

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

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## Abstract

A reductant counts for much in the hydrometallurgical recycling of valuable metals from spent lithium-ion batteries (LIBs). There is limited information about SnCl<sub>2</sub> as a reductant with organic acid (maleic acid) to recover value metals from spent LiCoO<sub>2</sub> material. The leaching efficiencies were 98.67% and 97.59% for Li and Co with 1 mol L<sup>-1</sup> of maleic acid and 0.3 mol L<sup>-1</sup> of SnCl<sub>2</sub> at 60°C and 40 min. And the kinetics and thermodynamics of the leaching process were inquired in the article to study the mechanism of leaching process clearly. According to the comparison of H<sub>2</sub>O<sub>2</sub> on the leaching efficiency, optimal leaching parameters and the activation energy, it is feasible to replace H<sub>2</sub>O<sub>2</sub> with SnCl<sub>2</sub> as a leaching reducer in the leaching process. In addition, when SnCl<sub>2</sub> is used in the acid-leaching process, Sn residue in leachate may has a positive effect on the re-synthesis of nickel-rich cathode materials. Therefore, the present study can provide a new direction for reductants selection for the hydrometallurgical recovery of valuable metals from spent LIBs

**Key words:** spent lithium ion batteries; recovery; maleic acid; reductant; SnCl<sub>2</sub>

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## 1. Introduction

Because of the increasingly serious environmental problems, people were beginning to explore new and clean energy. LIBs have been developed rapidly as a clean energy. In the last periods, LIBs have been widely used in electric vehicle and portable electronic equipment because of the low weight, high voltage, long service life, wide operating temperature range and safe performance[1-3]. With the economy developed rapidly, LIBs are in a high demand. Meanwhile, the consumption of LIBs has also

increased dramatically. It is estimated that the weight of these depleted batteries in China will exceed 200,000 tons by 2020[4-6]. There are high contents of heavy metals more than that in natural minerals, lithium salts and organic electrolyte which may produce harmful gases reacting with air in the spent LIBs[7-10]. Therefore, spent LIBs without appropriate disposal not only result in the waste of resource, but also lead to environmental pollution such as soil and underground water contamination.

At present, with people's attention to environmental protection and the development of

recovery technology, more and more attention has been paid to the recycling of spent LIBs. There are three topical recycling technologies for recycling spent LIBs: hydro-metallurgy, pyro-metallurgy and bio-metallurgy[11, 12]. Among the three processes, hydrometallurgy process has the advantages of high efficiency, low energy consumption, simple sample operation, etc., thus, it is the preferred process for recycling [13, 14]. The hydrometallurgical mainly includes the following steps: pretreatment, acid-leaching and reclamation[15]. Among the process, acid-leaching is a critical step that affect the recovery efficiency of metals of the spent LIBs. In the past, inorganic acid like HCl[16, 17], H<sub>2</sub>SO<sub>4</sub>[18-20] and H<sub>3</sub>PO<sub>4</sub>[21] as leaching agents have been investigated because of their low cost and high leaching efficiency. In recent years, organic acids with green source, little secondary pollution and the roughly the same leaching efficiency in comparison with inorganic acid has been attracted a lot of attention. Thus, a lot of studies have been conducted on leaching of spent LIBs materials using mild organic acid, such as L-tartaric acid[22] citric acid[12], formic acids[23], acetic acid[24], lactic acid[25] and succinic acid[26]. In addition, reducing agents were required to help increase the leaching efficiency. Because Co in the spent LIBs (like LiCoO<sub>2</sub> and LiNi<sub>x</sub>Co<sub>y</sub>Mn<sub>x</sub>O<sub>2</sub>) is mostly in the presence of Co<sup>3+</sup> which is not easy to dissolve. Reducing agents can reduce Co<sup>3+</sup> to Co<sup>2+</sup> which is easier to dissolve, so as to improve the leaching efficiency. The most commonly reducing agent is H<sub>2</sub>O<sub>2</sub>, because it does not introduce impurities into the system[24]. However, there are a few drawbacks of H<sub>2</sub>O<sub>2</sub> as the reducing agent, such as easily decomposition which leads to some issues in leaching, storage and transport process, as well as low efficiency of itself use. Hence, it is important and essential to find an efficient and stable substitute for H<sub>2</sub>O<sub>2</sub>. Some studies have been carried on to explore alternative reductants, like Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>[27], NaHSO<sub>3</sub>[28], NH<sub>4</sub>Cl[29],

glucose[30-32] and grape seed[33].

