiencies of Co and Li were around 55% and 88%, which is consistent with previous research based on cathode active materials only (Meshram et al., 2016). In contrast, for fractions >0.5 mm - in which the respective contents of Cu, Al, Fe were above 19.5 wt%, 12.8 wt% and 7.2 wt% - the associated leaching efficiencies of the target metals Co and Li increase to a level of at least 95%.

Additionally, the leaching kinetics with fractions: <0.125 mm and 0.5–1.0 mm, in which the Co and Li contents are nearly the same (Table 1), are outlined in Fig. 2. It is evident from Fig. 2a that the dissolution of the larger fractions (0.5–1.0 mm) have a faster dissolution kinetics for both Li and Co, when compared with the smaller fraction (<0.125 mm). Taking Co dissolution as an example, the Co leaching (0.5–1.0 mm) reaches the equilibrium at around 50 min, whereas leaching with the <0.125 mm fraction is unable to achieve equilibrium even with 150 min of reaction time. These results demonstrate clearly that the presence of metallic impurity components (Fe, Al, Cu) in the battery waste is beneficial for the extraction of Li and Co, as it increases both the leaching efficiency and the associated kinetics. Fig. 2b displays the behavior of other impurity metals during the leaching process, showing that the Fe, Al dissolution takes place rapidly and reaches nearly 100% at around 30 min for Fe and 60 min for Al. In addition, Cu partially dissolves and reaches ca. 45% after 60 min and 55% in 150 min. This suggests the presence of oxidants that can accept the electrons produced during the dissolution of Cu ($Cu - 2e^- = Cu^{2+}$). Based upon the observed enhanced dissolution of Li and Co, the assumption is that the target active materials and metallic components (e.g. Cu) can co-promote mutual dissolution. In order to study the mechanisms related to this phenomena, the acid leaching of active materials and metallic components were studied in more detail with pure substances (see in Section 3.3).

3.2. Investigation of acid leaching of underflow battery wastes (<2 mm) in the presence of overflow fractions as reducing agents

As a consequence of the positive effects determined with metallic components on the acid dissolution of active materials, the Cu and Al rich overflow fractions (OF, 2–6 mm) were investigated as additives to aid the extraction of Li and Co from the underflow fraction (UF, <2 mm). Results related to the Co and Li extraction in the absence and presence of the overflow fraction are displayed in Fig. 3a and b. As observed, Co and Li concentration increase markedly with the addition of the overflow fraction and findings demonstrate that higher ratios of overflow to underflow (OF/UF) give rise to the almost complete extraction of both Li and Co (>99%). Fig. 3c and d display the XRD patterns of the leach residues in the absence (Residue 1#) and presence (Residue 2#) of overflow additions (OF/UF = 1/10). Phase analysis of the XRD results was performed by HighScore software using Rietveld fitting (Mahieux et al., 2010) confirmed that the level of $LiCoO_2$ left in Residue 1# (8.4 wt%) was substantially greater *cf.* Residue 2# with an overflow addition (0.7 wt%). This is consistent with the chemical analyses of Residue 1# (Co: 5.40 wt%, Li: 0.27 wt%) and Residue 2# (Co: 0.07 wt%, Li: 0.03 wt%), shown in Fig. S3.

Fig. 4 displays the influence of acid concentration on the extraction of Co and Li with the addition of overflow fractions (OF: UF = 1/10) at 80 °C. From the results, it is evident that the leaching efficiency of Co and Li (with the addition of overflow fraction) increases with higher acid concentration. When $[H_2SO_4] \geq$ 2.0 mol/L, leaching efficiencies of Co and Li maintain a high level of above 99%, however, as H_2SO_4 concentration is decreased to 1.5 M, the extraction of Co and Li drops to ca. 93% and 95%, respectively. Additionally, the dissolution of Co and Li with lower acid concentration (1.5 mol/L H_2SO_4) exhibits lower leaching kinetics when compared to that with 2 and 2.5 mol/L H_2SO_4. For example, Co dissolution with both 2 and 2.5 mol/L H_2SO_4 reach a rapid equilibrium after 45 min, whereas when 1.5 mol/L H_2SO_4 is used, equilibrium is not achieved after 60 min irrespective of overflow fraction additions (Fig. 4a). The addition of overflow fractions can however, introduce more impurities (e.g. Al, Fe) that may increase the acid consumption, whilst simultaneously reducing Co and Li extraction. Nevertheless, as the addition of overflow fractions - at a ratio of OF/UF = 1/10 - adds only approximately 1.2 wt% Cu, 1.7 wt% Al and 0.2 wt% Fe to the total levels within the input mate-

