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Selective extraction of lithium (Li) and preparation of battery grade lithium carbonate (Li$_2$CO$_3$) from spent Li-ion batteries in nitrate system

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HIGHLIGHTS

- Selective extraction of Li from waste LIBs by nitration-roasting-leaching process.
- Further nitration of active materials happens during roasting process.
- Li concentration could be enriched up to 34 g/L by 4-stage cross-current water leaching.
- Battery grade Li$_2$CO$_3$ could be produced from the Li-rich water leaching solution.
- Overall recovery of Li was ∼90%, larger than the previously reported 60–80%.

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ABSTRACT

In this study, a novel method that allows selective extraction of lithium and production of battery grade Li$_2$CO$_3$ is introduced, which includes nitration, selective roasting, water leaching and Li$_2$CO$_3$ preparation. By this method, metallic components in Li-ion battery waste are firstly transformed into corresponding nitrates, and then decomposed into insoluble oxides during roasting except for lithium nitrate, which is ready to be extracted by water leaching. Under the optimum conditions of nitration (70 °C, 5 h, acid-to-scrap ratio of 30 mmol/g), selective roasting (250 °C, 1 h) and 4-stage cross-current water leaching (25 °C, liquid-to-solid ratio of 2:1), lithium extraction up to 93% is achieved, whereas extraction of other metals like cobalt, nickel, copper etc. are < 0.1%. The obtained lithium-rich solution (34.1 g/L lithium) is then subjected to a carbonation step at 95 °C for 30 min to form the desired Li$_2$CO$_3$. The purity of Li$_2$CO$_3$ produced is up to 99.95%, a level above the minimum standards required for battery grade Li$_2$CO$_3$. Application of this new process could significantly improve lithium recovery from waste Li-ion batteries, as the overall recovery of 90% for lithium achieved is much higher than previously reported lithium recovery of 60–80% from waste Li-ion batteries.

1. Introduction

Lithium - a key element in the modern energy revolution - has attracted ever-growing levels of research interest with the increasing demands for Li-ion batteries (LIBs) in everyday consumer electronics, electric vehicles and energy storage materials. This is exemplified by the Li-ion battery industry, which has expand rapidly in recent years and is still driving Li consumption - from 9760 t (2015) to predicted levels of 12,160 t by 2020 and 21,520 t by 2025 [1]. Although the current accessible global lithium reserves are up to 15–30 million tonnes [2], the present production of lithium from rock, clay, and brine resources is only just able to meet the steadily growing demand of lithium for LIBs due to a lack of capacity. For example, it is forecasted by Sonoc and Jeswiet [3] that the world will begin to face a severe scarcity of Li already as soon as the next decade and this future supply crisis can only be avoided by achieving a Li recycling minimum of 90% from spent LIBs [4]. Nevertheless, the prognosis for Li recycling from spent LIBs is not optimistic – a report from the UNEP reveals that the present global recovery of end-of-life Li is less than 1% [5]. Although spent LIBs are recycled worldwide by various companies (Toxco Inc., USA; Sony Corp., Japan; SNAM, France etc.), these industrial pyrometallurgical processes mainly focus on the valuable metals e.g. Co and Ni, whereas...
Li recovery is either neglected or only treat purely as a by-product [6,7]. One of the state-of-art technologies is the Umicore process (Belgium and Sweden), by which Co and Ni can be recovered by melting, whereas Li is lost in the related slags and dusts [7,8]. Consequently, recent research has moved to hydrometallurgical methods that allow for high recovery of Li. The most widely studied hydrometallurgical process typically involves the strong acid based leaching of waste LIBs scraps [9,10], purification [11], and extraction of target metals (e.g. Co, Ni, Mn) [12-14]. Li recovery from the raffinate by evaporation and lithium carbonate precipitation, although only ca. 60–80% Li can be recovered through this process [15,16]. One main reason for such a low Li recovery can be attributed to the fact that Li losses occur at numerous points within the complicated LIBs recovering flowsheet from acid leaching followed by Co, Ni extraction to evaporation and Li2CO3 precipitation. For example, research by Nan et al. [17] shows that up to 26.2% Li can be co-extracted by two-stage counter-current extraction for Co and Ni with 1 M Cyanex 272 and 5% TBP as modifier (O:A = 1:0.77, pH = 6.5). Additionally, in the evaporation process, lithium readily forms complex salts (e.g. Li2SO4 · Na2SO4) with sodium that is introduced from the treatment of impurities, extraction of valuable metals and pH adjustment process that leads to significant losses of Li [18].

