

Hydrometallurgical recycling of valuable metals from spent lithium-ion batteries by reductive leaching with stannous chloride

Liu-ye Sun, Bo-ruì Liu, Tong Wu, Guan-ge Wang, Qing Huang, Yue-feng Su, and Feng Wu

School of Materials Science and Engineering, Beijing Institute Technology, Beijing 100081, China
(Received: 10 March 2020; revised: 16 May 2020; accepted: 8 June 2020)

Abstract: The reductant is a critical factor in the hydrometallurgical recycling of valuable metals from spent lithium-ion batteries (LIBs). There is limited information regarding the use of SnCl_2 as a reductant with organic acid (maleic acid) for recovering valuable metals from spent LiCoO_2 material. In this study, the leaching efficiencies of Li and Co with $1 \text{ mol}\cdot\text{L}^{-1}$ of maleic acid and $0.3 \text{ mol}\cdot\text{L}^{-1}$ of SnCl_2 were found to be 98.67% and 97.5%, respectively, at 60°C and a reaction time of 40 min. We investigated the kinetics and thermodynamics of the leaching process in this study to better understand the mechanism of the leaching process. Based on a comparison with H_2O_2 with respect to leaching efficiency, the optimal leaching parameters, and the activation energy, we determined that it is feasible to replace H_2O_2 with SnCl_2 as a leaching reductant in the leaching process. In addition, when SnCl_2 is used in the acid-leaching process, Sn residue in the leachate may have a positive effect on the re-synthesis of nickel-rich cathode materials. Therefore, the results of this study provide a potential direction for the selection of reductants in the hydrometallurgical recovery of valuable metals from spent LIBs.

Keywords: spent lithium-ion batteries; recovery; maleic acid; reductant; stannous chloride

1. Introduction

In response to the increasingly serious environmental problems around the world, researchers are beginning to explore new and clean energy options. Lithium-ion batteries (LIBs) have developed rapidly as a clean energy option. In recent years, LIBs have been widely used in electric vehicles and portable electronic equipment because of their low weight, high voltages, long service life, wide operational temperature range, and safe performance [1–2]. With its rapidly developing economy, LIBs in China are in high demand and their consumption has increased dramatically. It is estimated that the weight of these depleted batteries in China will exceed 200000 tons by 2020 [3–5]. Spent LIBs contain higher contents of heavy metals than those in natural minerals, lithium salts, or organic electrolytes, and can produce harmful gases in reaction with air [6–9]. Therefore, spent LIBs that are not properly disposed of not only waste resources, but lead to environmental pollution such as soil and underground water contamination.

At present, with public interest focused on environmental protection and the development of recovery technologies, more attention is being paid to recycling spent LIBs. Three

types of recycling technologies are currently used to recycle spent LIBs: hydrometallurgical, pyro-metallurgical, and bio-metallurgical technologies [10–12]. Of these three processes, the hydrometallurgical process has the advantages of high efficiency, low energy consumption, and simple operation, which makes it the preferred process for recycling [13–15]. This process includes the following main steps: pretreatment, acid-leaching, and reclamation [15]. The most critical step is acid-leaching, which affects the efficiency of metal recovery from spent LIBs. In the past, inorganic acids like HCl [16–17], H_2SO_4 [18–20], and H_3PO_4 [21] were investigated as leaching agents because of their low cost and high leaching efficiency. In recent years, organic acids from green sources that generate little secondary pollution and have roughly the same leaching efficiency as inorganic acids have attracted a lot of attention. Many studies have been conducted on the leaching of spent-LIB materials by mild organic acids such as L-tartaric acid [22], citric acid [12], formic acids [23], acetic acid [24], lactic acid [25], and succinic acid [26]. Reducing agents are also needed to increase the leaching efficiency because the Co in spent LIBs (e.g., LiCoO_2 and $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$) is mostly in the form of Co^{3+} , which is not easily dissolved. Reducing agents can reduce Co^{3+} to the

more easily dissolved Co^{2+} to improve leaching efficiency. The most common reducing agent is H_2O_2 because it introduces no impurities to the system [24]. However, H_2O_2 has a few drawbacks as a reducing agent, such as being easily decomposed, which leads to some issues in leaching, storage, and transport processes, as well as its low leaching efficiency because of itself use. As such, it is vital that an efficient and stable substitute for H_2O_2 be found. A number of studies have been conducted to explore alternative reductants, including $\text{Na}_2\text{S}_2\text{O}_5$ [27], NaHSO_3 [28], NH_4Cl [29], glucose [30–32], and grape seed [33]. Other chemicals also have potential for use as a reducing agent in the recovery of valuable metals from spent LIBs. Furthermore, the resulting leachate can be used to resynthesize LIB cathode material [34–35]. Based on the safety and positive effects of Sn on LIB cathode materials, we used SnCl_2 as a reductant for leaching cathode materials from spent LIBs. In this work, we explore the effects of various parameters of the reductant SnCl_2 on the leaching efficiency, as well as the kinetics and thermodynamics of the leaching process. We also compare the leaching parameters when SnCl_2 and H_2O_2 are used as reducing agents.

2. Experimental

2.1. Materials

The spent LIBs used in this study were obtained from the Zhongguancun Electronic Market (Beijing, China). NaCl solution was used to discharge the residual power of the spent LIBs, and cathode materials were separated from Al foil by NaOH solution. Maleic acid was used as the leaching agent, and H_2O_2 and SnCl_2 were used as reductants. All the reagents used in the experiment were of analytical grade, and distilled water was used in the solutions.

