Recovery of cobalt and lithium from spent lithium ion batteries using organic citric acid as leachant

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ABSTRACT

In this work, a hydrometallurgical process based on leaching is applied to recover cobalt and lithium from spent lithium ion batteries (LIBs). Citric acid and hydrogen peroxide are introduced as leaching reagents and the leaching of cobalt and lithium with a solution containing $C_6H_8O_7·H_2O$ is investigated. When both $C_6H_8O_7·H_2O$ and H_2O_2 are used an effective recovery of Li and Co as their respective citrates is possible. The leachate is characterized by scanning electron micrography (SEM) and X-ray diffraction (XRD). The proposed procedure includes the mechanical separation of metal-containing particles and a chemical leaching process. Conditions for achieving a recovery of more than 90% Co and nearly 100% Li are achieved experimentally by varying the concentrations of leachant, time and temperature of the reaction as well as the starting solid-to-liquid ratio. Leaching with 1.25 M citric acid, 1.0 vol.% hydrogen peroxide and a S:L of $20\,g\,L^{-1}$ with agitation at 300 rpm in a batch extractor results in a highly efficient recovery of the metals within 30 min of the processing time at 90 °C. This hydrometallurgical process is found to be simple, environmentally friendly and adequate for the recovery of valuable metals from spent LIBs.

1. Introduction

Compared with nickel–cadmium (NiCd) or nickel–metal hydride (NiMH) batteries, lithium ion batteries (LIBs) are smaller, lighter, have no memory effect and provide much more energy per volume unit. Given these advantages, LIBs are mainly used as a power source for mobile phones, laptops and electronic devices. $LiCoO_2$ is the most popular LIBs cathode material because of its good performance. The demand for secondary batteries has steadily increased in recent times as portable electronic appliances such as cellular phones and laptop computers have become widely used [1]. World LIB production reached 500 million units in 2000 and is expected to reach 4.6 billion in 2010 [2]. LIBs contain heavy metals, organic chemicals and plastics. The metal residues are normally found at very high concentration levels, sometimes even higher than those found in natural ores. Dorella and Mansur [3] determined the metal content of the LIBs and found that valuable metals such as aluminum, cobalt, lead and lithium were the main species that needed to be separated. Disposal of these spent LIBs will result in environmental pollution. From an environmental viewpoint, the

recycling of spent LIBs is highly desirable. The current status of the recycling process has been reviewed in several studies and it is important that good recoveries are obtained during recycling of waste batteries. The recovery of major spent cell components is beneficial in terms of environmental protection and also for the provision of raw materials [4–8].

LIBs consist of two thin electrode films: the anode is made from metallic copper and the cathode from metallic aluminum. The cathode film is covered by an active material containing lithium and cobalt as a fine powder of $LiCoO_2$ aggregated with a polymeric binder PVDF while the anode is covered by powdered graphitic carbon. In LIBs, the anodes and cathodes are made from materials that allow the migration of Li-ions through an electrolyte solution. Several methods have been proposed to treat spent LIBs to recover some metal content. LIBs consist of heavy metals, organic chemicals and plastics in proportions of 5–20% cobalt, 5–10% nickel, 5–7% lithium, 15% organic chemicals and 7% plastics. A chemical process is required because physical separation methods like crushing, magnetic separation and floatation cannot fully recover the valuable metals.

Conventional routes comprise the following main steps: (1) a discharge pretreatment step to remove the excess capability, (2) dismantling of batteries to remove the plastic and metallic shells, (3) leaching with strong acid solutions and (4) metals separation. Lithium cobalt oxide ($LiCoO_2$) is an active material which is used as a cathode and it does not dissolve easily in common

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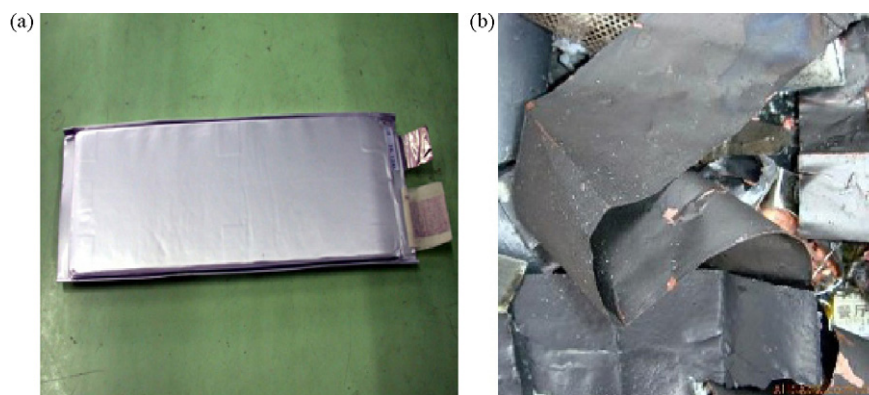 *E-mail addresses:* wufeng863@bit.edu.cn (F. Wu), chenrj@bit.edu.cn (R. Chen).