As a result, in order to increase Li recovery, some novel methods have been designed to simplify the Li recovery process by preferentially separating Li from other metals (e.g. Co, Ni, Mn), i.e. selective extraction of Li from spent LIBs. Organic acids like oxalic acid [19] and tartaric acid [20], for example, have been investigated and have shown good selectivity for Li over the other metals during waste LIBs leaching. Through this selective leaching process, Li can be enriched into the leaching solution in the form of soluble lithium-related salts (lithium oxalate and lithium tartrate), whereas the other metals (e.g. Co) are left in the leaching residue. Similar research has also been reported on the utilization of mild phosphoric acid as a leaching agent to selectively dissolve Li as LiH2PO4, whilst Co, Ni, Mn mainly remain in the solid phase as their respective phosphate precipitates [21,22]. In this case, Li can be directly extracted as Li2PO4 from the leaching solution - via an increase in pH - although final product purity only approximately 97%. In order to increase Li recovery, certain amount of reducing agents (e.g. 3–5 vol% H2O2) have to be consumed in the acid leaching process. Another interesting method is called oxidizing leaching [23,24], through which considerable amount of Li could be selectively leached out in the presence of acid and oxidizing agents (chlorine and sodium persulfate), whereas the other metals such as Co, Ni and Mn remain in solids at higher valences. In general, Li-rich leaching solutions with trace impurities can be obtained via selective acid leaching processes, and effectively shorten the overall Li recovery process. Nonetheless, these technologies involve high levels of organic or mineral acid consumption and additives - H2O2, chlorine or sodium persulfate. Another distinct disadvantage of these acid-based leaching processes is that significant quantities of alkali compounds are needed to neutralize the acidic leaching solution as Li recovery is best carried out under alkaline conditions (ca. pH 10–12) in order to ensure the high recovery and purity of final products.

Considering the abovementioned shortcomings of hydrometallurgical methods, researchers start to seek for combined methods to selectively extract Li from LIBs by e.g. roasting [25,26], vacuum evaporation or entraining gas evaporation [27] followed by water leaching. Among these methods, roasting-water leaching is considered as one of the most promising as the process has been previously shown to be effective in the Li industry as a way to treat the resistive minerals of lithium - spodumene (LiAlSi2O6) and petalite (LiAlSi4O10) [28]. A related technology, sulfidation-roasting-leaching for the preferential recovery of Li from waste LIBs has been developed and is based on the use of acidic sulfates (MgSO4, (NH4)2SO4, NaHSO4) to transform active materials (LiCoO2) into soluble Li2SO4 (or NaLiSO4) and insoluble Co2O3 by roasting between 600 and 800 °C [26,29]. This roast product is then subsequently treated by water leaching to produce a Li-rich sulfate solution from which pure Li2CO3 can be prepared. By utilization of this step-wise sulfidation-roasting and water leaching process, Li could be preferentially extracted from active materials with recovery levels of up to 90%. However, this method is not entirely suitable for the practical treatment of waste LIBs scraps, which contains both active materials and other components like carbon. Previous research [25] has shown that in the presence of C, part of lithium in active materials (LiCoO2) will be transformed into Li2CO3 (reaction 1), whose solubility is very low (13 g/L, 20 °C). Consequently, the formation of Li2CO3 during roasting process will greatly reduce the Li extraction efficiency.

\[
\text{LiCoO}_2 + C \rightarrow \text{Li}_2\text{CO}_3 + \text{Co} + \text{CO}_2
\]

Nevertheless, this behavior of Li containing active materials with carbon has been exploited in reduction roasting [30,31], which results in the transformation of LiNi0.5Co0.5Mn0.5O2 into Li2CO3, Ni, Co and MnO in the presence of graphite or lignite at ca. 650 °C for 3 h Li2CO3 produced via this method was then selectively extracted as LiHCO3 by leaching with carbonated water at ambient temperature. Like the sulfuration process, reduction roasting needs to be conducted at temperatures above 600 °C as C is otherwise too stable to react with Li2CO3 (e.g. 300 °C) as previously demonstrated by TGA-DSC analyses for the mixtures of Li2CO3 and C in air and argon atmospheres [25,30]. It is worth noting that only ca. 85% Li could be selectively extracted by the carbonated water leaching from the reduction roast produced, this resulted in LiHCO3 solution containing 4.4 g/L Li under optimum conditions. These findings suggest that the excess amount of water would need to be vaporized from the LiHCO3 solution in order to produce the desired Li2CO3 product.