2.2. Pretreatment

As shown in the flow chart in Fig. 1, spent LIBs were first fully discharged in NaCl solution to ensure safety during the subsequent experiments. Next, we manually removed the cases of the spent LIBs. We cut the cathode foil into pieces 1 cm × 1 cm in size. To separate the spent-LIB cathode materials from the Al foil, we soaked the cathode pieces in NaOH solution for 12 h, followed by drying at 60°C for approximately 24 h, and then calcination in a muffle furnace at 840°C for 5 h. The material was then cooled to room temperature to remove the acetylene black and poly vinylidene fluoride (PVDF). Finally, to improve leaching efficiency by increasing the surface area, we ground the calcined material into powder with a mortar and pestle for approximately 1 h.

2.3. Leaching process

All the leaching experiments were conducted in a 150-mL three-neck flask, in which active cathode material powder was mixed with a solution of maleic acid and reducing agent (H_2O_2 or SnCl_2), which was then heated in a water bath. The mixture was stirred at 270 $\text{r}\cdot\text{min}^{-1}$ by a mechanical stirrer to accelerate the reaction. Before the leaching experiments, we conducted an orthogonal experiment to estimate the approximate horizontal range of each parameter. And then following acid-leaching parameters were investigated: (a) concentrations of SnCl_2 (0.12–0.36 $\text{mol}\cdot\text{L}^{-1}$), concentration of maleic acid (0.5–2.5 $\text{mol}\cdot\text{L}^{-1}$), solid/liquid (S/L) ratio (10–50 $\text{g}\cdot\text{L}^{-1}$), temperature (40–80°C), and reaction time (20–60 min); (b) concentration of H_2O_2 (0.5–2.5vol%), concentration of maleic acid (0.5–2.5 $\text{mol}\cdot\text{L}^{-1}$), S/L ratio (5–40 $\text{g}\cdot\text{L}^{-1}$), temperature (50–90°C), and reaction time (30–70 min). After leaching, we separated the leach solution and residue and

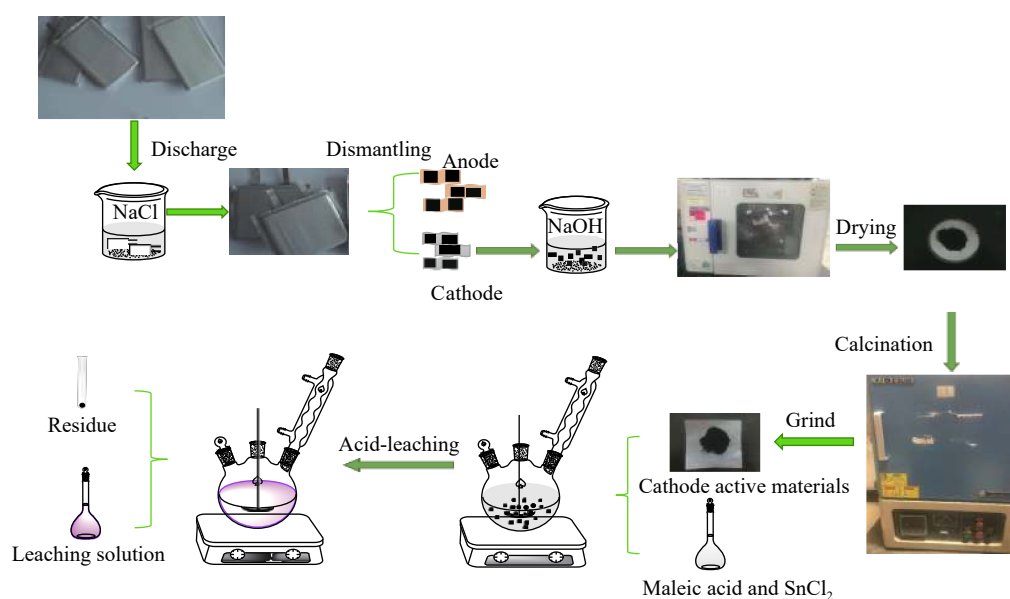


Fig. 1. Flow chart of metal recovery process from spent LIBs.

washed the leach residue with distilled water for analysis. To identify the acid-leaching mechanism, we studied the thermodynamics and kinetics of the leaching process. In addition, the residual Sn in the leachate can be extracted by 0.1 mol·L⁻¹ of Cyphos IL 104 to separate Sn from other valuable metals in the cathode materials [36].

To study the thermal behavior of the spent-LIB cathode materials after NaOH treatment, we employed thermo-gravimetric analysis and differential scanning calorimetry (TG/DSC). The measurements were performed in air atmosphere at a heating rate of 10°C·min⁻¹. X-ray diffraction (XRD) was used to characterize the crystal structures of the spent-LIB cathode materials and leaching residues. Scanning electron microscopy (SEM) was used to investigate the surface appearance of the materials. We also used inductively coupled plasma–optical emission spectrometry (ICP–OES) to quantitatively analyze the element contents of the active cathodic material powder dissolved by digestion and the leachate. The leaching efficiency of the metals was calculated using Eq. (1):

$$X = \frac{C_e}{C_0} \quad (1)$$

where X is the leaching efficiency (%), C_e is the concentration of metals in the leachate (mg·L⁻¹), and C_0 is the concentration of metals in the active cathode material (mg·L⁻¹).

