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Efficient recovery of lithium as Li_2CO_3 and cobalt as Co_3O_4 from spent lithium-ion batteries after leaching with *p*-toluene sulfonic acid

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ABSTRACT

Rechargeable lithium-ion batteries (LIBs) have been widely used in consumer electronics and electric vehicles. In terms of environmental restrictions and circular economy, proper treatment of spent LIBs is of great significance for achieving sustainable development. In this study, organic *p*-toluene sulfonic acid (PTSA) was employed to recycle valuable Li and Co elements from the spent LIBs for production of battery raw materials (e.g. Li_2CO_3 and Co_3O_4). Operation parameters such as PTSA concentration, hydrogen peroxide (H_2O_2) concentration, solid-to-liquid ratio, leaching temperature and leaching time, were systematically investigated. Under the optimal conditions (0.9 vol% H_2O_2, 1.5 mol L^{-1} PTSA, 30 g L^{-1} solid-to-liquid ratio, 80 °C, and 60 min), the leaching efficiencies of commercial $LiCoO_2$ could reach ~100% and 99% for Li and Co, respectively, while the corresponding values were about 95% and 93% for the spent $LiCoO_2$. In addition, the selective precipitation of Co-rich compounds in cooled leachate allowed an effective separation of Co from the mixture. The high recovery yield of Co_3O_4 and Li_2CO_3 demonstrated the great potential of the PTSA-assisted leaching strategy in hydrometallurgical recycling of the spent LIBs for practical applications. Overall, this proposed recovery process is simple, efficient, and environmentally friendly and is of vital importance for rational treatment of spent LIBs.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) can be found in almost every corner of our daily lives, owing to their excellent electrochemical performances. With the wide application of rechargeable LIBs, massive amounts of spent LIBs have been generated, thus causing significant environmental pollution, and posing serious health risks on account of their toxic contents, i.e., toxic electrolytes, heavy metals, plastic diaphragms, etc. (Xiao et al., 2020; Zhang et al., 2018). It was previously predicted that the worldwide generation of spent LIBs would reach 2 million metric tons per year by 2030 (Jacoby, 2019). There is no doubt that the large amounts of spent LIBs would cause immeasurable damages to the surrounding environment, if they were not properly treated. Furthermore, valuable lithium (Li) and cobalt (Co) resources are insufficient in China, due to the limitations of mining difficulties and other factors. As the circular economy of LIBs was widely recognized, recycling strategies with high feasibility and efficiency have been extensively investigated.

So far, the main recovery strategies of lithium-ion battery wastes are based on pyrometallurgy, hydrometallurgy and biohydrometallurgy (Golmohammadzadeh et al., 2018) processes. The pyrometallurgical processes are simple but has disadvantages. Particularly, the pyrometallurgical processes require relatively high temperatures (500–1000 °C), indicating a large energy consumption and the generation of excessive amounts of toxic gases during the recycling process. Besides the generation of environmental pollutants, metal containing compounds recovered from the pyrometallurgical processes were often low-grade compounds, which required further processing and purifications. Obviously, this could result in high cost and operation difficulty (Garcia et al., 2008; Joulié et al., 2017; Xu et al., 2008). The main step for a biohydrometallurgical process is to utilize the biological interactions between battery materials and microorganisms to reduce and reuse

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metals. Again, the biohydrometallurgical processes have their own disadvantages. The technical challenges include microbial cultivation and quantity control, bacterial pollution, difficulty in the operation of reaction processes as well as lengthy treatment times. Therefore, such strategy needs to be further improved for potential practical applications (Nayaka et al., 2016; Zhang et al., 2014; Zhao et al., 2008).

In contrast, the hydrometallurgical treatment of spent battery materials has multiple advantages, including high feasibility, appropriate reaction kinetics, environmental protection (no air pollution), less energy consumption, and high purity of recovered metal containing compounds (Garcia et al., 2008; Ku et al., 2016; Sun and Qiu, 2011; Sun et al., 2017). Previous studies have reported many different acidic, alkaline and reducing agents to leach valuable metals (Wang et al., 2016). Strong acids, such as HNO_3 (Lee and Rhee, 2003), H_2SO_4 (Yang et al., 2017) and HCl (Guzolu et al., 2017), were viewed as representatives of inorganic acid leaching agents, but can bring environmental problems due to wastewater production, soil pollution, as well as the emission of chlorine, sulfur and nitrogen oxides (Golmohammadzadeh et al., 2017; Gupta et al., 2012; Li et al., 2013). To address the above concerns, considerable attention has been brought to organic acid-assisted leaching technologies. It has been reported that utilizing organic acids as leaching agents could reduce the degree of corrosion of equipment, minimize harm to operators and achieve higher selective metal recovery (Chen et al., 2015; Horeh et al., 2016; Li et al., 2013; Zafar and Ashraf, 2007). Besides, the organic reagents do not produce harmful gases during the leaching processes (He et al., 2016; Li et al., 2018). However, there are indeed some drawbacks in using organic acids for metal leaching from cathode materials, among which the relatively low leaching efficiency is a critical one. Typically, the leaching assisted by organic acids had low efficiencies caused by their weak acidity, such as tartaric acid (He et al., 2016), aspartic acid (Li et al., 2013), succinic acid (Li et al., 2015), citric acid (Li et al., 2010b), malic acid (Li et al., 2013), formic acid (Gao et al., 2017), ascorbic acid (Li et al., 2012), and oxalic acid (Zeng et al., 2015). As a result, a low solid-to-liquid ratio, which was typically lower than 20 g L^{-1}, was usually adopted for effective leaching (Li et al., 2013; Li et al., 2015). Moreover, the hydrometallurgical process was complicated, because of a series of separation and purification processes of Co and Li, which would also lead to loss in product yield and extra consumption of chemicals. Therefore, continuous efforts need to be made to solve the technical challenges, including seeking for more effective organic acids and simplifying the subsequent procedures for the separation and recovery of Co and Li. The *p*-toluene sulfonic acid (PTSA) is a strong organic acid ($pK_a = -2.8$) and has a good solubility in water (67 g/100 mL). The PTSA has been reported as an economical and sustainable agent to dissolve wood lignin (Chen et al., 2017) and a high leaching efficiency (95%) was achieved, when using PTSA to leach $LiFePO_4$ (Yadav et al., 2020). Therefore, it is hypothesized that PTSA can be applied as a cost-effective and efficient organic acid to recycle Li and Co from the spent $LiCoO_2$ cathode materials.

In this study, effective recovery of Li as Li_2CO_3 and Co as Co_3O_4 from $LiCoO_2$ powder was conducted to address the existing technical challenges by leaching with PTSA, followed by pyrometallurgical treatment. By a combination of PTSA and hydrogen peroxide (H_2O_2), the effects of operation parameters, including leaching time, leaching temperature, concentrations of PTSA and H_2O_2, solid-to-liquid ratio, were systematically investigated and optimized. Moreover, the leaching kinetics were studied by observing the leaching of Li and Co from the spent LIBs to further explicate the metal leaching mechanisms. Then, through a simple cooling process of the obtained leachate, the cobalt-containing compounds precipitated as crystals while the Li contents remained dissolved in the supernatant liquid. Finally, Li and Co were successfully separated and recovered by the formation of Co_3O_4 and Li_2CO_3 after follow-up treatments.

