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Zhouguang Lu

Dawson Wai Shun Suen

See next page for additional authors

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Efficient recovery of lithium and cobalt from spent lithium-ion batteries by *p*-toluene sulfonic acid

Jiadong Liu^a, Tsz Yau Mak^b, Zhe Meng^a, Xuyang Wang^c, Zhouguang Lu^c, Dawson Wai-Shun Suen^b, Xiao-Ying Lu^{b,*}, Yuanyuan Tang^{a,*}

^a State Environmental Protection Key Laboratory of Integrated Surface Water-Groundwater Pollution Control, School of Environmental Science and Engineering, Southern University of Science and Technology, No.1088 Xueyuan Avenue, Shenzhen 518055, China.

^b Faculty of Science and Technology, Technological and Higher Education Institute of Hong Kong, Hong Kong, China.

^c Department of Materials Science and Engineering, Guangdong Provincial Key Laboratory of Energy Materials for Electric Power, Southern University of Science and Technology, Shenzhen, No.1088 Xueyuan Avenue, 518055, China

*Correspondence authors

E-mail address: tangyy@sustech.edu.cn; xylu@thei.edu.hk

Abstract

Rechargeable lithium-ion batteries (LIBs) are 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. Operation parameters such as PTSA concentration, hydrogen peroxide (H₂O₂) concentration, solid-to-liquid ratio, leaching temperature and time, were systematically investigated. Under the optimal conditions (0.9 vol% H₂O₂, 1.5 mol L⁻¹ PTSA, 30 g L⁻¹ solid-to-liquid ratio, 80 °C, and 60 min), while the leaching efficiencies of spent LiCoO₂ for Li and Co was 95 and 93% respectively, the leaching efficiencies of commercial LiCoO₂ was nearly quantitative. 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 Co₃O₄ and Li₂CO₃ demonstrated the great potential of the PTSA-assisted leaching method in metal recovery 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.

Keywords: Lithium cobalt oxide; Recovery; *p*-toluene sulfonic acid; Spent lithium-ion battery; Kinetics; Leaching

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 spent LIBs have been generated,

thus causing significant environmental pollution and poses 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 treated properly. 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 pyrometallurgy process is simple, but has an obvious disadvantage. Particularly, the pyrometallurgy process requires 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 pyrometallurgy process were often low-grade compounds, which requires further processing and purifications. Obviously, this pyrometallurgy process could result in high cost and operation difficulty (Garcia et al., 2008; Joulié et al., 2017; Xu et al., 2008). The main step for the biohydrometallurgy process is to utilize the biological

interactions between battery materials and microorganisms to reduce and reuse metals. Again, the biohydrometallurgy process has its own obvious 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 hydrometallurgy treatment of spent battery materials has multiple advantages, including high feasibility, appropriate reaction speed, 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 acids, alkalis and reducing agents to leach such 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 and 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 metal recovery selectivity (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), etc. 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 product yield loss 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. *p*-toluene sulfonic acid (PTSA) is a strong organic acid ($\text{pK}_a = -2.8$) and has a good solubility in water (67 g/100 mL). 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 found 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 and Co from LiCoO_2 powder was conducted to address the existing technical challenges by using hydrometallurgical leaching with PTSA, followed by pyrometallurgical treatment. By a combination of PTSA and hydrogen peroxide (H_2O_2), the effects of operation parameters, including time, 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 simply cooling process of the obtained leachate, the Co-containing compounds precipitated as a powder while the Li-containing compounds remained dissolved in the supernatant. Finally, the 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 (Samsang 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 LiCoO₂ 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 LiCoO₂, polyvinylidene fluoride (PVDF) binder and electrolyte. To obtain the spent LiCoO₂ powder, the electrode was placed in 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 LiCoO₂ powder and aluminum foil. Finally, the spent LiCoO₂ sample was manually ground into smaller particles (5-25 μm), which was beneficial for the subsequent organic acid-assisted leaching process. Additionally, *p*-toluene sulfonic acid (98.5%, Aladdin®) was used as the leaching agent, and hydrogen peroxide (35%, LingFeng®) was employed as the reducing agent. Succinic acid (99.5%, Aladdin®), citric acid (99.5%, Aladdin®), malonic acid (99.5%, Aladdin®), and oxalic acid (98%, Aladdin®) were also used for leaching performance comparison. 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 LiCoO₂ 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 optimal 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 optimal 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. Optimized 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. (Leaching conditions: 0.9 vol%

H₂O₂, 1.5 mol L⁻¹ organic acid concentration, 30 g L⁻¹ solid-to-liquid ratio, 80 °C, and 150 min).

2.3. Separation and recovery of Li and Co

The acid leaching was carried out under the optimal 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. After that, the crystalline samples were dried at 60 °C for 48 h, and weighed for the calculation of crystallization rate. 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 from filtration was allowed to cool to 60°C and then saturated NaOH solution was added to remove the remaining Co from the solution by precipitation. Next, saturated Na₂CO₃ solution (90°C) was added for the subsequent precipitation of Li₂CO₃. Finally, pure solid-phase Li₂CO₃ was obtained and purified with alcohol and hot water. For comparison, the hot leachate was also treated at room temperature for direct crystallization.

2.4. Analytical procedure and material characterization

The concentrations of metal elements (Li, Co, Ni, Mn, Fe, Cu) were measured by ICP-OES (PerkinElmer Optima 3300 DV). The leaching efficiency (X) was calculated by the equation as below:

$$X = \frac{C_0 V_0}{mw\%} * 100\% \quad (1)$$

where X represents the leaching efficiency; C_0 as the concentration of Co or Li in the leachate (g L^{-1}), V_0 as the volume of the leaching solution (L), m as the mass of initial LiCoO_2 (g) and $w\%$ as the percent by mass of Co or Li in the LiCoO_2 samples.

According to ICP-OES analyses, the content of LiCoO_2 samples powder was shown in Table S1. The crystal phases of all powder samples were characterized by an X-ray diffractometer (XRD, Rigaku) with high-intensity Cu-K α radiation (45kV 200mA). 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 $^\circ$ 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 $^\circ$ 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 illustrate 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 50 to 99% for Co. The improvement in the leaching performance was resulted from the higher concentration of hydrogen ions (H⁺) provided by the increased PTSA concentration. Moreover, the Li and Co leaching efficiency had already reached 100 and 99%, when the PTSA concentration was 1.5 mol L⁻¹. The above results confirmed that PTSA of 1.5 mol L⁻¹ should be considered as the optimal acid concentration for LiCoO₂ leaching. 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.