3. Results and discussion

3.1. Characterization of the cathode material

TG–DSC was applied to investigate the chemical reaction and weight-loss process of the cathode powder when the temperature ranged from room temperature to 1000°C. The results in Fig. 2 show three weight-loss stages and two distinct peaks. A weight loss of 1.5% occurred from 27 to 400°C, mainly due to the reduction of bound water in the material [16]. From 400 to 848°C, the weight loss of 1.84% indicates the removal of acetylene black and the binder

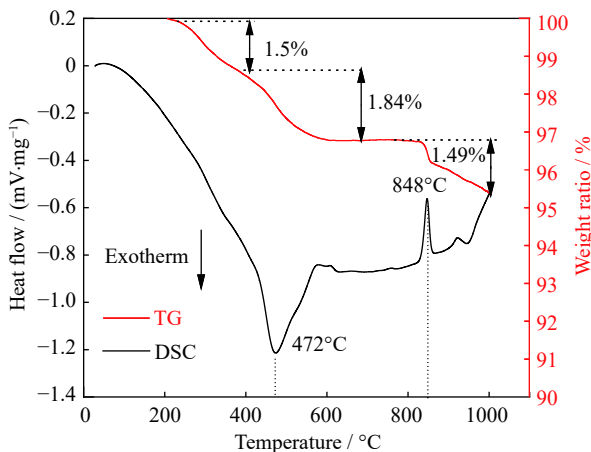
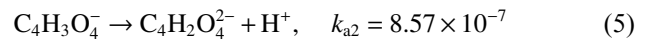
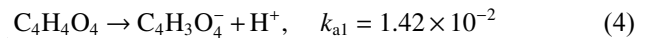
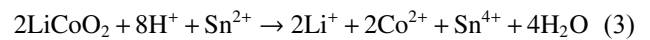
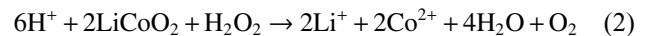


Fig. 2. TG–DSC curves of the spent cathodic powder.

(PVDF). Within the temperature range, there was an obvious DSC exothermic peak at 472°C, which indicates the degradation of acetylene black and the decomposition of PVDF. In addition, a weight loss of 1.49% was detected in the temperature range of 848–1000°C, with a DSC endothermic peak at 848°C, manifesting the phase transformation of the cathode material and the loss of lithium at high temperature [25]. In summary, the optimum calcination temperature is 840°C.

Fig. 3 shows the XRD patterns and SEM images of the spent-LIB cathodic material and the leaching residues. The XRD patterns in Fig. 3(a) indicate that the cathode materials of the spent LIBs are primarily LiCoO₂ and a small amount of Co₃O₄. In the leaching residues, there are characteristic peaks belonging only to Co₃O₄ whether H₂O₂ or SnCl₂ is used as the reducing agent. The SEM image in Fig. 3(b) shows that the particles of the cathode compounds from spent LIBs are irregular in shape with diameters ranging from 1 to 5 μm and have smooth edges. As can be seen in Figs. 3(c) and 3(d), the particle sizes of the leaching residues are smaller and the edges of the particles are cruder than those of the active LiCoO₂ material of the spent LIBs [35]. In addition, there is no significant difference between the particle sizes of the leaching residues from H₂O₂ and SnCl₂. These findings prove that using SnCl₂ as the reducing agent destroys the structure of the spent LiCoO₂.

According to the above characterization, the main component of the spent-LIB cathode materials in this study was LiCoO₂. The main reactions when using maleic acid as a leaching agent and different reductants in the leaching process are shown in the equations below (Eqs. (2) and (3)). Since maleic acid is a binary acid, one mole of maleic acid be used to calibrate two moles of H⁺. The dissociation steps and the dissociation constant that has an important influence on the H⁺ concentration and leaching efficiency are shown in Eqs. (4) and (5), respectively:



where k_{a1} and k_{a2} are dissociation constant of maleic acid.

A comparison of the dissociation constant of maleic acid with that of other organic acids that were used in previous studies [15] indicates the feasibility of using maleic acid as a leaching agent. Furthermore, as Co³⁺ is difficult to leach [37], we used a reducing agent to reduce the Co³⁺ to Co²⁺ to improve the Co leaching efficiency. In SnCl₂, Sn exists in the form of Sn²⁺, which can lose electrons and transform into high-valence Sn⁴⁺, thereby reducing high-valence metal ions to low-valence metal ions at the same time. Based on the standard electrode potential, $E^\ominus(\text{Co}^{3+}/\text{Co}^{2+}) = 1.83 \text{ V}$, $E^\ominus(\text{O}_2/\text{H}_2\text{O}_2) = 0.682 \text{ V}$, and $E^\ominus(\text{Sn}^{4+}/\text{Sn}^{2+}) = 0.151 \text{ V}$, SnCl₂