Fig. 1. Spent LIBs from (a) cellular phones and (b) the cathode and anode from a spent LIB.

leaching chemicals. Leaching of LIBs has been investigated using H_2SO_4 [9], HCl [10] and HNO_3 [11] as leaching agents followed by the treatment of the acid leachate and management of the final wastes. Metals were leached according to the following sequence in sulfuric media: aluminum > lithium > cobalt > copper [4]. H_2O_2 is usually added to convert all cobalt or manganese to their +2 state for subsequent recovery using electrochemical, precipitation or solvent extraction techniques [12–14]. It is possible to recover lithium as a carbonate (Li_2CO_3) or with cobalt as $LiCoO_2$ at 100 °C [15,16].

When a strong acid solution is used as leachant more than 99% lithium and cobalt can be recovered. However, Cl_2, SO_3 and NO_x are released during leaching and the acid obtained after leaching is a threat to the environment. A number of new processes are under development for future applications. Saeki [17] has presented an environmentally friendly process for the recovery of metal from spent LIBs. $LiCoO_2$ was subjected to co-grinding with PVC using a planetary ball mill to form Co- and Li-chlorides mechanochemically. As a result more than 90% Co and nearly 100% Li were recovered.

Citric acid is an organic acid and can be dissolved in water easily. It is often used as a raw material in the manufacturing industry. Sonmez and Kumar [18] studied the use of citric acid as a reagent in aqueous media to recover Pb and PbO from scrap battery paste. As a biodegradable natural acid, ($C_6H_8O_7$)·H_2O can be used for recovering metals from sewage sludge. Citric acid degrades easily under aerobic and anaerobic conditions so these waste solutions can be treated easily. The remaining citric acid can be recycled and reused for a subsequent leach.

In this work, we investigated reaction conditions using citric acid and hydrogen peroxide ($C_6H_8O_7$·H_2O and H_2O_2). Co and Li were recovered from the leaching solutions as their respective citrates. Our aim was to develop a new hydrometallurgical process that uses an environmentally friendly acid for leaching to recover lithium and cobalt from spent LIBs.

2. Experimental

2.1. Materials and reagents

Spent LIBs were collected for this study and Fig. 1 shows a spent LIB from a cellular phone as well as a cathode and an anode from a spent LIB. Citric acid was used for leaching and hydrogen peroxide (H_2O_2) was employed as a leaching agent. All solutions were prepared in distilled water and all reagents were analytical grade. Hydrochloric acid was used to completely leach the $LiCoO_2$ so that the cobalt and lithium content in the cathode could be determined. Chromatographically pure solutions of lithium and cobalt were

purchased from the National Institute of Metrology P.R. China for Atomic Absorption Spectrophotometry (AAS).

2.2. Dismantling, anode/cathode separation and metal characterization

Short-circuiting and self-ignition of battery rolls are potential dangers when anodes and cathodes contact each other during dismantling. Therefore, a discharging pretreatment step was used for the given process before the dismantling of the battery steel crusts. Fig. 2 shows a flowsheet of the process designed in this work. Spent LIBs were dismantled manually to remove both the plastic and steel cases that cover the batteries. The plastic cases around the batteries
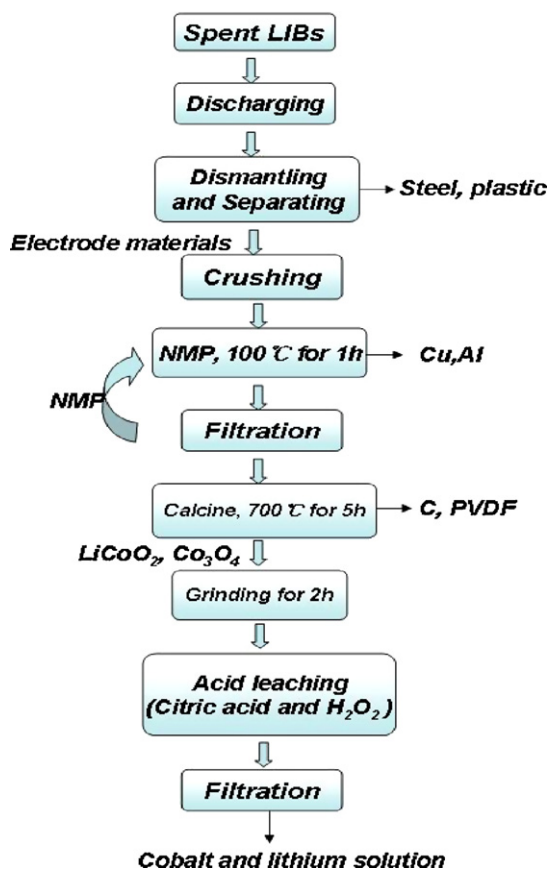