There are still some other chemicals which have the potential can be used as a reducing agent for recovery valuable metals from spent LIBs. What's more, the leachate can be used to resynthesize a lithium ion battery cathode material[34, 35]. Based on the safety and the positive effects of Sn on the lithium-ion batteries cathode materials, we employed SnCl<sub>2</sub> as a reductant for leaching of spent LIBs cathode materials. In this work, we explored the effects of various parameters of SnCl<sub>2</sub> as a reductant on the leaching efficiency, as well as the kinetics and thermodynamics of the leaching process. At the same time, we compared the parameters of leaching intuitively when SnCl<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> were used as reducing agents.

## 2. Materials and methods

### 2.1. Materials

The spent LIBs were from the Zhongguancun Electronic Market (Beijing, China). The NaCl solution was used for discharging residual power of the spent LIBs. And cathode materials were separated from the Al foil by NaOH solution. The maleic acid was used as the leaching agent, while the H<sub>2</sub>O<sub>2</sub> and SnCl<sub>2</sub> as the reductants. All the reagents in the experiment were analytical grade, and the water needed for solution is distilled water.

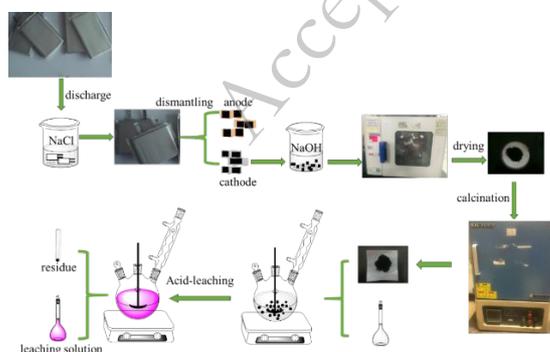
### 2.2 Pretreatment

As shown in the Fig. 1, the spent LIBs were firstly discharged fully through the NaCl solution for safety during the following experiments. Then spent LIBs were manually dismantled to remove the cases. The obtain cathode foil was cut into pieces of 1×1 cm<sup>2</sup>. The spent LIBs cathode materials and Al foil were separated by soaking the cathode pieces into NaOH solution for 12 hours. Then, the cathode material was dried at 60 °C for about 24 h and calcined in a muffle furnace at 840 °C for 5 h cooled to the room temperature

to remove the acetylene black and poly vinylidene fluoride (PVDF). Finally, the calcined material was ground into powder with mortar and pestle for about 1 h, a step that improve the leaching efficiency through improving the surface area.

### 2.3 Leaching process

All the leaching experiments were counted in a 150 mL three-necked by mixing active cathode material powder with solution of maleic acid and reducing agent ( $\text{H}_2\text{O}_2$ ,  $\text{SnCl}_2$ ), which was heated in a water bath. The mixture was stirred at 270 rpm by a mechanical stirrer to accelerate the reaction. The following acid-leaching parameters were investigated: (a) concentrations of  $\text{SnCl}_2$  (0.12-0.36 mol  $\text{L}^{-1}$ ), concentration of maleic acid (0.5-2.5 mol  $\text{L}^{-1}$ ), solid/liquid (S/L) ratio (10–50 g  $\text{L}^{-1}$ ), temperature (40–80 °C) and reaction time (20–60 min). (b) concentration of  $\text{H}_2\text{O}_2$  (0.5-2.5 vol%), concentration of maleic acid (0.5-2.5 mol  $\text{L}^{-1}$ ), solid/liquid (S/L) ratio (5–40 g  $\text{L}^{-1}$ ), temperature (50–90 °C) and reaction time (30–70 min). After leaching, the leach solution and residue were separated and the leach residue was washed by distilled water for analysis. In order to study the mechanism of acid-leaching, thermodynamics and kinetics of the leaching was conducted. In addition, the residual Sn in the leachate can be extracted by 0.1 mol  $\text{L}^{-1}$  Cyphos IL 104 to achieve the separation of Sn from other valuable metals in the cathode materials [36].