2. Materials and methods

2.1. Sample preparation

Two types of LIBs samples were used in this study: the first one being the powder obtained from the spent LIBs (Samsung company) and the second one being commercial $LiCoO_2$ (KeHeng®). The $LiCoO_2$ powder from the spent LIBs was prepared according to the following steps. First, the spent LIBs were immersed in Na_2SO_4 solution (10 *w*/*v*%) for 24 h to fully discharge. Then, the spent LIBs were cleaned with deionized water and dried for 12 h in an oven at 80 °C to completely discharge the remaining energy. After that, nozzle pliers were used to disassemble the battery into parts (e.g. aluminum plastic packaging film, insulator, diaphragm, anode and cathode etc.). The packaging film, diaphragm and negative electrode were classified and recycled, and the $LiCoO_2$ cathode was cut into 2 × 2 cm pieces for stripping of active materials. The cathode materials obtained in the above steps were composed of aluminum foil and coating material, wherein the coating material was mainly composed of $LiCoO_2$, polyvinylidene fluoride (PVDF) binder and electrolyte. To obtain the spent $LiCoO_2$ powder, the electrode was placed in a muffle furnace and calcined at 550 °C for 2 h. As a result, the PVDF and electrolyte were decomposed and removed, thus allowing the easy separation of $LiCoO_2$ powder and aluminum foil. Finally, the spent $LiCoO_2$ sample was manually ground into smaller particles (5–25 μm), which was beneficial for the subsequent organic acid-assisted leaching process. The metal content in the spent $LiCoO_2$ powder was analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, PerkinElmer Optima 3300 DV) after acid digestion by a mixed solution of HNO_3, HCl and H_2O_2. Table S1 shows Al (0.27%), Mn (0.12%), Fe (0.16%) and Cu (0.06%) as impurity elements in the spent $LiCoO_2$ powder but with very low contents, which demonstrates that the dismantling of spent LIBs was relatively complete without introducing impurities. Additionally, *p*-toluene sulfonic acid (98.5%, Aladdin®) was used as the leaching agent, and hydrogen peroxide (35%, LingFeng®) was also employed in the leaching process. Succinic acid (99.5%, Aladdin®), citric acid (99.5%, Aladdin®), malonic acid (99.5%, Aladdin®), and oxalic acid (98%, Aladdin®) were also used as leaching agents for the comparison of leaching performance. For elemental quantification, nitric acid (65%, LingFeng®) and hydrochloric acid (30%, LingFeng®) were used for sample digestion to measure the content of Li and Co in the spent and commercial $LiCoO_2$ samples. All solutions were prepared by deionized water with specific concentrations and all these chemicals were of analytical grade.

2.2. Leaching experiments

The leaching experiments were performed in 250 mL three-neck round-bottom flasks. A glass condenser was connected to one of the three ports to minimize water evaporation during the leaching experiments. The flask was placed in a heating mantle, equipped with magnetic stirring (800 rpm) and a temperature sensor. An appropriate amount of $LiCoO_2$ powder was carefully dispersed in the acidic solution containing PTSA and H_2O_2 to initiate the leaching experiments. For liquid sampling, about 1 mL of leaching solution was sampled regularly with a pipette, followed by syringe filtration for solid-liquid separation. The optimization of leaching conditions was based on operation parameters, including PTSA concentration, H_2O_2 concentration, leaching temperature and solid-to-liquid ratio. The effects of the above operation parameters were systematically investigated for a leaching period of 150 min. To determine the most suitable PTSA concentration for leaching, variables such as temperature, solid-to-liquid ratio and the concentration of H_2O_2 were held constant at 80 °C, 30 g L^{-1} and 0.9 vol % respectively. Next, the most suitable H_2O_2 concentration was determined by holding the concentration of PTSA at 1.5 mol L^{-1}, whilst holding other variables constant as before. Analogously, the solid-to-liquid ratio was optimized by altering the ratio from 5 to 60 g L^{-1} and the leaching temperature was optimized in the range of 25 to 100 °C. Most suitable operation parameters were as follows: H_2O_2 concentration (0.9 vol%), PTSA concentration (1.5 mol L^{-1}) and solid-liquid ratio (30 g L^{-1}). For comparison, the leaching performance of other organic acids (oxalic acid, malonic acid, citric acid, succinic acid) were also investigated as references using the leaching conditions: 0.9 vol% H_2O_2, 1.5 mol L^{-1} organic acid concentration, 30 g L^{-1} solid-to-liquid ratio at 80 °C, and 150 min.

2.3. *Separation and recovery of Li and Co*

The acid leaching was carried out under the most suitable conditions obtained from the experimental procedures above to obtain the leachate. Then, a direct crystallization process was involved in this study to achieve effective Li and Co separation. After 1 h of acid leaching, the solid-liquid mixture in the three-neck flask was immediately separated by a filter paper, and the hot leachate (about 80 °C) was directly placed in a 4 °C refrigerator for 12 h. Then, a pink precipitate was obtained via filtration and washing. After that, the crystalline samples were dried at 60 °C for 48 h, and weighed for the calculation of crystallization efficiency. The pink solid was heated to 800 °C under an oxygen atmosphere for 3 h, with an obvious color change of the solid from pink to black. The supernatant liquid from filtration was concentrated at 60 °C by evaporating most water contents and then saturated NaOH solution was added to remove the remaining Co from the solution by precipitation. Next, saturated Na_2CO_3 solution (90 °C) was added for the subsequent precipitation of Li_2CO_3. Finally, pure solid-phase Li_2CO_3 was separated by filtration and purified with alcohol and hot water.

2.4. *Analytical procedure and material characterization*

The concentrations of elements (Li, Co, Mn, Fe, Cu) were determined by ICP-OES. The leaching efficiency (X) was calculated by eq. (1):

$$X = \frac{C_0 V_0}{mw\%} * 100\% \tag{1}$$

where X represents the leaching efficiency; C_0 and V_0 represent the concentration of Co or Li (g L^{-1}), and volume of the leaching solution (L), respectively; m is the mass of initial $LiCoO_2$ (g) and w is the mass fraction of Co or Li (%/100) in the $LiCoO_2$ samples.

The crystal phases of all powder samples were characterized by an X-ray diffractometer (XRD, Rigaku) with high-intensity Cu-Kα radiation (45 kV, 200 mA). The surface morphologies were investigated by scanning electron microscopy (SEM, TESCAM MIRA3) analysis. Fig.S1 shows the XRD pattern and SEM image of the spent $LiCoO_2$ sample. The major 2θ diffraction peaks at 19.0, 37.4, 38.4 and 45.3° correspond well to the crystal planes of (003), (101), (006) and (104), respectively. Therefore, the crystal phase was identified as $LiCoO_2$ (PDF 50–0653). Meanwhile, two 2θ diffraction peaks located at 31.2 and 36.8° matched the crystal planes of Co_3O_4 (220) and (311), implying that the powder obtained from the spent LIBs contained a small amount of Co_3O_4.

3. Results and discussion

3.1. *Optimization of leaching operation parameters*

Figs.1a and b revealed the effect of PTSA concentration on Li and Co leaching efficiencies, respectively. A positive correlation was observed between the acid concentration and the leaching efficiencies, suggesting that the elevated acid concentration from 0.5 to 2.0 mol L^{-1} could improve leaching efficiency from 52% to 100% for Li and from 50% to 99% for Co. The improvement in the leaching performance was ascribed to the higher concentration of H^+ ions provided by the increased PTSA concentration, based on the balanced chemical reaction shown in Eq. (2). Moreover, the Li and Co leaching efficiency had already reached 100 and 99% when the PTSA concentration was 1.5 mol L^{-1}. Thus, the PTSA concentration of 1.5 mol L^{-1} was used as the optimal condition to investigate the effects of other operation parameters in the subsequent experiments.

