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Leaching Procedure and Kinetic Studies of Cobalt in Cathode Materials from Spent Lithium Ion Batteries Using Organic Citric Acid as Leachant

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ABSTRACT: An approach to recycle precious metals of cathode materials from spent lithium cobalt oxide batteries by using organic citric acid and hydrogen peroxide has been studied in this paper. The effects of molar ratio, solid-liquid ratio, reaction time and temperature on leaching efficiency of cobalt were investigated respectively. Meanwhile the leaching kinetics equation of cobalt was established, and the apparent activation energy of leaching reaction of cobalt was calculated out. The results show that when the molar ratio of citric acid to lithium cobalt oxides is 4:1, solid-to-liquid ratio is 15 g/L, the reaction temperature is 90 !, the reaction time is 5 h and concentration of H_2O_2 is 1.0 vol. %, the leaching efficiency could be up to 99.07%. The apparent activation energy of cobalt leaching reaction is 45.724 KJ/mol, and by means of conducting fitting test for the relationship between lithium cobalt oxides powder with different particle sizes and leaching efficiency, it can be concluded that the reaction of lithium cobalt oxides using citric acid and hydrogen peroxide is chemical reaction control.

Key words: Spent lithium cobalt oxides batteries, Citric acid, Leaching, Kinetics

INTRODUCTION

Compared to other batteries such as zinc-silver batteries, lead-acid batteries, Ni-MH batteries, Lithium Ion Batteries (LIBs) exhibit many advantages including small volume, light weight, high specific energy density, long cycle life, no memory effect, etc., thus they can be widely applied to portable equipments and electric vehicles (Lundblad *et al.*, 1997; Plichta *et al.*, 1987; Sabin, 1997; Ra *et al.*, 2006; Nan *et al.*, 2005; Xu *et al.*, 2008). It shows that the consumptions of LIBs will increase tremendously during the next 20 years. However the lifetime of lithium ion battery is generally 3~5 years, therefore there would be a great deal of spent lithium ion batteries upon completion of their service lives. Spent lithium ion batteries comprise about 5~15% cobalt and 2~7% lithium. If there are no proper safe methods to disposal, these spent lithium ion batteries may cause environmental pollution, scare resource waste and energy crisis (Lee et al., 2003).

The research on recycle technology of spent lithium ion battery was started in the 1990's, mostly focusing on the spent batteries with graphite as anode material and $LiCoO_2$ as cathode material. Basic procedures of various recycle technologies include pretreatment procedure (disassemble, classify, etc.) and recycle of cobalt and other metals. The difference mainly lies in the varieties of routes and methods to recycle metals. According to the literatures, the methods to recycle metals can be divided into physical methods and chemical process. The physical method mainly includes machinery, heat treatment, dissolution, etc. The chemical process mainly includes acid leaching, bioleaching, organic solvent extraction, chemical precipitation, electro-deposition, etc (Kondás *et al.*, 2006; Saeki *et al.*, 2004; Sonmez *et al.*, 2009).

Shin et al. proposed that spent lithium ion battery was first crushed and screened to get Al, Cu and plastics and then to get Fe using magnetic separation, further broken to get smaller particles for acid leaching. Lithium and cobalt shall be recycled in the form of filtrate (Shin *et al.*, 2005). Lee and Rhee

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*Corresponding author E-mail: changdeljw@163.com proposed that spent lithium ion battery was first heat-treated under the temperature of 100~150 °C for 1 h, and then disassembled by high speed grinder to separate electrode materials by shaking and screening. Subsequently carbon and binders were removed by heat treatment under 500~900 °C for 0.5~2 h. Finally cobalt was leached out using HNO_3, leach liquor would be placed in stainless steel crucible for roasting under 500~1000 °C for 2 h, so as to recycle cobalt oxide (Lee *et al.,* 2002). Y. N. Xu adopted a low-cost DMF for simple dis-solution to remove binder (PVDF) on electrode to recycle lithium ion battery (Xu *et al.,* 2014).

Acid leaching always uses inorganic acids such as sulfuric acid (Mantuano *et al.,* 2006; Jha *et al.,* 2011; Jha *et al.,* 2013), hydrochloric acid (Zhang *et al.*, 1998; Contestabile *et al.*, 2001), hydrogen nitrate (Catillo *et al.,* 2002), etc. The waste liquor generated after leaching comprises strong acidity, and the waste liquor may pollute water bodies without treatment before emission. However additional expenditure would be produced if conducting the follow-up processing. Therefore there is no significant economic benefit in recycling precious metal by inorganic acids. Sun et al. employed oxalic acid as leaching agent to precipitate the cobalt as cobalt oxalate. Aluminum and lithium in the liquor can be separated in the form of precipitation by precipitant of NaOH and Na_2CO_3 respectively (Sun *et al.,* 2012).

With the development of leaching technology, bioleaching methods appeared (Rohwerder *et al.,* 2003). Mishra et al. used acidithiobacillus ferro-oxidans to conduct bioleaching for cobalt and lithium in spent lithium ion battery (Mishra *et al.,* 2008). The efficiency of bioleaching was restricted by bacteria, and it can only propose the solution of low concentration of metal content. Meanwhile the velocity of bioleaching is slow, which results in unsatisfactory effects of industrial application. Pranolo et al. have studied a kind of mixed extraction solvent system to obtain pure cobalt and lithium from spent lithium ion battery leaching liquor. When the pH value of the system is less than 3.2, Fe, Co and Al are extracted in organic phase at the same time, realizing the effective separation from cobalt, nickel and lithium (Pranolo *et al.,* 2010). Castillo et al. took NaOH as precipitator, achieving the separation of Fe, Mn and Li by adjusting the pH value of solvent (Catillo *et al.,* 2002). Li et al. employ chemical precipitation method to synthesize new electrode material lithium cobalt oxides after the separation of cobalt and lithium in spent lithium ion battery (Li *et al.,* 2009).