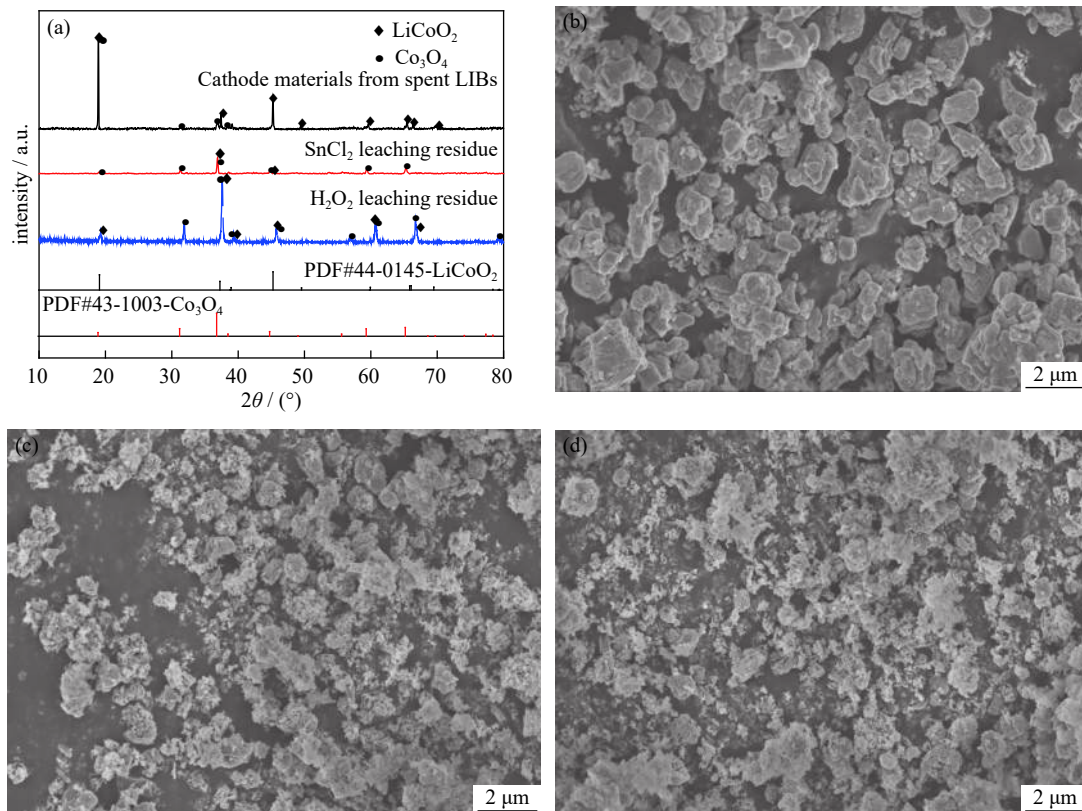


Fig. 3. (a) XRD patterns of the active cathodic material and leaching residues, (b) SEM images obtained before leaching, and (c–d) the leaching residues from H_2O_2 (c) and SnCl_2 (d).

can reduce Co^{3+} to Co^{2+} and it has the potential and feasibility to replace H_2O_2 as a reducing agent.

3.2. Effects of acid-leaching parameters on leaching efficiencies

The effect of maleic acid was studied under the following working conditions: SnCl_2 concentration of $0.3 \text{ mol}\cdot\text{L}^{-1}$, S/L ratio of $10 \text{ g}\cdot\text{L}^{-1}$, temperature of 60°C , and reaction time of 40 min. The leaching yields of Co and Li are reported in Fig. 4(a). Generally speaking, the leaching efficiencies of the metals increased with increases in the acid concentration [24]. This is because the acids ionize H^+ , which reacts with the spent LiCoO_2 materials and destroys the structure to dissolve the metals. In a certain concentration range, the higher is the acid concentration, the more easily the structure is destroyed [38]. As shown in the Fig. 4(a), the leaching efficiencies increased from 80.2% to 98.0% for Li and from 79.4% to 97.5% for Co with increases in the maleic-acid concentration from $0.5 \text{ mol}\cdot\text{L}^{-1}$ to $1 \text{ mol}\cdot\text{L}^{-1}$. The leaching efficiencies of Li and Co remained higher than 97.5% and nearly constant when the maleic-acid concentration was higher than $1 \text{ mol}\cdot\text{L}^{-1}$, which further shows that the influence of the acid concentration on the leaching efficiency is limited. In consideration of cost and efficiency, all further experiments were performed using $1 \text{ mol}\cdot\text{L}^{-1}$ of maleic acid.

It has been reported that adding a reductant can greatly

improve leaching efficiency [39]. In this work, SnCl_2 was used as a leaching reductant. The strong chemical bond between oxygen and cobalt makes LiCoO_2 difficult to dissolve. Adding SnCl_2 can reduce Co^{3+} to dissolved Co^{2+} . To study the effect of SnCl_2 on the leaching efficiency, the experiment was conducted using SnCl_2 ($0.12\text{--}0.36 \text{ mol}\cdot\text{L}^{-1}$) and $1 \text{ mol}\cdot\text{L}^{-1}$ of maleic acid at an S/L ratio of $10 \text{ g}\cdot\text{L}^{-1}$, at 60°C for 40 min, and the results are shown in Fig. 4(b). We can see that the leaching efficiency of Co increased progressively from 77.0% to 97.5%, with an increase in the SnCl_2 concentration from $0.12 \text{ mol}\cdot\text{L}^{-1}$ to $0.3 \text{ mol}\cdot\text{L}^{-1}$. With increases in the leaching efficiency of Co, the leaching efficiency of Li also increased. Because Li and Co exist in the same compound LiCoO_2 , and the dissolution of Co accelerates the structural destruction of the LiCoO_2 , the dissolution of Li also increases [18]. When the SnCl_2 concentration was higher than $0.3 \text{ mol}\cdot\text{L}^{-1}$, the leaching yields of Li and Co showed no significant improvement. Thus, $0.3 \text{ mol}\cdot\text{L}^{-1}$ was defined as the optimal SnCl_2 concentration.

To investigate the optimal S/L ratio, this ratio was controlled in the range of 10 to $50 \text{ g}\cdot\text{L}^{-1}$. Fig. 4(c) shows the effect of the S/L ratio under the conditions of $1 \text{ mol}\cdot\text{L}^{-1}$ of maleic acid, $0.3 \text{ mol}\cdot\text{L}^{-1}$ of SnCl_2 , 60°C , and a reaction time of 40 min. As we can see in the Fig. 4(c), the leaching efficiencies of Li and Co both decreased drastically when the S/L ratio was increased, which is because the effective area that