The positive role of hydrogen peroxide (H_2O_2) in the leaching process of $LiCoO_2$ has long been widely recognized (Golmohammadzadeh et al., 2018; Jung et al., 2021). Owing to the strong chemical bonds between Co and O in the lattice structure of $LiCoO_2$, proper use of reducing agents can significantly improve the leaching efficiency (Meshram et al., 2014; Pinna et al., 2017). Meanwhile, due to the better solubility of Co^{2+} over Co^{3+}, the participation of H_2O_2 as a reducing agent could probably promote the effective leaching of Li and Co. Thus, H_2O_2 was viewed as one of the most effective reducing agent for the hydrometallurgical recycling of Li and Co elements from the spent LIBs (Golmohammadzadeh et al., 2018). Chemical reduction was the major reaction mechanism involved in this process, implying the reduction of Co^{3+} in the lattice structure of $LiCoO_2$ to Co^{2+}, which was soluble in the leaching solution. Therefore, H_2O_2 was employed to assist the leaching of $LiCoO_2$ in PTSA and to optimize the H_2O_2 concentration after testing with different concentrations. From Figs.1c and d, when the concentration of H_2O_2 was increased from 0 to 0.9 vol%, the leaching efficiency was increased from 83 to 100% and 64 to 99% for Li and Co, respectively. However, further increase of the H_2O_2 concentration could not improve the leaching efficiency. Thus, H_2O_2 concentration of 0.9 vol% was adequate for $LiCoO_2$ leaching with a solid-to-liquid ratio of 30 g L^{-1}, given that leaching of $LiCoO_2$ could also be partially realized with the presence of PTSA. Similar phenomenon was also observed in previous studies, when citric acid was used as a leaching reagent, the optimal concentration of H_2O_2 was determined to be 1.0 vol % (Li et al., 2010b). Therefore, H_2O_2 concentration of 0.9 vol% was chosen to be the optimized parameter.

In addition, as shown in Figs.1e and f, the effects of solid-to-liquid ratio on PTSA's leaching efficiency were studied. The Li leaching efficiency was maintained at 100% when the solid-to-liquid ratio was increased from 5 to 45 g L^{-1}, but the leaching efficiency substantially decreased to 85%, when the solid-to-liquid ratio was controlled at 60 g L^{-1}. For Co element, the leaching efficiency reached 99%, when the solid-to-liquid ratio was increased from 5 to 30 g L^{-1}. The leaching performance was also decreased to 85 and 74%, when the solid-to-liquid ratios were controlled at 45 and 60 g L^{-1}, respectively. Therefore, solid-to-liquid ratio of 30 g L^{-1} was considered as the most suitable condition for the leaching of $LiCoO_2$.

Furthermore, the leaching performances of Li and Co were examined with PTSA in the temperature range of 25 to 100 °C. As shown in Figs. 1g and h, the leaching efficiency of Li and Co increased from 95 to 100% and 90 to 99%, respectively, with the increase in temperature from 25 to 80 °C. Previous studies suggested that the dissociation of organic acid was endothermic in nature (Li et al., 2013; Li et al., 2012), and the leaching of Li and Co from $LiCoO_2$ was also endothermic (Li et al., 2013). Thus, the increase of leaching temperature could facilitate the metal extraction by the dissociated acid. Although the increase of the leaching temperature from 80 to 100 °C could slightly improve the leaching efficiencies, from the viewpoint of energy conservation, the most suitable temperature was determined to be 80 °C in this study. It should be mentioned that the possible leaching reaction involved in the leaching process was suggested as Eq. (2):

$$2LiCoO_2 + 6C_7H_8O_3S + H_2O_2 \rightarrow 2C_7H_7O_3SLi + 2(C_7H_7O_3S)_2Co + 4H_2O + O_2(g) \tag{2}$$

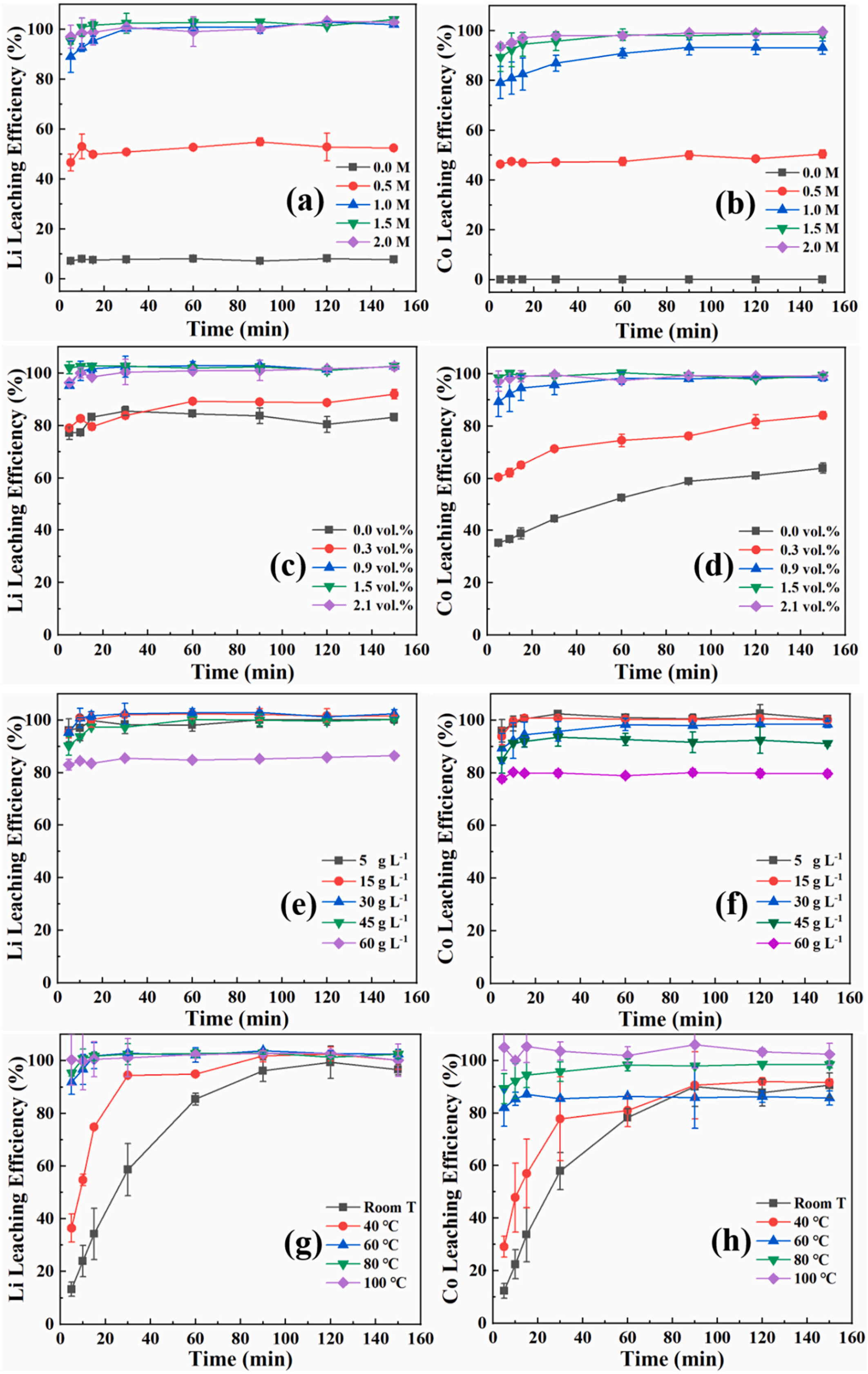

Fig. 1. The effect of (a, b) PTSA concentration, (c, d) H_2O_2 concentration, (e, f) solid-to-liquid ratio, and (g, h) temperature on leaching efficiencies of Li and Co. (Other conditions unless varied were: temperature of 80 °C, solid-to-liquid ratio of 30 g L^{-1}, H_2O_2 concentration of 0.9 vol%, PTSA concentration of 1.5 mol L^{-1}).

Table 1
Comparison of leaching performance of PTSA with the previously reported organic acids for $LiCoO_2$ cathode materials.