In this paper citric acid was selected as leaching agent to conduct leaching of hydrometallurgy for cathode material of spent lithium cobalt oxides. Citric acid is a common weak organic acid, hence seldom causing secondary pollution to the environment. This paper discussed the chemical reaction mechanism of hydrometallurgical leaching, and investigated the impacts of different molar ratio, solid-to-liquid ratio, reaction temperature, reaction time and concentration of H_2O_2 on leaching efficiency, and determined the apparent activation energy and reaction control principle of efficient leaching re-action of hydrometallurgy of lithium cobalt oxides by citric acid through experiments and theoretical calculation.

MATERIALS & METHODS

Spent $LiCoO_2$ LIBs were provided by Hubei Nuobang Chemical Company of China. Citric acid and hydrogen peroxide (H_2O_2) used as leaching agents were both purchased by Tianjin Kaitong Chemical Company of China. Dimethyl acetamide (DMAC) and other chemicals in the experiments were all analytical-grade reagents. Chromato-graphically pure solutions of cobalt were purchased from the National Institute of Metrology P.R. China for determination of Inductive Coupled Plasma Emission Spectrometer (ICP).

Fig. 1 shows a flowchart of the whole hydro-metallurgical recycling process for spent LIBs in this work. Firstly a discharging pretreatment step was used for the given process before the dismantling of the battery steel shell. Secondly the spent LIBs were manually dismantled by steel saw and knife to get cell core, and then the cell core got dismantled to separate the cathode and anode plate. Thirdly the cathode plate was soaked in the organic solvent to separate the cathode materials and current collector for the following leaching. Finally the spent materials were leached out by citric acid and hydrogen peroxide in the optimal conditions.

Firstly the discharged battery was dismantled by steel saw, manually removing the battery core. Secondly the soft packing of battery core was cut with scissors, also manually removing the winding cathode and anode plates together. Finally the cathode and anode plates were manually separated using the small knife, wherein the diaphragm and anode plates were reserved for other use, the cathode plates were used for separating experiment. All steps in this dismantling procedure were carried out using safety glasses, gloves and gas masks for safe opera- tion.

The cathode plates were soaked by DMAC in thermostatic water bath to effectively separate spent electrode materials and aluminum foils, and the residuals on aluminum foils could be wiped out manually. And then the received black powders were dried at 60 °C for 24 h for the following thermal pretreatment. Finally the cathode materials from the spent batteries were calcined at 600 °C for 2 h in a muffle to eliminate carbon and PVDF in the cathodic active materials.

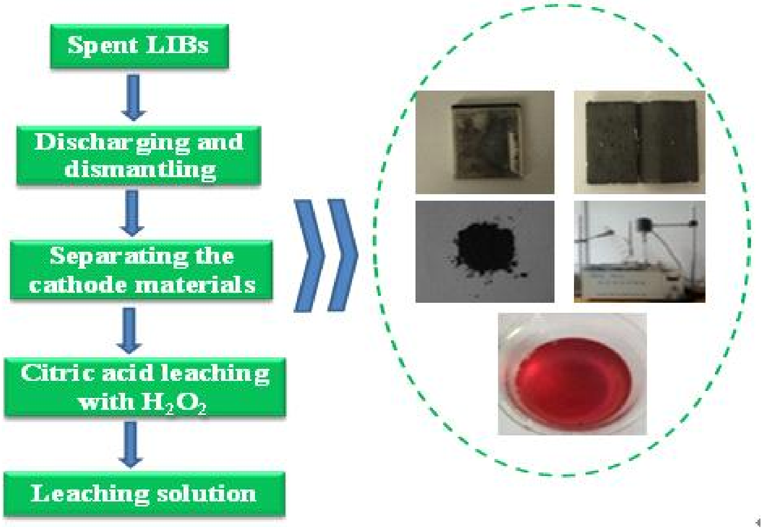


Fig. 1. The flowchart of hydrometallurgical recycling process for spent LIBs in this work

The leaching experiments were carried out in a 250 mL three-necked round-bottomed reactor with thermostatic water bath device. The reactor was fitted with an impeller stirrer, a vapor condenser to reduce the loss of water by evaporation and a thermometer. First a certain amount of citric acid and distilled water were placed into the reactor to reach thermal equilibrium. And then other amount of spent $LiCoO_2$ powder and H_2O_2 solution were added to the reactor with agitation. The optimal leaching conditions, i.e. mol ratio of $LiCoO_2$ to citric acid, solid-to-liquid ratio, leaching temperature, leaching time and using of H_2O_2 on leaching efficiency were investigated in details. Finally after filtration and washing with water, a black residue and a pink solution were obtained shown in Fig. 1. The samples during the leaching process were taken for determination of cobalt ions by ICP at regular intervals.