**Fig. 1. Flow sheet of recovery metals from spent LIBs**

To study the thermal behavior of spent LIBs cathode materials after NaOH treatment, thermogravimetric analysis and differential scanning calorimetry (TG/DSC) were employed. The measurements were performed in an air atmosphere at a heating rate of 10 °C  $\text{min}^{-1}$ . The X-ray diffraction (XRD) was used to characterize crystal structures of spent LIBs cathode materials and leaching residues. The scanning electron microscopy (SEM) was used to investigate surface appearance of materials. Moreover, element contents of the active cathodic material powder dissolved by digestion and the leachate were analyzed quantitatively by inductively coupled plasma optical emission spectrometer (ICP-OES). The leaching efficiency of the metals was calculated with the Eq (1):

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

Where the X is the leaching efficiency (%),  $C_e$  is the concentration of metals in the leachate (mg  $\text{L}^{-1}$ ),  $C_0$  represents the concentration of metals in the active cathode material (mg  $\text{L}^{-1}$ ).

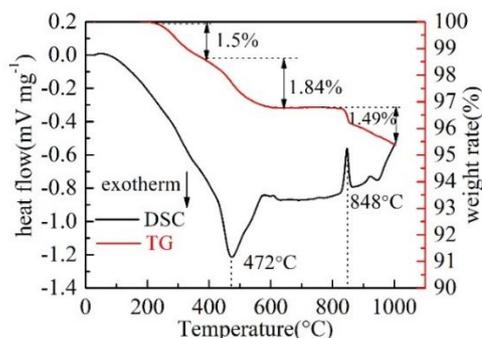
## 3. Results and discussion

### 3.1 Characterization of the cathode material

TG-DSC was applied to investigate the chemical reaction and weight loss process in the cathode powder when the temperature ranged from room temperature to 1000 °C. And the result was shown in Fig. 2. It is clear that three weight-loss stages and two distinct peaks were observed. A weight loss of 1.5% was discovered from 27 to 400 °C, mainly due to the reduction of bound water in the material<sup>[16]</sup>. From 400 to 848 °C, a mass loss of 1.84% indicated the removal of acetylene black and binder (PVDF). In the temperature range, there was an obvious DSC exothermic peak at 472 °C representing the degradation of acetylene black and decomposition of PVDF. In addition, the weight loss of 1.49% was detected in the temperature range of 848-1000 °C with a exothermic DSC

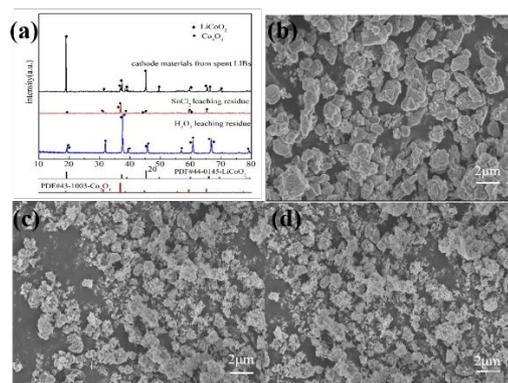
endothermic peak at 848 °C, manifesting a phase transformation of the cathode material and the loss of lithium at high temperature[25]. In summary, the optimum calcination temperature is 840°C.

XRD patterns and SEM images of the spent LIBs cathodic material and the leaching residues



**Fig. 2. TG-DSC curves of the spent cathodic powder**

are shown in Fig. 3. From the XRD patterns in Fig. 3(a), the cathode materials of spent LIBs were almost  $\text{LiCoO}_2$  and a little  $\text{Co}_3\text{O}_4$ . There were only characteristic peaks belonging to  $\text{Co}_3\text{O}_4$  in the leaching residues whether  $\text{H}_2\text{O}_2$  or  $\text{SnCl}_2$  was as the reducing agent. SEM images in Fig. 3(b) shows that particles of the cathode compounds of spent LIBs is irregular shapes with diameters of 10 to 50  $\mu\text{m}$  and the edges of particles are smooth. As can be seen in the Fig. 3(c) and Fig. 3(d), the particle size of the leaching residues is smaller and the edges of the particles are cruder compared to the active  $\text{LiCoO}_2$  material of spent LIBs[35]. And there is no significant difference between particle sizes of the leaching residues from  $\text{H}_2\text{O}_2$  and  $\text{SnCl}_2$ . These phenomena proved that  $\text{SnCl}_2$  as the reducing agent destroyed the structure of spent  $\text{LiCoO}_2$ .