Therefore, it is meaningful to develop a process to selectively extract Li from spent LIBs with high recovery at lower temperatures. It is well known that most nitrates readily decompose at low temperatures, for example, Al(NO3)3 at ca. 125–175 °C, Cu(NO3)2 at 150–225 °C, Co (NO3)2 at ca. 150–225 °C [32], and Ni(NO3)2 at ca. 150–250 °C [33], whilst in contrast LiNO3 has a decomposition temperature at ca. 600 °C [34,35]. Based on this significantly large difference, the authors suggest that selective extraction of Li from waste LIBs by a ‘nitration-roasting-leaching’ process route would be favorable when compared to the previously reported ‘reducing roasting-leaching’ [30] and ‘sulfidation-roasting-leaching’ processes [26]. After nitration, most of the constituent elements in LIBs scrap are transformed into their corresponding nitrates; these can then be easily decomposed into insoluble oxides at the appropriate roasting temperatures (< 300 °C) with the exception of lithium nitrates. Subsequent water leaching of the roast allows the selective dissolution of lithium nitrate, in preference to the other insoluble oxides. Furthermore, in the lithium recovery step, the high energy-consuming evaporation step that is widely utilized in sulfate system, can be avoided due to the fact that lithium nitrate has a high solubility [36] and furthermore lithium concentration can be effectively increased by cross-current leaching. In terms of the nitrogen oxides gases produced in the roasting process, these can be recycled into nitric acid either by pressurized acid adsorption, catalyst or oxidizing agents (e.g. H2O2, ozone), which has previously been proved to be feasible for the treatment of tail gases from nitric acid plants, pickling units or catalyst calcinatory [37–39]. The nitric acid produced via this methodology could then be recycled for use in the earlier nitration step of the proposed process. Thus, a sustainable and closed-loop process can be achieved with lower roasting temperatures and higher Li extraction compared to earlier published literature.

2. Experimental

2.1. Materials and characterization

A company working in the recycling business of batteries and accumulators provided the input materials (< 2 mm) used in this
and V are the concentration and the volume of water leaching solution. In order to avoid nitrous (NOx) gas build-up, the waste gas was fed sequentially via two nickel, manganese mainly exist as LiCoO2 and LiCo0.25Ni0.65Mn0.1O2.

Fig. 1a reveals that lithium, cobalt, copper, nickel, manganese mainly exist as LiCoO2 and LiCo0.25Ni0.65Mn0.1O2 forms. In contrast, copper is in the elementary form, whereas aluminum is observed in both elementary and oxide forms.

2.2. Experimental procedures

Acid-mixing (nitrification) process: The nitrification process was carried out using a two gram sample of LIBs scrap, which was mixed in a cylindrical alumina crucible with various amounts of nitric acid, before being placed in a shaking bath (200 rpm) at 70 °C for 5 h. In order to obtain homogenous mixing and prevent any explosive reactions, the concentrated nitric acid was diluted to 45% (10 mol/L) with distilled water prior to the addition of the LIBs scrap.

Selective roasting process: After the nitrification process, roasting of the acid-scrap mixture in a ventilated preheated furnace (SCANDIA, Type K4/PDI 40) was investigated with the parameters of roasting time of 30–90 min, roasting temperature of 100–300 °C and acid dosage of 5–35 mmol/g (acid-to-scrap ratio). In order to prevent any corrosive nitrous (NOx) gas build-up, the waste gas was fed sequentially via two Dreschel bottles that contained 250 mL alkaline solution (2 M NaOH and 5% H2O2) in order to achieve neutralization [41].

Table 1

<table>
<thead>
<tr>
<th>Elements</th>
<th>Li</th>
<th>Co</th>
<th>Ca</th>
<th>Cu</th>
<th>Ni</th>
<th>Al</th>
<th>Mn</th>
<th>Fe</th>
<th>Zn</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
<td>3.65</td>
<td>23.6</td>
<td>6.24</td>
<td>2.72</td>
<td>1.73</td>
<td>0.66</td>
<td>0.01</td>
<td>57.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Equation (2):

\[ \chi = \frac{(C \times V)/(m_i \times w_i)}{100} \]  

where \( m_i \) (g) and \( w_i \) (wt.%) are the mass of the input materials and the compositions of element (i), respectively; C and V are the concentration of element (i) and the volume of water leaching solution. In order to ensure the accuracy of these findings, the leaching residue were also analyzed to further verify the results. Some experiments were repeated three times and the variations of the results were presented where appropriate as error bars.