The kinetic studies in leaching procedure of cobalt by citric acid were investigated. Changes of leaching efficiency under different temperatures with the passage of leaching time were discussed, and changes of leaching efficiency under different particle sizes with the passage of leaching time were also discussed, so as to summarize the kinetics reaction equation under different temperatures. The reaction activation energy and reaction control type of citric acid leaching were determined.

XRD characterization of spent $LiCoO_2$ was performed on D/MAX 2550 X-ray diffraction analyzer (from Japan) using Cu K_ radiation (λ=1.54 Å) at 300 mA and 40 kV. The morphology of spent $LiCoO_2$ was examined by ESEM Quanta-200FEG FEI scanning electron microscopy (SEM) technique. The concentrations of Co^{2+} in leachate were measured by ICP method. The leaching efficiency in this work was defined as the concentration of Co^{2+} in leachate : Total Co in $LiCoO_2$ powders.

RESULTS & DISCUSSION

The XRD and SEM results of spent $LiCoO_2$ after separation of cathode materials and current collector can be observed in Fig. 2. From the X-ray diffraction, the phase components of $LiCoO_2$ from spent LIBs are observed to be $LiCoO_2$ and Co_3O_4. The Co_3O_4 contained in the cathode materials may come from the decomposition or transformation of $LiCoO_2$. Meanwhile the intensities and 2-theta positions of some diffraction peaks of $LiCoO_2$ have much difference with the raw $LiCoO_2$. From the SEM image, the morphology and particle size of spent $LiCoO_2$ appear much irregular with many agglomerations, which are different than the raw $LiCoO_2$. Therefore the spent $LiCoO_2$ from spent LIBs cannot be directly used as the active material of new battery, and need to be recovered.

Meanwhile the EDX results of spent $LiCoO_2$ after separation of cathode materials and current collector are shown in Fig. 3. They indicate that some particles in spent $LiCoO_2$ mainly comprise cobalt and other particles mainly carbon. This means that after several charge and discharge cycles, the adhesives (mainly PVDF) in spent batteries begin to form a lump, and spent $LiCoO_2$ particles are mostly agglomerated. According to the above results, Fig. 4 illustrates the mechanism of battery invalid. On one hand the layered structure of $LiCoO_2$ appears structural deformation after several inserting and removing of lithium ions in the cathode materials, on the other hand the lump of adhesives prevent the electronic transmission and

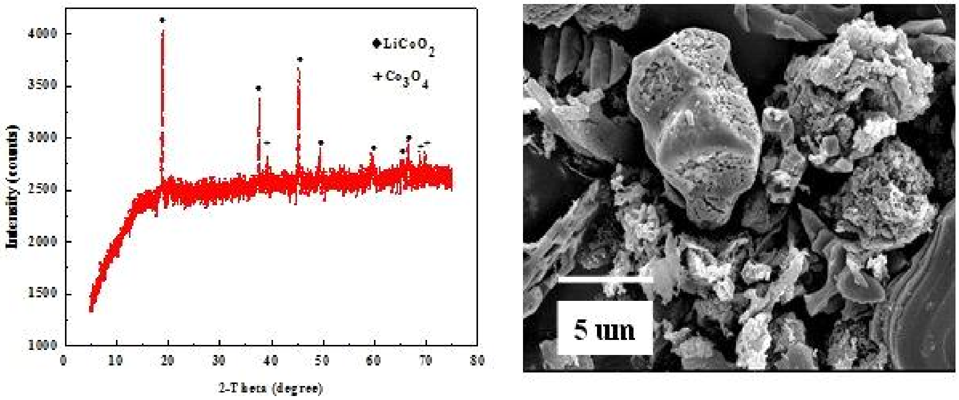


Fig. 2. XRD pattern and SEM image of $LiCoO_2$ from spent LIBs after separation of cathode materials and current collector

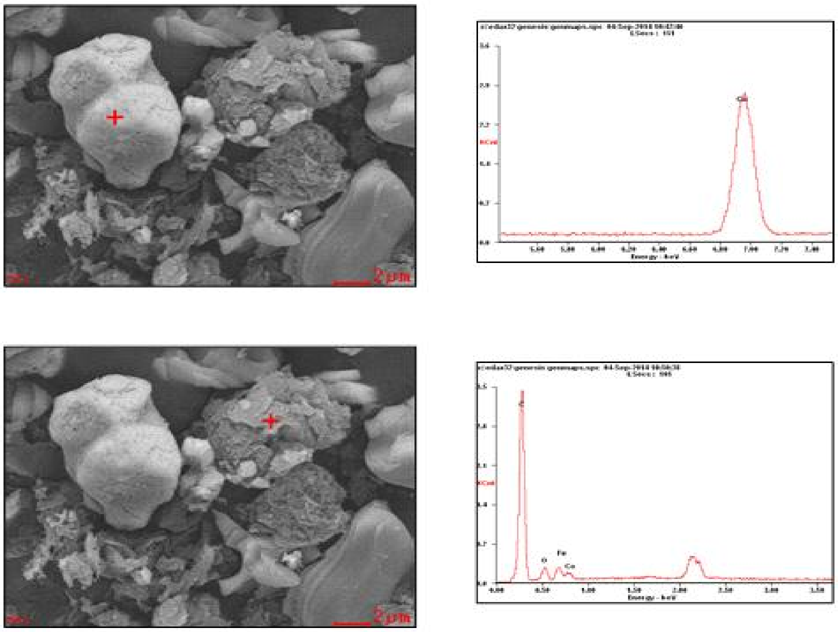


Fig. 3. EDX results of $LiCoO_2$ from spent LIBs after separation of cathode materials and current