**Fig. 3. XRD patterns of the active cathodic material and the leaching residues (a); SEM images obtained before leaching (b), the leaching residues from  $\text{H}_2\text{O}_2$  (c) and  $\text{SnCl}_2$ (d).**

According to the above characterization, the main components of the spent LIBs cathode materials in this paper are  $\text{LiCoO}_2$ . The main reactions of maleic acid as leaching agent with different reducers in leaching process are as follows equations (Eqs. (2)–(3)). Since maleic acid is a binary acid, one mole of maleic acid calibrate two moles of  $\text{H}^+$ . The dissociation steps and dissociation constant that has an important influence on  $\text{H}^+$  concentration and leaching efficiency are as follows equations (Eqs. (4)–(5)):

$$6\text{H}^+ + 2\text{LiCoO}_2 + \text{H}_2\text{O}_2 \rightarrow 2\text{Li}^+ + 2\text{Co}^{2+} + 4\text{H}_2\text{O} + \text{O}_2 \quad (2)$$

$$2\text{LiCoO}_2 + 8\text{H}^+ + \text{Sn}^{2+} \rightarrow 2\text{Li}^+ + 2\text{Co}^{2+} + \text{Sn}^{4+} + 4\text{H}_2\text{O} \quad (3)$$

$$\text{C}_4\text{H}_4\text{O}_4 \rightarrow \text{C}_4\text{H}_3\text{O}_4^- + \text{H}^+ \quad k_{a1}=1.42 \times 10^{-2} \quad (4)$$

$$\text{C}_4\text{H}_3\text{O}_4^- \rightarrow \text{C}_4\text{H}_2\text{O}_4^{2-} + \text{H}^+ \quad k_{a2}=8.57 \times 10^{-7} \quad (5)$$

Compared maleic acid and other organic acids which have been used in previous studies[15] with the dissociation constant, maleic acid as a leaching agent is feasible. Furthermore, the  $\text{Co}^{3+}$  is difficult to leach [37]. Therefore, a reducing agent is used to reduce the  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  so as to improve the leaching efficiency of Co. Sn exists  $\text{SnCl}_2$  in form of  $\text{Sn}^{2+}$  which can lose electrons and transform into high valence  $\text{Sn}^{4+}$  and reduce high valence metal ions to low valence metal ions

at the same time. Based on the standard electrode potential,  $\Phi^{\ominus}(\text{Co}^{3+}/\text{Co}^{2+}) = 1.83$ ,  $\Phi^{\ominus}(\text{O}_2/\text{H}_2\text{O}_2) = 0.682$ ,  $\Phi^{\ominus}(\text{Sn}^{4+}/\text{Sn}^{2+}) = 0.151\text{V}$ , the  $\text{SnCl}_2$  can reduce  $\text{Co}^{3+}$  into  $\text{Co}^{2+}$  and it is potential and feasibility to replace  $\text{H}_2\text{O}_2$  as a reducing agent in this work.

### 3.2 Effects of acid-leaching parameters on leaching efficiencies

In order to study the influence of various parameters on the leaching efficiency during the leaching process, meanwhile, to estimate the approximate horizontal range of each parameter, the orthogonal experiment was carried out (Table S1-S2). The effect of maleic acid was studied under the following working condition:  $\text{SnCl}_2$  concentration of  $0.3 \text{ mol L}^{-1}$ , S/L ratio of  $10 \text{ g L}^{-1}$ , temperature of  $60 \text{ }^{\circ}\text{C}$ , reaction time of 40 min, and the leaching yields of Co and Li were reported in Fig. 4(a). Generally speaking, the leaching efficiencies of metals increased with the acid concentration increasing[24]. Because acid can ionize  $\text{H}^+$  which reacted with spent  $\text{LiCoO}_2$  materials and destroyed the structure to dissolve metals. In a certain concentration range, the higher the acid concentration is, the easier the structure is destroyed[38]. As we can see, the leaching efficiencies heightened from 80.2% to 98% for Li, and from 79.4% to 97.5% for Co with the maleic acid concentration increasing from 0.5 to  $1 \text{ mol L}^{-1}$ . The leaching efficiencies of Li and Co remained over 97.5% and almost constant when the maleic acid concentration was more than  $1 \text{ mol L}^{-1}$ , which further shows that the influence of acid concentration on the leaching efficiency is limited. In consideration of the cost and efficiency, all further experiments were carried out using  $1 \text{ mol L}^{-1}$  maleic acid.

