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Separation of Li and Al from spent ternary Li-ion batteries by in-situ aluminum-carbon reduction roasting followed by selective leaching

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Abstract

During the reduction roasting of waste ternary Li-ion batteries (LIBs), a large amount of carbon reductant is introduced in the recycling process, which is not conductive to achieve the goal of carbon peaking and carbon neutrality. This research proposes to make full use of aluminum and carbon – main constituents of waste LIBs – as reductants in the roasting process. Results show that the aluminum-carbon reduction roasting method has a higher efficiency compared with the traditional carbon reduction. Lithium present in ternary materials can be almost completely transformed into soluble Li_2CO_3, while the associated Ni, Co and Mn are all converted into insoluble metal elements or their corresponding oxides at 650 °C (t = 90 min). The presence of Al decreases the carbothermal roasting temperature, while the presence of waste carbon allows Li to be converted into easily soluble lithium carbonate in preference to lithium aluminate. The optimal amount of carbon and Al in the spent LIBs were 14.7% and 7.0%, respectively. After roasting, > 97% of Li could be selectively leached by carbonated water leaching, while only < 0.5% of Al, Ni, Co, and Mn dissolved. The leach residues obtained were purified by alkali treatment with 3 mol/L NaOH at 90 °C to achieve > 99% Al separation. These results suggest that the in- situ aluminum-carbon reduction roasting, followed by selective leaching of Li and Al, mitigates several of the challenges related to battery recycling: (i) Li extraction is increased substantially above the state-of-the-art recovery efficiencies, (ii) Al - known to decrease battery metals extraction in hydrometallurgical processing - is selectively removed after making full use of its reducibility and (iii) battery metal-rich residues with low im- purity levels is produced for further refining, therefore paving the way towards more economical, efficient and environmentally friendly spent LIBs recycling.

Keywords: Waste LIBs; Sustainable recycling; Aluminum-carbon reduction: Selective separation

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1. **Introduction**

The LIBs are widely used in electric vehicles (BEVs) and various electronic products due to their high energy density, high conversion efficiency, long lifetime and good safety properties (Goodenough and Park, 2013; Huang et al., 2016; Huang et al., 2018; Yang et al., 2016). Moreover, a majority of national strategies currently being adopted worldwide are putting emphasis on the need for increased electrification of society supported by batteries and this is coinciding with a rapid development phase within the LIBs industry. The range of applications for LIBs are constantly broadening and there has been a concurrent increase in the overall market share of LIBs (Jung et al., 2021; Liu et al., 2021; Zhang et al., 2021). However, the average effective life of LIBs for BEVs is relatively short, which means that a large number of LIBs will start to reach their end-of-life (EoL) over the next few years (Ghassa et al., 2021; Meshram et al., 2020; Wang et al., 2020a). The global amounts EoL battery materials in 2035 are predicted to be equivalent to ca. 104 GWh (Chen et al., 2016; Ku et al., 2016). In addition to Li, waste LIBs also contain other valuable metals such as Ni, Co, Mn as well as toxic organic substances (Lebedeva and Boon-Brett, 2016; Sun et al., 2016; Yang et al., 2017), therefore there are both economic and envi- ronmental aspects related to the efficient recycling of LIBs (Cao et al., 2018; Zeng et al., 2014; Zhang et al., 2018).

The predominant recycling process for spent LIBs that has been used in recent times has been based on pyrometallurgical high temperature smelting. Umicore of Belgium, Toxco Inc. of the United States, and Sony Corp of Japan all use smelting processes to recover the valuable metals from waste batteries. Such processes provide good recovery efficiencies for the valuable metals like Ni, Co and Cu, whereas Li and Mn are lost or treated as a by-product only (Heydarian et al., 2018; Zhang et al., 2013). Consequently, recent research has focused on the development of hydrometallurgical methods that can allow high recovery not only for Ni, Co and Cu but also for currently under-recovered elements like Li and Mn. Nevertheless, most hydrometallurgical processes investigated for the treatment of spent LIBs tend to be relatively long and complicated. A typical flowsheet consists of sulfuric acid leaching, neutralization and precipitation of iron, Cu recovery, solvent extraction of Ni/Co/Mn fol- lowed by crystallization of each at a battery grade purity, and finally precipitation of lithium carbonate. In such a process, the total recovery of Li can reach only 60–80% due to Li losses at each of the separate stages (Chen et al., 2021a; Hu et al., 2017; Torkaman et al., 2017). Moreover, a substantial number of reducing agents (such as H_2O_2, $NaHSO_3$, $Na_2S_2O_3$, ascorbic acid, metallic elements, etc.) are needed during the leaching process to dissolve metals from the cathode mate- rials (Chen et al., 2021b; Liu et al., 2019; Pinna et al., 2017; Zheng et al., 2018). In order to decrease Li losses in different unit processes, several researchers have focused on the recovery of Li as the initial step in the hydrometallurgical recycling process of LIBs. However, the production and use of a large number of organic acids such as oxalic acid and tartaric acid required for such an approach increases the recycling cost and environmental impacts, which makes the industrialization of these processes a challenge (Mocellin et al., 2017; Musariri et al., 2019; Quijada et al., 2020; Vieceli et al., 2018).

Considering the shortcomings of single hydrometallurgical methods and pyrometallurgical methods for the recovery of LIBs, roasting pre- treatment combined with hydrometallurgical separation has attracted widespread attention within the industry (Jian et al., 2021; Mocellin et al., 2017; Nan et al., 2005; Peng et al., 2019b; Quijada et al., 2020; Yadav and Banerjee, 2018). In the pretreatment stage, sulfate roasting (Wang et al., 2018a), nitrate roasting (Peng et al., 2019b) and carbon reduction roasting methods (Hu et al., 2017) are often adopted to achieve the selective transformation of Li, Ni, Co and Mn present in spent LIBs. After such roasting, Li is transformed into a soluble metal sulfate, nitrate or carbonate, whereas Ni, Co, Mn and other metals are present as insoluble metals or their oxides. Subsequently, Li can be separated from Ni, Co, Mn and other metals by simple water leaching or low acid leaching without the need for any reducing agent. Although sulfate roasting has been demonstrated to be efficient and applicable to all types of spent LIBs, the roasting temperature and required chemical inputs are both relatively high. Alternatively, nitrate roasting can significantly reduce the roasting temperature, and > 95% of Li can be selectively transformed into soluble $LiNO_3$ at <300 °C. Nevertheless, due to the relatively high cost of nitric acid and related highly corrosive nature to metal infrastructure in particular, such a process remains a challenge to upscale to an industrial level. Moreover, the introduction of a large amount of sulfuric acid or nitric acid during the roasting stage causes NOx or SOx formation, which requires the addition of gas purification methods to avoid the atmospheric release of such toxic components. In contrast, carbon reduction roasting has been shown to result in almost 85% Li extraction from spent LIBs with a ~ 20% carbon dosage and an optimum temperature of 650 °C for 3 h (Hu et al., 2017). Furthermore, as carbon is often a key component within spent LIBs, it is possible that the reductant can be sourced from the battery waste itself.

In addition to carbon, Fe, Al and Cu metals cannot be completely separated from the active material ($LiNixCo_yMn_zO_2$) by currently used industrial pretreatment processes. Peng et al. (2019a) found that Cu residues left in the waste can be used as a reducing agent to achieve effective reduction of LiNixCoyMnzO2 cathode materials during the acid leaching process. Furthermore, the presence of Fe as an impurity has also been found to catalyze the oxidation-reduction reaction between Cu and cathode materials (Porvali et al., 2020). These results indicate that impurity metals like Cu and Fe present in spent LIBs can act as an in-situ reducing agent, reducing the costs and/or environmental burden caused by alternative virgin reductants such as H_2O_2, $NaHSO_3$ and $Na_2S_2O_3$. Compared with Fe and Cu, the dosage of Al in waste LIBs is higher, and its maximum dosage can reach as much as 15% - this is mainly due to Al being the base of the cathode that is coated by active ternary cathode material mixed with conductive agent. Chernyaev et al. (2021) suggested that the reductive power of Al can be fully utilized for Fe^{3+}/Fe^{2+} catalyzing $LiNi_xCo_yMn_zO_2$ leaching during sulfuric acid leaching, however, as Al is hard to selectively remove it can also cause subsequent solution purification issues. Wang et al. (2020b) have also proposed that Al can be used as a reducing agent in the reduction roasting stage to achieve the reduction and transformation of spent LIBs, and then roasting products can be further leached by alkali (2.5 mol/L) to achieve good Li extraction (> 93%). Nevertheless, their results also indicated that >95% of Al dissolves into the leachate, which can lead to difficulties with Al and Li separation.