No.	Acid name	H_2O_2 Concentration (vol %)	Acid Concentration (mol L^{-1})	Solid-to-liquid ratio (g L^{-1})	Temperature (°C)	Leaching time (min)	Leaching efficiency (%)	References
1#	DL-malic acid ($C_4H_5O_6$)	2.00	1.5	20	90	40	Co: 93 Li: 94	(Li et al., 2010a)
2#	Citric acid ($C_6H_8O_7$)	1.25	2.0	30	60	120	Co: 81 Li: ~92	(Golmohammadzadeh et al., 2017)
3#	Oxalic acid ($C_2H_2O_4$)	N.A.	1.0	15	95	150	Co: 98 Li: 97	(Zeng et al., 2015)
4#	Acetoacetic acid ($C_4H_6O_4$)	1.50	1.5	10	70	60	Co: 98 Li: 99	(Liu et al., 2019)
5#	Succinic acid $(CH_2)_2(CO_2H)_2$	4.00	1.5	15	70	40	Co: 100 Li: 98	(Li et al., 2015)
6#	Aspartic acid ($C_4H_7NO_4$)	4.00	1.5	10	90	120	Co: ~60 Li: ~60	(Li et al., 2013)
7#	PTSA	0.90	1.5	30	80	60	Co: ~99 Li: ~100	This work

3.2. *Comparison of leaching performance*

Table 1 summarizes the reported results of the organic acid-assisted $LiCoO_2$ leaching in previous studies, which confirmed the superior leaching performance of PTSA. For example, the requirement of H_2O_2 concentration by the PTSA leaching was only 0.9 vol%, which was lower than previous studies using succinic acid (4 vol%) and aspartic acid (4 vol%). Moreover, the most suitable solid-to-liquid ratio for effective leaching with PTSA was 30 g L^{-1}, which was much higher than previous studies using DL-malic acid (20 g L^{-1}), aspartic acid (10 g L^{-1}) and oxalic acid (15 g L^{-1}). Furthermore, to highlight the superior leaching performance of PTSA, a series of organic acids reported in previous studies, including oxalic acid, citric acid, succinic acid and malonic acid, were employed to compare leaching performance with PTSA. The experiment was conducted with acid concentration of 1.5 mol L^{-1}, a solid-to-liquid ratio of 30 g L^{-1}, H_2O_2 concentration of 0.9 vol%, at 80 °C and for 150 min. As shown in Figs.2a and b, when PTSA was applied to leach $LiCoO_2$, the leaching efficiencies of Li and Co reached 100 and 99%, respectively. In addition, the leaching efficiency of 90% could be achieved for both Li and Co with PTSA, even within a very short leaching time (5 min), while the efficiencies were generally lower than 72% by using the other acids (Figs.2a and b). Therefore, it can be concluded that a higher leaching performance was observed by using PTSA as the leaching agent, in terms of leaching rate and leaching efficiency. Previous studies suggested that pK_a value could be regarded as an important indicator for choosing appropriate leaching reagents (Golmohammadzadeh et al., 2018). Strength of organic acids is generally based on the functional groups within their molecular structure including, $-COOH$, $-SO_3H$, enol, alcohol, thiol and phenol groups (Theron, 2011). From the comparison of the pK_a value (−2.8 for PTSA while 1.24–4.2 for other acids), it can be concluded that the high acidity of leaching agents played a crucial part in the leaching of $LiCoO_2$. This could be attributed to the sulfonyl group ($-SO_2OH \rightarrow -SO_2O^- + H^+$) of PTSA which is more likely to ionize in aqueous solution to produce H^+ ions than the functional groups from other leaching agents (Serjeant and Dempsey, 1979).

3.3. *Kinetic study based on the leaching of spent $LiCoO_2$*

To confirm the feasibility of PTSA for practical application, the PTSA was further used to leach $LiCoO_2$ samples from spent LIBs with leaching temperatures ranging from 25 to 80 °C. As illustrated in Figs. 3a and b, when leaching temperature was 80 °C, the leaching efficiencies of 95 and 93% can be achieved for Li and Co, respectively. Then, the leaching data obtained after this experiment were employed for the investigation of leaching kinetics. Previous studies have implied that the leaching kinetics of $LiCoO_2$ were composed of two stages (Jha et al., 2013; Yang et al., 2014). Mathematical fitting of shrinking core model was adopted to determine the leaching mechanism of spent $LiCoO_2$ (Levenspiel, 1998), detailed mathematical expressions are in Eq. (3) and (4):

$$\text{Chemical reaction control}: 1-(1-X)^{\frac{1}{3}}=kt \tag{3}$$

$$\text{Diffusion control}: 1-\frac{2}{3}X-(1-X)^{\frac{2}{3}}=kt \tag{4}$$

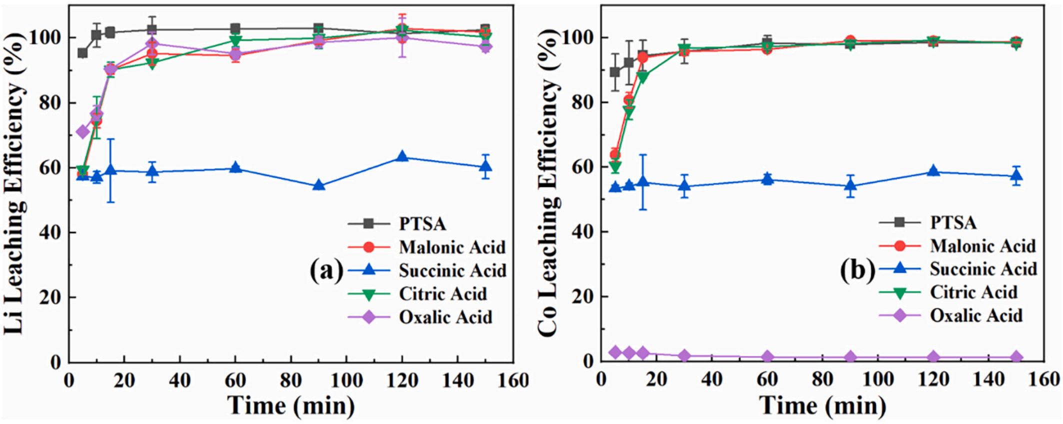

Fig. 2. Comparison of PTSA leaching performance for (a) Li and (b) Co with malonic acid, succinic acid, citric acid and oxalic acid. (Note that the performance comparison experiment was conducted with leaching temperature of 80 °C, acid concentration of 1.5 mol L^{-1}, H_2O_2 concentration of 0.9 vol% and solid-to-liquid ratio of 30 g L^{-1}).

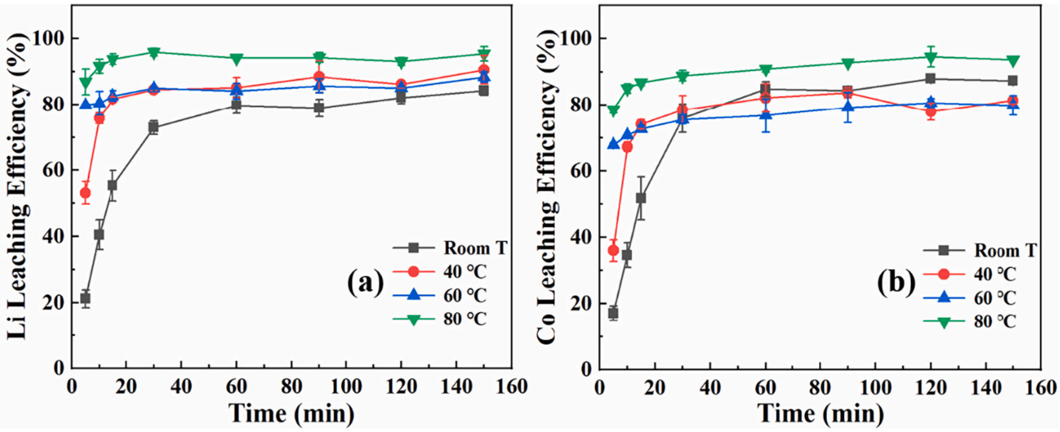

Fig. 3. Effect of temperature on PTSA leaching of Li (a) and Co (b) from spent $LiCoO_2$ (Note that leaching experiment of spent $LiCoO_2$ was conducted with leaching temperature of 80 °C, acid concentration of 1.5 mol L^{-1}, H_2O_2 concentration of 0.9 vol% and solid-to-liquid ratio of 30 g L^{-1}).