It has been reported that adding a reductant can greatly improve the leaching efficiency [1]. In this work,  $\text{SnCl}_2$  was a leaching reductant. The strong chemical bond between oxygen and cobalt makes  $\text{LiCoO}_2$  difficult to dissolve. Adding the

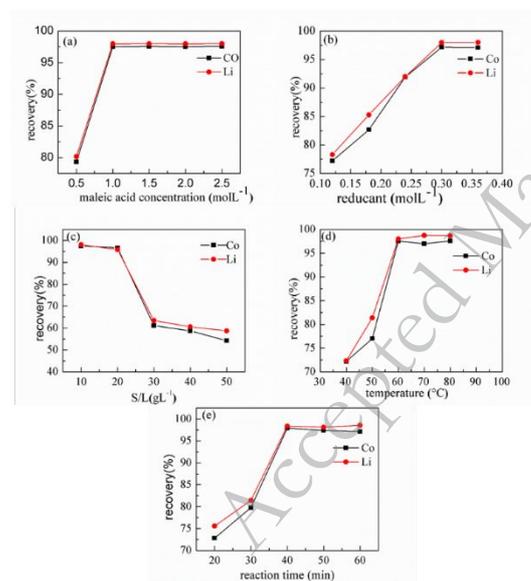
$\text{SnCl}_2$  reduced  $\text{Co}^{3+}$  that is not easily dissolved to dissolved  $\text{Co}^{2+}$ . In order to study the effect of  $\text{SnCl}_2$  on leaching efficiency, the experiment was applied with  $\text{SnCl}_2$  ( $0.12\text{-}0.36 \text{ mol L}^{-1}$ ),  $1 \text{ mol L}^{-1}$  maleic acid,  $10 \text{ g L}^{-1}$ ,  $60 \text{ }^{\circ}\text{C}$  and 40 min and the result was shown in Fig. 4(b). The leaching efficiency of Co increased progressively from 77% to 97.2%, with an increase in the  $\text{SnCl}_2$  concentration from  $0.12 \text{ mol L}^{-1}$  to  $0.3 \text{ mol L}^{-1}$ . With the leaching efficiency of Co increasing, the leaching efficiency of Li also increased. Because Li and Co exists in the same compound  $\text{LiCoO}_2$  and the dissolution of Co accelerated the structural destruction of the  $\text{LiCoO}_2$ , the dissolution of Li increased[18]. When the  $\text{SnCl}_2$  was above  $0.3 \text{ mol L}^{-1}$ , leaching yields of Li and Co showed no significant improvement. Thus,  $0.3 \text{ mol L}^{-1}$  was defined as the optimal  $\text{SnCl}_2$  concentration.

To investigate the optimal S/L ratio, the S/L ratio was controlled in the range of 10 to  $50 \text{ g L}^{-1}$ . Fig. 4(c) shows the effect of S/L ratio under conditions of  $1 \text{ mol L}^{-1}$  maleic acid,  $0.3 \text{ mol L}^{-1}$   $\text{SnCl}_2$ ,  $60 \text{ }^{\circ}\text{C}$  and 40 min. As we can see in the Fig. 4(c), the leaching efficiencies of Li and Co both decrease drastically, when the S/L ratio increased, which due to the fact that the effective area that can be contacted per unit volume is decreasing [13]. While S/L increase from 10 to  $20 \text{ g L}^{-1}$ , the leaching efficiencies decreased slightly, for Li barely decreased from 98% to 96% and for Co decreased from 97.5% to 96.6%. Therefore, considering both the leaching efficiency and economic benefit, S/L= $20 \text{ g L}^{-1}$  is the best leaching parameter.

To study the effect of temperature, the reaction temperature was varied from 40 to  $80 \text{ }^{\circ}\text{C}$ , in the same time, the other parameter were held as following:  $1 \text{ mol L}^{-1}$  maleic acid,  $10 \text{ g L}^{-1}$  S/L,  $0.3 \text{ mol L}^{-1}$   $\text{SnCl}_2$  and 40 min. Fig. 4(d) shows that the leaching efficiencies increased with the increasing of temperature between 40 and  $60 \text{ }^{\circ}\text{C}$ , indicating that leaching metals from spent

LiCoO<sub>2</sub> is an endothermic process[26, 28, 39]. Moreover, increasing the temperature can accelerate mass transfer in the solution[19, 39] and can cause more frequent and more energetic collisions<sup>[13]</sup>, thereby, enhancing reaction at the surface of the particles<sup>[16]</sup>. What's more, when the temperature continued to increase 60 to 80 °C, the leaching efficiency was not significantly improved. Thus, 60 °C was chosen as the optimum reaction temperature.