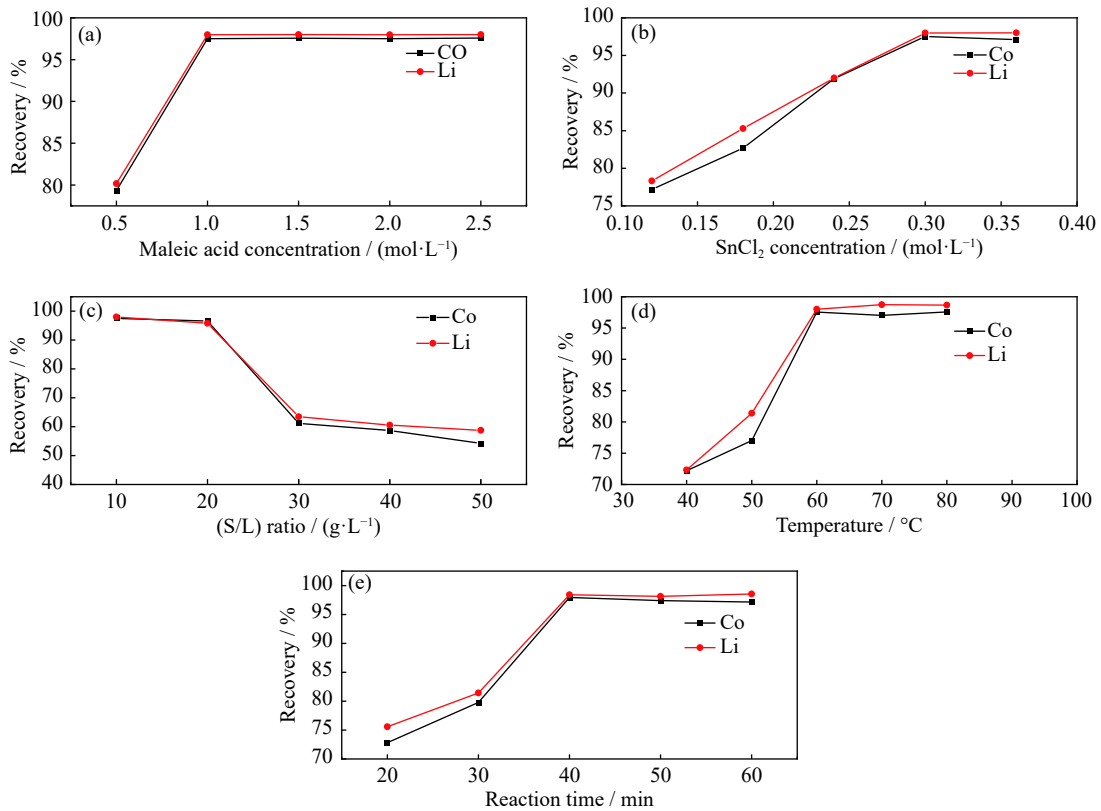


Fig. 4. Effects of acid-leaching parameters on the leaching efficiency with SnCl₂: (a) maleic-acid concentration; (b) SnCl₂ concentration; (c) S/L ratio; (d) temperature; (e) reaction time.

can be contacted per unit volume was decreasing [13]. When the S/L ratio was increased from 10 to 20 g·L⁻¹, the leaching efficiencies decreased slightly, with that for Li barely decreasing from 98.0% to 96.0% and that for Co decreasing from 97.5% to 96.6%. Therefore, considering both the leaching efficiency and economic benefit, an S/L ratio of 20 g·L⁻¹ is the best leaching parameter.

To study the effect of temperature, we varied the reaction temperature from 40 to 80°C, while holding constant the other parameters at 1 mol·L⁻¹ of maleic acid, a 10 g·L⁻¹ S/L ratio, 0.3 mol·L⁻¹ of SnCl₂, and a reaction time of 40 min. Fig. 4(d) shows that the leaching efficiencies increased with increases in temperature from 40 to 60°C, which indicates that leaching metals from spent LiCoO₂ is an endothermic process [26,28,40]. Moreover, increasing the temperature can accelerate the mass transfer in the solution [19,40], which can cause more frequent and more energetic collisions [13], thereby enhancing reactions at the surface of the particles [16]. When the temperature continued to increase from 60 to 80°C, the leaching efficiency did not significantly improve. Thus, we chose 60°C as the optimum reaction temperature.

Next, we investigated the influence of the reaction time with SnCl₂ as a reducing agent on the leaching of spent LiCoO₂ with a maleic-acid concentration of 1 mol·L⁻¹, SnCl₂ concentration of 0.3 mol·L⁻¹, temperature of 60°C, and S/L ratio of 10 g·L⁻¹. In Fig. 4(e), it is clear that the leaching effi-

ciency increased with increases in the reaction time up to 40 min. However, when the reaction time exceeded 40 min, the recovery efficiencies of Li and Co showed no significant differences. Thus, 40 min can be regarded as the optimum reaction time.

3.3. Kinetics of leaching process.

Kinetics analysis is essential for investigating the leaching behavior and feasibility of using SnCl₂ as a reductant for leaching reactions. The main purpose of kinetics investigations is to recognize the rate-controlling steps of the reaction. The leaching process of LiCoO₂ is a typical heterogeneous reaction, which means the shrinking-core model can be used to represent the leaching kinetics [28–29,33]. In this model, the unreacted core will gradually shrink and disappear during the leaching process, as shown in Fig. 5. This model has three main control steps: liquid film diffusion control (Eq. (6)), chemical reaction control (Eq. (7)), and inert-ash-layer diffusion control (Eq. (8)), which are represented as follows:

$$\text{Model 1 : } X = K_1 t \tag{6}$$

$$\text{Model 2 : } 1 - (1 - X)^{1/3} = K_2 t \tag{7}$$

$$\text{Model 3 : } 1 - 3(1 - X)^{2/3} + 2(1 - X) = K_3 t \tag{8}$$

where X is the leaching efficiency of Li or Co; K_1 , K_2 , and K_3 are the reaction rate constants of the control model (min⁻¹); t is the leaching time (min).