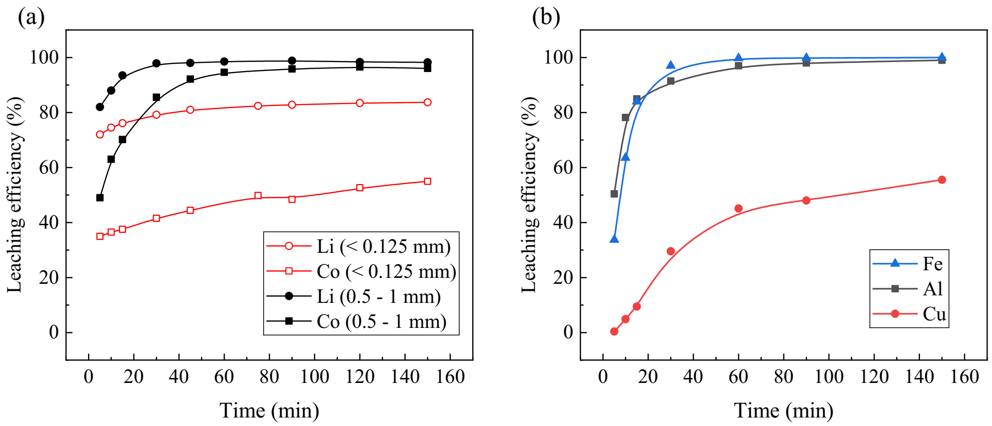

Fig. 2. (a) Leaching efficiency of Li and Co as a function of time using battery waste fractions <0.125 mm and 0.5–1.0 mm; (b) Leaching efficiency of impurity elements as a function of time with the 0.5–1.0 mm battery waste fraction (T = 80 °C, t = 2.5 h, *S/L* = 100 g/L, $[H_2SO_4]$ = 2 mol/L).