The influence of the reaction time with SnCl<sub>2</sub> as a reducing agent on the leaching of spent LiCoO<sub>2</sub> was reviewed in acid concentration = 1 mol L<sup>-1</sup>, SnCl<sub>2</sub> concentration = 0.3 mol L<sup>-1</sup>, temperature = 60 °C, S/L = 10 gL<sup>-1</sup>. In the Fig. 4(e), it is clearly that the leaching efficiency increased with the reaction time increasing until 40 min. However, when the reaction time was above 40 min, the recovery efficiencies of Li and Co showed no significant differences. Thus, 40 min would be regarded as the optimized reaction time.



**Fig. 4. Effects of the acid-leaching parameters on the leaching efficiency with SnCl<sub>2</sub>; (a) maleic acid concentration; (b) SnCl<sub>2</sub> concentration; (c) S/L ratio; (d) temperature; (e) reaction time.**

### 3.3 Kinetics of leaching process.

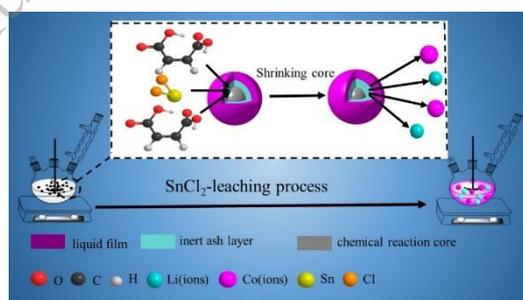
Kinetic analysis is very necessary to investigate the leaching behavior and feasibility of SnCl<sub>2</sub> as reductant for leaching reactions. The main purpose of kinetics investigation is to recognize the rate-controlling steps of the reaction. The leaching process of LiCoO<sub>2</sub> is a typical heterogeneous reaction, therefore the shrinking-core model could 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, which was 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)) are represented as following:

$$\text{Model 1: } X = K_1 t \quad (6)$$

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

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

where  $x$  is the leaching efficiencies of Li and Co,  $k_1$ ,  $k_2$  and  $k_3$  (min<sup>-1</sup>) are the reaction rate constant of control model,  $t$  (min) is the leaching time.



**Fig.5. Illustration of the kinetic mechanism of the SnCl<sub>2</sub>-leaching process**

To recognize the rate-controlling step of SnCl<sub>2</sub>-leaching process, the dissolution kinetics behavior of Co and Li in the acid-solution system was studied at various reaction time (10-60 min) and temperatures (40-80 °C), while other leaching parameters were maintained as the optimum level obtained in Section 3.2. Based on the above

models, the leaching data of SnCl<sub>2</sub>-leaching process was fitted. The fitting result of chemical reaction control (Eq. (7)) in Fig. 6 shown the best relevance. Thus, the SnCl<sub>2</sub>-leaching process is mainly controlled by surface chemical reaction[40]. The reaction product is soluble, therefore, the inert ash diffusion does not exist. There is only one layer of liquid film and the resistance is very small. In addition, the reaction was carried out under stirring at 270 rpm, reducing the influence of diffusion resistance, and the resistance effect of external diffusion can be basically eliminated[41]. Therefore, the rate-controlling step of acid-leaching process is surface chemical reaction. According to the fitting results, we can get the surface chemical reaction constants at different temperatures. And there is a relationship between reaction rate constant and reaction temperature, which is in accordance with the Arrhenius equation (Eq. (9)):

$$k = Ae^{-E_a/RT} \quad \ln k = \ln A - \frac{E_a}{RT} \quad (9)$$

Where the K is the reaction rate constant(min<sup>-1</sup>), A is pre-exponential factor, R is molar gas constant (8.314472J K<sup>-1</sup> mol<sup>-1</sup>), E<sub>a</sub> is activation energy (K · J mol<sup>-1</sup>) and T is thermodynamic temperature (K).

The activation energy of Li and Co dissolution was calculated by plotting of the ln K vs 1/T in Fig. 6. The E<sub>a</sub> for leaching of Li was 36.28 K J mol<sup>-1</sup> and for Co was 22.97 K J mol<sup>-1</sup>.