Fig. 2. Flowsheet of the hydrometallurgical recycling process for lithium ion secondary rechargeable batteries.

were removed using a small knife and a screwdriver. The metallic shell that covers the battery was removed by immersing it in liquid nitrogen for 4 min and then it was attached to a lathe to prevent flames or explosions. The metallic shell was then cut with a saw and the ends of the metallic shell were removed first. A longitudinal cut allowed access to the internal material of the battery and this was removed using pliers. All steps in the experimental procedure were carried out using safety glasses, gloves and gas masks for safe operation.

Once dismantled, the anodes and cathodes were manually uncurled and separated then treated with N-methylpyrrolidone (NMP) at 100 °C for 1 h. The cathodic active materials were effectively separated from their support substrates and the recovery of both copper and aluminum in their metallic form was achieved. Furthermore, NMP can be reused for the next process.

After drying at 60 °C for 24 h, thermal pretreatment was necessary to eliminate carbon and PVDF in the cathodic active materials. The cathode picks from the spent batteries were calcined at 700 °C for 5 h in a muffle and then cooled to room temperature. The off gases were purified in a system that consisted of a cooler, a condensation chamber, filters with activated carbon for heavy metals removal and bag filters. After roasting and cooling the cathodic active materials, dried samples of the powdered materials that covered the cathode foils were submitted for X-ray diffraction (XRD) and inductively coupled plasma atomic emission spectrometer (ICP) for qualitative analysis. The lithium cobalt oxide was ground with a planetary ball mill for 2 h to enable easy leaching. Smaller particle sizes lead to better dissolution and increased leaching efficiency.

2.3. Metal leaching

All batch-leaching experiments were carried out in a 100 mL three-necked and round-bottomed thermostatic Pyrex reactor with a temperature control facility. The reactor was fitted with an impeller stirrer, a vapor condenser to reduce the loss of water by evaporation and a thermometer. The leaching experiments were conducted in the apparatus. The reflux condenser was used to avoid vapor loss at high temperature and heating was provided by an electric mantle with temperature control. A known strength and amount of citric acid was poured into the reactor and allowed to reach thermal equilibrium. A measured amount of waste $LiCoO_2$ powder and H_2O_2 solution were added to the reactor with agitation provided by the magnetic stirrer. To obtain the optimum conditions, leaching experiments were tested under various conditions, i.e. changing the citric acid concentration, the S/L ratio, the temperature and the H_2O_2 concentration. During the leaching experiment, samples were taken at scheduled intervals. After filtration and washing with water, a black residue and a pink solution were obtained. The residual acid solution was reused for the treatment of new samples of leached solids. Other organic acids such as malic acid and acetic acid were chosen as candidates to examine their leaching behavior towards cobalt and lithium in the cathodic material.

2.4. Analytical methods

To determine the total amounts of cobalt and lithium, a sample of cathodic active material was dissolved completely in concentrated HCl and analyzed by AAS. The concentration of various metallic ions in the cathode was determined using an inductively coupled plasma atomic emission spectrometer. The amounts of cobalt and lithium in the filtrate were also measured to calculate the leaching efficiency, which is defined as the ratio of the amount of a component in the leachate to the total amount of Co and Li in the cathode. A chemical analysis of the cathodic active material

Table 1
Li, Co, Mn and Ni content in cathodic active material of the spent LIBs.

Element	Content (w/w)
Li	4.40%
Co	53.8%
Mn	0.97%
Ni	0.80%

before and after calcination was carried out with an X-ray diffractometer (Rigaku, Cu-Kα). The leach residues were filtered, dried, weighed and subjected to XRD and SEM analysis.