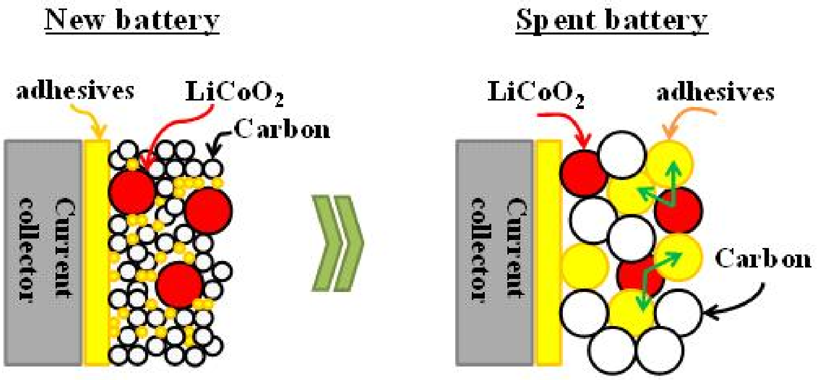


Fig. 4. The schematic diagram for explaining the mechanism of battery invalid

electrochemical reactions (shown as the green arrows) because they are themselves insulators.

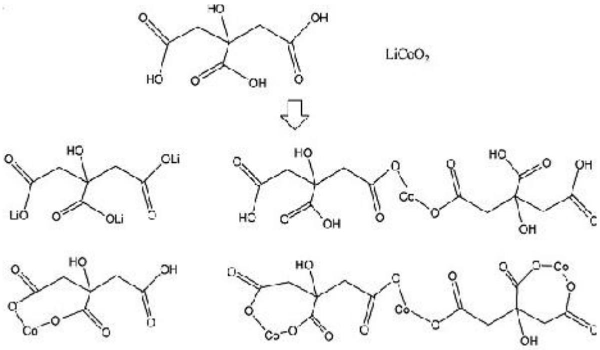
Citric acid is a kind of weak organic acid, and it cannot be fully dissolved in the solution. The reaction using citric acid as leaching agent to get $LiCoO_2$ can be described as a three-stage reaction. The leaching reaction between $LiCoO_2$ and $C_6H_8O_7\cdot(H_2O)$ can be described as follows (Li *et al.*, 2010). The electrovalence of Co in $LiCoO_2$ is +3, Co^{3+} is not easy to be dissolved in water with strong oxidizing property, and Co is generally existed as the form of Co^{2+} in water. Therefore, we can see from the above equation that the leaching of Co in $LiCoO_2$ electrode is a process of reduction leaching, and it can only have a better leaching effect in a system with reducing condition. The reducing agent of hydrogen peroxide can facilitate the reaction, and the equation of (3-1) is a main leaching reaction to reduce trivalence cobalt ions to bivalence ions. Therefore, adding reducing agent of H_2O_2 solution during the leaching process of $LiCoO_2$ can increase the leaching efficiency of cobalt.

The principle of leaching is to destroy the structure of spent $LiCoO_2$ by using citric acid, thus making the cobalt in $LiCoO_2$ dissolved in solution. Heterogeneous reaction procedure between citric acid and lithium cobalt oxides includes the following steps: (1) the reactant of citric acid is diffused to the surface of $LiCoO_2$ from the bulk phase; (2) the production of cobalt citrate could be produced on the surface of $LiCoO_2$ by the reactant of citric acid via adsorption and reaction, realizing the chemical reaction procedures of interface throughout the process of formation, growing and desorption of crystal nucleus of acid leaching product; (3) the acid leaching product cobalt citrate would leave the solid-liquid interface by diffusion.

Assuming that the reaction of citric acid and lithium cobalt oxides is fully developed, the equation shall be shown as follows:

We can see from the equation (3-4) that leaching of 1 mol $LiCoO_2$ shall be theoretically leached out by 1 mol citric acid. However, the citric acid is weak organic acid, and it is impossible to have full reaction with $LiCoO_2$ during the actual reactions. Hence in the experimental procedure, taking excessive citric acid to react with lithium cobalt oxides is necessary. Fig. 5 shows the relation between the leaching efficiency and the mol ratio of $LiCoO_2$ to citric acid. It can be observed that when the mol ratio of $LiCoO_2$ to citric acid is 1:1, the leaching efficiency is only 56.74%; when the mol ratio is increased to 1:2.5, the leaching efficiency is up to 85.83%; when the mol ratio reaches 1:3, 1:3.5 and 1:4, the leaching efficiencies are accordingly increased to 93.83%, 96.28% and 97.86% respectively. It can be seen that the leaching efficiency increases with the increasing of mol ratio of $LiCoO_2$ to citric acid, and when the mol ratio comes to 1:4, the optimum reaction condition has been achieved.