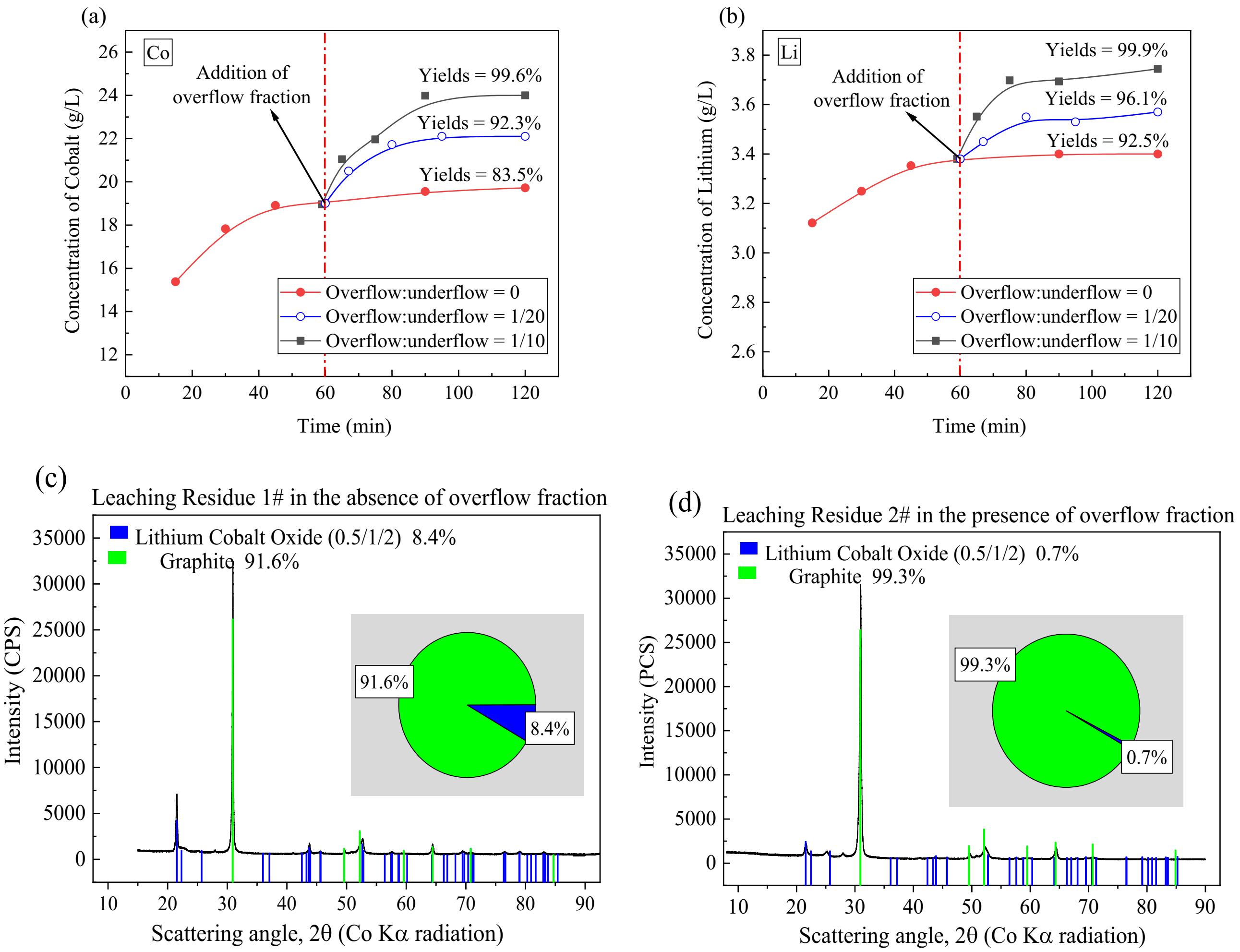

Fig. 3. Comparison of LIBs leaching in the absence and presence of overflow fractions (T = 80 °C, S/L = 100 g/L, $[H_2SO_4]$ = 2 mol/L). (a) Co extraction as a function of time; (b) Li extraction as a function of time; XRD patterns of leach residue in the (c) absence (Residue 1#) and (d) presence (Residue #2) of the overflow fraction (OF:UF = 1/10).