3. Results and discussion

3.1. Dismantling and characterization of lithium cobalt oxygen in spent LIBs

The spent LIBs were dismantled and calcined by the hydrometallurgical route described above. Table 1 shows the metal content of the samples from the cathodes of spent LIBs. Metal values such as cobalt, lithium, manganese and nickel from the inner part of the batteries are desired substances in this recycling process. ICP analysis of the cathode revealed small amounts of Ni and Mn are contained in the cathode and this is due to doping and surface modification used to increase the capacity of the LIBs. As shown in Table 1, 4.4% Li and 54.8% Co were found in the cathode to be high according to environmental standards so LIBs need to be recycled.

Analysis of the $LiCoO_2$ present in the cathode after dismantling and calcination was carried out with an X-ray diffractometer. The crystalline $LiCoO_2$ phase was clearly identified by XRD analysis as shown in Fig. 3 thus corroborating the findings from previous studies. Fig. 3 shows XRD patterns of the cathodic active materials before and after calcination at 700 °C as well as XRDs of the leach residues. From the results of X-ray diffraction, the cathode composition of the spent LIBs was found to be $LiCoO_2$, Co_3O_4 and C. The Co_3O_4 present in the cathode comes from a transformation of the active material ($LiCoO_2$) [19]. Co_3O_4 peaks were identified confirming that the polyvinylidene fluoride (PVDF) binder decomposed and that HF was released during calcination. At the same time, Co_3O_4 was present in the calcined dust. XRD data indicated that the cathodic material contained $LiCoO_2$ and Co_3O_4 as the carbon and binder were burnt off by calcination at 700 °C.

Fig. 4 shows scanning electron micrographs (SEM) of $LiCoO_2$ powders from the cathode of the spent LIBs and the commercial
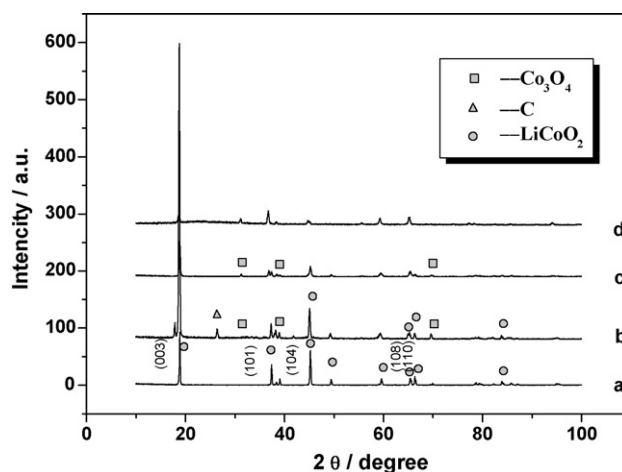