The effect of solid-to-liquid ratio on the leaching efficiency of cobalt was studied at 90 ^oC and 5 h, and using the molar ratio of citric acid to $LiCoO_2$ at 4:1, and the H_2O_2 concentration of 1.0 vol.%. The solid-to-liquid ratios are changed from 15 g/L to 30 g/L to conduct the experiment. The results between solid-to-liquid ratio and leaching efficiency are displayed in Fig. 6. It can be seen that, when the solid-to-liquid ratio is increased from 10 g/L to 15 g/L, the leaching efficiency is up to 99.07%; when the solid-to-liquid ratio reaches 20 g/L, the leaching efficiency reduced; when the solid-to-liquid ratio is up to 25 g/L and 30 g/L, the leaching efficiency is tend to decrease gradually. From the above results, we can see that the increasing of solid-to-liquid ratio cannot make leaching efficiency increase. It is because that the density of resultant of reaction in the bulk solution would increase with high solid-to-liquid ratio, which makes it difficult for the resultant of material surface to spread to the bulk of solution. Therefore, the leaching efficiency is decreased. Hence, the optimum solid-to-liquid ratio of leaching reaction is 15 g/L.



$$6H_3Cit + 2LiCoO_2 + H_2O_2 = 2Li^+ + 6H_2Cit^- + 2Co^{2+} + 4H_2O + O_2 \quad (3\text{-}1)$$

$$6H_2Cit^- + 2LiCoO_2 + H_2O_2 = 2Li^+ + 2Co^{2+} + 6HCit^{2-} + 4H_2O + O_2 \quad (3\text{-}2)$$

$$6HCit^{2-} + 2LiCoO_2 + H_2O_2 = 2Li^+ + 2Co^{2+} + 6Cit^{3-} + 4H_2O + O_2 \quad (3\text{-}3)$$

$$2H_3Cit + 2LiCoO_2 + H_2O_2 = 2Li^+ + 2Cit_3^{''} + 2Co^{2+} + 4H_2O + O_2 \quad (3\text{-}4)$$

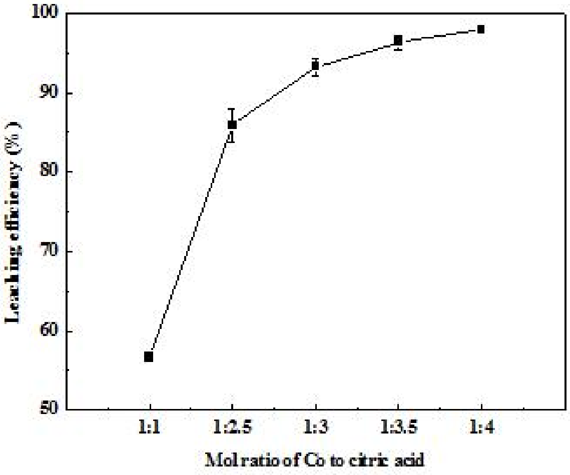


Fig. 5. Effect of mol ratio of $LiCoO_2$ and citric acid on leaching efficiency

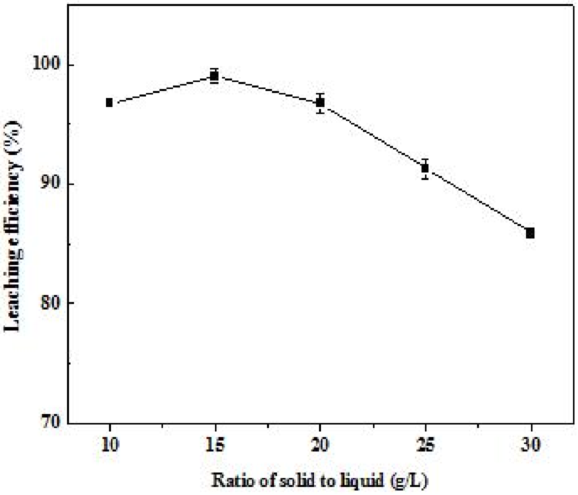


Fig. 6. Effect of solid-to-liquid ratio on the leaching efficiency at 90 °C, 5 h,the molar ratio of citric acid to $LiCoO_2$ at 4:1, and the H_2O_2 concentration of 1.0 vol.%

The effect of temperature on the leaching efficiency of cobalt was studied at 5 h, and using the molar ratio of citric acid to $LiCoO_2$ at 4:1, solid-to-liquid ratio of 15 g/L, and the H_2O_2 concentration of 1.0 vol.%. The temperatures are changed from 70 °C to 90 °C, and the results between temperature and leaching efficiency are shown in Fig. 7. As it shown in the figure, the leaching efficiency increased significantly accompanying the increasing of temperature. The leaching efficiency of cobalt could be up to 99.07% under the temperature of 90 °C. Due to the need of endothermic reaction in the dissociation process of citric acid, and more hydrogen ion appeared in the solution with the increasing of temperature, the leaching efficiency of $LiCoO_2$ is increased with the increasing of temperature. When the temperature is up to 90 °C, a highest leaching efficiency can be achieved. However, the citric acid gradually evaporated from the solution when the temperature over 90!. Therefore, the optimum reaction temperature for $LiCoO_2$ is 90 °C.

The effect of time on the leaching efficiency of cobalt was studied at 90 °C, and using the molar ratio of citric acid to $LiCoO_2$ at 4:1, solid-to-liquid ratio of 15 g/L, and the H_2O_2 concentration of 1.0 vol.%. The relations between time and leaching efficiency are shown in Fig. 8. It can be seen from the figure that, as time goes on, the leaching efficiency increases, which means the increasing of reaction time is obviously benefit for the leaching of cobalt. When the reaction time is more than 5 h, the increasing trend of leaching efficiency tends to be smooth and steady, there is no significant increasing in leaching efficiency of cobalt. Therefore, the optimum reaction time for leaching efficiency of $LiCoO_2$ is 5 h.