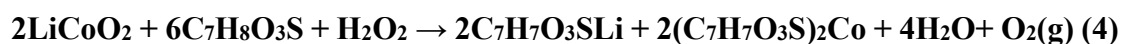
Owing to the strong chemical bonds between Co and O in the lattice structure of LiCoO₂, proper use of reducing agents can significantly improve the leaching efficiency (Meshram et al., 2014; Pinna et al., 2017). Meanwhile, due to the better solubility of Co²⁺ over Co³⁺, the participation of H₂O₂ as reducing agent could probably promote the effective leaching of Li and Co. Thus, H₂O₂ was viewed as one of the most commonly-used reducing agents in the effective recycling of Li and Co from spent LIBs

(Golmohammadzadeh et al., 2018). Furthermore, applying H₂O₂ as reducing agent in the leaching system would introduce no impurities (Setiawan et al., 2019). Chemical reduction was the major reaction mechanism involved in this process, implying the reduction of Co³⁺ in the lattice structure of LiCoO₂ to Co²⁺ with good solubility in the solution. The oxidation-reduction potential of H₂O₂ and Co³⁺ can be expressed as below:



By comparing the potential values given in Eq. (2) and Eq. (3), it was inferred that H₂O₂ could be employed to reduce Co³⁺ to Co²⁺. However, based on the Nernst equation, when the H₂O₂ amount exceeded the required amount, rather than a reducing agent, it would act as an oxidant, or be potentially decomposed into H₂O and O₂ (Golmohammadzadeh et al., 2017; Skoog, 1982). Therefore, the optimization of H₂O₂ concentration should be determined via the leaching experiments with various H₂O₂ concentrations. From Figs.1c and d, it could be seen that when the concentration of H₂O₂ was increased from 0 to 0.9 vol%, the leaching efficiencies correspondingly increased from 83 to 100% and 64 to 99% for Li and Co, respectively. However, further increase of the H₂O₂ concentration could not further improve the leaching efficiency. Similar phenomenon was also observed in previous studies, when citric acid was used as leaching reagent, the optimal concentration of H₂O₂ was determined to be 1.0 vol% (Li et al., 2010b). Therefore, H₂O₂ concentration of 0.9 vol% was chosen to be the

optimized parameter. It should be mentioned that the possible leaching reaction involved in the leaching process was suggested as follows:



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 such a value was 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 optimal condition for the leaching LiCoO₂.

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, when the temperature was increased from 25 to 80 °C, the leaching efficiency of Li was correspondingly increased from 95 to 100%, and Co efficiency increased from 90 to 99%. 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 LiCoO₂ 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 optimal temperature condition was determined to be 80 °C in this study.

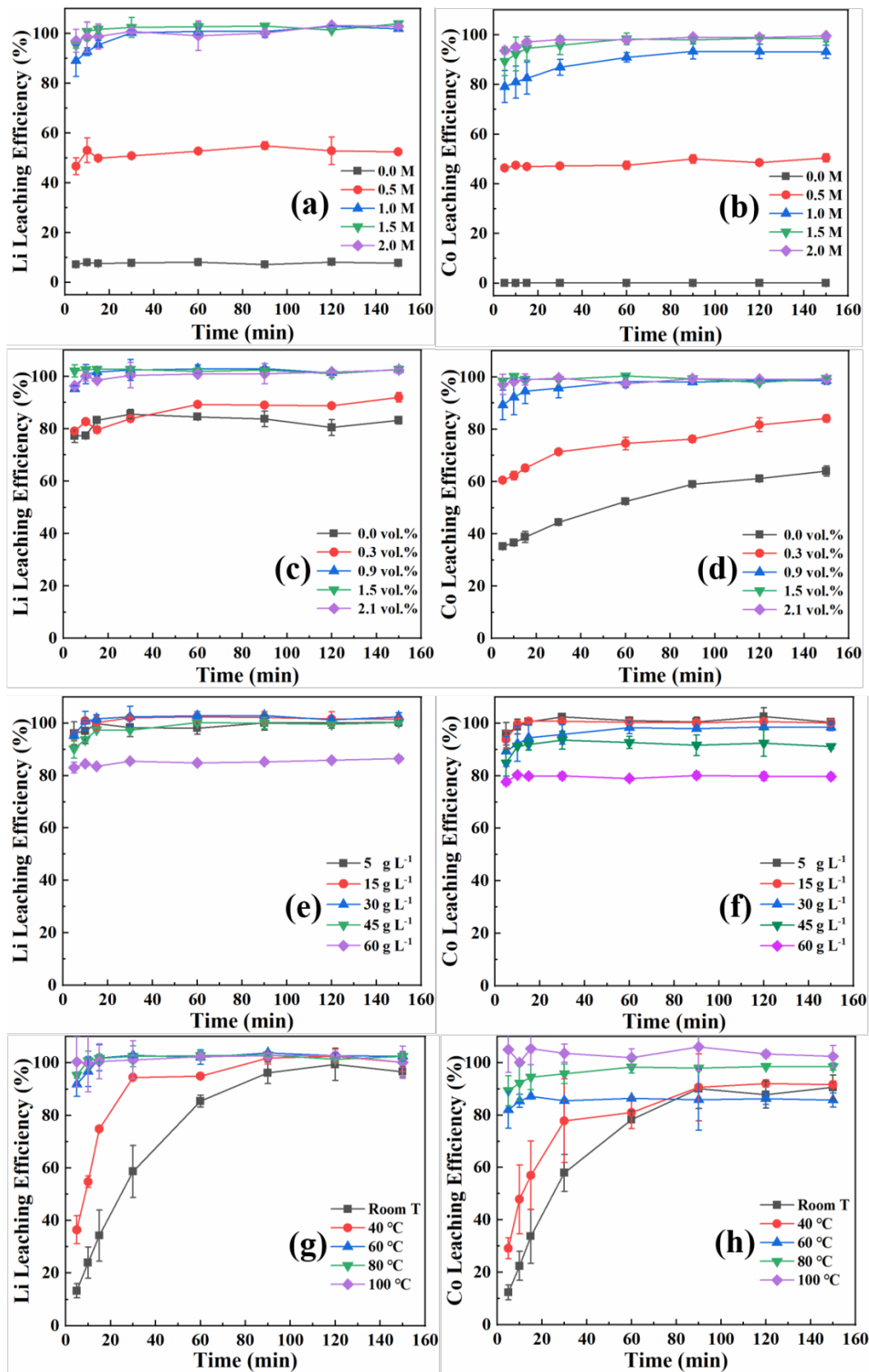


Fig. 1 The effect of (a, b) PTSA concentration, (c, d) H_2O_2 concentration, (e, f) solid-to-liquid ratio, and (g, h) temperature on leaching efficiencies of Li and Co.

3.2. Leaching performance comparison

Table. 1 Comparison of the leaching performance of PTSA with the other previously reported organic acids for LiCoO₂ cathode materials.