In contrast to the above aluminum thermal reduction method, the current research detailed here is based on a process where Al and Li are dominantly present in separate phases, rather than as lithium aluminate. In the early exploration experiments, it was found that the simultaneous presence of carbon and aluminum can substantially improve the reduction roasting kinetics of waste LIBs: Li forms lithium oxide or lithium carbonate, whereas Al is present as oxides. Lithium can then be further separated from Al and other impurities by use of a carbonated water leaching process. In order to further reduce production costs and improve the recycling process for spent LIBs, an in-situ aluminum-car- bon reduction roasting process was proposed and further optimized to find the most suitable carbon-aluminum ratio, roasting temperature and roasting time. This research not only optimizes the existing carbon thermal reduction or aluminum thermal reduction process used for the treatment of spent LIBs, thereby making the existing processes more economical and environmentally friendly, but this work also provides a valuable technical reference for the pretreatment (disassembling, crushing, magnetic separation and screening) of spent LIBs.

2. Experimental

2.1. Experimental procedure

2.1.1. Selective transformation of Li

The input materials used in this research were obtained from a battery recycler based in southern China and the spent LIBs had been subjected to a pretreatment - dismantling, crushing, sieving. The in-situ aluminum-carbon reduction roasting experiments were performed in a horizontal tube furnace (Hanjun TLL-3, Shanghai Hanjun, China). The temperature was measured by a K-type thermocouple controlled by a Keithley 2000 multimeter intelligent temperature controller (accuracy of ±1 °C, Tektronix, Inc., Beaverton, United States). Within the furnace, the flow of protective inert gas (Ar) was precisely controlled by a digital mass flow controller (KW7000, Halma, Alicat Scientific, USA). Low-Al raw materials were used as a base to configure experimental raw ma- terials with different controlled aluminum dosage (0.27%, 1.0%, 3.0%, 5.0%, 7.0%, 10.4%) through the addition of Al powder. A pre-determined amount of reduced carbon powder (7.1%, 10.4%, 14.7%, 21.5%, 25.7%), was also added to the experimental materials (mixture of aluminum powder and low-aluminum battery raw materials) and thoroughly mixed within the matrix. Samples were placed in an Al_2O_3 crucible prior to insertion into the cold furnace, which was then heated at a rate of 5 ◦C/min under a protective argon (99.999 vol%) atmosphere to the desired target temperature (550 °C, 600 °C, 650 °C, 700 °C, 750 °C). Once the required temperature was achieved, the roasting reaction was carried out according to the set roasting durations (30 min, 60 min, 90 min, 120 min, 150 min). Once roasting treatment was complete, the furnace was cooled to room temperature at a rate of 5 °C/min. The degree of reduction that occurred during the roasting was determined based on the sample mass change measured before and after the experiments.

2.1.2. Selective separation of Li

The main objective of the experiment was to achieve the selective separation of Li from the remaining metals. Carbonated water leaching was used to selectively recover Li from the roasted cathode materials. Leaching experiments were carried out with a CO_2 flow rate of 50 mL/ min and a liquid-solid ratio of 25:1 (mL/g) at a stirring speed of 300 rpm at 30 °C for 2 h. The leaching results were utilized to evaluate the efficiencies of the aluminum-carbon reduction roasting process. After leaching, the slurry was vacuum filtered, the filtrate was collected and its volume recorded. The leachates were sampled and analyzed by ICP- OES to calculate the amount of Li, Ni, Co and Al successfully leached. Leach residues obtained were also characterized by XRD and SEM-EDS to confirm the main phases present and their associated morphologies. Extraction of Li Ni, Co, Mn and Al (%E) were calculated based on the solution samples via Eq. (1):

$$\%E = (Ci \times V)/(m_o \times w_o) \times 100\% \qquad (1)$$

where m_o(g) and w_o (%) are the mass of the material and the compositions (i.e. %(w/w)) of element (i) after the roasting transformation of the waste LIBs, respectively, and V and Ci are the volume of the leach so- lution and the concentration of element (i).

2.1.3. Selective separation of Al

After selective separation of Li, alkaline leaching was performed in a 200 mL cylindrical reactor with magnetic stirring (300 rpm) and the temperature was controlled by a water bath. The experiments were conducted to study the influence of the NaOH concentration (0.5–3.0, mol/L), leaching time (10–90, min), leaching temperature (35–90 °C), and liquid-to-solid (L/S) ratios (10–50, mL/g). Following leaching, the slurry was vacuum filtered, and the filtrate was collected and the volume recorded. The leachates were sampled and analyzed by ICP-OES to calculate the leaching efficiencies of Ni, Co, Mn and Al. The leach residues obtained were also characterized by XRD to confirm the main mineral phases of the components.

2.2. Analysis and characterization

The physical composition of the raw material, roasted products and leach residues were characterized using an X-ray diffraction spectrometer (K_{α} = 1.5406 A, MiniFlex600, Rigaku, Japan) with a Cu target in the range of 10 to 80°. The morphology and elemental distribution behaviors in the roasted products and leach residues were determined by SEM-EDS (MIRA 3 LMH, TESCAN Brno, S.r.o, Brno, Czech), whereas the concentrations of Li, Ni, Co, Mn and Al in the leachate were determined by ICP-OES (ICAP-AES 7400, HORIM) of TR788-DGS-III.

3. **Results and discussion**

3.1. Materials and characterization

The waste LIBs were used in the experiments as received and the chemical composition of the two types of raw material (high-Al material and low-Al material) investigated are presented in Table 1. The results show that the contents of Li, Ni, Co, and Mn in the high-Al material were 5.6%, 21.5%, 8.7%, and 14.6%, respectively, while the contents of Li, Ni, Co, and Mn in low-Al materials were 6.0%, 25.6%, 10.2%, and 14.0%, respectively. The dosage of Al in high-Al materials was as high as 10.4%, whereas the level of Al in low-Al materials was only 0.3%. In addition to the metal elements, the carbon dosage in high-Al and low-Al waste LIBs materials were 1.9% and 3.0%, respectively. Characterization of the LIBs waste by XRD and SEM - shown in Fig. 1 and Fig. 2 - revealed that Li, Co, Ni and Mn exist primarily as LiNi0.5Co0.2Mn0.3O2 with a regular sphere morphology (particle size of 2–10 μm). Additionally, Al phases were found in the high-Al material, whilst the diffraction peaks of Cu, Fe, and C were not found due to their low content.

A map of the main elements within the high Al material is shown in Fig. 3. The distribution regions of Ni, Co and Mn were coincident and found to be combined with each other without any obvious distribution boundaries. In contrast, Al, Cu, and C exist as separate phases with discernable phase boundaries – these are mainly as a result of the pre- treatment process – and are consistent with the XRD analysis (Fig. 1).

3.2. Exploration of different thermal reduction

In the exploration stage of the research, the low-Al cathode materials and high-Al cathode materials were directly subjected to thermal reduction treatment. It was found that the low-Al cathode materials could not realize the complete transformation of waste ternary materials (Fig. 4a), and the extraction of Li was only 66% (Table 2). For high-Al materials, if the carbon dosage is insufficient, most of the Li is con- verted into lithium aluminate, not easily soluble lithium carbonate (Fig. 4b), and the leaching of Li is only almost 50%. Whereas, when enough carbon is introduced into the high-Al cathode materials, the resulting product is lithium carbonate instead of lithium aluminate (Fig. 4c), and the leaching of Li is over 97%.