In eqs. (3) and (4), X represents the fraction of metals leached by PTSA, *k* is the apparent rate constant (min^{-1}) and *t* is the reaction time (min).

Table S2 summarizes the fitting results of leaching kinetics at different temperatures by the shrinking core model, which clearly indicated that the leaching of Li was controlled by diffusion ($R^2 = 0.98$) model and that of Co was controlled by chemical reaction ($R^2 = 0.99$). As displayed in Fig. 4a and b, the plots of $1\text{-}(1\text{-}X)^{1/3}$ versus *t* and $1–2/3\times$-$(1\text{-}X)^{2/3}$ versus *t* further examine the leaching models of Li and Co, respectively. Poor linear fittings with low correlation coefficients (Li: $R^2 < 0.79$; Co: $R^2 < 0.82$) for the leaching data between 40 and 80 °C, suggest that the shrinking core model could not account for the leaching kinetics at higher temperatures. In addition, a second-order rate law (Eq. (5)) was further adopted to fit the leaching kinetics. The fitting results according to Eq. (6) are also summarized in Table S2, which show good correlation fitting (Li: $R^2 > 0.99$; Co: $R^2 > 0.96$) at leaching temperatures between 40 and 80 °C but poor results for the data at 25 °C (Li: $R^2 \sim 0.95$; Co: $R^2 \sim 0.84$). The fittings of t/C_t versus *t* for the leaching of Li and Co are depicted in Figs.4c and d, respectively. This confirms that the leaching process could follow the second-order rate law between 40 and 80 °C:

$$\frac{dC_t}{dt} = k(C_e - C_t)^2 \tag{5}$$

where *k* is the second-order leaching rate constant (L g^{-1} min^{-1}), C_e is the saturated concentration of soluble Li (or Co) (g L^{-1}), *t* is the leaching

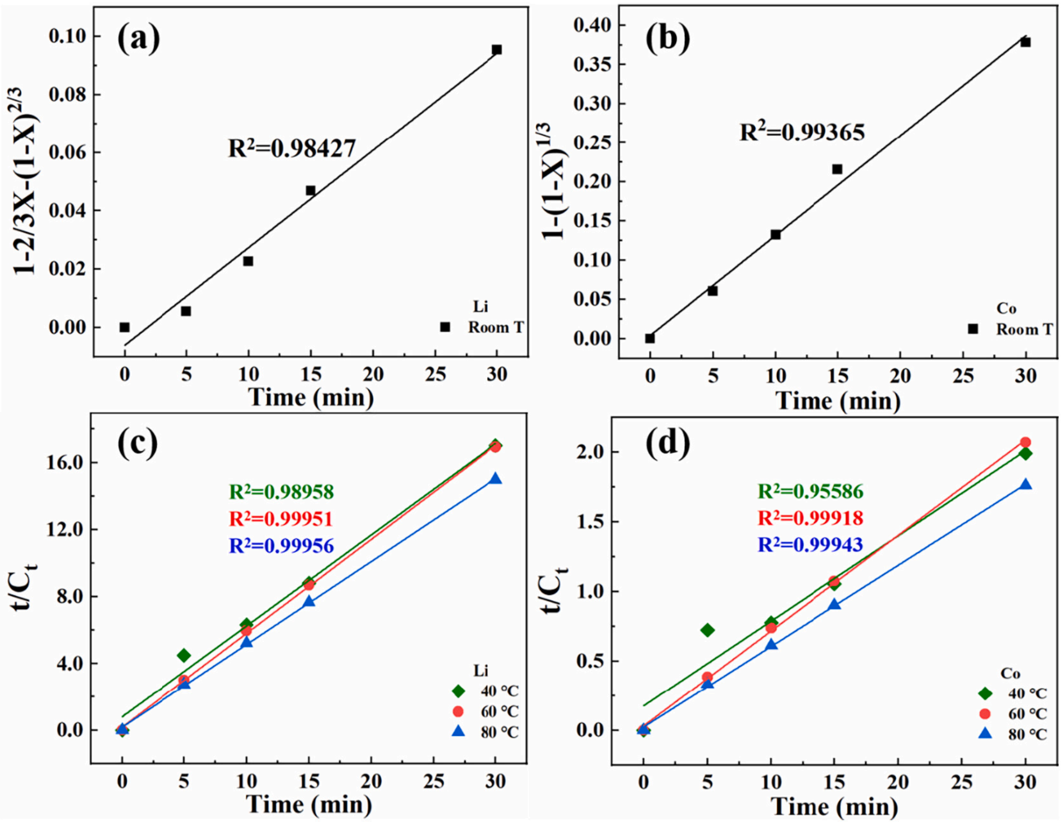

Fig. 4. Fitting of kinetic models for leaching: (a) shrinking core diffusion model for Li at 25 °C, (b) shrinking sphere chemical reaction model for Co at 25 °C, (c) second-order reaction model for Li and (d) second-order reaction model for Co (40–80 °C).

time (min), C_t is the concentration of leached Li (or Co) in the suspension at any time t. As C_t varies from 0 to C_t while t is extended from 0 to t, the function can be integrated to:

$$\frac{t}{C_t} = \frac{1}{kC_e^2} + \frac{t}{C_e} \tag{6}$$

According to Eq. (2), the reaction products (e.g. $C_7H_7O_3SLi$ and $(C_7H_7O_3S)_2Co$) were unable to immediately diffuse into the leaching solution, due to energy limitation at room temperature. As a result, the solid products might precipitate on the surface of the unreacted $LiCoO_2$ sample and could slow down the chemical interaction between the PTSA and the unreacted core of $LiCoO_2$. The different rate-determining mechanism of Li and Co is probably due to stronger Co—O chemical bond in the crystal structure of $LiCoO_2$ as it needs a reducing agent according to Eq. (2). Therefore, the chemical reaction was more likely to be the rate-determining step for Co leaching kinetics. At temperature ≥ 40 °C, the leaching rate of Li and Co is controlled by a second order reaction. The dissolution of leaching products on the surface may be described as follows:

$$C_7H_7O_3SLi\ (s) \rightarrow C_7H_7O_3S^-\ (aq) + Li^+\ (aq) \tag{7}$$

$$(C_7H_7O_3S)_2Co\ (s) \rightarrow 2C_7H_7O_3S^-\ (aq) + Co^{2+}\ (aq) \tag{8}$$

3.4. *Recycling and regeneration*

3.4.1. *Separation of Li^+ and Co^{2+} by direct crystallization*

Interestingly, as depicted in Figs.5c and d, when the high-temperature leachate (80 °C) was placed in a low-temperature environment, pink crystals were spontaneously formed and precipitated at the bottom. This phenomenon could be observed for every leachate obtained from the leaching processes with different solid-to-liquid ratios. Figs.5a and b illustrates the changes of Li^+ and Co^{2+} concentrations in the leachate before and after the direct crystallization process, implying that the concentration of Co^{2+} in the solution decreased dramatically after direct crystallization with only a slight drop in the concentration of Li^+. Therefore, it was inferred that the pink crystal precipitated from the leachate after cooling was a Co-rich compound (hereinafter referred to as precursor A). A small amount of Li^+ was adsorbed on the surface of precursor A, resulting in a slight decrease of Li^+ concentration after crystallization (Fig. 5a). The mass contents of Co and Li in Fig.S2 further confirmed the predominance of Co in the precipitation process. Therefore, after treating with alcohol to remove possible impurities on the solid surface, the as-obtained crystals were further characterized by XRD. The pattern in Fig.S3 indicated that the predominant crystalline phase was well attributed to cobalt toluene sulfonate hexahydrate ($C_{14}H_{14}CoO_6S_2 \cdot 6H_2O$, PDF 48–2314). From the results above, this direct crystallization process proved to be an effective method for the separation of Li and Co, thus making the recycling strategy environmentally and economically proficient, especially in comparison with complicated separation treatments in previous studies (e.g. chemical precipitation, solvent extraction). For example, after leaching of the spent $LiCoO_2$ by methane sulfonic acid, Li and Co ions in the leachate were separated by the addition of precipitating agents (e.g. ammonia and urea) for the formation of precipitates (Wang et al., 2019).