Water leaching process: The roast obtained at 250 °C with 6.0 mL HNO3 (45%), 10 mol/L per 2.0 g of LIB scrap (acid-to-scrap ratio = 30 mmol/g) were leached with distilled water at room temperature. The influence of the liquid-solid (L/S) ratio (from 1:1 to 20:1) and contact time (from 5 to 480 min) on the water leaching process were studied. In addition, a four-stage cross-current water leaching process was conducted by contacting the pregnant leaching solution (PLS) successively with fresh rinse for 30 min at room temperature with a fixed L/S ratio of 2:1. The leaching residue produced were collected and then further treated by a two-stage water leaching for 30 min with L/S = 2:1. The concentrated PLS produced by the four-stage cross-current water leaching were utilized as the input solution for the preparation of lithium carbonate.

Preparation of lithium carbonate: Lithium-rich PLS obtained from the leaching process was firstly purified by increasing the pH value to 12.0 with 2M NaOH followed by filtering to remove the precipitated impurities. The clear filtrate was added dropwise into sodium carbonate solution (Na2CO3, 300 g/L) with a fixed molar ratio of Na2CO3:Li+ = 0.6:1, at different temperatures to produce lithium carbonate. In order to investigate the influence of lithium concentration, Li-bearing solutions of different concentrations were prepared from the clear filtrate by dilution and evaporation. The obtained lithium carbonate products were washed two times with hot distilled water (ca. 95 °C) before being dried in an oven for 2 h at 240 °C to completely remove the residual water. Purity of Li2CO3 and the contents of impurities were measured according to methods proposed by Standardization Administration of PRC, including acid-base titration, AAS and ICP-OES [42]. The particle size distribution of Li2CO3 was analyzed with a Malvern Mastersizer 3000.

3. Results and discussion

3.1. Nitrification and selective roasting

3.1.1. Acid mixing (nitrification)

The chemical reactions between nitric acid and the various components present with waste LIBs are by definition relatively complex. In order to define the amount of acid to achieve the desired nitrification process, reactions between waste LIBs components and nitric acid were simplified as outlined in reaction 3–8, where Co, Ni, Mn were assumed to exist as LiCoO2, LiNiO2, LiMnO2, and the other metals were assumed to be elementary forms. The minimum stoichiometric nitric acid (45%) needed for the nitrification process was found to be approximately 22.5 mmol per gram of waste LIBs scrap. Therefore, in order to ensure the maximum conversion of the scrap in nitrate mixture, 35 mmol nitric acid (45%) per gram of LIB scrap (equivalent to an acid-to-scrap ratio, 35 mmol/g) was used.

LiCoO2 + 4HNO3 = LiNO3 + Co(NO3)2 + NO (g) + O2 (g) + H2O  

LiNiO2 + 4HNO3 = LiNO3 + Ni(NO3)2 + NO (g) + O2 (g) + H2O  

LiMnO2 + 4HNO3 = LiNO3 + Mn(NO3)2 + NO (g) + O2 (g) + H2O  

Fe + 4HNO3 = Fe(NO3)3 + NO (g) + 2H2O
In order to accelerate the nitration process, acid-scrap mixture were placed in a shaking bath (200 rpm) at 70 °C for 5 h before the resultant mixture was dissolved with distilled water (L/S = 25:1) for 30 min at ambient temperature. From the XRD patterns of the residue displayed in Fig. 1b, peaks corresponding to active materials (Li0.61CoO2 and LiCoO2) could be clearly identified. This indicates an incomplete nitration of the active materials even after treatment at 70 °C for 5 h. The respective extraction rates for Co and Li were ca. 80% and 85%, which is consistent with previous research that has shown nitric acid can only dissolve approximately 80% of the active materials (LiCoxNiyMnzO2) in the absence of reducing agents [40].

\[
\begin{align*}
Al + 4HNO_3 & = Al(NO_3)_3 + NO(g) + 2H_2O \\
1.5Cu + 4HNO_3 & = 1.5Cu(NO_3)_2 + NO(g) + 2H_2O
\end{align*}
\]

In order to accelerate the nitration process, acid-scrap mixture were placed in a shaking bath (200 rpm) at 70 °C for 5 h before the resultant mixture was dissolved with distilled water (L/S = 25:1) for 30 min at ambient temperature. From the XRD patterns of the residue displayed in Fig. 1b, peaks corresponding to active materials (Li0.61CoO2 and LiCoO2) could be clearly identified. This indicates an incomplete nitration of the active materials even after treatment at 70 °C for 5 h. The respective extraction rates for Co and Li were ca. 80% and 85%, which is consistent with previous research that has shown nitric acid can only dissolve approximately 80% of the active materials (LiCoO2) in the absence of reducing agents [40].