Fig. 3. XRD patterns of the samples (a) commercial $LiCoO_2$, (b) the dismantled cathodic material from a spent LIB, (c) the cathodic material after dismantling and calcination at 700 °C for 5 h and (d) leach residues.
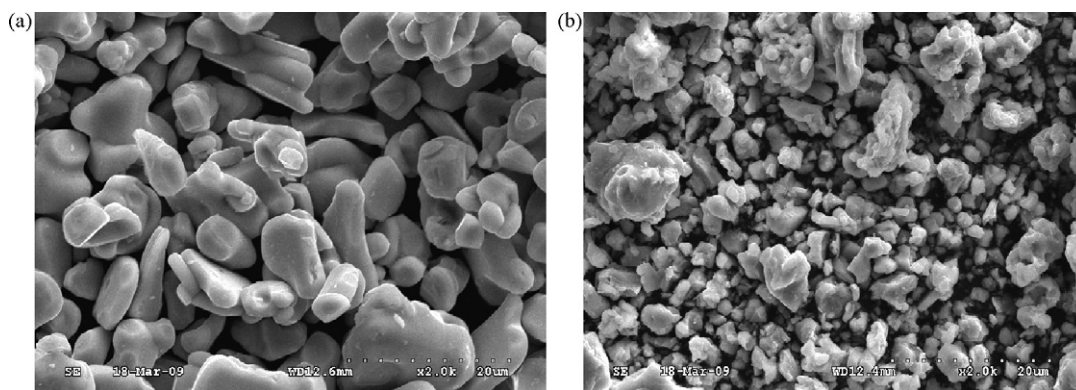
Fig. 4. SEM images of (a) commercial $LiCoO_2$ and (b) the cathodic material after dismantling and calcination at 700 °C for 5 h.
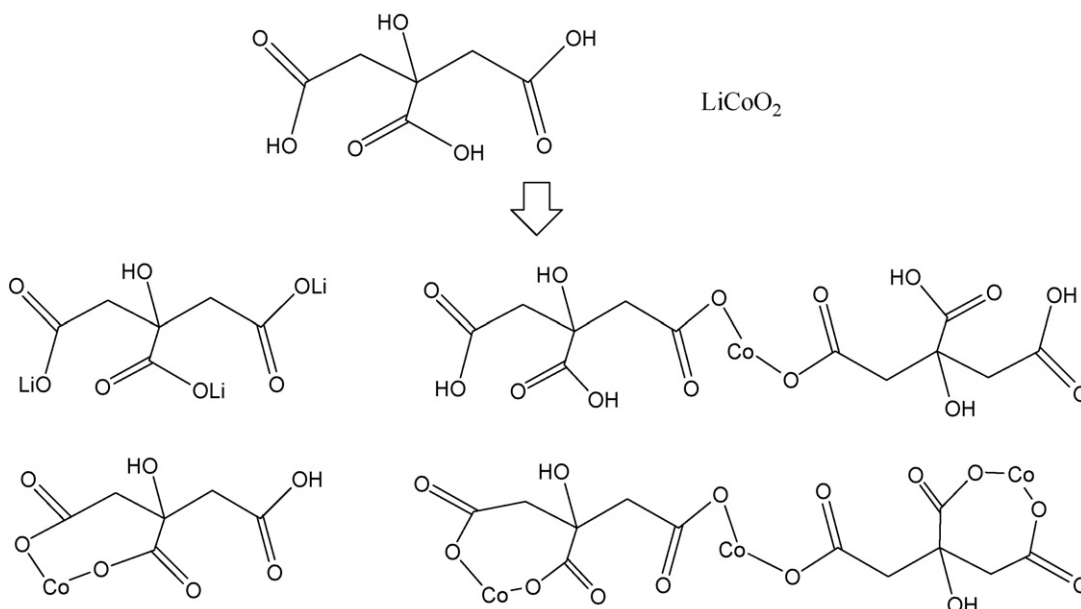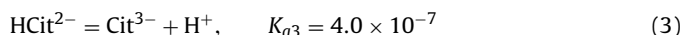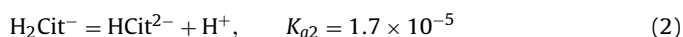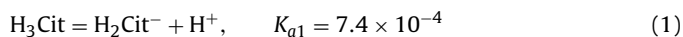

Fig. 5. Possible reaction products for citric acid and $LiCoO_2$.

$LiCoO_2$ powder. $LiCoO_2$ powders after becoming ineffective have irregular morphologies compared with commercial $LiCoO_2$ powder and seem to contain larger agglomerates as well. A uniformity of particle size resulted from the charge and discharge cycles. By comparison, the commercial powder is composed of more round-shaped and smooth particles. $LiCoO_2$ powders that are obtained from spent LIBs can, therefore, not be directly used as an active material in the cathode unless it is recovered and reused.
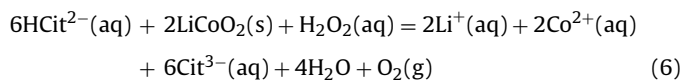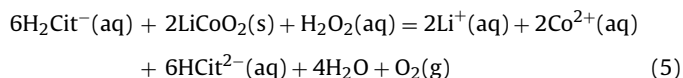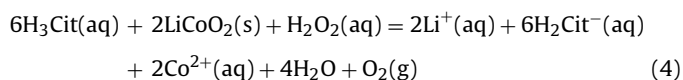
3.2. Leaching of waste $LiCoO_2$

Citric acid is a common weak organic acid and its possible reaction products are shown in Fig. 5. Three carboxyls are contained in one $C_6H_8O_7$ molecule and upon dissociation of 1 mol citric acid in distilled water 3 mol H^+ is theoretically produced. In fact, not all the H^+ is released to the solution. The dissociation reaction of citric acid can be expressed as follows:

$$H_3Cit = H_2Cit^- + H^+, \qquad K_{a1} = 7.4 \times 10^{-4} \tag{1}$$

$$H_2Cit^- = HCit^{2-} + H^+, \qquad K_{a2} = 1.7 \times 10^{-5} \tag{2}$$

$$HCit^{2-} = Cit^{3-} + H^+, \qquad K_{a3} = 4.0 \times 10^{-7} \tag{3}$$

Leaching of waste $LiCoO_2$ using citric acid as a leachant can be described as a three-tier reaction. The leaching reaction of waste