3.4.2. *Metal recovery and material regeneration*

The schematic diagram in Fig. 6 (a) reveals the entire procedure for the recovery and regeneration of Li and Co in this study. It was reported

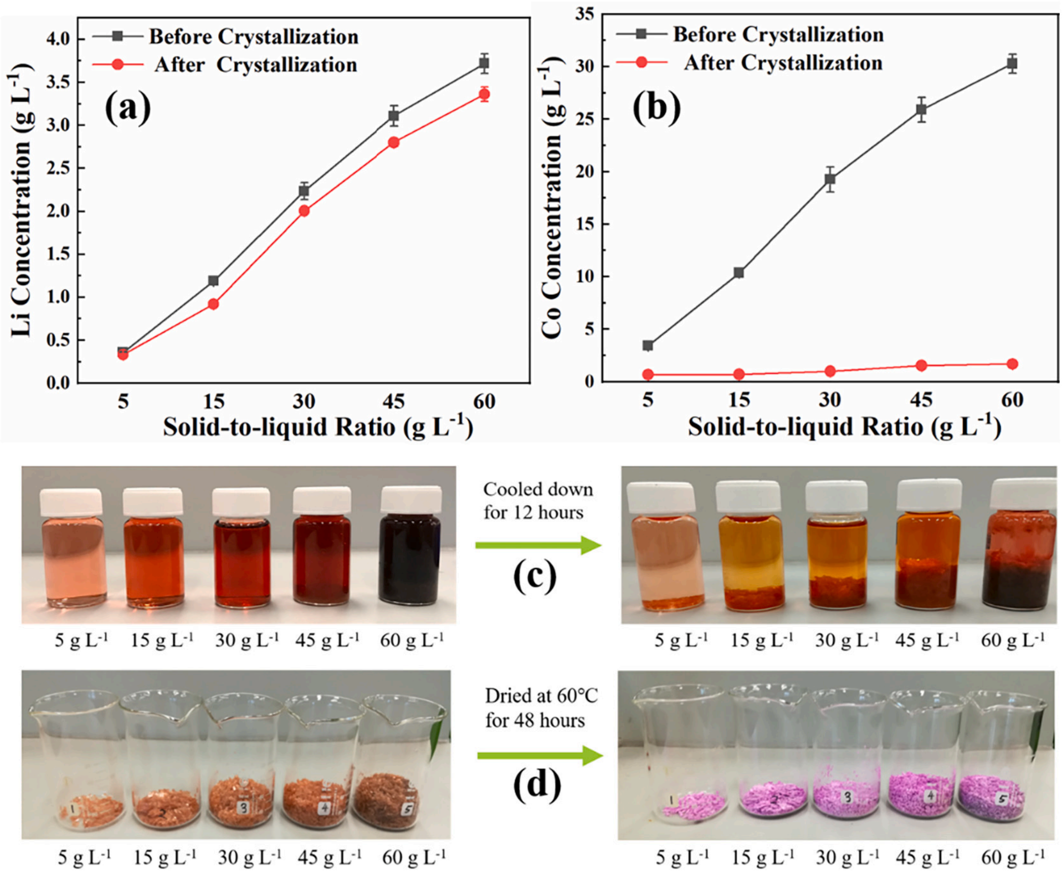

Fig. 5. Concentration of metal ions in leachates produced at different S/L ratios at 80 °C before and after crystallization: (a) Li; (b) Co; and appearance after cooling/crystallization at 4 °C for 12 h (c) and after drying at 60 °C for 48 h (d) (Note that the leaching experiment was conducted with H_2O_2 concentration of 0.9 vol%, PTSA concentration of 1.5 mol L^{-1}, solid-to-liquid ratio of 5–60 g L^{-1} and leaching time of 60 min).

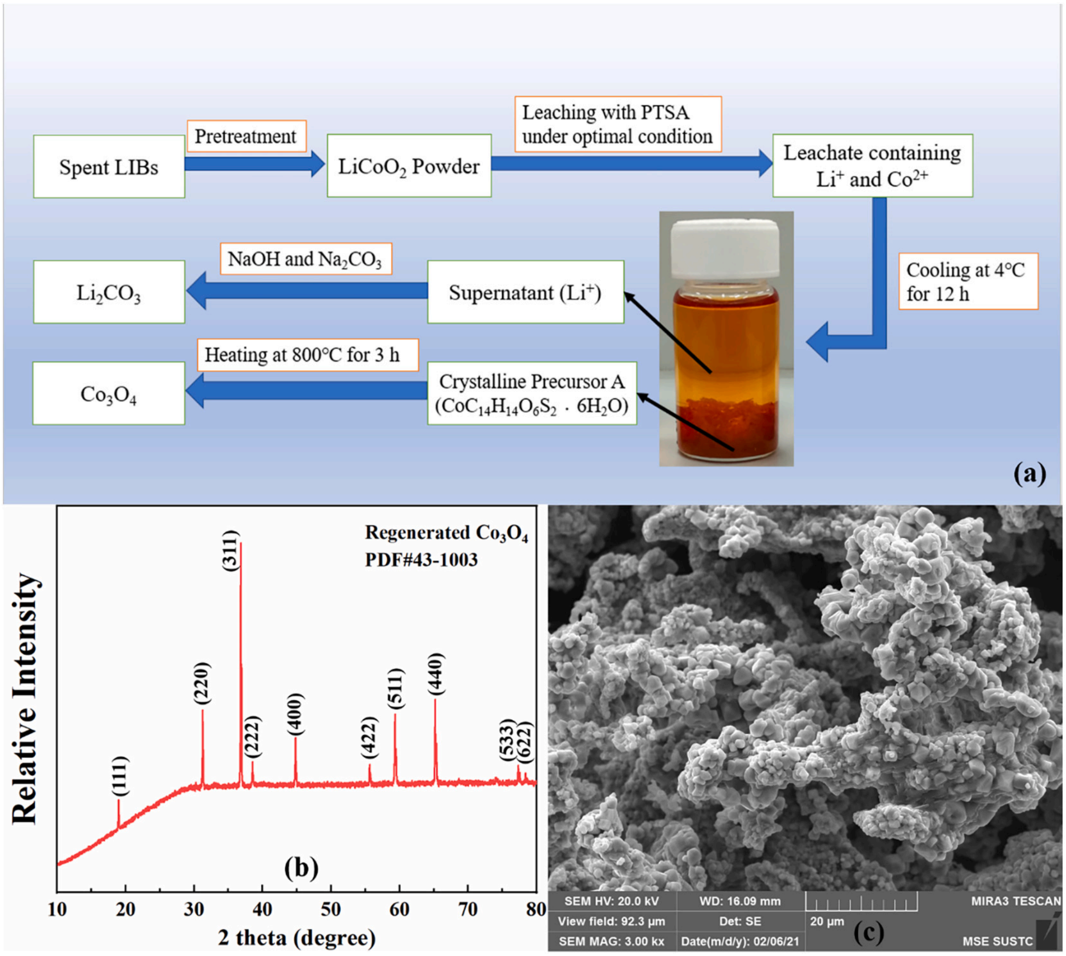

Fig. 6. (a) The flowchart of the process to recover Li_2CO_3 and Co_3O_4 from spent LIBs. (b) XRD pattern and (c) Typical SEM image of the regenerated Co_3O_4 under the most suitable condition.