3.1.2. Selective roasting

The roasting of acid-scrap mixture with respect to acid dosage i.e. acid-to-scrap ratios, roasting time, and roasting temperatures were investigated and the results are presented in Fig. 2a, Fig. 2b and c, respectively. The roasted material obtained were treated by water leaching (L/S = 25:1, 30 min, room temperature) to evaluate the efficiency of the combined nitration-selective roasting process. It can be observed from Fig. 2a and b that selective extraction of Li towards other metals could be achieved with acid-to-scrap ratio above 25 mmol/g and roasting time above 1 h at 250 °C. The Li extraction reached up to 98%, much higher than that achieved in the absence of roasting (85%). This means roasting step was beneficial for Li extraction, which could be also observed from Fig. 2c, concerning the influence of roasting temperatures between 100 and 275 °C.

As comparison, results after acid mixing in the absence of the roasting step are also included in Fig. 2c (denoted in red). It can be seen that roasting of the acid-scrap mixture at 100 °C for 1 h results in no change when compared to the metals dissolution into the water directly after nitration (in the absence of roasting). XRD patterns of nitrat-roasted (100 °C) LIBs waste in Fig. 3a reveal clearly peaks corresponding to nitrates of lithium, cobalt and copper, which disappear after water leaching in Fig. 3b, the XRD patterns of leaching residue. Although peaks corresponding to Al, Fe, Ni, Mn could not be clearly identified in the XRD of roast (100 °C, Fig. 3a), most of these metals can still be assumed to be in the form of nitrates prior to water leaching because they could be analyzed in the solution (Fig. 2c). It is worth noting that peaks related to Li0.61CoO2 can be identified in both Fig. 3a and b. This suggests an incomplete nitration of the active materials (e.g. LiCoO2) by acid-mixing followed by roasting at 100 °C for 1 h. As roasting temperatures increase from 100 to 150 °C in Fig. 2c, the extraction of Fe and Al show significant decrease - from 88% to 3.5% (Fe) and 77%–26.5% (Al), whereas Cu undergoes only a slight reduction (from 60% to 55%). This behavior can be attributed to the partial decomposition of corresponding nitrates, i.e. aluminum nitrate and iron nitrate starting at ca. 125 °C, copper nitrate at ca.150 °C. Conversely, extraction of Li, Co, Ni and Mn show the opposite trend, with increases of 10–15% (from 80-85%–95% for Ni, Co, Mn; 88%–98% for Li) determined under the same conditions. With the further increase in roasting temperature from 150 to 250 °C, the extraction of all metals - except for Li - is shown to decrease before levelling off below 0.1% at 250 °C. At these conditions Li extraction remains almost constant.
The XRD patterns of roasts after 250 °C (Fig. 3c) show that the peaks related to copper and cobalt nitrates (Fig. 3a) disappear while the peaks that correspond to lithium nitrates remain and only disappeared after the water leaching step (Fig. 3d). By contrast, the peaks related to carbon can be identified in all samples, which is consistent with previous research that demonstrated that C stability is such that there is a very limited reaction with either oxygen or LiCoO2 at temperatures below 600 °C [25,30]. In addition, it can be also observed that peaks corresponding to Li0.61CoO2 that exist in Fig. 3a and b disappear in Fig. 3c and d. This suggests further nitration of the active materials can take place during the roasting step.

SEM morphologies of the samples roasted at 250 °C (Fig. S2b) comprise of finer particles and tend to be more amorphous without phase boundaries when compared to the waste cathode materials (Fig. S2a). This can partly explain why there are no clear phases related to Ni, Mn, Al, Cu etc. identified in the XRD analysis (Fig. 3c and d). In order to further determine the more exact form of these elements (Ni, Mn, Al, Cu etc.), mapping analysis of the roast of 250 °C (Fig. S2c) and its leaching residue (Fig. S2d) were conducted. Results reveal that the distribution regions of O, Co, Ni, Mn, Al, Cu and Fe are coincident and combined with each other without any obvious distribution boundaries in either the roast or its leaching residue, which is in contrast to their distribution in the raw material (Fig. S1) where Co, Al and Cu exist as separate phases with discernable phase boundaries. This change in the elemental distribution is suggested to be attributed to the fact that these metals are firstly dissolved as nitrates during nitration process and then decomposed as related insoluble oxides simultaneously at 250 °C. It should be noted that elements like lithium and nitrogen are generally unable to be detected by means of EDS, consequently there are no Li and N distribution regions present in Fig. S2c, although the LiNO3 phase is clearly identified by XRD (Fig. 3c).

