

Vacuum pyrolysis and hydrometallurgical process for the recovery of valuable metals from spent lithium-ion batteries

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ABSTRACT

Spent lithium-ion batteries contain lots of strategic resources such as cobalt and lithium together with other hazardous materials, which are considered as an attractive secondary resource and environmental contaminant. In this work, a novel process involving vacuum pyrolysis and hydrometallurgical technique was developed for the combined recovery of cobalt and lithium from spent lithium-ion batteries. The results of vacuum pyrolysis of cathode material showed that the cathode powder composing of LiCoO_2 and CoO peeled completely from aluminum foils under the following experimental conditions: temperature of 600°C , vacuum evaporation time of 30 min, and residual gas pressure of 1.0 kPa. Over 99% of cobalt and lithium could be recovered from peeled cobalt lithium oxides with 2 M sulfuric acid leaching solution at 80°C and solid/liquid ratio of 50 g L^{-1} for 60 min. This technology offers an efficient way to recycle valuable materials from spent lithium-ion batteries, and it is feasible to scale up and help to reduce the environmental pollution of spent lithium-ion batteries.

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1. Introduction

Lithium-ion batteries (LIBs) are usually composed of cathode, anode, organic electrolyte and separator. The cathode is the main component that determines the cost and the charge efficiency of LIBs, and the most commonly used cathode material is LiCoO_2 [1]. As LIBs are widely used as electrochemical power sources in mobile telephones, personal computers, video-cameras and other modern-life appliances due to their characteristics of light weight, high energy density, long storage life and other good performances, the generation of spent LIBs is increased significantly in the parallel way [2]. According to International Telecommunications Union (ITU), the world consumers of mobile phones have surpassed 5.2 billion in 2010. The more consumption of LIBs means the more amount of scrap. It is estimated that 200–500 MT of spent LIBs are produced annually. In spent LIBs, the cobalt and lithium contents are respectively 5–15 wt.% and 2–7 wt.%, which are higher than those found in natural ores or even concentrated natural ores [3–6]. Besides cobalt and lithium, spent LIBs also contain many hazardous materials such as toxic and flammable electrolyte, which are considered as both an attractive secondary resource and environmental contaminant. It is considered to be a beneficial and urgent way of recycling valu-

able metals from spent LIBs to prevent environmental pollution [7–9].

The existing methods for recycling spent LIBs are mainly pyrometallurgy and hydrometallurgy processes [2,10]. Though the traditional pyrometallurgical processes can burn off all the organic electrolyte and binder and make leaching valuable metals more easily [1,11,12]. In the hydrometallurgical processes, the dismantled electrodes are first dissolved in concentrated acids [13,14]. Then, the resultant solution, which contains metal ions, can be recovered by precipitation [14–16], extraction [9,17,18] or electrodeposition [1,19,20]. The hydrometallurgical processes are more favorable from an environmental protection viewpoint.

Although many techniques have been introduced to recycle valuable metals from spent LIBs, their economic and environmental effect is less than satisfactory and there are still some problems to be solved. Firstly, the existing hydrometallurgical processes may produce wastewater containing fluorine and pollute the environment due to the incomplete recycling of the organic binder and electrolyte (usually LiPF_6 , of high cost), and it is also difficult and expensive to treat the wastewater [4]. Secondly, it may be difficult to recover the valuable aluminum foils with the existing processes for recycling spent LIBs. Although the recovery of both copper and aluminum can be conveniently achieved with the process presented by Contestabile et al. [7], in which the battery rolls were treated with N-methylpyrrolidone (NMP) for the separation and recovery of LiCoO_2 , the recovery effects of LiCoO_2 were demon-