No	Acid name	H ₂ O 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 ₄ H ₅ O ₆)	2.00	1.5	20	90	40	Co: 93 Li: 94	(Li et al., 2010a)
2#	Citric acid (C ₆ H ₈ O ₇)	1.25	2.0	30	60	120	Co: 81 Li: ~92	(Golmohammadzadeh et al., 2017)
3#	Oxalic acid (C ₂ H ₂ O ₄)	N.A.	1.0	15	95	150	Co: 98 Li: 97	(Zeng et al., 2015)
4#	Acetoacetic acid (C ₄ H ₆ O ₄)	1.50	1.5	10	70	60	Co: 98 Li: 99	(Liu et al., 2019)
5#	Succinic acid (CH ₂) ₂ (CO ₂ H) ₂	4.00	1.5	15	70	40	Co: 100 Li: 98	(Li et al., 2015)
6#	Aspartic acid (C ₄ H ₇ NO 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

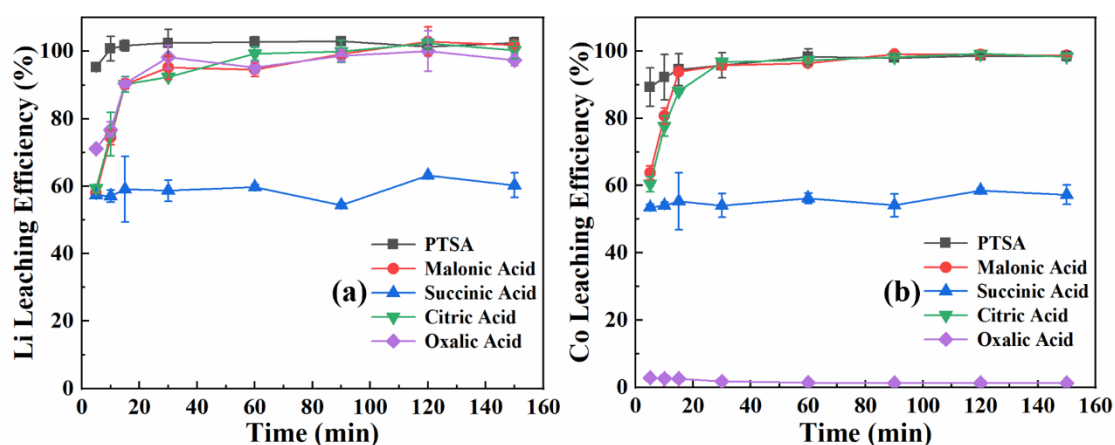


Fig. 2 Comparison of PTSA leaching performance for (a) Li and (b) Co with malonic acid, succinic acid, citric acid and oxalic acid.

Table 1 summarized the previously reported results of the organic acid-assisted LiCoO₂ leaching in published studies, which confirmed the superior leaching performance of PTSA. For example, the requirement of H₂O₂ 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 optimal 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, H₂O₂ 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 LiCoO₂, 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&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. From the comparison of the pK_a value (-2.8 for PTSA while 1.24-4.2 for other organic acids), it can be concluded that the high acidity of leaching agents played a crucial role in the leaching of LiCoO₂. Strong acidity of PTSA originated from the sulfonyl group (-SO₃H) of its molecular, which are more likely to ionize in aqueous

solution to produce hydrogen ions (H^+) than the functional groups from other leaching agents, such as carboxyl group ($-COOH$) from malonic acid, succinic acid, oxalic acid and citric acid (Serjeant and Dempsey, 1979).

3.3. Kinetics study based on the leaching of spent $LiCoO_2$

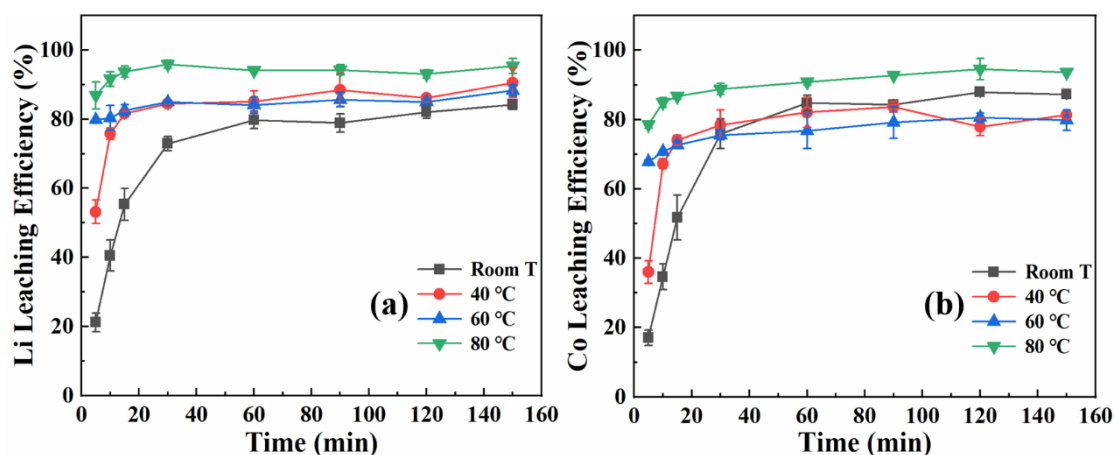


Fig. 3 Application of PTSA for leaching of spent $LiCoO_2$ at different leaching temperatures.

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. The concentration of H_2O_2 was controlled at 0.9 vol%, the solid-to-liquid ratio was kept at 30 g L^{-1} , and the PTSA concentration was maintained at 1.5 mol L^{-1} for this experiment. **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 LiCoO₂ 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 LiCoO₂ (Levenspiel, 1998), detailed equations were given as following:

Chemical reaction control: $1 - (1 - X)^{\frac{1}{3}} = kt$ (5)

Diffusion control: $1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}} = kt$ (6)

In equations (5) and (6), X represents the leaching efficiency of Li (or Co), k is the reaction rate constant (min⁻¹) and t is the reaction time (min).