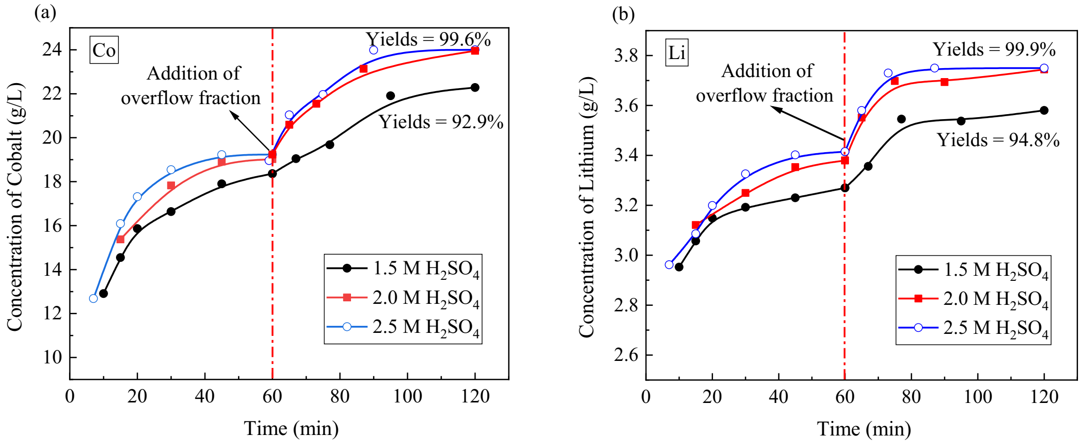

Fig. 4. Behaviors of (a) Co and (b) Li as a function of H_2SO_4 concentration and time (T = 80 °C, S/L = 100 g/L, $[H_2SO_4]$ = 1.5, 2.0, 2.5 mol/L, mass ratio of OF:UF = 1/10).

rial, this will only consume a limited amount of acid (~0.1 mol H_2SO_4 per 10 g of overflow fraction added).

From the results it is clear that addition of overflow fractions can enhance the extraction of both Co and Li to >99%, resulting in leaching residue that contains only 0.07 wt% Co and 0.03 wt% Li (as shown in Fig. S3). For comparison, the extraction of Co and Li in the presence of one of the most commonly reported reductants - hydrogen peroxide - was also studied, based on our previous research (Aaltonen et al., 2017). With the addition of an optimum 5% (v/v) H_2O_2, Co recovery was only ~95% and the Co present within the leach residue was over 2% (Fig. S3). This is probably resulted from the fact that H_2O_2 can readily decompose in the presence of metal ions like Fe^{2+}, Mn^{2+}, Cu^{2+} and Cr^{3+} (Magalhães et al., 2007). Furthermore, the Li (1.4 wt%) and Co (8.4 wt%) present in the overflow fractions, due to association with the electrode materials, can also be recovered when using overflow fractions as additives.

In addition, neutralization tests with leaching solutions (Table S1) in the absence and presence of overflow fractions (OF/UF = 1/10) were investigated and the results, detailed in Fig. S4, reveal that the introduction of impurities from overflow fractions do not cause any discernible increase in the chemical burden for the subsequent purification stage. Details about the neutralization process can be found in supporting materials.

3.3. Influence of metallic components on the dissolution of $LiCoO_2$

In order to determine the effect of the individual elements present in the overflow material on the reduction and yield of Co and Li, experiments that utilized pure substances were undertaken as outlined in Table 2. It is clear from Fig. 5a that acid dissolution of pure $LiCoO_2$ (0.2 mol) has slow kinetics in the absence of reduction agents (*E1-Co*), with Co dissolution only seen to increase from 38% to 55% over 180 min. With the addition of metallic Cu (0.05 mol), Co dissolution displays a marginal increase from 55% to 60% (*E2-Co*), which suggests that metallic copper has only a minor reductive effect on the dissolution of $LiCoO_2$. The addition of a small quantity Fe (0.006 mol) increased Co dissolution (*E3-Co*, Fig. 5a) up to 77% and an equilibrium was reached within 120 min. A similar trend can also be observed for the Cu dissolution in Fig. 5b, which also accelerated after the addition of Fe (*E3-Cu*), which demonstrates that Fe addition promotes both the oxidation (of Cu) and reduction (of $LiCoO_2$) processes. The results suggest that the presence of dissolved Fe ions (Fe^{2+} or Fe^{3+}) play the key role in enhancing the leaching kinetics. Nevertheless, electrons produced by the dissolved Fe ions ($Fe^{2+} \leftrightarrow Fe^{3+}$, 0.006 mol e^-) are not sufficient to provide all the reductive power for the dissolution of $LiCoO_2$ from 58% to 78% ($LiCoO_2 \rightarrow Co^{2+}$, 0.04 mol e^-) or the dissolution of Cu from 25% to 100% after 120 min ($Cu \rightarrow Cu^{2+}/Cu^{+}$, 0.0375–0.075 mol e^-). Therefore, it is postulated that the dissolved Fe ions have a catalytic action (Hiroyoshi et al., 1997), (Hidalgo et al., 2018), that facilitates electron transfer between $LiCoO_2$ and Cu via the following reactions (Eqs. (3) and (4)):