The effect of concentration of H_2O_2 on the leaching efficiency of cobalt was studied at the temperature of 90 °C and 5 h, and using the molar ratio of citric acid to $LiCoO_2$ at 4:1, the solid-to-liquid ratio of 15 g/L. The volume concentrations of H_2O_2 are changed from 0.0% to 1.5%. The results between concentration of H_2O_2 and leaching efficiency are shown in Fig. 9. From the figure, it can be observed that very low amount of cobalt can be leached out when the concentration of H_2O_2 is lower than 1.0 vol.%. It is well known that the function of H_2O_2 involves the reduction of Co^{3+} in the solid to Co^{2+} in the aqueous phase, and the effect of H_2O_2 was related to a change in the leaching kinetics of $LiCoO_2$. When the concentrations of H_2O_2 are increased to 1.0 vol.%, the leaching efficiency almost reaches the maximum. However, at 1.5 vol.% H_2O_2 the leaching efficiency did not increase significantly. Therefore, the optimal concentration of H_2O_2 is choosed to be 1.0 vol.% in this experiment.

As the leaching time goes on, the relationship between different reaction temperature and leaching efficiency is shown in Fig. 10. Based on the experimental results of Fig. 10, assuming that the leaching reaction of citric acid and $LiCoO_2$ is chemical reaction control, the leaching data can be fitted in accordance with chemical reaction control velocity equation: $1-3(1-X)^{2/3}+2(1-X)=k_c t$, and the result is shown in Fig. 11.

According to the Fig. 11, kinetic equation of leaching process under different temperatures can be summarized as below (equation 3-5 to 3-9):

X in the above equations refers to leaching efficiency (%) and t refers to time. The correlation

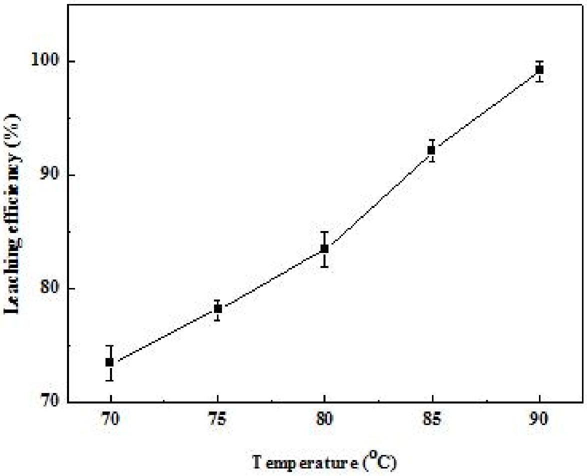


Fig. 7. Effect of temperature on the leaching efficiency at 5 h, the molar ratio of citric acid to $LiCoO_2$ at 4:1, solid-to-liquid ratio of 15 g/L, and the H_2O_2 concentration of 1.0 vol.

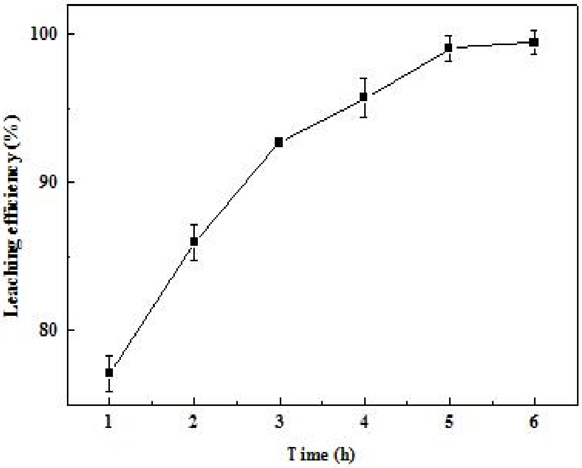


Fig. 8. Effect of time on the leaching efficiency of cobalt at 90 ℃, the molar ratio of citric acid to $LiCoO_2$ at 4:1, solid-to-liquid ratio of 15 g/L, and the H_2O_2 concentration of 1.0 vol. %

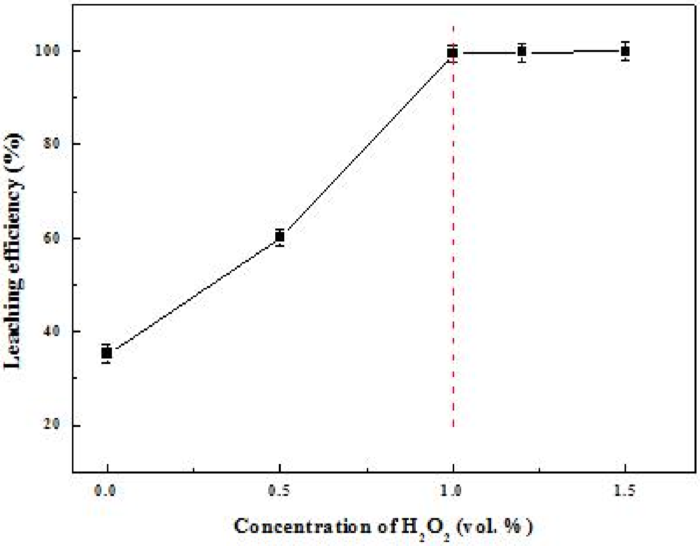


Fig. 9. Effect of concentration of H_2O_2 on the leaching efficiency of cobalt at the temperature of 90 °C and 5 h, using the molar ratio of acetic acid to $LiCoO_2$ at 4:1, the solid-to-liquid ratio of 15 g/L

coefficient R^2 in the above equations (3-5) to (3-9) is 0.9779, 0.9981, 0.9984, 0.9653 and 0.9941 respectively, and they are all higher than 0.96, which means the degree of fitting is high.