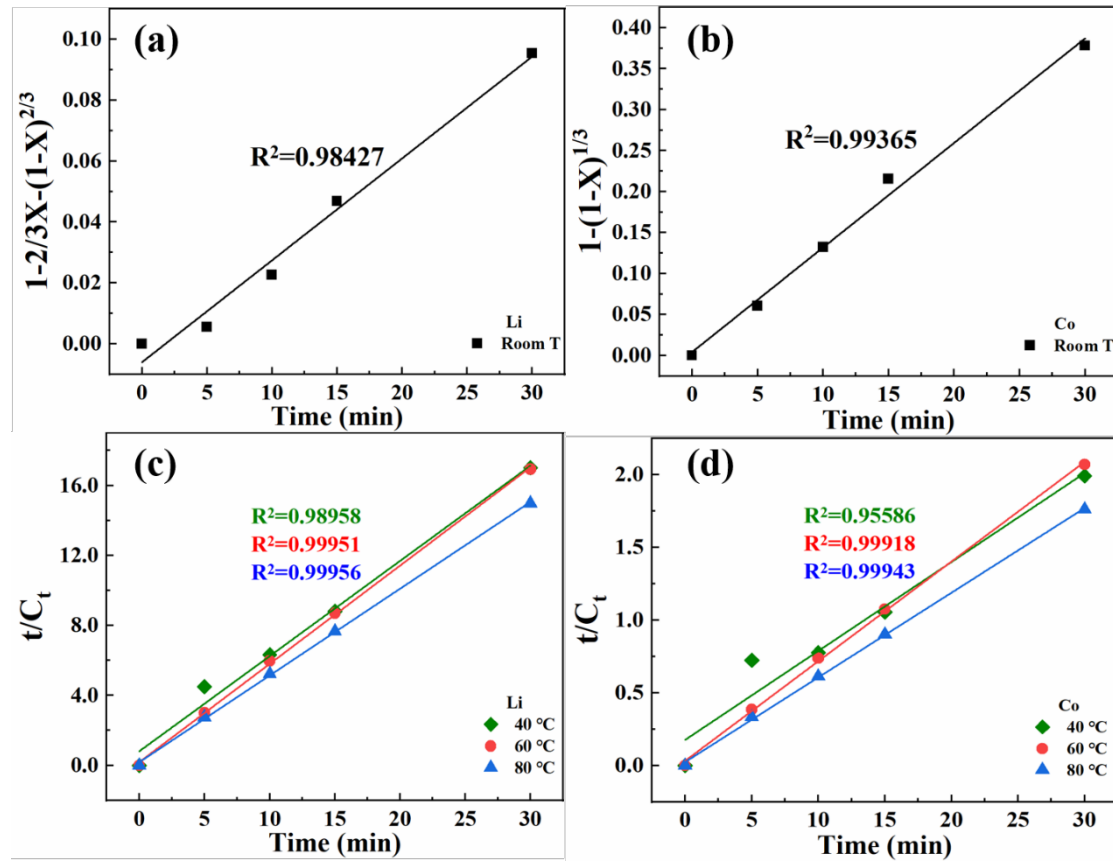


Fig. 4. (a) Diffusion model fitting of Li at room temperature (25 °C), (b) chemical

reaction model fitting of Co (25 °C), second-order fitting of (c) Li and (d) Co (40-80 °C)

Table S2 summarized 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 ($R^2 = 0.98427$) model and that of Co was controlled by chemical reaction ($R^2 = 0.99365$). As displayed in Fig.4a and b, the plots of $1-(1-X)^{1/3}$ versus t and $1- 2/3X- (1-X)^{2/3}$ versus t were further given for the leaching models of Li and Co, respectively. Poor linear fittings with low correlation coefficients (Li: $R^2 < 0.79$; Co: $R^2 < 0.82$) were obtained for the leaching data between 40 and 80 °C, suggesting that the shrinking core model could not account for the leaching kinetics at higher temperatures. In addition, a second-order rate law (Equation (7)) was further adopted to fit the leaching kinetics. The fitting results according to Equation (8) were also summarized in Table S2, which showed 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 were depicted in Figs.4c and d, respectively. This confirmed that the leaching process followed the second-order rate law between 40 to 80 °C.

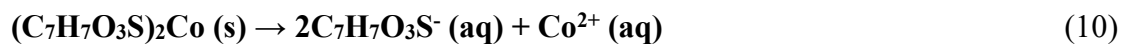
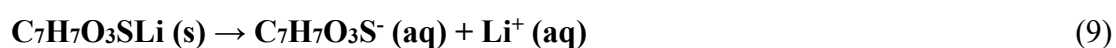
$$\frac{dC_t}{dt} = k(C_e - C_t)^2 \quad (7)$$

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) ($g L^{-1}$), and t is the leaching time (min). C_t is the concentration of leached Li (or Co) in the suspension at any time. As C_t varies from 0

to C_t while t is extended from 0 to t , the function can be integrated to:

$$\frac{t}{C_t} = \frac{1}{kC_e^2} + \frac{t}{C_e} \quad (8)$$

As shown in Equation (4), the reaction products (e.g. $C_7H_7O_3SLi$ and $(C_7H_7O_3S)_2Co$) were unable to diffuse into the solution immediately, 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 core $LiCoO_2$. The different rate-determining mechanism of Li and Co is probably due to stronger Co-O chemical bond in the crystal structure of $LiCoO_2$. Therefore, the chemical reaction was more likely to be the rate-determining step for Co leaching kinetics. As temperature increased (≥ 40 °C), the leaching rate of Li and Co might be controlled by the sample dissolution after complete suspension, and the chemical reactions involved in the dissolution of leaching products may be described as follows:



3.4. Recycling and regeneration

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

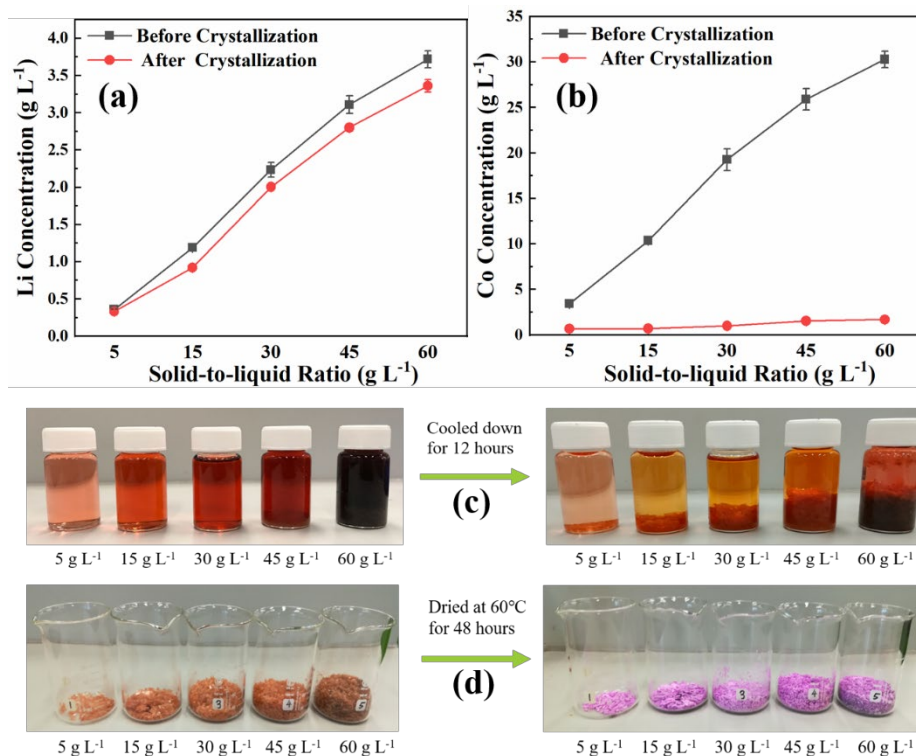


Fig. 5 (a) Li concentration in the leachate before and after crystallization (b) Co concentration in the leachate before and after crystallization (c) cooling and (d) drying process of precursor A