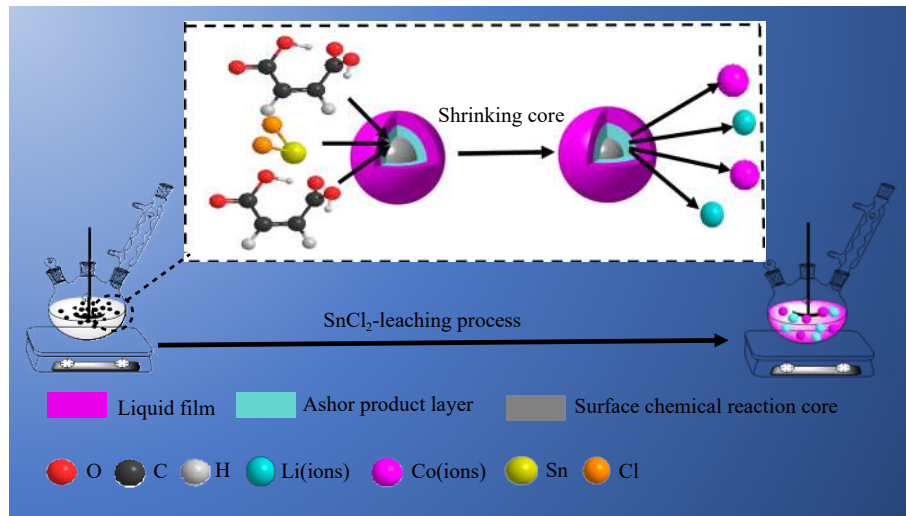


Fig. 5. Illustration of the kinetics mechanism of the SnCl_2 -leaching process.

To identify the rate-controlling step of SnCl_2 -leaching process, the dissolution kinetics behaviors of Co and Li in the acid-solution system were studied at various reaction times (10–60 min) and temperatures (40–80°C), while other leaching parameters were maintained at the optimum levels obtained in section 3.2. Based on the above models, we fitted the leaching data of the SnCl_2 -leaching process. The fitting result of the chemical reaction control (Eq. (7)) in Fig. 6 was best. Therefore, the SnCl_2 -leaching process is mainly controlled by the surface chemical reaction [41]. As the reaction

product is soluble, there was no inert ash diffusion. There was only one layer of liquid film and the resistance was very small. In addition, the reaction was performed under stirring at $270 \text{ r}\cdot\text{min}^{-1}$, thereby reducing the influence of diffusion resistance, so the resistance effect of external diffusion can be eliminated [42]. As such, the rate-controlling step of the acid-leaching process is the surface chemical reaction. According to the fitting results, we can obtain the surface chemical reaction constants at different temperatures. We find there to be a relationship between the reaction rate constant and reaction

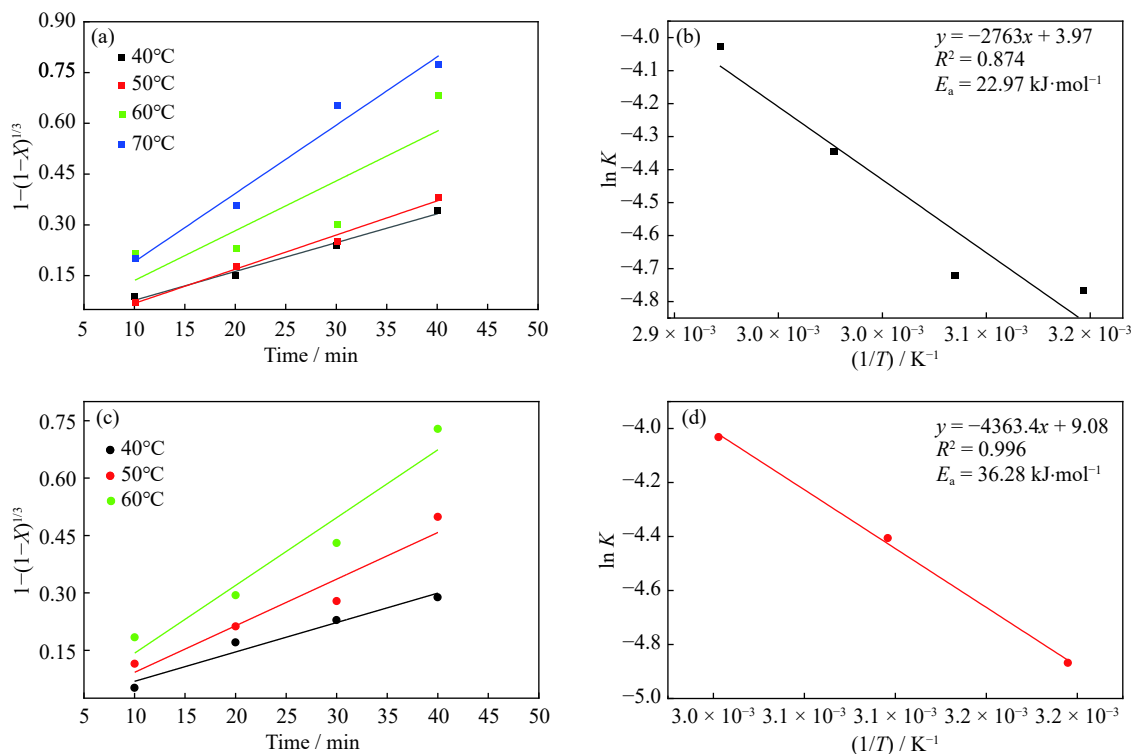


Fig. 6. Kinetics analysis of Co (a) and Li (c) in maleic-acid leaching process with SnCl_2 (chemical surface reaction model); Arrhenius plots for leaching of Co (b) and Li (d).

temperature, which accords with the Arrhenius equation (Eq. (9)):

$$K = A \exp(-E_a/RT), \quad \ln K = \ln A - \frac{E_a}{RT} \quad (9)$$

where K is the reaction rate constant (min^{-1}), A is pre-exponential factor, R is the molar gas constant ($8.314472 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), E_a is the activation energy ($\text{kJ}\cdot\text{mol}^{-1}$), and T is the thermodynamic temperature (K).