Under different temperatures, the calculation results of ln k_c of comprehensive reaction rate constant in the process of leaching is shown in Table 1. Arrhenius curve (shown in Fig. 12) of cobalt leaching

$$90\ ^{o}C:\quad 1-3(1-X)^{2/3}+2(1-X)=0.0019t+0.0503 \qquad (3\text{-}5)$$

$$85\ ^{o}C:\quad 1-3(1-X)^{2/3}+2(1-X)=0.0016t+0.0065 \qquad (3\text{-}6)$$

$$80\ ^{o}C:\quad 1-3(1-X)^{2/3}+2(1-X)=0.0012t+0.0002 \qquad (3\text{-}7)$$

$$75\ ^{o}C:\quad 1-3(1-X)^{2/3}+2(1-X)=0.0010t+0.0108 \qquad (3\text{-}8)$$

$$70\ ^{o}C:\quad 1-3(1-X)^{2/3}+2(1-X)=0.0008t-0.0050 \qquad (3\text{-}9)$$

reaction is drawn in accordance with the results in table. Based on the formula $\ln t_T = -\frac{E}{RT} + I$, we can find that the slope of Arrhenius curve is E/R. And based on the Fig. 12 and calculation, we can find that the slope of rectilinear is 5.4996, the apparent activation energy of leaching reaction is 45.724 KJ/mol > 42 KJ/mol, which means the leaching reaction is chemical reaction control.

In this experiment, with the increasing of the time (20 min, 60 min, 120 min, 180 min and 240 min), the relationship between different average particle sizes of initial reaction and leaching efficiency is shown in Fig. 13. Data of Fig. 13 is fitted in accordance with chemical reaction control velocity equation $1-3(1-X)^{2/3}+2(1-X)=k_c t$, and the result is shown in Fig. 14.

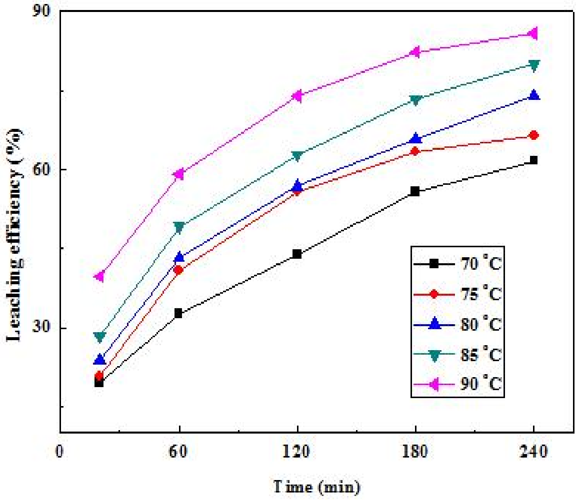


Fig. 10. Relationship between temperature and leaching efficiency with the increasing of time

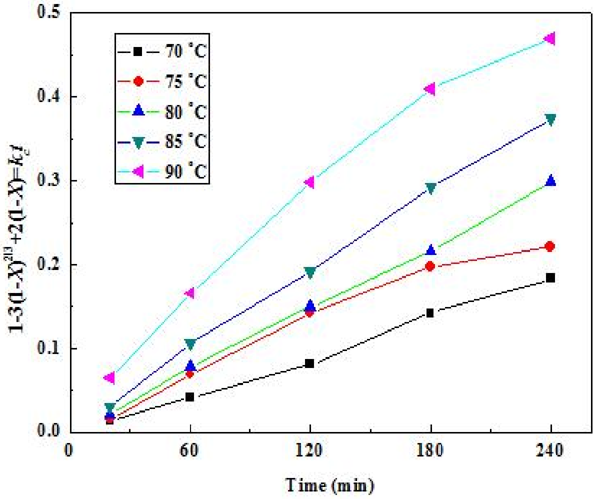


Fig. 11. Leaching kinetic curves under different reaction temperatures (70 °C, 75 °C, 80 °C, 85 °C, 90 °C)

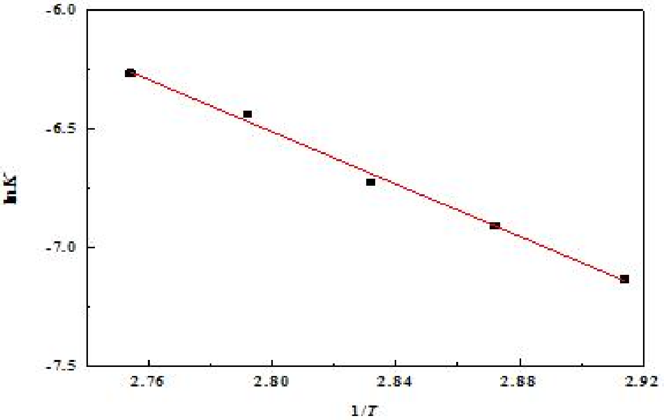


Fig. 12. Arrhenius curve of leaching reaction of citric acid and $LiCoO_2$

Table 1. Comprehensive reaction rate constant and its $\ln k_c$ under different temperatures