that the solubility of $(C_7H_7O_3S)_2Co{\cdot}6H_2O$ decreased continuously with decreasing temperature (Yu et al., 2016). Hence, to obtain a fully crystalized product, the hot leachates were placed in refrigerator (4 °C) for 12 h. After previous leaching steps, the as-obtained pink crystals were employed to regenerate Co_3O_4, which was considered as one of the critical raw materials for industrial production of $LiCoO_2$. When heat treatment was performed on the pink crystals, it could be transformed into Co_3O_4 materials. It is worth noting that Li is volatile at high temperatures (Lundblad et al., 2000; Tennakoon et al., 1997). Therefore, the residual Li contents in precursor A, as shown in Fig.S2 was evaporated upon thermal treatment. The purity of the regenerated Co_3O_4 was further confirmed by ICP-OES after acid digestion, and the results showed no Li detected (detection limit for Li: 0.002 mg/L). Fig. 6b illustrates the typical XRD pattern of the pink crystal treated at 800 °C for 3 h. The crystal phase of thermal treated sample in black color could be identified as Co_3O_4 (PDF 43–1003). Fig.S4 shows the formation of well-crystallized Co_3O_4 from the leaching processes with different solid-to-liquid ratios. The SEM image in Fig. 6c revealed that particle size of the regenerated Co_3O_4 sample was between 1 and 2 μm.

The recovery yield of Co, which was determined by the mass ratio of recovered Co to the total Co in the original $LiCoO_2$, is considered as one of the criteria to evaluate the effectiveness of the recovery strategy. Fig. 7 shows the calculated Co recovery yield (solid-to-liquid ratio ranging from 5 to 60 g L^{-1}) after every step in this study, including leaching by PTSA/H_2O_2, precipitation of Co-rich crystals, and heat treatment (800 °C, 3 h). The results implied that Co recovery yield was correspondingly increased with the increase of solid-to-liquid ratio up to 30 g L^{-1}. Low solid-to-liquid ratio (< 30 g L^{-1}) suggested a relatively low Co concentration in the leachate (Figs.5a and b), which could subsequently result in less Co precipitation. However, when the solid-to-liquid ratio was larger than 30 g L^{-1}, a significant decrease in Co recovery yield was observed. As suggested in Fig. 1h, this is due to the decreased leaching efficiency. It can be seen from Fig. 7 that little loss of Co was observed for the conversion from Co-rich crystal to Co_3O_4 during heat treatment process. Overall, in terms of Co recovery yield during these three steps, 30 g L^{-1} was confirmed to be the most suitable solid-

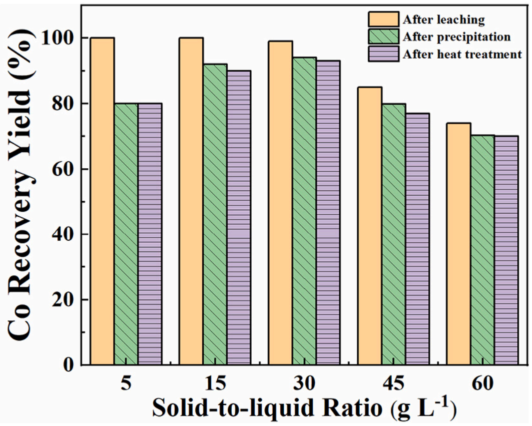

Fig. 7. Effects of solid-to-liquid ratios on Co recovery yields.

to-liquid ratio, and the total Co recovery yield could reach as high as 94%.

Once 30 g L^{-1} was identified as a practical condition for the whole recovery pathway, the Li-containing supernatant liquid was then utilized to regenerate Li_2CO_3, which was viewed as one of the indispensable raw materials in the production of LIB cathode materials. The Li-containing solution was firstly purified with NaOH solution to remove a small amount of Co^{2+}, followed by the treatment of Na_2CO_3 solution (Barik et al., 2016) and finally leading to the formation of Li_2CO_3, which was further confirmed by the XRD pattern (Fig.S5). The obtained Li_2CO_3 was then purified by washing with alcohol to remove possible organic impurities and the final recovery yield of Li was able to reach up to 80%. The regenerated Co_3O_4 and Li_2CO_3 could react together at high temperatures to regenerate active cathode materials $LiCoO_2$ (Shi et al., 2018). Overall, the proposed recovery strategy is highly recommended, owing to its concise flow path and high recovery yield.

4. Conclusions

In conclusion, PTSA was proved to be an effective leaching agent for battery recycling applications. Under the optimized leaching conditions (H_2O_2: 0.9 vol%, PTSA concentration: 1.5 mol L^{-1}, temperature: 80 °C, solid-to-liquid ratio: 30 g L^{-1}), nearly 100% of Li and 99% of Co could be successfully extracted out in 1 h. Detailed kinetic studies demonstrated that leaching temperature could significantly affect the leaching efficiencies of Li and Co from the spent $LiCoO_2$. By cooling the leachate, Co ions could be easily separated from Li ions via direct crystallization of Co $(OTs)_2 \cdot 6H_2O$ at low temperatures. Afterwards, the well-crystallized Co_3O_4 materials were regenerated after heat treatment while the Li_2CO_3 was recovered from the supernatant liquid with a final recovery yield of 94% Co and 80% Li. Owing to the superiority in Co and Li recovery from the $LiCoO_2$, PTSA might have great potentials to be applied for the recovery of other battery materials, such as ternary cathode materials NCA and NCM, etc. Overall, this study successfully confirmed that PTSA-assisted recycling strategy could be regarded as one of the potential processes to achieve green, sustainable, and effective regeneration of Co_3O_4 and Li_2CO_3 materials, thus achieving circular economy of rechargeable LIBs industry.

CRediT authorship contribution statement

Yuanyuan Tang and Xiao-ying Lu co-supervised the whole work with conceptualization, methodology and fund acquisition. Jiadong Liu conducted the experiments, analyzed data and wrote the draft manuscript. Tsz Yau Mak, Zhe Meng, Xuyang Wang, Yulin Cao, Zhouguang Lu and Dawson Wai-Shun Suen were also involved in conducting experiments, analyzing data and revising the manuscript.

Declaration of Competing Interest

The authors declare that there are no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References

Barik, S.P., Prabaharan, G., Kumar, B., 2016. An innovative approach to recover the metal values from spent lithium-ion batteries. Waste Manag. 51, 222–226.

Chen, L., et al., 2017. Rapid and near-complete dissolution of wood lignin at ≤80°C by a recyclable acid hydrotrope. Sci. Adv. 3 (9), e1701735.

Chen, X., Luo, C., Zhang, J., Kong, J., Zhou, T., 2015. Sustainable recovery of metals from spent Lithium-ion batteries: a green process. ACS Sustain. Chem. Eng. 3 (12), 3104–3113.

Gao, W., et al., 2017. Lithium carbonate recovery from cathode scrap of spent Lithium-ion battery: a closed-loop process. Environ. Sci. Technol. 51 (3), 1662–1669.

Garcia, E.M., Santos, J.S., Pereira, E.C., Freitas, M.B.J.G., 2008. Electrodeposition of cobalt from spent Li-ion battery cathodes by the electrochemistry quartz crystal microbalance technique. J. Power Sources 185 (1), 549–553.

Golmohammadzadeh, R., Rashchi, F., Vahidi, E., 2017. Recovery of lithium and cobalt from spent lithium-ion batteries using organic acids: process optimization and kinetic aspects. Waste Manag. 64, 244–254.

Golmohammadzadeh, R., Faraji, F., Rashchi, F., 2018. Recovery of lithium and cobalt from spent lithium ion batteries (LIBs) using organic acids as leaching reagents: a review. Resour. Conserv. Recycl. 136, 418–435.

Gupta, V.K., Ali, I., Saleh, T.A., Nayak, A., Agarwal, S., 2012. Chemical treatment technologies for waste-water recyclin‡ an overview. RSC Adv. 2, 6380–6388.