From these results, it can be inferred that synergistic thermal reduction of aluminum and carbon enables efficient Li extraction. In order to determine the reaction process, the Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) (NETZSCH STA 449 F3, Germany) analysis were conducted in argon atmosphere at a heating speed of 5 °C/min with mixture of commercially pure $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ powders and reductant (aluminum and carbon). From Fig. 5(a-b), it can be further demonstrated that both carbon and aluminum can be used as reductant to realize the transformation of the ternary cathode wastes. It can be observed that there is a sharp endo- thermic peak accompanying with little weight loss in the temperature range of 620–680 ◦C, which can be assigned to the reaction of $LiNi_{0.5}$-$Co_{0.2}Mn_{0.3}O_2$ and Al into Li_2O, NiO, CoO, MnO and Al_2O_3 (Eq. (2–3)). Fig. 5(b) shows that the carbon reduction reaction of $LiNi_{0.5}$- $Co_{0.3}Mn_{0.2}O_2$ occurs at 680–700 °C, and the main reactions are Eq. (4–5). From Fig. 5(c-d), it also can be further seen that aluminum and carbon can synergistically react with the ternary cathode powder when carbon and aluminum coexist in the reaction system, and the aluminothermic reduction reaction occurs preferentially. The diagram of Gibbs free energy as a function of temperature (Fig. S1, LiCoO2 as an example because of the lack of LiNi0.5Co0.2Mn0.3O2 thermodynamic data) for this reaction system also confirmed the sequence of aluminum and carbon reduction roasting reactions. When the Li in the waste LIBs are reduced to lithium oxide by Al, the obtained lithium oxide will preferentially react with carbon dioxide to generate lithium carbonate instead of lithium aluminate, which ensures the efficient separation of Li in the subsequent leaching stage.

$$6LiNi_xCo_yMn_{1-x-y}O_2+2Al = 3Li_2O+6xNiO+6yCoO+6(1-x-y)MnO+Al_2O_3 \quad (2)$$

$$Li_2O + Al_2O_3 = 2LiAlO_2 \quad (3)$$

$$8LiNi_xCo_yMn_{1-x-y}O_2+2C = 4Li_2O+8xNiO+8yCoO+8(1-x-y)MnO+2CO_2 \quad (4)$$

$$Li_2O + CO_2 = Li_2CO_3 \quad (5)$$

Roasting conditions: temperature (650 °C), time (90 min).

Carbonate leach conditions: S/L ratio (25:1 mL/g), stirring speed (300 rpm), leach reagent (H_2O + 50 mL/min CO_2), leach time (2 h), leaching temperature (30 °C).

3.3. In-situ aluminum-carbon reduction roasting

In order to obtain the optimal technological conditions for selective lithium extraction by in-situ aluminum-carbon reduction roasting process, the effects of roasting temperature, roasting time, Al dosage and carbon dosage on lithium extraction were investigated in detail, and the results are shown in Fig. 6.

Fig. 6(a) shows that the roasting temperature has a significant effect on the extraction of Li from spent cathode materials. The extraction of Li from the high-Al materials (10.4% Al) and low-Al materials (0.27% Al) increased from 70% and 62% to 97% and 94%, respectively, with increase in roasting temperature from 550 °C to 650 °C. When the roasting temperature was below 650 °C, the extraction of Li from the low-Al material was about 10% lower than that achieved with the high-Al materials. Nevertheless, the difference in the extraction of Li from high-Al and low-Al materials become smaller when the roasting temperature is > 650 °C. Furthermore, Li extraction decreased gradually with the increase in roasting temperature from 650 °C to 750 °C, whereas the extraction of Ni, Co, Mn and Al remained at approximately < 0.5% over the temperature range investigated. As can be seen in Fig. 6 (b), over 80% of Li could be extracted from high Al cathode materials (10.4% Al) after only 30 min of roasting. When the roasting time was increased from 30 min to 120 min, Li extraction increased from 82 to 97%, and the extraction of the impurities remained at a low level (< 0.5%). A further prolongation of the roasting time beyond 90 min only resulted in a slight increase in the level of extraction of both Li and impurities. Under the same roasting conditions, the average extraction of Li in low-Al materials was about 10% lower than that of high-Al materials over a time range of 30 to 90 min. With the increase of in LIBs waste undergoes some significant changes - from stable $LiNi_xCo_yMn_{1-x-y}O_2$ to Ni, Co and Mn metals or oxides. However, the extraction of Ni, Co, Mn and Al remains at a low level (< 0.1%) due to the low solubility of Ni, Co, Mn and Al metals and their oxides in the carbonated water used for the leaching process. The SEM results show that both high-Al materials and low-Al materials were decomposed after reduction roasting, with the morphology ranging from a relatively regular ellipsoid shape (Fig. 2) to an amorphous polyhedron (Fig. S3) with 14.7% carbon dosage. This is conducive to the dissolution of Li in the subsequent leaching reaction as the selective separation of Li can be achieved as transformed Li2CO3 obtained from roasting stage can be further converted into more soluble $LiHCO_3$ (Eq. 6).

$$Li_2CO_{3(s)} + H_2O_{(aq)} + CO_{2(g)} = 2LiHCO_{3(aq)} \qquad (6)$$

These results highlight that in-situ Al and C reduction can achieve selective leaching of Li due to an efficient transformation. When combined with the XRD results, it can be inferred that the conversion process of waste LIBs that occurs during reduction process is as follows (Eq. 7):

$$LiNi_xCo_yMn_{1-x-y}O_2, C, Al \rightarrow Li_2O, MnO, NiO, CoO, CO_2, Al_2O_3 \qquad (7a)$$

$$Li_2O, MnO, NiO, CoO, CO_2, Al_2O_3 \rightarrow Li_2CO_3, MnO, Ni, Co, Al_2O_3 \qquad (7b)$$

The above results indicate that the spent cathode materials can be efficiently reduced by in-situ aluminum-carbon reduction roasting, which has the beneficial effects of decreasing both the consumption of reductant and energy required. The most suitable aluminum-carbon reduction roasting conditions were determined to be a carbon dosage of 14.7% and an aluminum dosage of 7.0% with a roasting temperature of 650 °C for 2 h. After the roasting transformation, the Li can be effectively separated from spent LIBs by using carbonated water leaching. The XRD results (Fig. 8) illustrate that the diffraction peak of Li_2CO_3 has almost disappeared, whereas the diffraction peak of other mineral phases present in the roasted products undergo no significant change. This indicates that the selective extraction of Li could be achieved through the aluminum-carbon synergistic roasting followed by carbonated water leaching. Under the optimal conditions, > 97% Li can be separated from waste ternary battery material, while the extraction efficiencies of Ni, Co and Mn were below 0.5%. Fig. S4 shows that the distribution regions of Ni, Co and Mn are coincident and combined with each other without any obvious distribution boundaries, whereas Al clearly exists in the form of separate phases with discernable phase boundaries. Additionally, Mn, Al and O are observed to be more closely associated, which is consistent with the XRD analysis results (Fig. 8) that show Ni and Co mainly exist as elemental metals in the leach residues, whilst Mn and Al are primarily in the form of oxides.

3.4. **Selective separation of Al**

The presence of Al in the leach residues is not conducive to the subsequent separation and recovery of valuable metals such as Ni, Co and Mn. Based on the fact that Al can be effectively dissolved in sodium hydroxide solution, an alkaline leaching process was proposed to separate Al from Ni, Co and Mn. The influence of the main parameters on the leaching behaviour was investigated, and the results are shown in Fig. 9. As outlined in Fig. 9, the selective separation of Al can be achieved by using alkaline leaching. Fig. 9(a) shows that an increase in the NaOH concentration provides an improved separation of Li from leach residues containing Al_2O_3. As the concentration of NaOH is raised from 0.5 mol/L to 3.0 mol/L, Al extraction increases significantly from 37% to 98%, and there is almost no Ni, Co and Mn found within the alkaline leachate. From Fig. 9(b), it is clear that > 95% of Al could be extracted from the cathode wastes after 70 min of leaching. Further studies into the effect of leaching temperature in Fig. 9(c), shows that the leaching efficiency of Al increased from 60% to 98% as the leaching temperature was increased from 35 ◦C to 90 ◦C. In order to obtain the best separation efficiency, a temperature of 90 ◦C was selected as being optimum in this study. Fig. 9(d) highlights the effect of the liquid-to-solid (L/S) on the extraction of Al, Ni, Co and Mn. It was found that the extraction of Al gradually increased with increased L/S. maximum Al leaching efficiency of > 99% was evident under the optimum conditions of 3 mol/L NaOH, T = 90 °C, t = 70 min and L/S of 30 mL/g, whereas the extraction of Ni, Mn and Co remained at approximately <0.01%. Following alkaline leaching, almost all of the diffraction peaks associated with Al_2O_3 disappear and the leach residues were found to be mainly composed of Ni, Co metals and MnO (Fig. S5), which can be further subjected to oxidative sulfuric acid leaching to recover Ni, Co and Mn.