To sum up, the selective extraction of Li from waste LIBs can be achieved through the combination of nitration (acid-to-scrap of 30 mmol/g, 75 °C, 5 h), selective roasting (roasting time of 1 h, roasting temperature of 250 °C) and water leaching (L/S = 25:1, room temperature, 20 min).

The different trends seen for Li, Co, Ni, Mn with respect to those of Fe, Al and Cu at temperature range from 100 to 150 °C (Fig. 3c) can be attributed to the further nitration of the residual active materials (e.g. LiCo0.5Ni0.5Mn0.9O2) in the acid-scrap mixture during the roasting process. Nevertheless, nitric acid readily decomposes at temperatures above 100 °C and Fig. 2d shows the pH values with the respective titrated H+ concentration of the water leaching solution of acid-scrap mixture and roast. It can be observed that H+ concentration in water leaching solutions from raw material roasted at temperature higher than 100 °C were ≤ 10−3 mol/L, which is significantly lower than that obtained from the acid-scrap mixture prior to the roasting step. This indicates that nearly all the excess nitric acid has been decomposed or vaporized at T > 100 °C and that active material (e.g. LiCo0.5Ni0.5Mn0.9O2) nitration cannot take place with nitric acid during the roasting process. In other words, the further nitration of active materials (e.g. LiCo0.5Ni0.5Mn0.9O2) during roasting step must happens with other nitrates, for example nitrates of aluminum, copper and iron.

In order to prove the above hypothesis, Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) analysis were conducted in air atmosphere at a heating speed of 5 °C/min with the mixture of pure LiCoO2 powders and aluminum nitrate, iron nitrate as well as copper nitrate, respectively. Taking aluminum nitrate as an example, Fig. 4 summarizes the TGA-DSC results of a) LiCoO2, b) Al(NO3)3⋅9H2O, c) the mixture of Al(NO3)3⋅9H2O and LiCoO2 powders as well as d) Co(NO3)2⋅6H2O. It can be observed that there is no distinct DSC thermogram peaks and weight loss transitions for LiCoO2 whereas for Al(NO3)3⋅9H2O, a sharp endothermic peak accompanying with great weight loss can be identified in the temperature range of 125–175 °C, which can be assigned to the decomposition of aluminum nitrate into Al2O3. For the mixture of 80% Al(NO3)3⋅9H2O and 20% LiCoO2 powders in Fig. 4c, two extra DSC thermogram transitions at ca. 175 and 250 °C could be identified, compared with that of single chemicals in Fig. 4a and b. Based on previous research [32,33], these two thermogram peaks are probably corresponding to the decomposition behaviors of cobalt nitrate, of which the DSC results are presented in Fig. 4d.

The XRD patterns of roasts produced at 150 and 250 °C with mixture of 80% Al(NO3)3⋅9H2O and 20% LiCoO2 are presented in Fig. S3. The diffraction peaks of lithium nitrate and cobalt nitrate can be clearly discerned from roasts at 150 °C (Fig. S3a). When the temperature increased to 250 °C (Fig. S3b), the peaks corresponding to the cobalt nitrates disappear, whereas those associated with lithium nitrate are remained and even more obvious. This formation of cobalt nitrate and...
its subsequent decomposition can be visually confirmed via the change in color of the roasts from pink to black (in Fig. S3). In order to quantify how much LiCoO₂ were transformed into dissolvable nitrates, the roasts obtained at 150 and 250 °C were further subjected to water leaching with S/L = 150 g/L at room temperature for 20 min. Results show that leaching efficiency of Li increase from 49.5% (roasts at 150 °C) to 77.5% (roasts at 250 °C). This finding confirms the phenomenon that the active materials (e.g. LiCoO₂) can react with metallic nitrates (e.g. Cu(NO₃)₂; Al(NO₃)₃; Fe(NO₃)₃), to form lithium nitrate and cobalt nitrate during the roasting process in a manner similar to that reported for the sulfidation roasting process, where active materials (LiCoO₂) react with acidic sulfates like MgSO₄, (NH₄)₂SO₄ or NaHSO₄.