$$LiCoO_2(s) + Fe^{2+} + 4H^{+} \rightarrow Fe^{+3} + Co^{2+} + Li^{+} + 2H_2Oc \quad \Delta_r G_m^{\theta} = -138.21 \text{ kJ/mol} \tag{3}$$

$$2Fe^{3+} + Cu \rightarrow Cu^{2+} + 2Fe^{2+} \quad \Delta_r G_m^{\theta} = -66.71 \text{ kJ/mol} \tag{4}$$

Similar effects between Fe and Al were also found (Fig. 5c and d) as the addition of Al only lead to a minor increase in Co dissolution, whereas after the addition of Fe (0.006 mol) Co dissolution increased by 20% from 55% to 75% ($LiCoO_2 \rightarrow Co^{2+}$, 0.04 mol e^-). Moreover, the Al dissolution kinetics were seen to improve in the

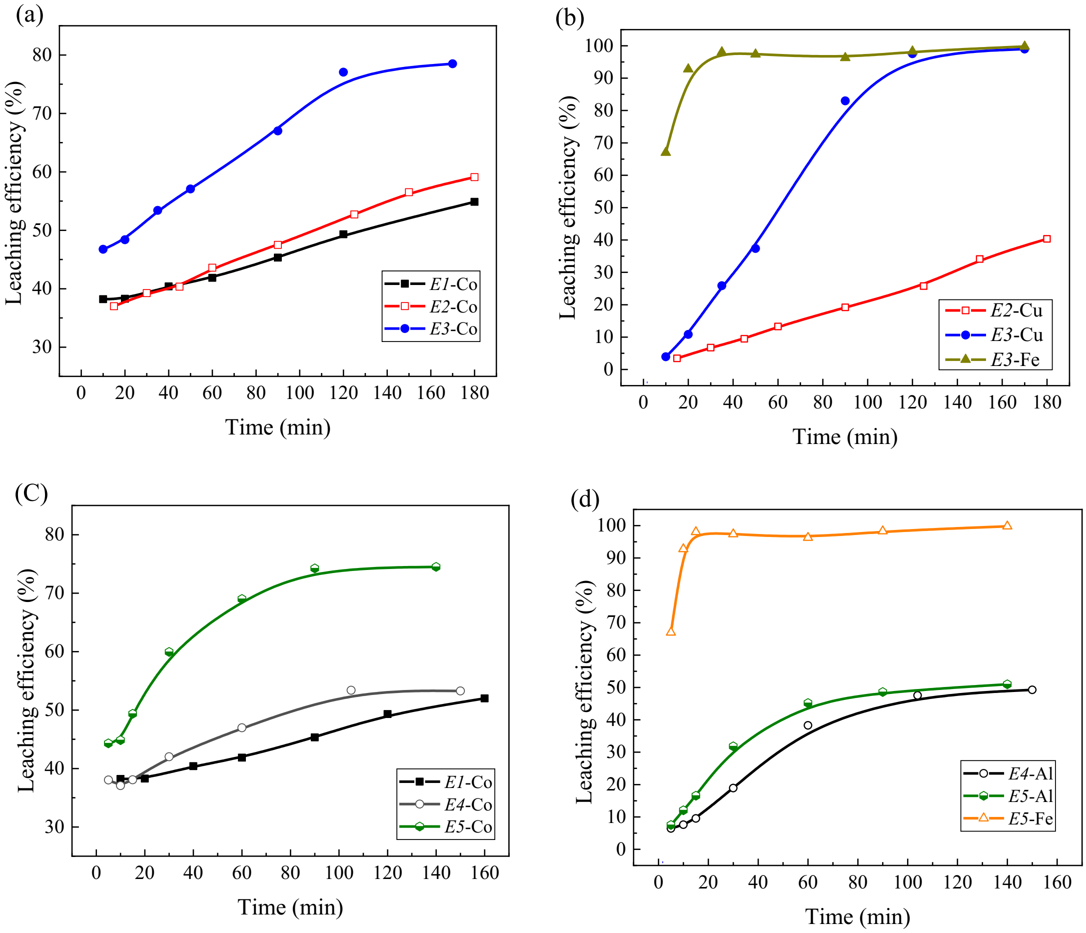

Fig. 5. Leaching of (a) Co in experiments *E1*, *E2*, *E3*; (b) Cu and Fe in experiments *E2*, *E3*; (c) Co in experiments *E1*, *E4*, *E5*; and (d) Al and Fe in experiments *E4*, *E5*. Input materials are as follows: *E1*: $LiCoO_2$, *E2*: Cu + $LiCoO_2$, *E3*: Cu + Fe + $LiCoO_2$, *E4*: Al + $LiCoO_2$, *E5*: Al + Fe + $LiCoO_2$.

initial stage of leaching after Fe was added. This behavior might result from the reactions between Al and Fe^{3+} (Eq. (5)), however, due to the passivation of Al, the equilibrium dissolution of Al only increases ca. 5%.

$$3Fe^{3+} + Al(s) \rightarrow Al^{3+} + 3Fe^{2+} \quad \Delta_r G_m^{\theta} = -679.91 \ \text{kJ/mol} \tag{5}$$

Based on these results, it can be determined that although the addition of Cu and Al separately had only a marginal positive effect on the dissolution of $LiCoO_2$, the co-addition of Fe clearly enhances both Co and Cu (Al) dissolution, primarily as a result of the catalytic effect of Fe ions on electron transfer for Co dissolution. A comparison of the dissolution behavior determined with industrially produced waste fractions containing Cu, Fe, Al (Fig. 2b) shows the results with pure Fe in Fig. 5 exhibits a similar behavior, whereas dissolution of the Cu and Al (Fig. 5b and d) are different from that observed in Fig. 2b. Complete dissolution of the simulated Cu could be achieved as shown in Fig. 5b after 120 min, whereas Fig. 2b shows only ca. 