$LiCoO_2$ with a $C_6H_8O_7 \cdot (H_2O)$ solution may be represented as follows:

$$6H_3Cit(aq) + 2LiCoO_2(s) + H_2O_2(aq) = 2Li^+(aq) + 6H_2Cit^-(aq)$$
$$+ 2Co^{2+}(aq) + 4H_2O + O_2(g) \tag{4}$$

$$6H_2Cit^-(aq) + 2LiCoO_2(s) + H_2O_2(aq) = 2Li^+(aq) + 2Co^{2+}(aq)$$
$$+ 6HCit^{2-}(aq) + 4H_2O + O_2(g) \tag{5}$$

$$6HCit^{2-}(aq) + 2LiCoO_2(s) + H_2O_2(aq) = 2Li^+(aq) + 2Co^{2+}(aq)$$
$$+ 6Cit^{3-}(aq) + 4H_2O + O_2(g) \tag{6}$$

From Eqs. (4) to (6), it can be predicted that the addition of a reductant can facilitate the forward reaction and Eq. (4) is the primary leaching reaction since Co(III) in the reactant is reduced to Co(II) [13]. Therefore, a study to improve the leaching efficiency of cobalt by adding the reducing H_2O_2 solution during the acid leaching of waste $LiCoO_2$ was carried out. In the leaching reaction, cobalt and lithium were leached as $Co(C_6H_7O_7)_2$, $Li(C_6H_7O_7)$, Co^{2+} and Li^+, respectively. XRD patterns indicate that most of the $LiCoO_2$ was dissolved in the leaching reaction. The residues were Co_3O_4 and
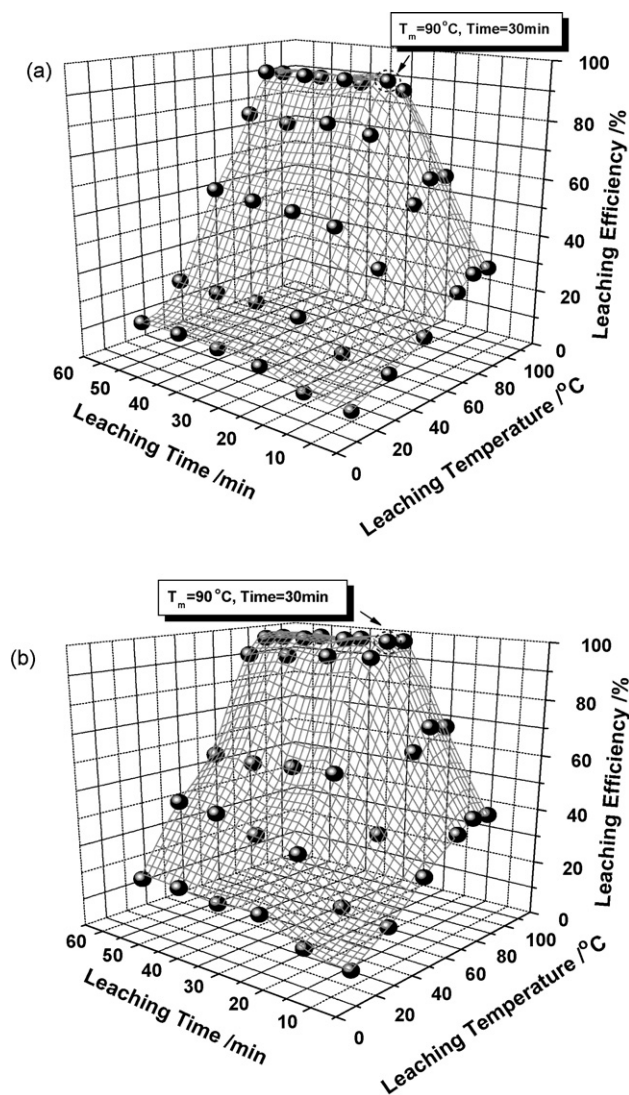
Fig. 6. Effect of leaching temperature and leaching time on the leaching of waste LiCoO₂ with 1.25 M citric acid (H₂O₂ = 1 vol.%, S:L = 20 g L⁻¹ and agitation speed = 300 rpm). (a) Leaching efficiency of Co and (b) leaching efficiency of Li.

C which cannot be leached because Co_3O_4 does not dissolve completely in citric acid.