3.2. Water leaching process

3.2.1. Influence of L/S ratios and leaching time

Extraction of Li from the roasts (acid-to-scrap = 30 mmol/g, roasting time = 1 h, roasting temperature = 250 °C) by water leaching was investigated at 25 °C with different L/S ratios of water to roasts (1:1 to 20:1 mL/g) and reaction times (between 5 and 480 min). Li concentration in the water leaching solution was measured by ICP-OES and from these results the Li extraction was calculated based on the assumption that the solution volume remained constant throughout the water leaching process.

The results in Fig. 5a show that with an increase in the L/S ratio, Li extraction improves resulting in the gradual decrease of Li concentration in solution. When the L/S ratio is 20:1, Li extraction reaches 97.9%, from a Li concentration of 1.5 g/L in solution, however, at lower L/S ratios (e.g. 1:1–5:1, mL/g), the Li extraction is lower ca. 80–90% (room temperature, 30 min) even though LiNO₃ readily dissolves in water with a solubility of 70.1 g per 100 mL H₂O at 20 °C. Theoretically, Li extraction should maintain a high level at different L/S ratios, rather than increase with higher L/S ratios. In order further investigate this phenomenon, the dissolution kinetics of Li with an L/S = 2:1 was studied, in more detail (Fig. 5b). As can be observed, ca. 80% of Li dissolves very rapidly during the first 5 min, after which the dissolution kinetics decreases significantly with only a ca. 5% increase in Li extracted over the next 25 min. For the residual 15% Li, dissolution takes place even more slowly with equilibrium reached only after 480 min, although the final Li extraction reaches up to 97% a value very close to that achieved with L/S = 20:1 after 30 min (Fig. 5a). These results suggest that the low Li extraction at low L/S ratios in Fig. 5a are the result of the system kinetics, i.e. Li extraction at low L/S ratios is unable to reach equilibrium after 30 min. One possible reason for the slow dissolution kinetics observed in Fig. 5b, is that the LiNO₃ particles present may be trapped by some of the other phases that are produced during the roasting process. For example, based on the mapping analysis results of roasted materials produced at 250 °C (Fig. S2), the distribution of Co, Ni, Mn, Fe, Cu, Al and O were found to be coincident, which suggests these elements mainly exist in the oxide form and that these oxides are embedded or combined with each other. This finding may also explain the measured Li kinetics as it is highly likely that also a portion of Li containing material is trapped by the other oxides during the roasting process, which would limit the Li dissolution. From the results shown in Fig. 5a and b, it can be concluded that a majority of Li is extracted after only 30 min and that the residual Li can be more effectively extracted with higher dilutions (e.g. L/S = 20:1) or longer leaching times (e.g. 480 min).

Previous research by Zhu et al. [43] has shown that the precipitation efficiency of Li₂CO₃ product by carbonation directly correlate with lithium concentration in solution. Consequently, in order to improve both the concentration of Li in solution and the final Li extraction, a
cross-current multistage leaching process that comprised multiple contacts of water leaching raffinate with fresh roast material was performed using an L/S ratio of 2:1 and leaching time of 30 min (Fig. 6). Since Li extraction is only ca. 85% after 30 min with L/S = 2:1 (as shown in Fig. 5b), the wet leaching residues that still contain part of the Li were then collected and washed twice more with fresh water for a few hours. At each stage, the leachate was separated by centrifugation at 600 rpm for 10 min after the leaching process.

As outlined in Fig. 6, Li concentration can be effectively enriched from 12.0 g/L to 34.2 g/L by contacting solution with fresh roasts in four stages. Washing solution (W1) that had a 6.0 g/L Li can also be reused as the leaching agent at the first water leaching step in the process. The final leach residue was subjected to total dissolution with aqua regia after drying at 80 °C for 24 h, followed by ICP analysis. Chemical analysis revealed that the final leaching residue consisted of 0.28% Li, 24.6% Co, 6.5% Cu, 2.8% Ni, 1.8% Mn. Overall, the total recovery of Li was calculated to be 93% based on Li content in the leach residue following equation (9):

$$\gamma = (1 - \frac{m_{t} \times w_{l}}{m_{w} \times w_{o}}) \times 100\%$$  (9)

Where $\gamma$ is the extraction of Li (%); $m_{t}$ and $m_{w}$ are the mass of leaching residue and roasts (g), respectively; $w_{l}$ and $w_{o}$ are the contents of Li in the leaching residue and roasts (%), respectively.