3.5. Flowsheet development

From above results, a new process for the selective separation of Li and Al from spent LIBs based on the combination of in-situ aluminum- carbon reduction roasting, carbonated water leaching and Al alkaline leaching is outlined in Fig. 10. The composition of raw material and by- products obtained from the proposed flowsheet are shown in Table 3, and the mass balance of the valuable metals throughout the recovery process is shown in Fig. S6. Application of this new process could significantly improve the separation and recovery of Li and Al from spent LIBs. The reduction performance of Al and C can be fully utilized to avoid the introduction of a large amount of reducing agents. Consequently, this research provides a reference case for the dismantling, sorting, and valuable metal recovery from waste LIBs.

The high purity LiHCO3 solution obtained can be further treated to prepare battery-grade lithium carbonate, whereas the sodium aluminate solution byproduct can be used to prepare Al products via the Bayer process. Moreover, considering the high content of Ni/Co metal elements in the final alkaline leach residue, oxidative acid leaching method will be carried out to extract these valuable metals such as Ni, Co and Mn (Hu et al., 2017). The oxidative acid leach solution can be further treated to recover Ni, Co and Mn by using standard technologies such as selective precipitation or solvent extraction (Dutta et al., 2018; Perez et al., 2016; Wang et al., 2018b).

4. Conclusions

This research proposes an efficient method to selectively extract Li and Al from waste ternary battery materials. Results show that:

(1) Through the in-situ aluminum-carbon reduction roasting, the Li, Ni, Al, Co, and Mn in the waste ternary battery materials were selectively converted into readily soluble Li2CO3 and insoluble elemental metals or oxides. The selective extraction of Li can be achieved by carbonated water leaching.

(2) > 97% Li can be separated from waste ternary battery material under optimal conditions of the carbon dosage of 14.7% and aluminum dosage of 7.0% with a roasting temperature of 650 °C

and a roasting time of 90 min, while the extraction rates of Ni, Co and Mn were below 0.5%.

(3) The Al in carbonated water leach residue can be separated from Ni, Co and Mn, and >99% of Al can be extracted with 3 mol/L NaOH at 90 ◦C within 70 min. Compared with single carbon reduction roasting, in-situ aluminum-carbon reduction roasting process not only enables the reductive nature of Al to play a role but also reduces the need for virgin reductants for the trans- formation of LIBs waste. Based on these findings, the overall process outlined paves the way towards more environmentally friendly recycling operations that have a reduced level of asso- ciated carbon dioxide emissions.

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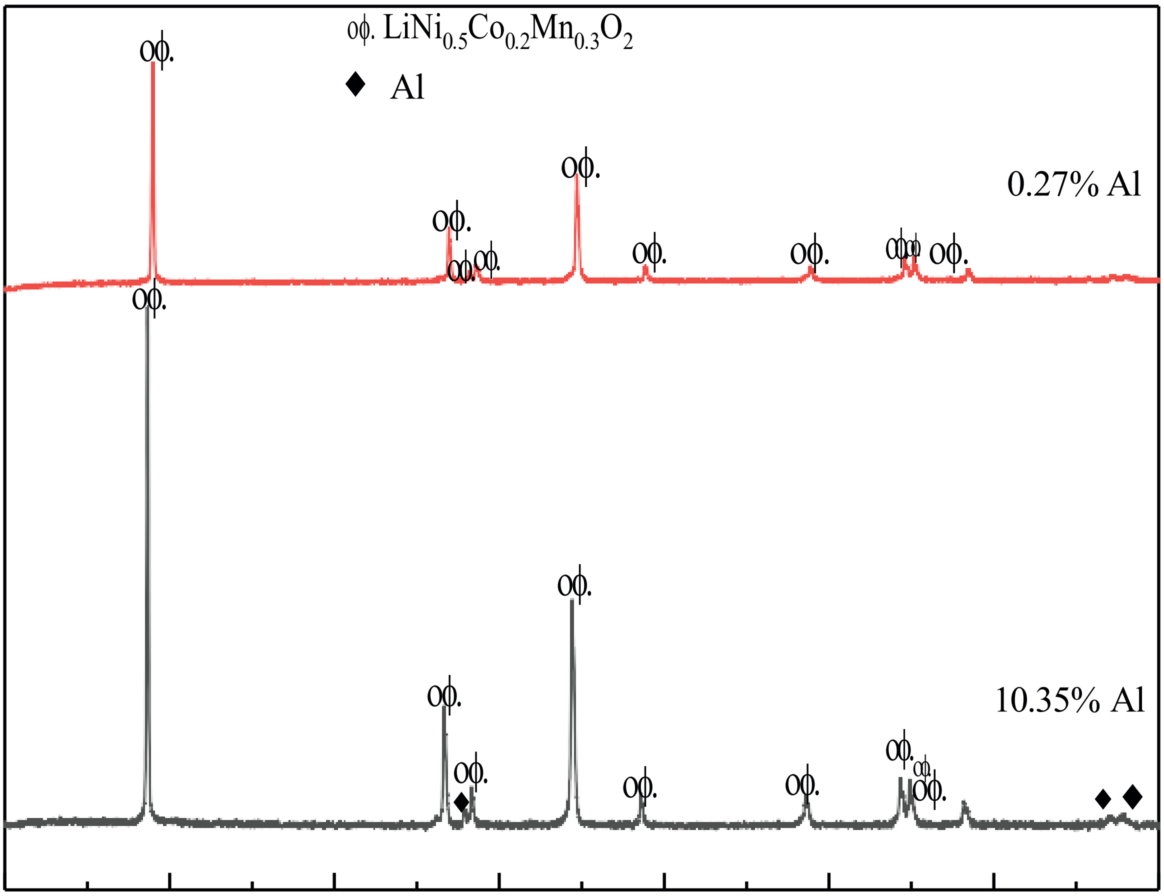