The E_a values of the Li and Co dissolutions were calculated by plotting $\ln K$ vs. $1/T$, as shown in Fig. 6. The E_a for leaching of Li was $36.28 \text{ kJ}\cdot\text{mol}^{-1}$ and that for Co was $22.97 \text{ kJ}\cdot\text{mol}^{-1}$.

3.4. Thermodynamics of leaching process

In addition to the kinetics analysis, the thermodynamics of the leaching reactions are important in the study of this mechanism. The Gibbs free energy (ΔG), an important thermodynamic parameter, is related only to the temperature and pressure. Moreover, ΔG is only based on the initial and final states of the reaction system, which reflect the extent of the chemical reaction. To calculate the ΔG s of the leaching reactions, thermodynamically favorable leaching products must first be identified. As a leaching agent, maleic acid can pro-

duce H^+ and radical ions by dissociation. In the leaching process, H^+ extracts Li^+ and Co^{2+} in association with the reduction process by SnCl_2 , during which the Co^{3+} in the material is reduced to Co^{2+} , and Sn^{2+} is oxidized to Sn^{4+} . During the reaction, metal complexes of metal and radical ions can form [34,43]. In Fig. 7, we can see that according to the valance states of the metal ions and the molecular structure of the radical ions, only one structure is possible for the Li complex, but two structures are possible for Co complexes (A and B in Fig. 7) and three are possible for Sn complexes (C, D, and E in Fig. 7). In our previous work, we found the formation energy of cobalt complex A to be lower than that of cobalt complex B, which means that the Co leaching product exists in the form of Co complex (a) [38]. This result is in agreement with Eqs. (4) and (5), for which the dissociation constant k_{a2} of maleic acid is much smaller than k_{a1} . This shows that the secondary dissociation of maleic acid can be ignored compared with the first dissociation. Therefore, each maleic-acid molecule can only provide one complexation site for metal ions after the dissociation and leaching process. Under these circumstances, Co and Sn are more likely to form Co complex A and Sn complex C, as shown in Fig. 7. Based on the above results, the acid-leaching processes by SnCl_2 and H_2O_2 can be expressed as shown in Eqs. (10) and (11):

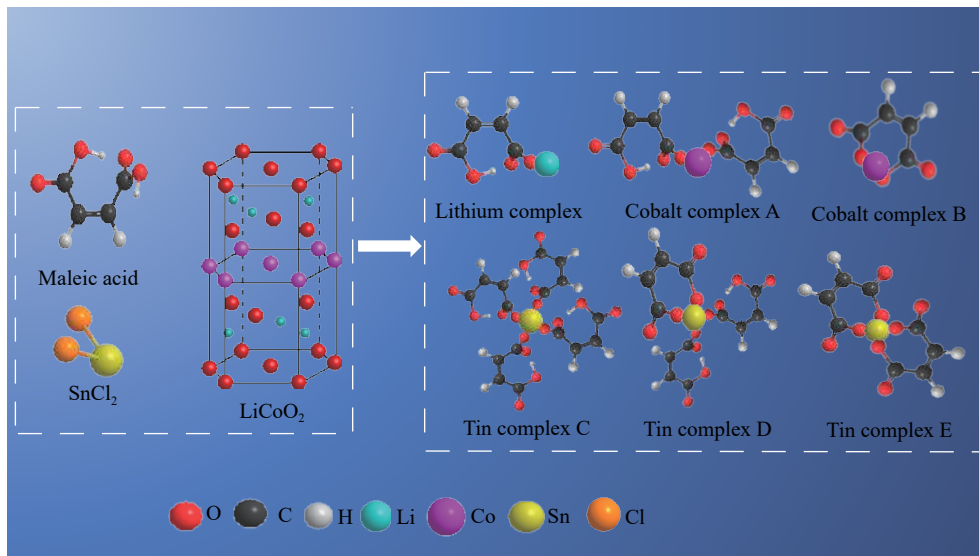
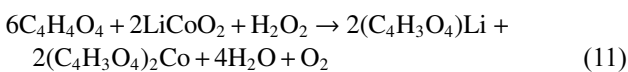
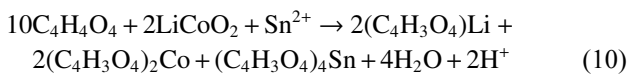


Fig. 7. Possible leaching products in the SnCl_2 -leaching process.



The ΔG values of the leaching reactions in which H_2O_2 and SnCl_2 were applied as reductants were calculated using the following formula under the conditions 333 K and 101 kPa:

$$\Delta G = -RT \ln k \quad (12)$$

where k is the equilibrium constant.

The value of k can be calculated based on the concentration of the final state of each substance in the reaction system. The concentration of each reaction substance can be obtained from the measurement and stoichiometric ratios using Eqs. (10) and (11), respectively. Table 1 lists the values of k and ΔG , in which we can see that the ΔG value of the H_2O_2 -leaching reaction is smaller than that of the SnCl_2 -leaching

reaction. This indicates that the range in which the H_2O_2 -leaching reaction can proceed is larger than that of the SnCl_2 -leaching process, which is consistent with the fact that the efficiency of the H_2O_2 -leaching reaction is slightly higher than that of the SnCl_2 -leaching reaction (as described in section 3.5). However, from a thermodynamic point of view, it is feasible to replace H_2O_2 with SnCl_2 , as the difference between the ΔG values of the two leaching reactions is insignificant.