Leaching temperature (K)	$1/T$ ($\times 10^3$)	k_c	$\ln k_c$
343.15	2.914	0.0008	-7.131
348.15	2.872	0.0010	-9.908
353.15	2.832	0.0012	-6.725
358.15	2.792	0.0016	-6.438
363.15	2.754	0.0019	-6.266

(Note: *T* is Kelvin degree, and *K* is comprehensive reaction rate constant)

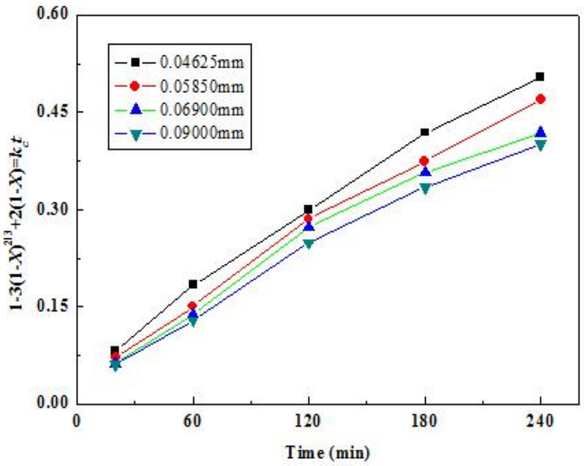


Fig. 13. Relationship between particle size of initial reaction and leaching efficiency with the increase of time

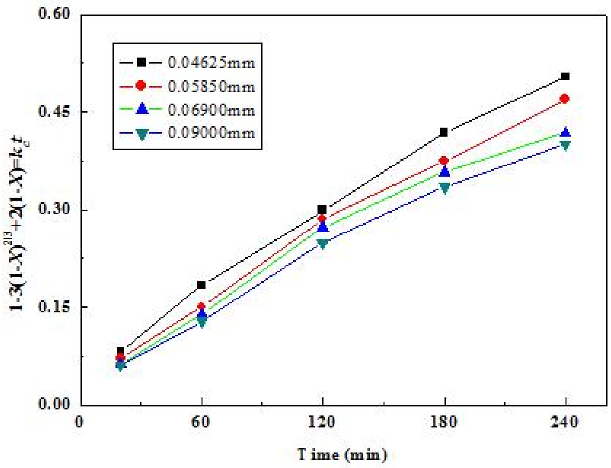


Fig. 14. Leaching kinetic curve of different particle sizes of initial reaction

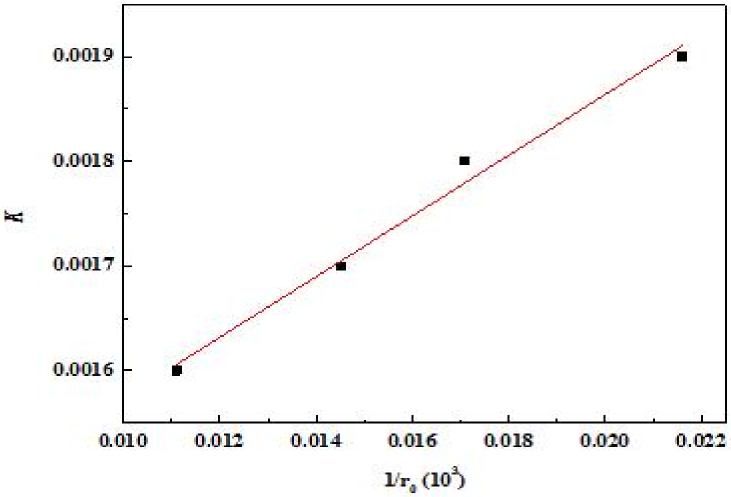


Fig. 15. Relationship between $1/r_0$ and K

On the basis of Fig. 14, we can calculate that the comprehensive reaction rate constant K of particle size of initial reaction (0.04625 mm, 0.05850 mm, 0.06900 mm and 0.09000 mm) is 0.0019, 0.0018, 0.0017 and 0.0016 respectively. Then the curve is drawn with the K and reciprocal of corresponding particle size of initial reaction $1/r_0(\times 10^3)$, as shown in Fig. 15. A linear relationship has been observed between the comprehensive reaction rate constant and reciprocal of particle size of initial reaction, which means the leaching reaction of citric acid is chemical reaction control.

CONCLUSIONS

(1) The optimum reaction conditions for leaching of cobalt in spent $LiCoO_2$ battery by citric acid are: the molar ratio of spent $LiCoO_2$ and citric acid is 1:4, the solid-to-liquid ratio is 15 g/L, the reaction temperature is 90 °C, the reaction time is 5 h, and concentration of H_2O_2 is 1.0 vol. %, the leaching efficiency of cobalt can be up to 99.07%.

(2) Leaching kinetics of $LiCoO_2$ in spent lithium ion battery by adopting citric acid can be described by leaching kinetic equation $1-3(1-X)^{2/3}+2(1-X)=k_c t$. The apparent activation energy of the reaction is 45.724 KJ/mol, and the leaching process is verified to be controlled by the chemical reaction procedure via the impacts of particle size of initial reaction on the leaching efficiency.

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