55% Cu was dissolved from spent LIBs fractions after 150 min. This is because a majority of the active materials ($\sim$97%) has already dissolved (Fig. 5b) and there is insufficient active materials left to act as an electron acceptor for Cu oxidation. Conversely, dissolution of Al from spent LIBs fractions occurs more rapidly reaching nearly 100% after 60 min when compared with the dissolution of simulated pure Al scraps. This indicates that no obvious Al passivation occurs during the leaching with industrially produced waste LIBs fractions (Fig. 2b) in contrast to that observed with simulated pure Al scraps (Fig. 5d).

4. Conclusions

In this paper, the influence of metallic components (Cu, Al, Fe) on the acid dissolution of Li and Co from the industrially produced waste LIBs was studied. Leaching experiments using industrial battery waste fractions with different contents of metallic components revealed that the leaching efficiency of Li and Co were enhanced by the increased levels of Cu, Al and Fe in the waste fractions.

Furthermore, the use of industrial battery waste overflow (>2 mm fraction) rich in Cu and Al foil, normally processed via smelting, was proven to support the dissolution of Co and Li from the underflow fractions. This new approach indicates that the large size fractions should not be deeply separated from Co-rich smaller fractions (as conducted in the state-of-the-art industrial pretreatment processes). Acid leaching experiments with pure metallic substances indicate that the presence of Fe in solution is crucial, as it has a catalyzing effect on the reductive behavior of both Al and Cu that results in increased leaching efficiencies of Co and Li up to almost 100%. Consequently, the findings indicate categorically that the emerging circular economy of metals for critical battery materials like Co and Li could be markedly improved by the hydrometallurgical recycling of both OF and UF fractions.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2019.06.048.

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