Interestingly, as depicted in Figs.5c&d, when the high-temperature leachate (80 °C) was placed in a low-temperature environment (i.e. room temperature or lower), 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&b illustrated the changes of Li⁺ and Co²⁺ concentrations in the leachate before and after the direct crystallization process, implying that the concentration of Co²⁺ in the solution was 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. Therefore, after treated with alcohol to remove possible impurities on the solid surface, the as-obtained crystal was further characterized by XRD. The pattern in Fig.S3 indicated that the predominant crystalline phase was well attributed to cobalt toluene sulfonate hexahydrate ($\text{C}_{14}\text{H}_{14}\text{CoO}_6\text{S}_2 \cdot 6\text{H}_2\text{O}$, 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 precipitations. (Wang et al., 2019).

3.4.2. Metal recovery and material regeneration

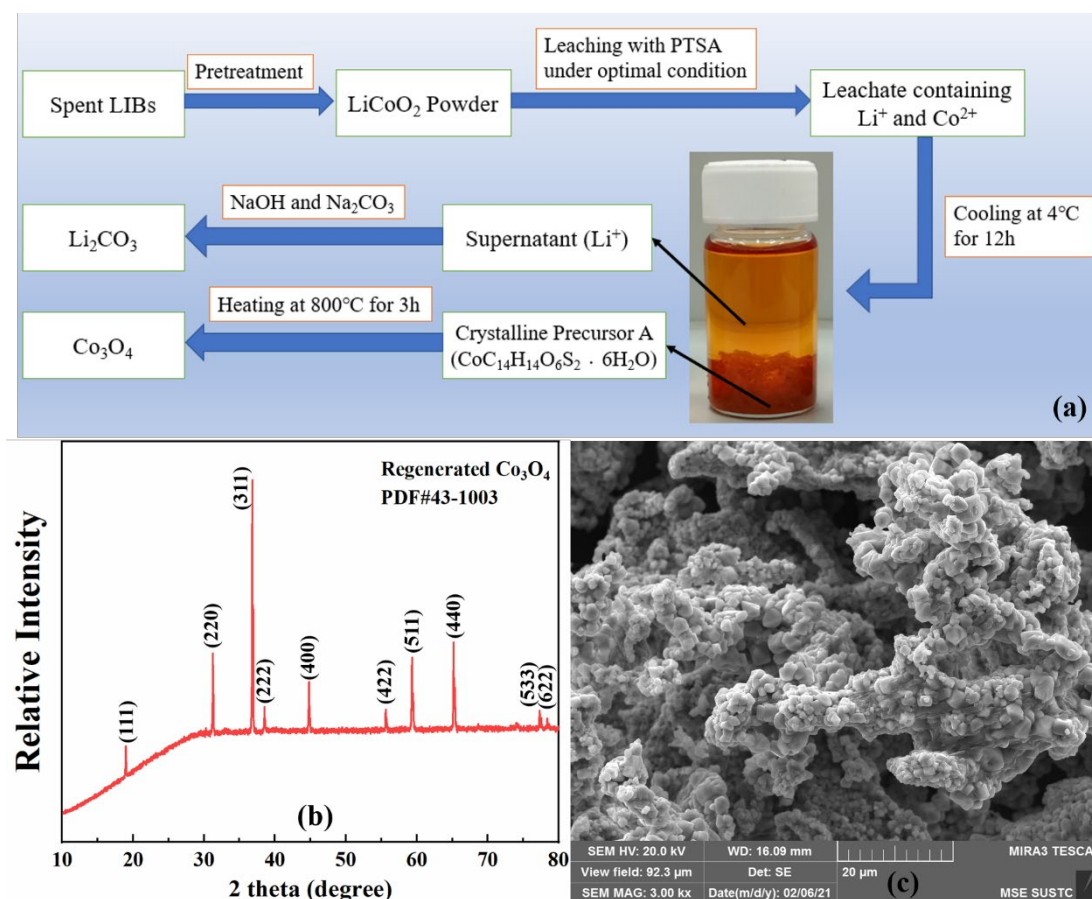


Fig.6 (a) The flowchart of the recovery process of spent LIBs. (b) XRD pattern and (c) SEM image of the regenerated Co₃O₄ under optimized condition.

To understand the direct crystallization process for the formation of C₁₄H₁₄CoO₆S₂·6H₂O, crystallization treatment temperature and time were also optimized in this study. As shown in **Fig S4**, after transferring the hot leachate (~80 °C) to a cooler environment, the crystallization efficiency of Co increased quickly, with the decrease of the treatment temperature for the leaching solution. When the leaching sample was directly treated at room temperature, the complete crystallization of Co could be achieved in about 3 h, and the final crystallization rate was about 84%. When treated at 4 °C, the crystallization efficiency was significantly increased to 89% in the

first 3 h, and reached about 92% at 12 h. Obviously, this is higher than that of room temperature crystallization. This phenomenon was consistent with the change trend of $(C_7H_7O_3S)_2Co \cdot 6H_2O$'s solubility at different temperatures (Yu et al., 2016). Here, Although direct crystallization at 4 °C for 12 h could achieve higher crystallization efficiency, it is recommended that direct crystallization at room temperature for element separation was highly preferred, due to energy saving process. The schematic diagram in Fig.6 (a) demonstrated the entire procedure for the recovery and regeneration of Li and Co in this study. After previous leaching steps, the as-obtained pink crystal was 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 would transform into Co_3O_4 materials. It is worth noting that Li is volatile at high temperatures (Lundblad et al., 2000; Tennakoon et al., 1997), hence the low Li content in precursor A, as shown in Fig.S2, and therefore would be evaporated during the heat treatment. As a result, Co_3O_4 with high purity was obtained as the final recovered product (Table S3). Fig.6b illustrated the 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.S5 further showed 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 to 2 μm .