Guzolu, J.S., Gharabaghi, M., Mobin, M., Alilo, H., 2017. Extraction of Li and co from Li-ion batteries by chemical methods. J. Inst. Engineers (India): Series D 98 (1), 43–48.

He, L.-P., Sun, S., Mu, Y.-Y., Song, X., Yu, J., 2016. Recovery of Lithium, nickel, cobalt, and manganese from spent Lithium-ion batteries using l -tartaric acid as a Leachant. ACS Sustain. Chem. Eng. 5.

Horeh, N.B., Mousavi, S.M., Shojaosadati, S.A., 2016. Bioleaching of valuable metals from spent lithium-ion mobile phone batteries using aspergillus Niger. J. Power Sources 320, 257–266.

Jacoby, M., 2019. It’s Time to Recycle Lithium-ion Batteries, 97. C&EN Global Enterprise.

Jha, M.K., et al., 2013. Recovery of lithium and cobalt from waste lithium ion batteries of mobile phone. Waste Manag. 33 (9), 1890–1897.

Joulié, M., Billy, E., Laucournet, R., Meyer, D., 2017. Current collectors as reducing agent to dissolve active materials of positive electrodes from Li-ion battery wastes. Hydrometallurgy 169, 426–432.

Jung, J.C.-Y., Sui, P.-C., Zhang, J., 2021. A review of recycling spent lithium-ion battery cathode materials using hydrometallurgical treatments. J. Energy Storage 35, 102217.

Ku, H., et al., 2016. Recycling of spent lithium-ion battery cathode materials by ammoniacal leaching. J. Hazard. Mater. 313, 138–146.

Lee, C.K., Rhee, K.-I., 2003. Reductive leaching of cathodic active materials from lithium ion battery wastes. Hydrometallurgy 68 (1), 5–10.

Levenspiel, O., 1998. Chemical Reaction Engineering. John Wiley & Sons.

Li, L., et al., 2010a. Environmental friendly leaching reagent for cobalt and lithium recovery from spent lithium-ion batteries. Waste Manag. 30 (12), 2615–2621.

Li, L., et al., 2010b. Recovery of cobalt and lithium from spent lithium ion batteries using organic citric acid as leachant. J. Hazard. Mater. 176 (1), 288–293.

Li, L., et al., 2012. Ascorbic-acid-assisted recovery of cobalt and lithium from spent Li-ion batteries. J. Power Sources 218, 21–27.

Li, L., et al., 2013. Recovery of metals from spent lithium-ion batteries with organic acids as leaching reagents and environmental assessment. J. Power Sources 233, 180–189.

Li, L., et al., 2015. Succinic acid-based leaching system: a sustainable process for recovery of valuable metals from spent Li-ion batteries. J. Power Sources 282, 544–551.

Li, L., et al., 2018. Economical recycling process for spent lithium-ion batteries and macro- and micro-scale mechanistic study. J. Power Sources 377, 70–79.

Liu, B., et al., 2019. Maleic, glycolic and acetoacetic acids-leaching for recovery of valuable metals from spent lithium-ion batteries: leaching parameters, thermodynamics and kinetics. R. Soc. Open Sci. 6 (9), 191061.

Lundblad, A., Schwartz, S., Bergman, B., 2000. Effect of sintering procedures in development of LiCoO2-cathodes for the molten carbonate fuel cell. J. Power Sources 90 (2), 224–230.

Meshram, P., Pandey, B.D., Mankhand, T.R., 2014. Extraction of lithium from primary and secondary sources by pre-treatment, leaching and separation: a comprehensive review. Hydrometallurgy 150, 192–208.

Nayaka, G.P., Pai, K.V., Manjanna, J., Keny, S.J., 2016. Use of mild organic acid reagents to recover the co and Li from spent Li-ion batteries. Waste Manag. 51, 234–238.

Pinna, E.G., Ruiz, M.C., Ojeda, M.W., Rodriguez, M.H., 2017. Cathodes of spent Li-ion batteries: dissolution with phosphoric acid and recovery of lithium and cobalt from leach liquors. Hydrometallurgy 167, 66–71.

Serjeant, E.P., Dempsey, B., 1979. IUPAC chemical data series. In: Ionisation constants of organic acids in aqueous solution, 23. Pergamon Press, Oxford, 989 pp.

Shi, Y., Chen, G., Chen, Z., 2018. Effective regeneration of LiCoO2 from spent lithium-ion batteries: a direct approach towards high-performance active particles. Green Chem. 20 (4), 851–862.

Sun, L., Qiu, K., 2011. Vacuum pyrolysis and hydrometallurgical process for the recovery of valuable metals from spent lithium-ion batteries. J. Hazard. Mater. 194, 378–384.

Sun, Z., et al., 2017. Toward sustainability for recovery of critical metals from electronic waste: the hydrochemistry processes. ACS Sustain. Chem. Eng. 5 (1), 21–40.

Tennakoon, T.M.T.N., Lindbergh, G., Bergman, B., 1997. Performance of LiCoO2 cathodes, prepared using the Pechini method, in molten carbonate fuel cells. J. Electrochem. Soc. 144 (7), 2296–2301.

Theron, M.M., 2011. Organic Acids and Food Preservation. CRC Press. https://doi.org/10.1201/9781420078435.

Wang, B., et al., 2019. Recycling LiCoO2 with methanesulfonic acid for regeneration of lithium-ion battery electrode materials. J. Power Sources 436, 226828.

Wang, D., Wen, H., Chen, H., Yang, Y., Liang, H., 2016. Chemical evolution of LiCoO2 and NaHSO4·H2O mixtures with different mixing ratios during roasting process. Chem. Res. Chin. Univ. 32 (4), 674–677.

Xiao, J., Li, J., Xu, Z., 2020. Challenges to future development of spent Lithium ion batteries recovery from environmental and technological perspectives. Environ. Sci. Technol. 54 (1), 9–25.

Xu, J., et al., 2008. A review of processes and technologies for the recycling of lithium-ion secondary batteries. J. Power Sources 177 (2), 512–527.

Yadav, P., Jie, C.J., Tan, S., Srinivasan, M., 2020. Recycling of cathode from spent lithium iron phosphate batteries. J. Hazard. Mater. 399, 123068.

Yang, X., Zhang, J., Fang, X., 2014. Rare earth element recycling from waste nickel-metal hydride batteries. J. Hazard. Mater. 279, 384–388.

Yang, Y., Xu, S., He, Y., 2017. Lithium recycling and cathode material regeneration from acid leach liquor of spent lithium-ion battery via facile co-extraction and co-precipitation processes. Waste Manag. 64, 219–227.

Yu, C., Huang, Z., Zeng, Z., Xue, W., 2016. Thermodynamic models for correlation of solubility of Hexaquocobalt(II) Bis(p-toluenesulfonate) in liquid mixtures of water and ethanol from 288.15 to 333.15 K. J. Solut. Chem. 45 (3), 395–409.

Zafar, Z.I., Ashraf, M., 2007. Selective leaching kinetics of calcareous phosphate rock in lactic acid. Chem. Eng. J. 131 (1), 41–48.

Zeng, X., Li, J., Shen, B., 2015. Novel approach to recover cobalt and lithium from spent lithium-ion battery using oxalic acid. J. Hazard. Mater. 295, 112–118.

Zhang, X., et al., 2018. Toward sustainable and systematic recycling of spent rechargeable batteries. Chem. Soc. Rev. 47 (19), 7239–7302.

Zhang, Z., et al., 2014. Recovery of Lithium cobalt oxide material from the cathode of spent Lithium-ion batteries. ECS Electrochem. Lett. 3 (6), A58–A61.

Zhao, L., Yang, D., Zhu, N.-W., 2008. Bioleaching of spent Ni–cd batteries by continuous flow system: effect of hydraulic retention time and process load. J. Hazard. Mater. 160 (2), 648–654.