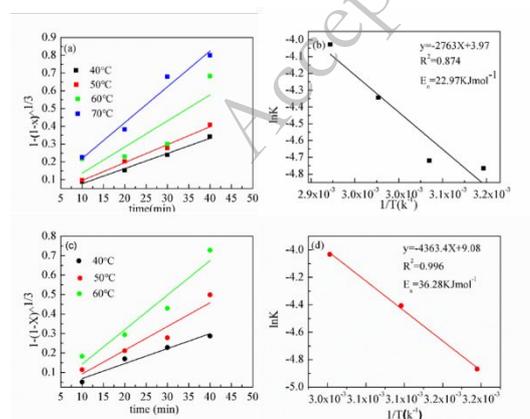


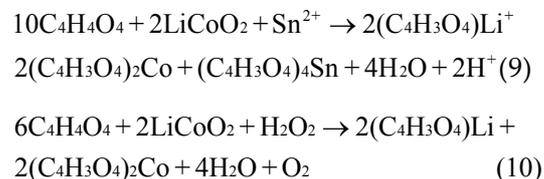
Fig. 6. Kinetics study of Co (a) and Li (c) in maleic

acid-leaching process with SnCl<sub>2</sub>(chemical surface reaction model); Arrhenius plots for leaching of Co (b) and Li (d)

### 3.4 Thermodynamic of leaching process.

In addition to kinetics analysis, thermodynamics is also important for the study on the mechanism of leaching reactions. The Gibbs free energy ( $\Delta G$ ) is an important thermodynamic parameter which is only related to temperature and pressure. Moreover,  $\Delta G$  is only based on the initial and final states of the reaction system, reflecting the extent where the chemical reaction proceeded. To calculate  $\Delta G$  of the leaching reactions, the thermodynamic favorable leaching products need to be determined firstly. As the leaching agent, maleic acid can produce H<sup>+</sup> and radical ions through dissociation. In the leaching process, the H<sup>+</sup> extracted Li<sup>+</sup> and Co<sup>2+</sup> with the reduction process by SnCl<sub>2</sub>, during which the Co<sup>3+</sup> in the material was reduced to Co<sup>2+</sup>, while the Sn<sup>2+</sup> was oxidized to Sn<sup>4+</sup>. During the reaction, metal complexes can be formed by metal ions and radical ions [34, 42]. It can be seen from the Fig.7 that according to the valance states of metal ions and molecular structure of radical ion, there is only one structure for Li complex, but two possible structures for Co complexes ((a) and (b) in Fig.7) and three possible structures for Sn complexes ((a), (b) and (c) in Fig.7). According to our previous work, the formation energy of cobalt complex (a) is lower than that of cobalt complex (b), indicating that the Co leaching product exist in the form of Co complex (a)[38]. This result was agreement with Eq (3) and (4) that the dissociation constant  $k_{a2}$  of maleic acid is much smaller than  $k_{a1}$ , illustrating that the secondary dissociation of maleic acid can be ignored compared with the first dissociation. Therefore, each maleic acid molecular can only provide one complexation site for metal ions after dissociation and leaching process. Under this

circumstance, Co and Sn are more likely to form Co complex (a) and Sn complex (a) in Fig.7. Based on the above results, acid leaching process by SnCl<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> can be symbolized by Eq (9)-(10):



The Gibbs free energy ( $\Delta G$ ) of the leaching reactions that H<sub>2</sub>O<sub>2</sub> and SnCl<sub>2</sub> were applied as reductants was calculated based on the following formula:

In the case of state (333 K, 101 kPa)

$$\Delta G = -RT \ln K \quad (11)$$

Where the K is Equilibrium constant. Where the R is the universal gas constant (8.314 J·mol<sup>-1</sup>·K<sup>-1</sup>) and T is the absolute temperature (K).