Fig. 1. XRD pattern of high-Al and low-Al spent ternary LIBs

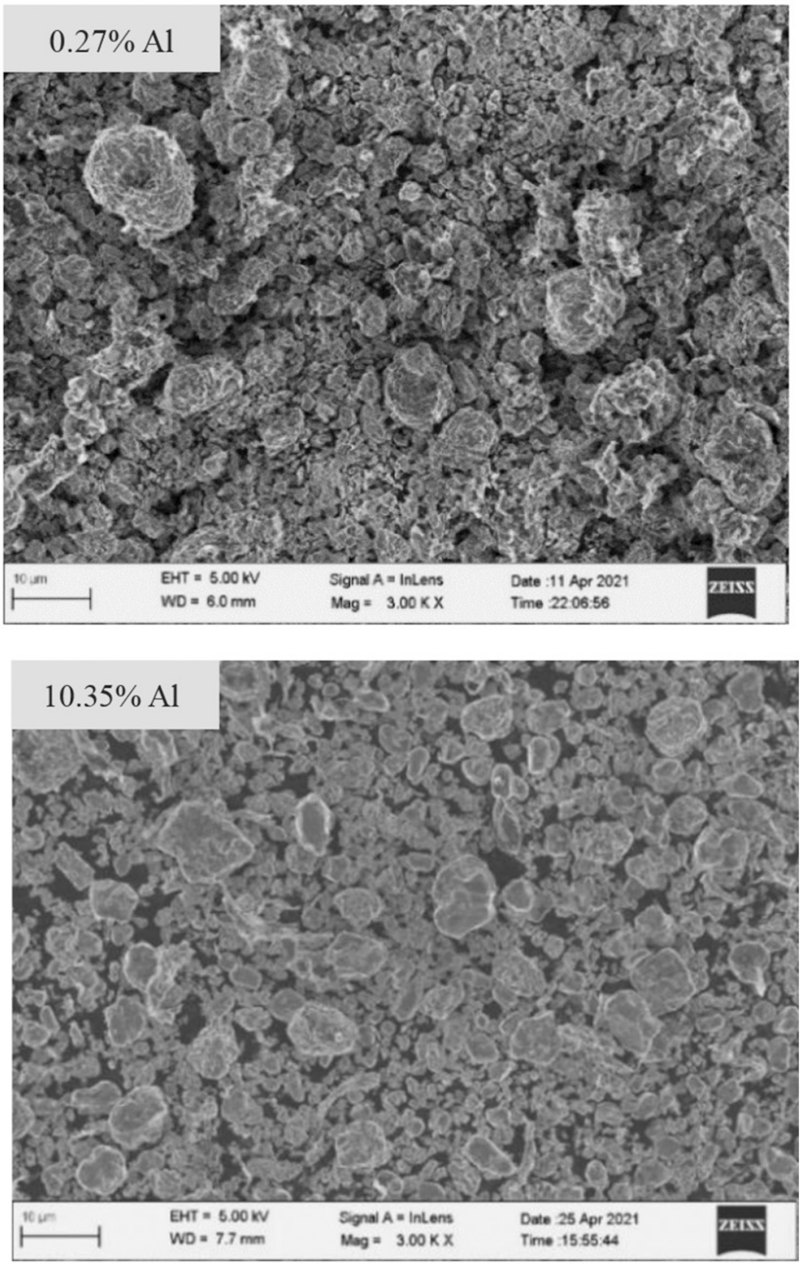

Fig. 2. SEM images of high-Al and low-Al spent ternary LIBs.

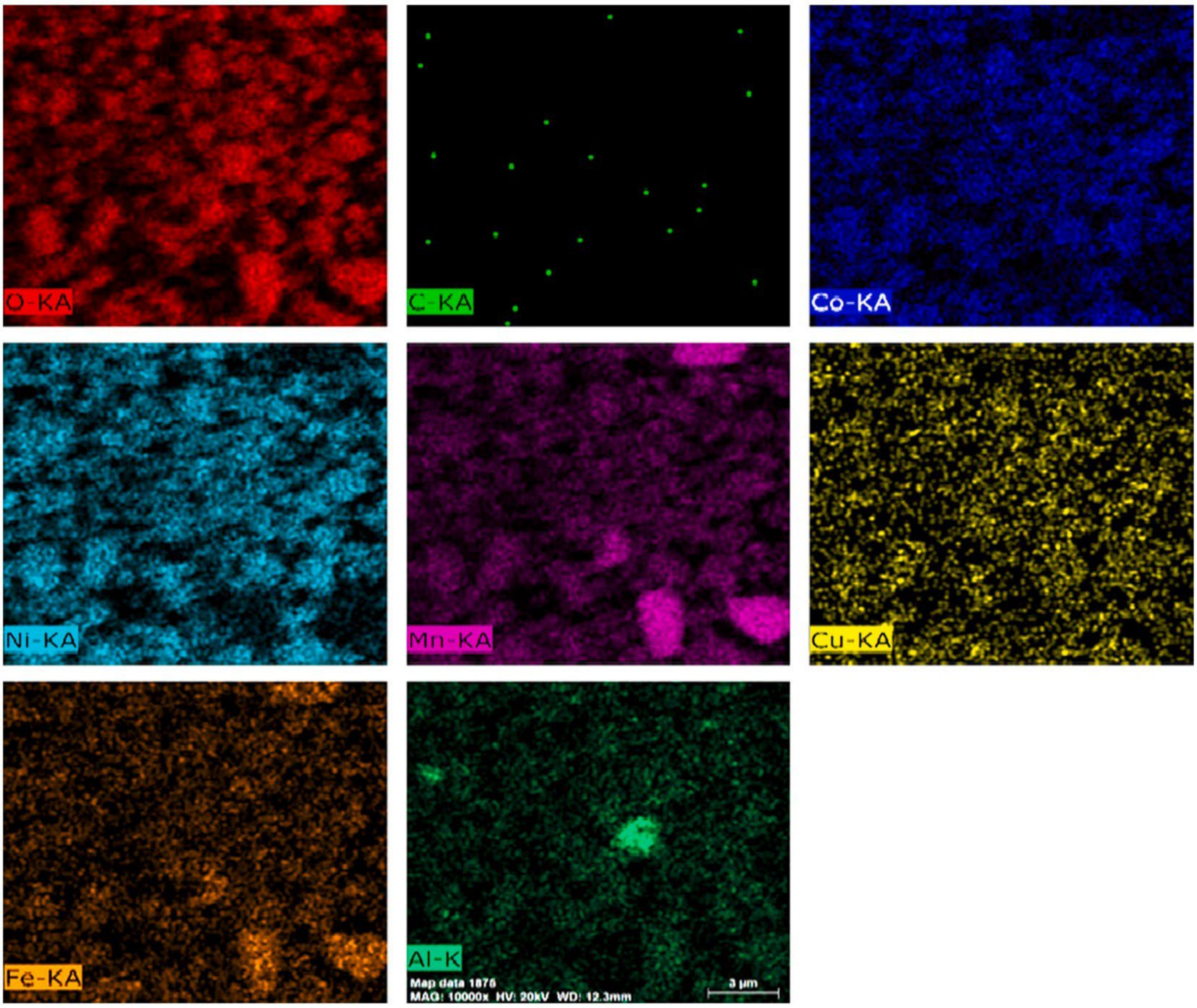

Fig. 3. Elemental maps of high Al spent ternary cathode materials.

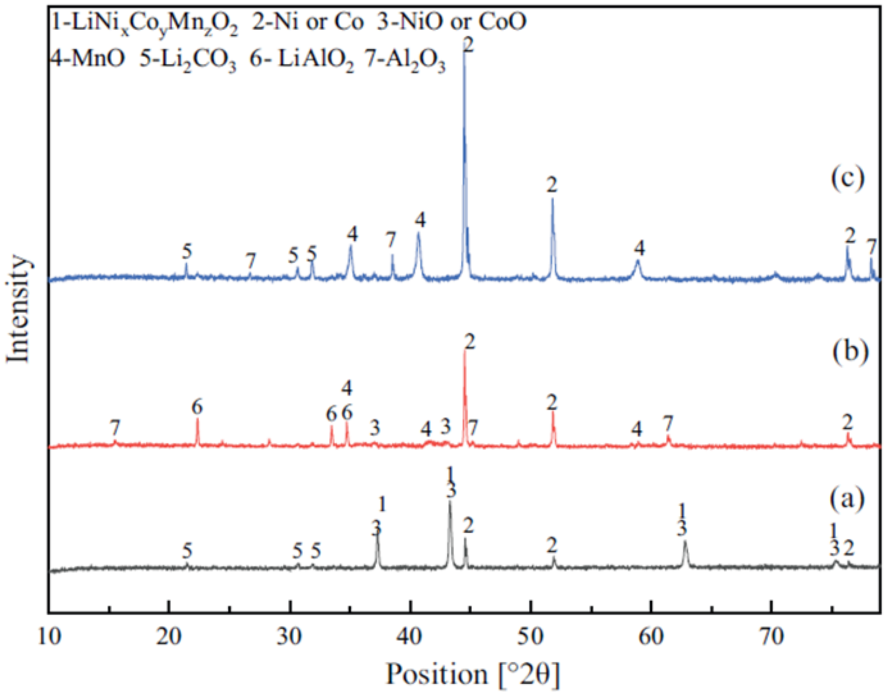

Fig. 4. XRD patterns of roasted products with different reductant composition: (a) 0.27% Al + 3.0% C; (b) 10.4% Al + 1.9% C; (c) 10.4% Al + 14.7% C (T = 650 ◦C, t = 90 min).