The recovery yield of Co, as the mass ratio of recovered Co to the total Co in the original

LiCoO_2 , is one critical criterion to evaluate the effectiveness of the method. Thus, Fig.7 demonstrated the calculated Co recovery yield (solid-to-liquid ratio ranging from 5 - 60 g L^{-1}) after every step in this study, including leaching by PTSA, Co-rich crystal precipitation, and heat treatment (800 °C, 3 h). The results implied that Co recovery yield was increased with the increasing of solid-to-liquid ratio up to 30 g L^{-1} . Low solid-to-liquid ratio ($< 30 \text{ g L}^{-1}$) suggested a relatively low Co concentration in the leachate (Figs.5a&b), which could subsequently result in less Co precipitation. However, when the solid-to-liquid ratio was larger than 30 g L^{-1} , an obvious decrease in Co recovery yield was observed, which was resulted from the decreased leaching efficiency, as shown in Fig.1f. It can be seen from Fig.7 that very 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 optimal solid-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 was then utilized to regenerate Li_2CO_3 , which was viewed as one of the indispensable raw materials in the production of LIB cathodes. 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.S6). The obtained Li_2CO_3 was then washed by 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 can 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 concise flow path and high recovery yield.

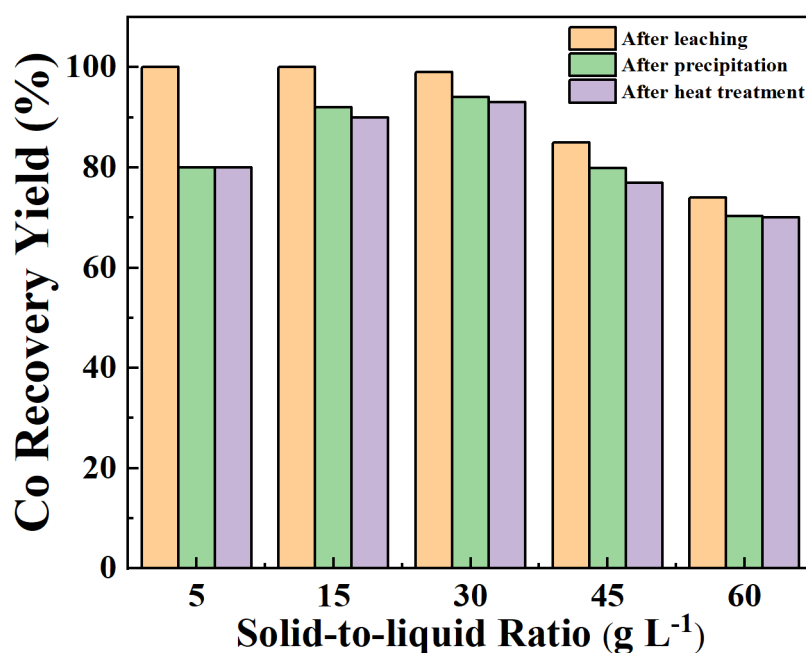


Fig.7. Effects of solid-to-liquid ratios on Co recovery yields

4. Conclusions

In conclusion, *p*-toluene sulfonic acid (PTSA) was proved to be an effective leaching agent for battery recycling applications. Under the optimized leaching conditions (H_2O_2 amount: 0.9 vol%, PTSA concentration: 1.5 mol L^{-1} , temperature: $80 \text{ }^\circ\text{C}$, solid-to-liquid ratio: 30 g L^{-1}), nearly 100% of Li and 99% of Co can be successfully extracted out in 1 h. Detailed kinetic studies demonstrated that leaching temperature could obviously affect the leaching mechanisms of Li and Co from the spent LiCoO_2 . By cooling the

leachate, Co ions can be easily and directly separated from Li ions via direct crystallization of $C_{14}H_{14}CoO_6S_2 \cdot 6H_2O$ at low temperatures (e.g. 4 °C or room temperature). Afterwards, the well-crystallized Co_3O_4 materials were regenerated after heat treatment while the Li_2CO_3 was recovered from the supernatant with a final recovery yield of 94 and 80% for Co and Li, respectively. 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 cathode materials, such as 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.

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.

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, analyzing data and writing the draft manuscript. Tsz Yau Mak, Zhe Meng, Xuyang Wang,

Zhouguang Lu and Dawson Wai-Shun Suen involved in conducting experiments, analyzing data and revising the manuscript.

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**Efficient recovery of lithium and cobalt from spent lithium-ion
batteries by *p*-toluene sulfonic acid**

Jiadong Liu^a, Tsz Yau Mak^b, Zhe Meng^a, Xuyang Wang^c, Zhouguang Lu^c, Dawson Wai-Shun Suen^b, Xiao-Ying Lu^{b,*}, Yuanyuan Tang^{a,*}

^a State Environmental Protection Key Laboratory of Integrated Surface Water-Groundwater Pollution Control, School of Environmental Science and Engineering, Southern University of Science and Technology, No.1088 Xueyuan Avenue, Shenzhen 518055, China.

^b Faculty of Science and Technology, Technological and Higher Education Institute of Hong Kong, Hong Kong, China.

^c Department of Materials Science and Engineering, Guangdong Provincial Key Laboratory of Energy Materials for Electric Power, Southern University of Science and Technology, Shenzhen, No.1088 Xueyuan Avenue, 518055, China

*Correspondence authors

E-mail address: tangyy@sustech.edu.cn; xylu@thei.edu.hk

Elements	Li	Co	Al	Cu	Fe	Mn
Contents (wt. %)	7.56	60.32	0.27	0.06	0.16	0.12

Table S1. Chemical composition of the LiCoO₂ cathode material recovered from LIBs waste.

Fitting model	Shrinking core model				Second-order model	
	Chemical reaction control		Diffusion control			
Temperature (°C)	R ² (Li)	R ² (Co)	R ² (Li)	R ² (Co)	R ² (Li)	R ² (Co)
Room temperature	0.96388	0.99365	0.98427	0.96043	0.79229	0.61205
40	0.69180	0.74716	0.78164	0.81993	0.98958	0.95586
60	0.44493	0.47280	0.50778	0.56497	0.99951	0.99918
80	0.54771	0.51068	0.61629	0.59410	0.99956	0.99943

Table S2. Parameters of acid leaching kinetics models.