3.2.1. Effect of temperature and time on leaching

The effect of temperature and time on the leaching efficiency of cobalt and lithium was studied using 1.25 M citric acid. During the leaching process, the S:L was maintained at 20 g L⁻¹ and the H_2O_2 concentration was 1 vol.%. Results are shown in Fig. 6 and indicate that only 8% of the cobalt and 15% of the lithium can be leached at 25 °C. With an increase in temperature, the metal leaching efficiency also increased. When the temperature was increased to 60 °C, the recovery of cobalt and lithium was more than 50% respectively. At 80 °C, 74% of the cobalt and 83% of the lithium were leached. Fig. 6 illustrates that the metal leaching efficiency was significantly affected by temperature and time. It is apparent that increasing the reaction time is beneficial to metal leaching. At reaction times of more than 30 min, the leaching efficiencies of cobalt and lithium did not increase significantly. Initially, the leaching rate was fast but the reaction rate decreased at interval times of more than 30 min. The dissolution of $LiCoO_2$ seemed to be controlled by a surface chemical reaction [11]. At 90 °C and for 30 min, 99% Li and 91% Co was leached. However, at 100 °C the efficiency of leaching Li and Co showed almost no change.
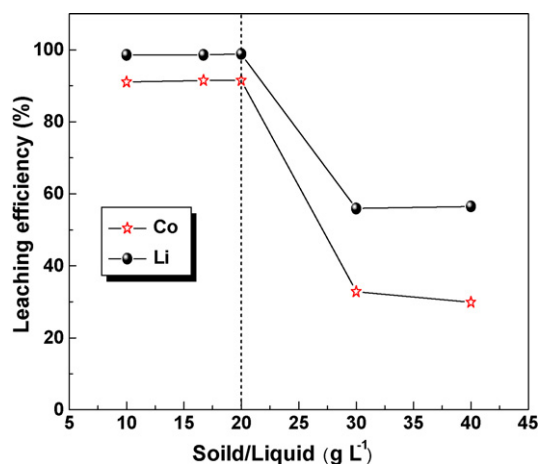
An increase in temperature remarkably enhanced the leaching efficiency of the metals. This is due to the dissociation process of citric acid which undergoes an endothermic reaction and more H^+ is present in the solutions as the temperature increases. Therefore, the leaching velocity of $LiCoO_2$ also increased with an increase in the leaching efficiency for both cobalt and lithium. When the temperature increases to 90 °C, the citric acid starts to vaporize gradually from solution.

3.2.2. Metal dissolution at different solid/liquid ratios

The effect of solid/liquid ratio (S:L) on the leaching efficiency for cobalt and lithium was studied from 10 to 40 g L⁻¹ under experimental conditions of 90 °C, 1.25 M $C_6H_8O_7$, 30 min reaction time and 1.0 vol.% H_2O_2. Fig. 7 indicates that the leaching efficiencies of cobalt and lithium increased as the S:L decreased and that 91% cobalt as well as 99% lithium were leached at 20 g L⁻¹. At a S:L of 30 g L⁻¹, the leaching efficiency of both Co and Li was not very high and the citric acid was not sufficient to leach the $LiCoO_2$ powder.

A S:L of 20 g L⁻¹ was, therefore, considered to be suitable to leach the waste $LiCoO_2$. Considering the lower chemical consumption and a relatively better leaching efficiency, the best conditions for the leaching of cobalt and lithium from waste $LiCoO_2$ was therefore determined.

3.2.3. Effect of citric acid concentration on leaching

The citric acid concentration dependency for leaching cobalt and lithium is shown in Fig. 8. The concentration of $C_6H_8O_7$ was varied from 0.3 M to 1.5 M at a S:L of 20 g L⁻¹ while using a temperature of 90 °C, a concentration of 1 vol.% H_2O_2 and a leaching time of 30 min. When the concentration of citric acid was 1.25 M, nearly all the $LiCoO_2$ dissolved. The leaching efficiency increased from 16% to 91% for cobalt and 36% to 99% for lithium as the $C_6H_8O_7$ concentration increased from 0.3 M to 1.25 M. However, with a further increase in the $C_6H_8O_7$ concentration from 1.25 M to 1.5 M, the leaching efficiency of Co and Li decreased rapidly.