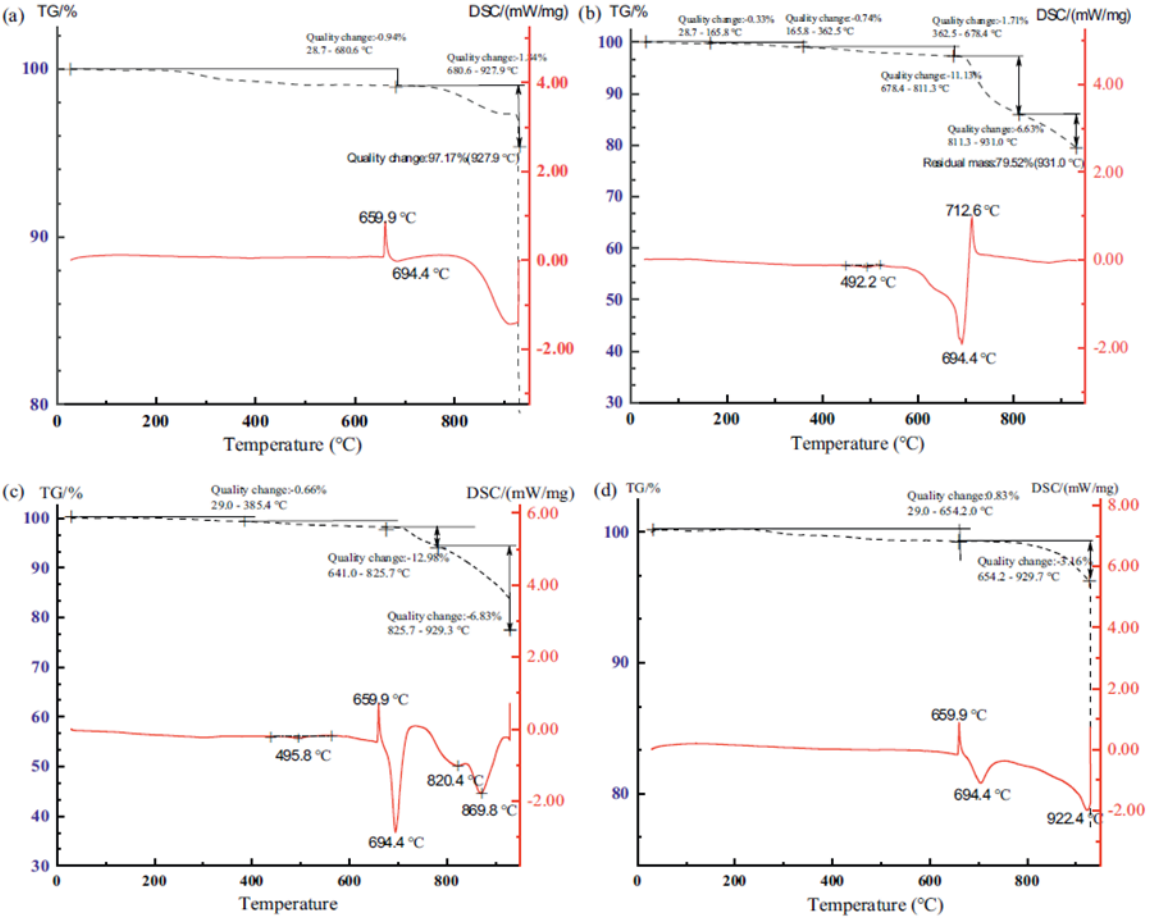

Fig. 5. TG-DSC analysis of pure: (a) $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ + 10.4% Al + 0.0% C; (b) $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ + 0.0% Al + 14.7% C; (c) $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ + 10.0% Al + 3.0% C; (d) $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ + 10.0% Al + 10.0% C.

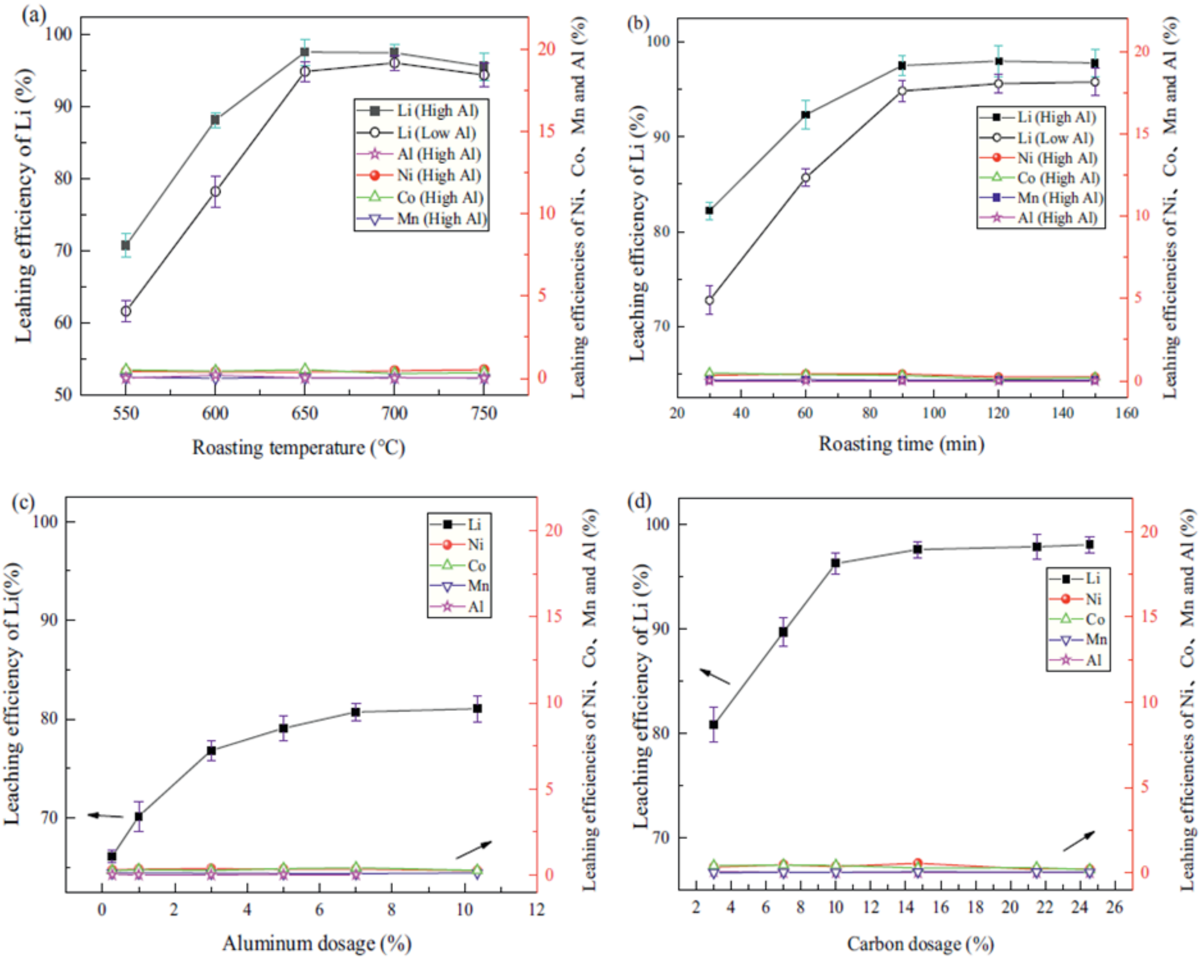

Fig. 6. Leaching efficiencies of Li, Ni, Co, Mn and Al from waste LIBs: (a) effect of roasting temperature (t = 90 min, carbon dosage = 14.7%, aluminum dosage = 0.27% or 10.4%); (b) effect of roasting time (T = 650 °C, carbon dosage = 14.7%, aluminum dosage = 0.27% or 10.4%); (c) effect of aluminum dosage (T = 650 °C, t = 90 min, carbon dosage = 3.0%); (d) effect of carbon dosage (T = 650 °C, t = 90 min, aluminum dosage = 7.0%).