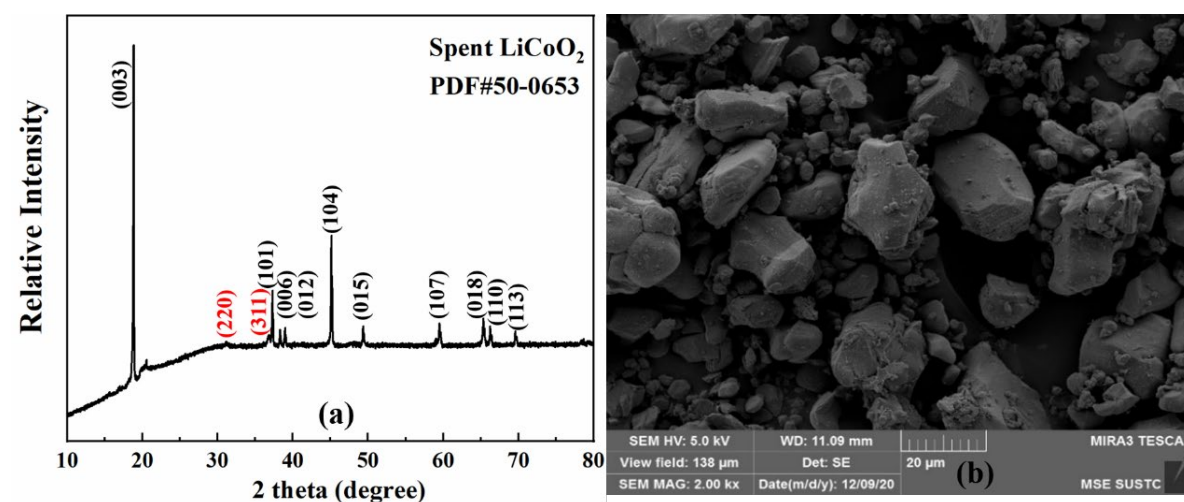


Fig. S1. (a) XRD pattern and (b) SEM image of the spent cathode material (LiCoO₂) after pre-treatment.

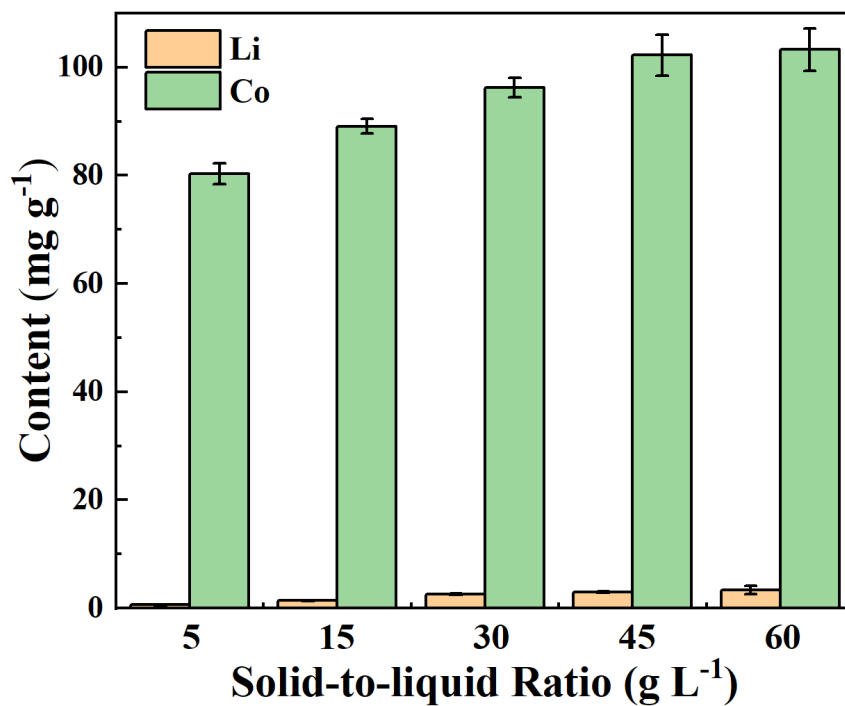


Fig. S2. The content of Li and Co in the pink crystal precipitated from the leachate of LiCoO₂ with different solid-to-liquid ratios

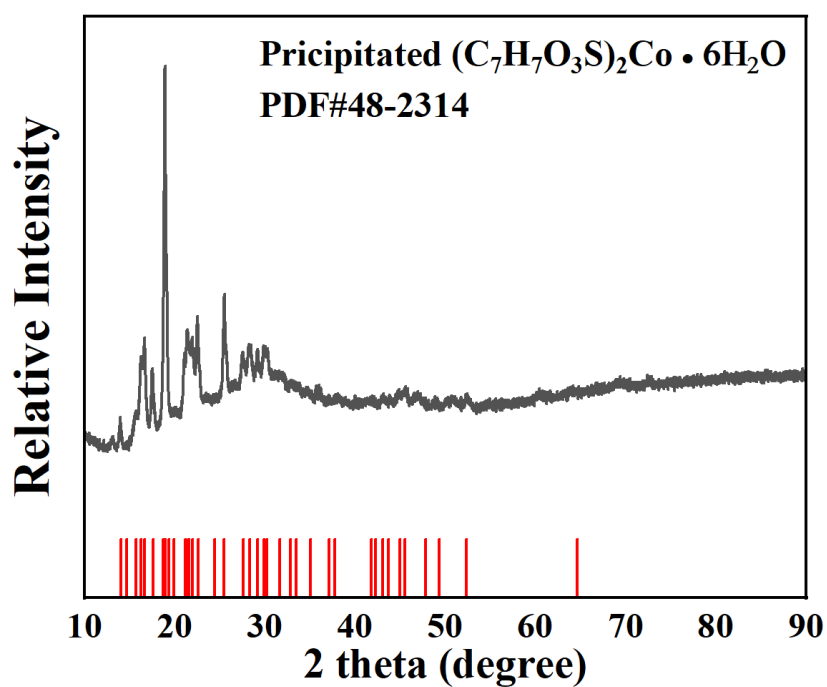


Fig. S3. XRD pattern of the **purified** Co-rich compound (pink crystal, precursor A) precipitated from the leachate