3.3. Preparation of lithium carbonate

The concentration of metals in PLS4 obtained from the 4-stage circular leaching process – outlined in Fig. 6 - are presented in Table 2. As

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Chemical compositions of Li-bearing solution for the precipitation of Li$_2$CO$_3$ before (PLS4) and after purification (PLS5).</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLS</td>
<td>pH</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>PLS4</td>
<td>6.6</td>
</tr>
<tr>
<td>PLS5</td>
<td>12.0</td>
</tr>
<tr>
<td>Purification efficiency %</td>
<td>0.0</td>
</tr>
</tbody>
</table>
distribution of the produced Li₂CO₃ in Fig. 7b show that the specific surface area and volume weighted mean diameter were 24.10 m²/g and 5.10 μm, respectively, which is superior to that produced from a synthetic sulfate solution under the same conditions. Overall, the Li₂CO₃ produced had a purity of 99.95% and a mean diameter of 5.10 μm making it suitable for use as battery grade Li₂CO₃, whose requirements are > 99.5% purity and a d₉₀ (the diameter of 90% particles) of between 9 and 15 μm [46]. In comparison, most of the produced Li₂CO₃ by other methods with purity of 90.0% [44], 98.1% [47], 98.9% [30], 99.1% [45] does not meet the standards required for battery grade Li₂CO₃, which indicates additional processes such as precipitation with蜥蜴和钠化物Na₂CO₃ solution [24] are necessary in order to improve the purity of Li₂CO₃.

It is noteworthy that the residual solution produced from the Li₂CO₃ precipitation are rich in NO₃⁻ (4.9 mol/L), Na⁺ (5.9 mol/L), Li⁺ (0.25 mol/L), CO₃²⁻ (0.6 mol/L) etc. Referring to the industrial practice about treating the low-Li high-Na sulfate solution [45], one of the feasible methods to treat this type of nitrate solution is to firstly recover Li with Na₃PO₄ and then remove the residual CO₃²⁻ by adjusting pH values, producing quite pure sodium nitrate solution (ca. 500 g/L NaNO₃), which can be utilized to produce by-product of NaNO₃ by evaporation and crystallization.

3.4. Base metal extraction from the leach residue

Due to the high content of valuable metals in the leaching residue after water leaching, acid leaching of this material with 2 M H₂SO₄ and 2% (v/v) H₂O₂ at 75 °C for 2 h with L/S = 10:1 was explored as a method to extract these valuable metals. As shown in Fig. S5, the peaks that represent cobalt oxides totally disappear after acid leaching. Residual contents of Co, Ni, Mn, Cu in the acid leach residue were determined to be 0.18%, 0.07%, 0.04%, 0.03%, respectively. The acid leaching solution obtained was found to be rich in Co (24.3 g/L), Ni (2.75 g/L), Mn (1.75 g/L), Cu (6.35 g/L) and can be treated using classic state-of-art technologies such as selective precipitation or solvent extraction [12–14]. A proposed flowsheet for treating LIB scrap as a whole is outlined in Fig. 8.

4. Conclusions

This research proposes an efficient method to selectively extract Li and produce battery grade Li₂CO₃ from waste LIBs by 'nitrification-roasting-water leaching' followed by carbonization process as summarized in Fig. 8. The study shows that:

1. Li could be selectively extracted from waste LIBs scrap by nitrification, roasting and water leaching as nitrates of Al, Fe, Co, Ni, Mn, Cu etc. readily decompose into their insoluble oxides during roasting, while lithium remains as lithium nitrate throughout the proposed roasting process.

2. Extraction of Li could be increased by ca. 10% at roasting process (> 100 °C) when compared to process in the absence of roasting. This can be explained by the further nitrification of active materials (e.g. LiCoO₂Ni₇MnO₂) with other nitrates (e.g. Al(NO₃)₃).

3. A 4-stage cross current water leaching process (instead of vaporization) was proved to be effective to enrich lithium concentration in PLS to 34.2 g/L at ambient temperature with L/S = 2.1.

4. Battery grade Li₂CO₃ (99.95%) could be produced from the purified Li-rich nitrate solution by carbonation with purified Li-rich solution (pH 12.0) added dropwise into Na₂CO₃ solution (300 g/L) at 95 °C for 30 min. The obtained Li₂CO₃ with a volume weighted mean diameter of ~5 μm, was compatible to the reported commercial Li₂CO₃ and much finer than that achieved with synthetic sulfate solution of the same concentration, the equivalent volume weighted mean diameter of which was of ~63 μm.

Fig. 7. Characterization of the prepared Li₂CO₃. a) Impurities contents of prepared Li₂CO₃ in nitrate system with XRD patterns as an inset, b) Particle size distribution of Li₂CO₃ prepared from nitrate and sulfate system.
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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpowsour.2019.01.072.
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