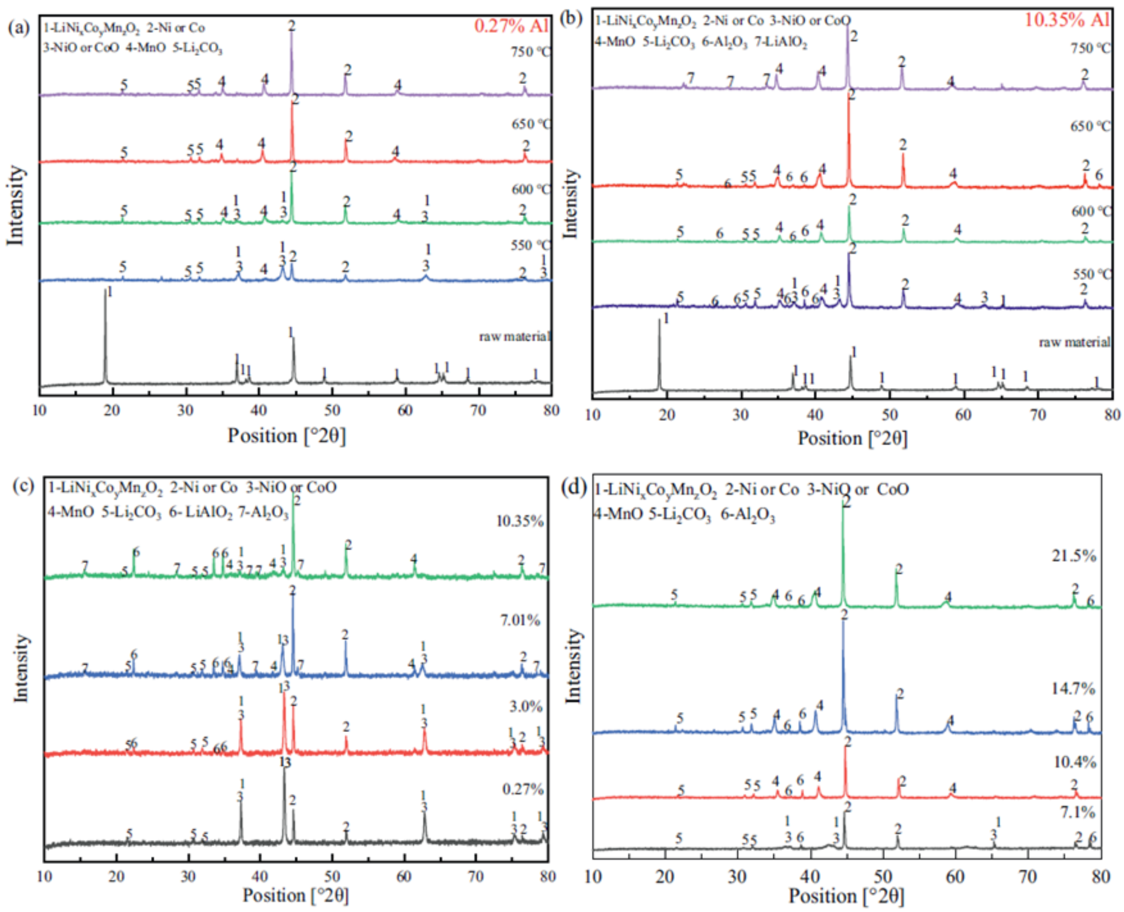

Fig. 7. XRD patterns of the raw materials and the roasted residues: (a-b) effect of roasting temperature ((t = 90 min, carbon dosage = 14.7%, aluminum dosage = 0.27% (a) or 10.4% (b)); (c) effect of aluminum dosage (T = 650 °C, t = 90 min, carbon dosage = 3.0%); (d) effect of carbon dosage (T = 650 °C, t = 90 min, aluminum dosage = 7.0%).

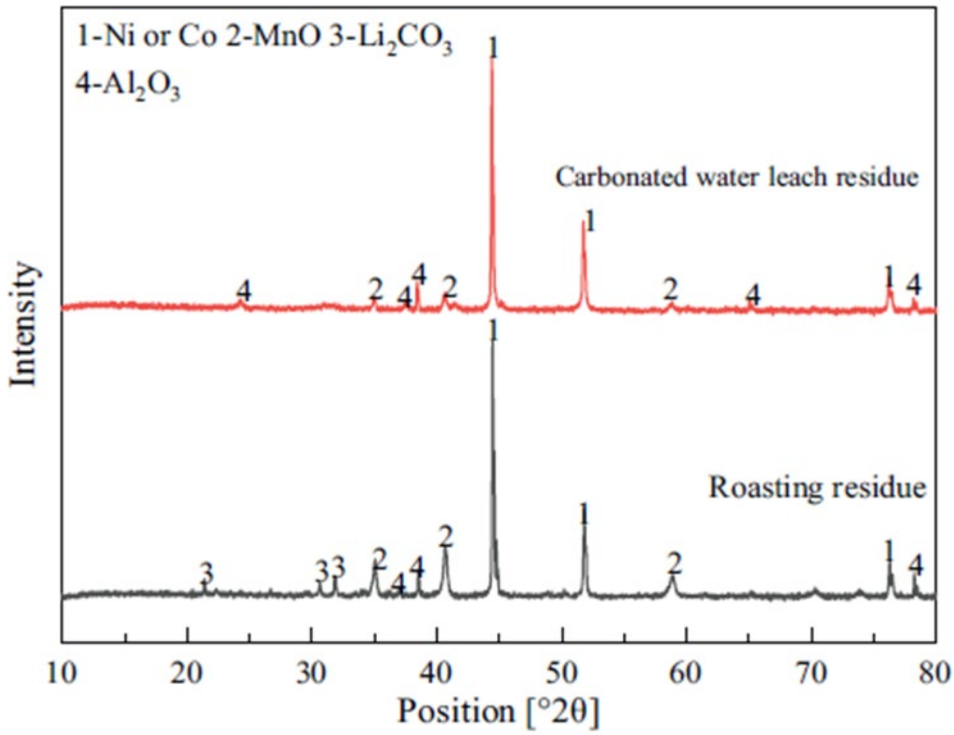

Fig. 8. XRD patterns of roasted products (T = 650 °C, t = 90 min, carbon dosage = 14.7%, aluminum dosage = 7.0%) and carbonated water leach residue (T = 30 °C, t = 120 min, CO_2 flow rate = 50 mL/min, L/S = 25 mL/g).