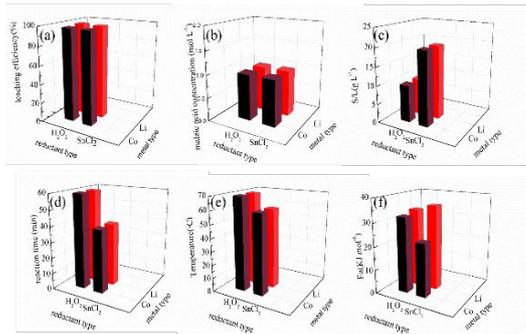
The K can be calculated based on the concentration of the final state of each substance in the reaction system. The concentration of each reaction substance can be obtained from measurement and stoichiometric ratio by Eq (9)-(10). The results of K and  $\Delta G$  are shown in Table S5. As can be seen in Table S5,  $\Delta G$  of the H<sub>2</sub>O<sub>2</sub>-leaching reaction is smaller than that of the SnCl<sub>2</sub>-leaching reaction, indicating that the extent where H<sub>2</sub>O<sub>2</sub>-leaching reaction could proceed is larger than that of SnCl<sub>2</sub>-leaching process, which is consistent with the fact that the leaching efficiency of H<sub>2</sub>O<sub>2</sub>-leaching is slightly higher than that of SnCl<sub>2</sub>-leaching (as shown in Section 3.5). But it is feasible to replace H<sub>2</sub>O<sub>2</sub> with SnCl<sub>2</sub> from a thermodynamic point of view, since there is insignificant difference between the  $\Delta G$  of the two leaching reactions.



Fig.7. Possible leaching products in the acid-leaching processes of the SnCl<sub>2</sub>-leaching process.

### 3.5 Comparison of the H<sub>2</sub>O<sub>2</sub> and SnCl<sub>2</sub> as the reductant.

In order to better confirm the feasibility of SnCl<sub>2</sub> replacing H<sub>2</sub>O<sub>2</sub> as a leaching reductant, the performance of SnCl<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> as a leaching reductant was compared based on our previous study[38]. For a more intuitive comparison the availability and efficacy of H<sub>2</sub>O<sub>2</sub> and SnCl<sub>2</sub> as the leaching reductant, the leaching efficiency, optimal leaching parameters and the activation energy for the two reductant were made comparison into a histogram (Fig.8). As can be seen in Fig.8(a) and Fig.8(b), the leaching efficiency of metals from spent LIBs and the optimal maleic acid concentration with the two reductants were almost the same. When SnCl<sub>2</sub> was the reductant of the leaching process the optimal S/L<sup>-1</sup> was higher than H<sub>2</sub>O<sub>2</sub> in Fig.8(c). The order of the optimal reaction time and temperature was SnCl<sub>2</sub><H<sub>2</sub>O<sub>2</sub> in Fig.8(d) and (e). What's more, the activation energy of Co that SnCl<sub>2</sub> was the reductant is significantly lower than H<sub>2</sub>O<sub>2</sub>. More importantly, SnCl<sub>2</sub> is safer than H<sub>2</sub>O<sub>2</sub> in the leaching process. H<sub>2</sub>O<sub>2</sub> as a reducing agent, gas may be generated during the leaching process, which will increase the pressure of the reaction vessel actually and an explosion might occur in more serious situation. While there is no gas in the leaching process of SnCl<sub>2</sub> as a reductant. Therefore, SnCl<sub>2</sub> is an efficient and feasible reducing agent for the acid leaching process.



**Fig. 8.** Comparison between the two reductants in the leaching efficiency (a), optimal maleic acid concentration (b), optimal S/L ratio (c), optimal temperature (d), optimal reaction time (e), activation energy (Ea) (f).

#### 4. Conclusions

In this study, a stable reductant  $\text{SnCl}_2$  with maleic acid has been used to enhance the leaching efficiencies from spent LIBs. Based on the leaching result, over 98% Li and 97% Co can be recovered with  $1 \text{ mol L}^{-1}$  maleic acid,  $0.3 \text{ mol L}^{-1} \text{SnCl}_2$ ,  $20 \text{ g L}^{-1}$ ,  $60 \text{ }^\circ\text{C}$  and 40 min. Compared with our previous work that  $\text{H}_2\text{O}_2$  was used as a reducing agent the leaching efficiencies are almost equal. However, the leaching parameter of  $\text{SnCl}_2$  is easier to achieve. And the results from leaching kinetics implies that the processes fit with the shrinking-core model. The activation energy of Co and Li of  $\text{SnCl}_2$ -leaching reaction is lower than that of  $\text{H}_2\text{O}_2$ -leaching reaction. What's more,  $\text{SnCl}_2$  can be used as a reducing agent to recover other cathode materials like  $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ , and Sn in leaching solution may produces good effects in the subsequent synthesis of Ni-rich cathode materials[43]. In general, comprehensive consideration of leaching efficiency, energy consumption and safety issues,  $\text{SnCl}_2$  can be used as a leaching reducing agent instead of  $\text{H}_2\text{O}_2$ .

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