Table 1. k and ΔG of H_2O_2 and SnCl_2 as reducing agents

Reducing agents	k	$\Delta G / (\text{kJ}\cdot\text{mol}^{-1})$
H_2O_2	0.66	1.2
SnCl_2	0.39	2.6

3.5. Comparison of H_2O_2 and SnCl_2 as reductants

To better confirm the feasibility of using SnCl_2 as a leaching reductant as a replacement for H_2O_2 , we compared the performances of SnCl_2 and H_2O_2 as leaching reductants based on our previous study [38]. For a more intuitive comparison, we plotted a histogram of the availability and efficacy of

H_2O_2 and SnCl_2 as leaching reductants, including their leaching efficiencies, optimal leaching parameters, and activation energies (Fig. 8). As can be seen in Figs. 8(a) and 8(b), the leaching efficiency of metals from spent LIBs and the optimal maleic-acid concentrations for the two reductants are almost the same. When SnCl_2 was the reductant in the leaching process, the optimal S/L ratio was higher than that of H_2O_2 , as shown in Fig. 8(c). The order of optimal reaction times and temperatures is $\text{SnCl}_2 < \text{H}_2\text{O}_2$ in Figs. 8(d) and 8(e), respectively. Furthermore, the activation energy of Co when SnCl_2 was the reductant is significantly lower than for H_2O_2 . More importantly, SnCl_2 is safer than H_2O_2 during the leaching process. When H_2O_2 is used as a reducing agent, gas can be generated during the leaching process, which increases the pressure of the reaction vessel such that an explosion might occur in more serious situations. In contrast, no gas is generated in the leaching process when SnCl_2 is used as a reductant. In addition, the Sn in the leaching solution may produce good effects in the subsequent synthesis of Ni-rich cathode materials [44]. Therefore, SnCl_2 is an efficient and feasible reducing agent for the acid-leaching process.

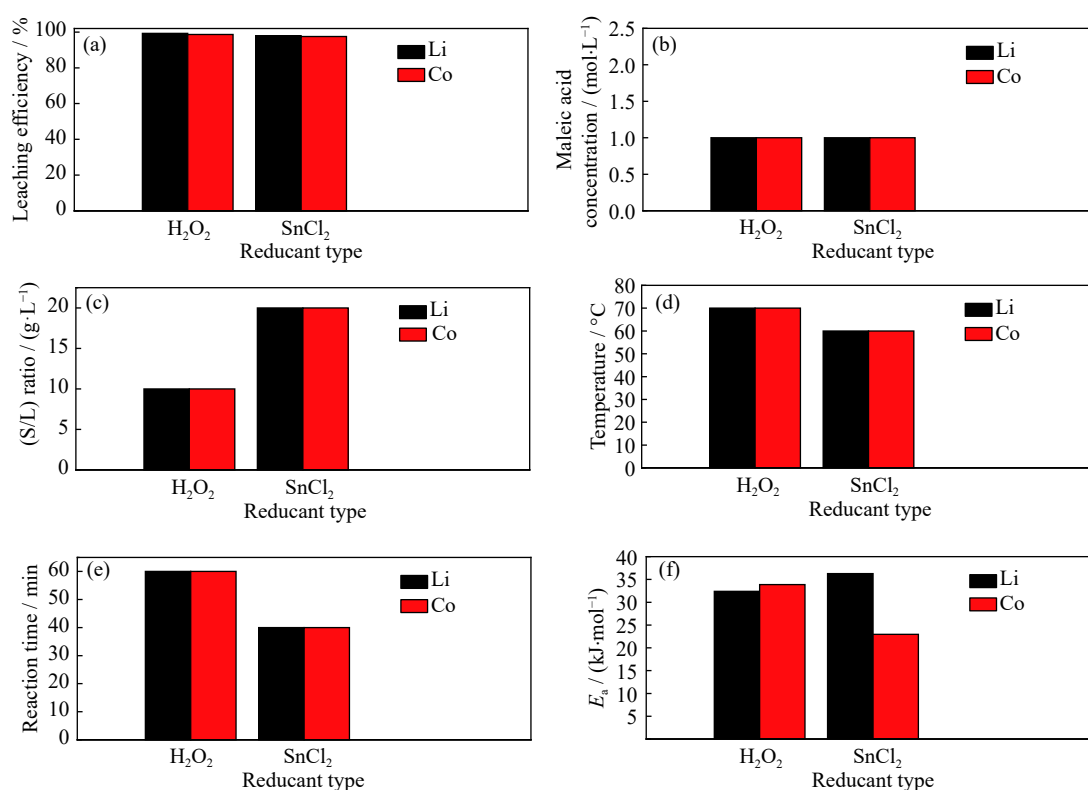


Fig. 8. Comparison of the two reductants with respect to (a) leaching efficiency, (b) optimal maleic-acid concentration, (c) optimal S/L ratio, (d) optimal temperature, (e) optimal reaction time, and (f) activation energy (E_a).

4. Conclusion

In this study, we used the stable reductant SnCl_2 with maleic acid to enhance the leaching efficiencies from spent

LIBs. The results reveal that more than 98% of Li and 97% of Co can be recovered using $1 \text{ mol}\cdot\text{L}^{-1}$ of maleic acid, $0.3 \text{ mol}\cdot\text{L}^{-1}$ of SnCl_2 , a $20 \text{ g}\cdot\text{L}^{-1}$ S/L ratio, 60°C , and a reaction time of 40 min. Compared with our previous work in which

H₂O₂ was used as a reducing agent, the obtained leaching efficiencies are almost equal. However, the leaching parameters of SnCl₂ are easier to achieve and the leaching kinetics analysis indicates that the processes fit the shrinking-core model. The activation energies of Co and Li for the SnCl₂-leaching reaction are lower than those for the H₂O₂-leaching reaction. Furthermore, SnCl₂ can be used as a reducing agent to recover other cathode materials such as LiNi_xCo_yMn_zO₂. In general, after comprehensive consideration of the leaching efficiency, energy consumption, and safety issues, we can conclude that SnCl₂ can be used as a leaching reducing agent instead of H₂O₂.

Acknowledgements

This work was financially supported by the National Key R&D Program of China (No. 2016YFB0100301) and the National Natural Science Foundation of China (Nos. 21875022 and U1664255).

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