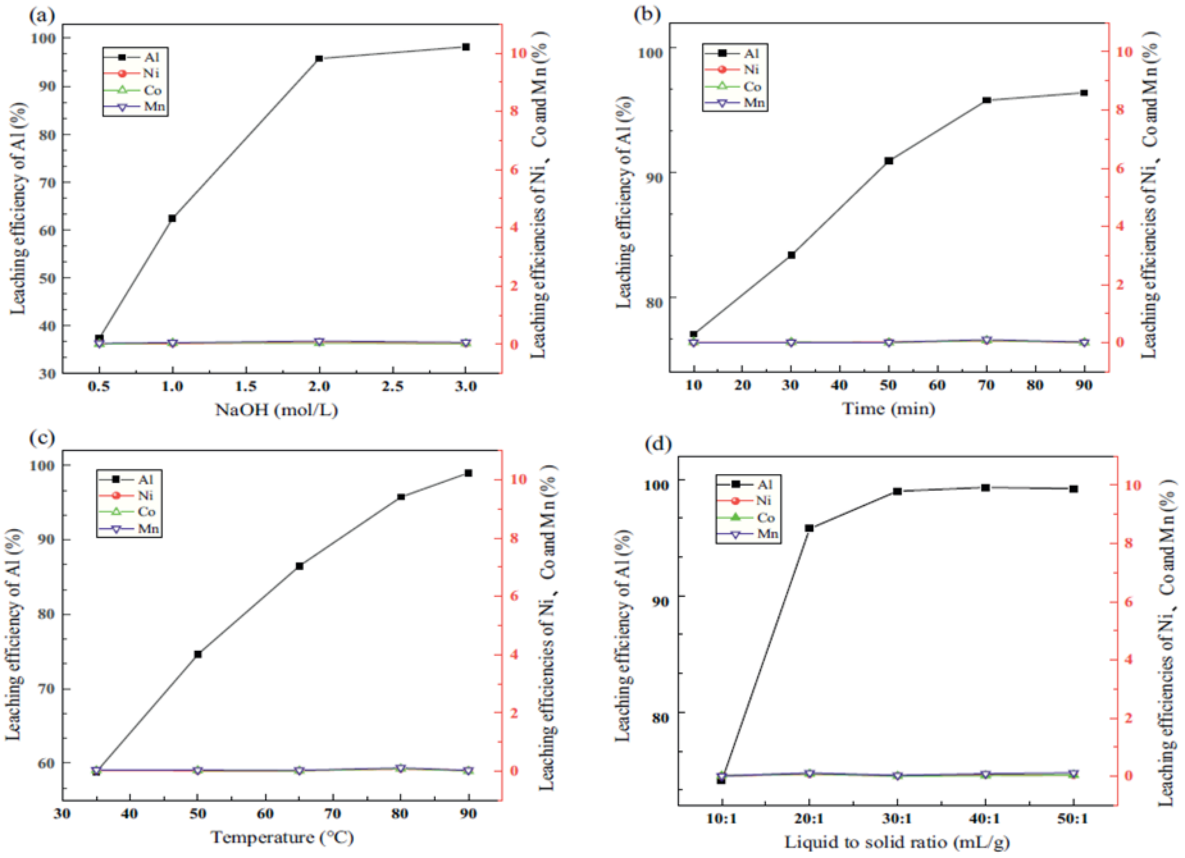

Fig. 9. Leaching efficiencies of Al, Ni, Co and Mn: (a) effect of NaOH concentration (T = 80 °C, L/S = 20 mL/ g, t = 70 min); (b) effect of leaching time (NaOH = 2.0 mol/ L, T = 80 °C, L/S = 20 mL/ g); (c) effect of leaching temperature (NaOH = 2.0 mol/ L, L/S = 20 mL/ g, t = 70 min); (d) effect of L/S (NaOH = 2.0 mol/ L, T = 80 °C, t = 70 min).

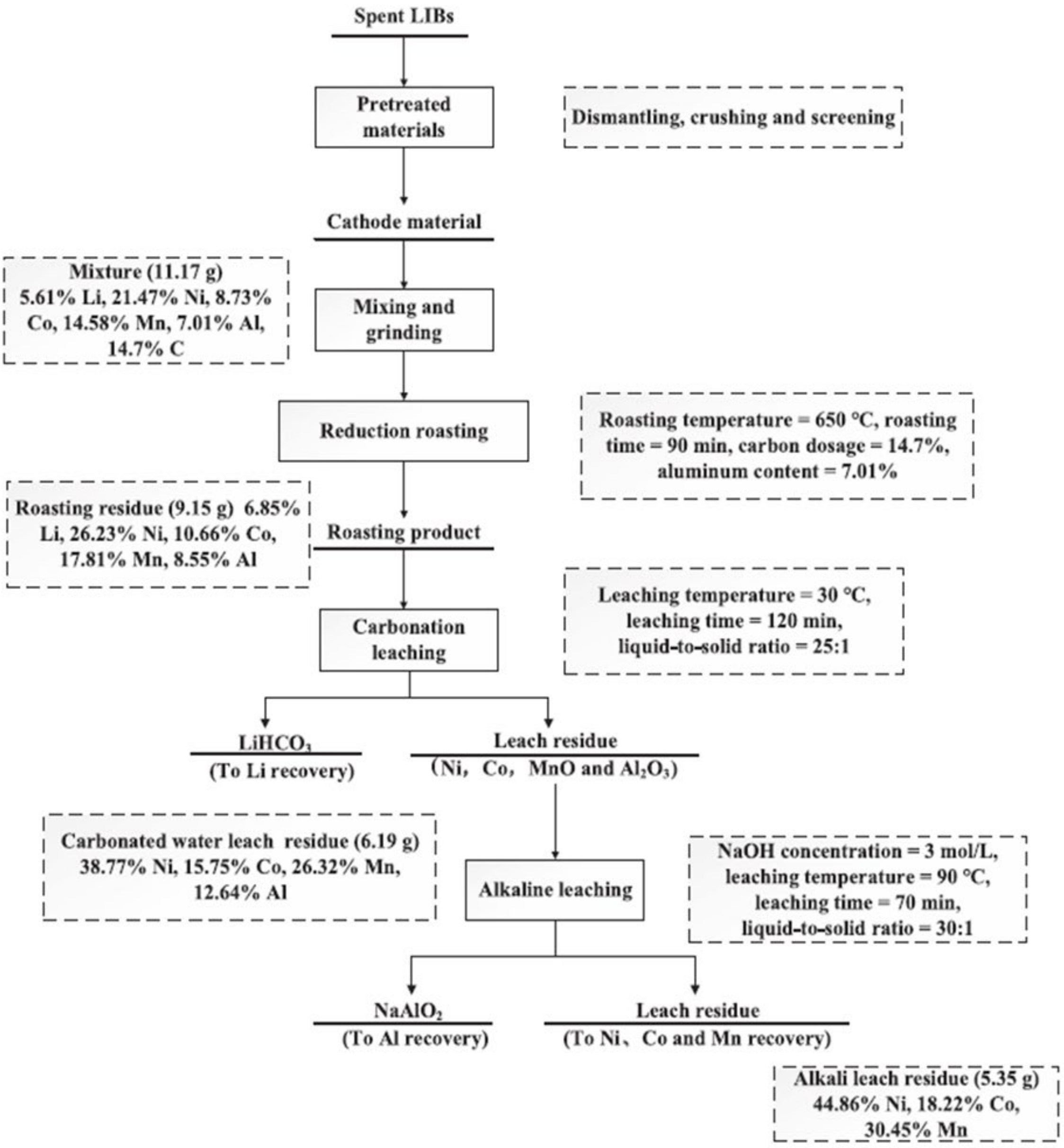

Fig. 10. Proposed flowsheet for selective separation of Li and Al from waste LIBs scraps.

Table 1. Chemical composition of high-Al and low-Al spent ternary LIBs.

Samples	**Li**	**Co**	**Cu**	**Ni**	**Al**	**Mn**	**Fe**	**C**
High Al (% w/w)	5.61	8.73	< 0.01	21.47	10.35	14.58	0.03	1.91
Low Al (% w/w)	6.03	10.15	< 0.01	25.64	0.27	13.98	0.03	3.01

Table 2. Extraction efficiencies of valuable metals with different reductant composition.

Reductant composition	Li (%)	Ni (%)	Co (%)	Mn (%)	Al (%)
3.01% C + 0.27% Al	66.11	0.29	0.24	0.11	< 0.01
1.91% C + 10.4% Al	49.72	0.23	0.25	0.08	<0.01
14.7% C + 10.4% Al	97.55	0.55	0.27	0.46	< 0.01

Table 3. Elemental composition of raw material and by-products obtained from the proposed flowsheet.

Samples description and units of elemental assay	Li	Ni	Co	Mn	Al	Sample mass (g) or volume (mL)
Raw materials (% *w*/w)	5.61	21.47	8.73	14.58	7.01	11.17 g
Roasting products (% w/w)	6.85	26.23	10.66	17.81	8.55	9.15 g
Carbonated leach residues (% w/w)	0.31	38.77	15.75	26.32	12.64	6.19 g
Carbonated leach solution (g/L)	2.43	0.05	0.02	0.03	0.02	250 ml
Alkaline leach residues (% w/w)	0.40	44.86	18.22	30.45	0.15	5.35 g
Alkaline leach solution (g/L)	<0.01	0.02	<0.01	0.01	3.87	200 mL

Roasting conditions: Solid particle size (2-10 µm), temperature (650 ˚C), time (90 min), reductant (14.7%C + 7.0%Al), initial total mass (11.17 g), final total mass (9.15 g).

Carbonate leach conditions: S/L ratio (25:1 mL/g), stirring speed (300 rpm), leach reagent (H_2O + 50 mL/min CO_2), leach time (2 h), leaching temperature (30 ˚C), initial mass used for leaching (9.15 g), mass of leach residue(6.19 g).

Alkaline leach conditions: NaOH concentration (2.0 mol L^{-1}), leaching temperature (80 ˚C), S/L ratio (20:1 mL/g), leaching time (70 min), initial mass used for leaching (6.19 g), mass of leach residue (5.35 g).