3.2.4. Effect of hydrogen peroxide on leaching

The effect of H_2O_2 concentration on leaching is shown in Fig. 9. During leaching, the temperature was maintained at 90 °C and the leaching time was 30 min while the S:L was maintained at 20 g L⁻¹ and the concentration of citric acid was 1.25 M. We found that 25% of the cobalt was leached in the absence of H_2O_2 whereas 54% of the lithium was leached under the same conditions. We observed that the leaching efficiency of cobalt and Li increased significantly with
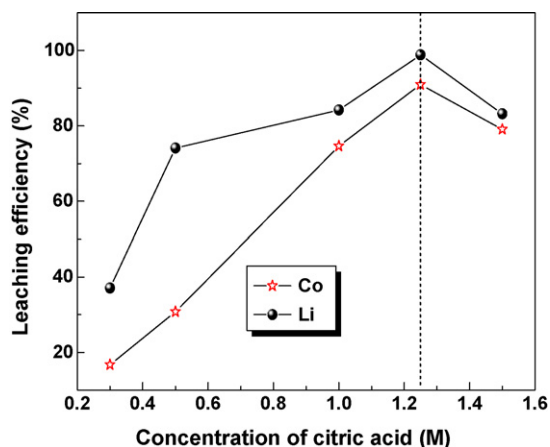
Fig. 7. Effect of solid/liquid ratio on the leaching of waste LiCoO₂ with 1.25 M citric acid at 90 °C for 30 min (H₂O₂ = 1 vol.% and agitation speed = 300 rpm).

Fig. 8. Effect of citric acid concentration on the leaching of waste $LiCoO_2$ at 90 °C for 30 min (H_2O_2 = 1 vol.%, S:L = 20 g L^{-1} and agitation speed = 300 rpm).
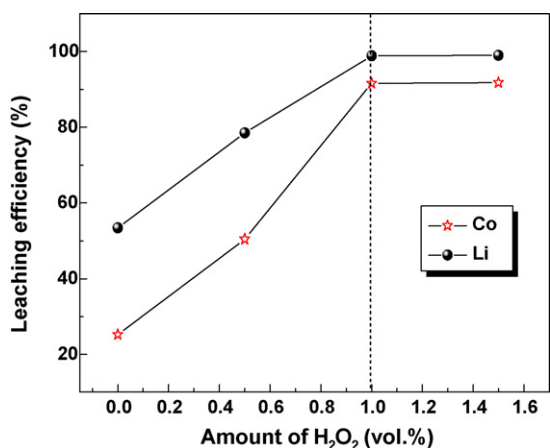

Fig. 9. Effect of H_2O_2 amount on the leaching of waste $LiCoO_2$ with 1.25 M citric acid at 90 °C for 30 min (S:L = 20 g L^{-1} and agitation speed = 300 rpm).

an increase in H_2O_2 concentration by comparison to the leaching efficiency in the absence of H_2O_2. The leaching efficiencies of cobalt and lithium increased from 25% to 91% and 54% to 99%, respectively when the concentration of H_2O_2 increased to 1.0 vol.%. However, at 1.5 vol.% H_2O_2 the leaching efficiency did not increase significantly. Ferreira et al. [20] found that the effect of H_2O_2 was possibly related to a change in the leaching kinetics of $LiCoO_2$. The solubilization of $LiCoO_2$ involves the reduction of Co^{3+} in the solid to Co^{2+} in the aqueous phase. Eqs. (4)–(6) suggest that the leaching efficiency of lithium and cobalt is dependent on the H_2O_2 concentration. In addition, lithium dissolves more easily in the presence of citric acid than cobalt does. With the addition of more H_2O_2 to the solution, no significant increase in the leaching efficiency of cobalt and lithium was observed as hydrogen peroxide decomposed when heated according to Eq. (7):

$$H_2O_2(l) \rightarrow H_2O(l) + \frac{1}{2}O_2(g) \tag{7}$$

4. Conclusions

Spent LIBs are important raw materials for metals such as lithium, cobalt and aluminum, and by recycling the environmental benefits are obvious. For LIBs, the recovery of cobalt seems attractive because of the high price of this metal. In this paper, a hydrometallurgical route for the recovery of cobalt from spent LIBs was investigated and consisted of: (1) manual dismantling to separate the steel scraps, plastic and battery dust containing the cobalt to be recovered, (2) an anode/cathode manual separation and treatment with NMP to recover Cu and Al and (3) leaching with citric acid and hydrogen peroxide to transfer metals from the cathodic active material to the aqueous solution.

Based on the above investigation and by considering the lower energy consumption, lower chemical consumption and relatively better leaching efficiency the best conditions for the leaching of cobalt and lithium from waste $LiCoO_2$ were determined. Using 1.25 M citric acid, 1.0 vol.%. hydrogen peroxide, a leaching temperature of 90 °C, a S:L ratio of 20 g L^{-1} and a time interval of 30 min nearly 100% Li and more than 90% Co were extracted from the spent LIBs.

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