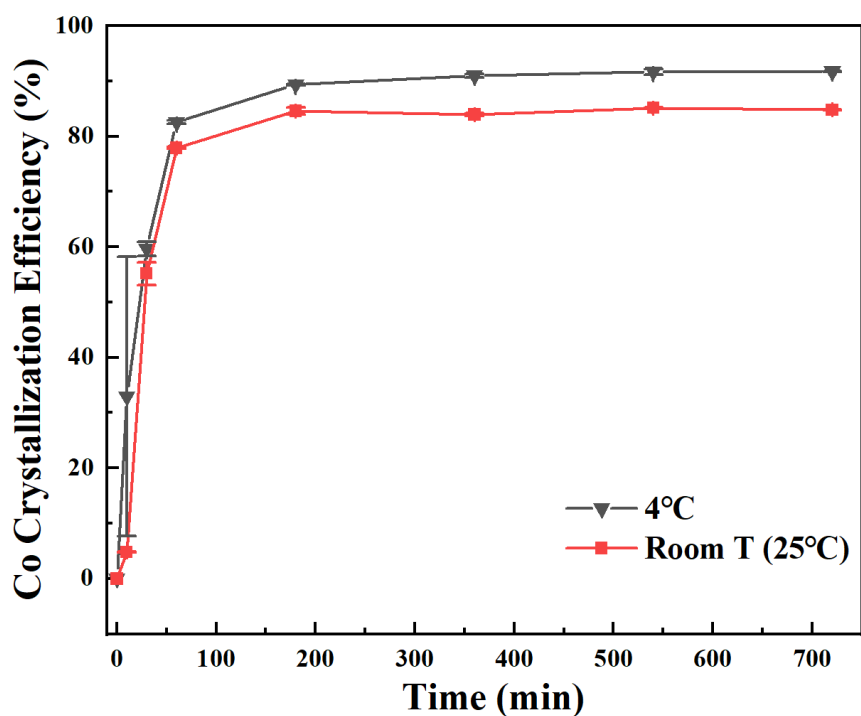


Fig.S4 The effect of temperature on the crystallization efficiency of Co

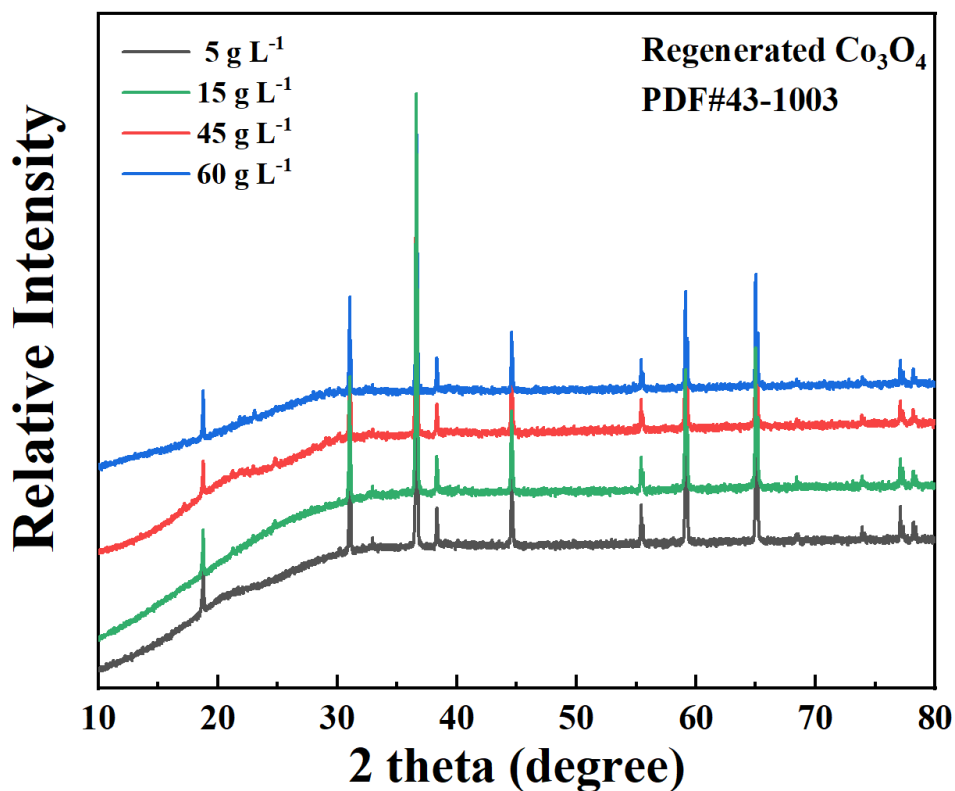


Fig. S5. Typical XRD patterns of the regenerated Co_3O_4 after heating the pink crystal precipitated from the leachate of different solid-to-liquid ratios (5 g L⁻¹ to 60 g L⁻¹)

Solid-to-liquid ratio (g L ⁻¹)	5	15	30	45	60
Purity (%)	>99	>99	>99	>99	>98

Table S3 Purities of the regenerated Co₃O₄ after heating the pink crystal precipitated from the leachate of different solid-to-liquid ratios (5 to 60 g L⁻¹)

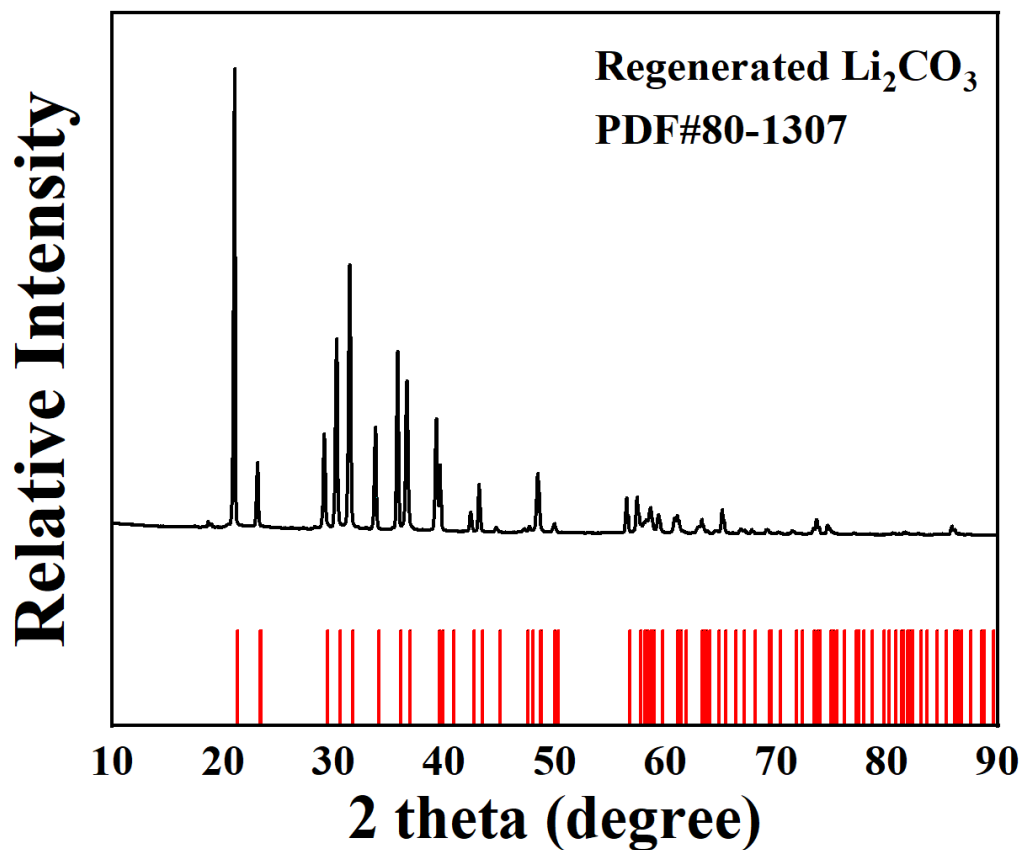


Fig. S6. XRD pattern of the regenerated Li₂CO₃