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strated to be influenced by the used adhesive agents and rolling methods of electrodes [21]. The recovery cost is also high and the process is hard to protect the environment and the employees' health due to the emission of toxic gases. Thirdly, the cathode material LiCoO_2 is usually linked together with aluminum foils through adhesive agents with good chemical stability and mechanical performance such as polyvinylidene fluoride (PVDF) binder, which are not able to react with most of the strong acid and base, most of the strong oxidant and halogen. PVDF could not be dissolved in organic reagents such as fatty hydrocarbon and alcohol at room temperature either, making leaching reactions more difficult to achieve [2]. Almost all the previous works are started with mechanical pretreatment processes such as crushing, sieving, magnetic separation, fine crushing and classification after dismantling or separating the different components from spent LIBs [13,22]. However, mechanical separation processes have a disadvantage of not completely making all kinds of components in spent LIBs get separated from each other [23]. In addition, harmful gas is produced in the crushing process because of the strength and tenacity of the cathode materials, and the powdered metal oxide (LiCoO_2) may be lost as they usually adhere to the nonmetallic powder produced in the crushing process. So pretreatment is really necessary for recycling of valuable metals from spent LIBs [2,13]. In view of the problems of the recycling technologies mentioned above, it is believed that an effort must be made to find a more advanced technology without negative environmental effects for recycling spent LIBs.

Vacuum pyrolysis can be considered as an alternative pretreatment method for recycling spent LIBs. In the pyrolysis process (heating under the absence of oxygen), the organic material is decomposed to low molecular products (liquids or gases), which can be used as fuel or chemical feedstock. Furthermore, the fine layer of powdered metal oxide on aluminum foils becomes crisp and easy to fall off, while the inorganic material such as metals can keep fairly intensity and can be recycled. Due to removing organic binders, vacuum pyrolysis can also bring about good conditions for the subsequent hydrometallurgical processes so that wet purification becomes simple and easy, resulting in better metal recovery efficiencies. In fact, there are many other advantages by using vacuum pyrolysis [24], such as: (1) preventing the toxic gases from harming environment; (2) lowering the decomposition temperature of organic compounds; (3) protecting valuable metals from being oxidized so that not only cobalt and lithium can efficiently be recycled, but also copper and aluminum can be recycled in their metallic forms with lower costs; (4) pyrolysis products or volatiles from electrolyte (e.g., LiPF_6) and binder (e.g., PVDF) could be collected and reused; (5) the separation of valuable metals from aluminum foils could be accomplished without any scraping or sieving procedures; (6) the leaching solution from vacuum pyrolysis residues is fluorine-free. To develop an environmentally friendly and economically recycling method, a new process consisted of vacuum pyrolysis and hydrometallurgical technique for the combined recovery of cobalt and lithium from spent lithium-ion batteries is proposed in this work.

2. Experimental

2.1. Materials and reagents

Spent LIBs used in mobile phones with different manufacturers and sizes were chosen in this study. Analytically pure sulfuric acid, nitric acid, hydrochloric acid and hydrogen peroxide solution was employed in the experiment. All the solutions at specified concentrations were prepared in distilled water.

2.2. Dismantling and separation

A flowsheet of the process was illustrated in Fig. 1. Spent LIBs were discharged firstly for security considerations. After discharging pretreatment step, spent LIBs were dismantled into different components such as cathode electrodes, anode electrodes, organic separators and iron scraps with pincers and saws. The cathode electrodes were uncurled manually after dismantling.

2.3. Vacuum pyrolysis

In this study, the pyrolysis system mainly consisted of vacuometer, vacuum furnace, and vacuum pump as shown in Fig. 2. The cathode electrodes were initially placed into the reactor. The pyrolysis was first pumped and the system pressure was kept lower than 1.0 kPa. The condensation temperature of the cold trap was -10°C . Then the reactor was heated to 600°C with a heating rate of $10^\circ\text{C}/\text{min}$, and it was held at the desired temperature for 30 min. After exiting the reactor, the volatiles entered the condensers and were condensed. Non-condensable gases were extracted by vacuum pump and collected by the gas collector finally. To research the effects of the heating conditions, the cathode electrodes were first cut into small pieces with a certain length and placed into the furnace, and then heated under atmospheric or vacuum at different temperatures. The peeled lithium cobalt oxide from aluminum foils was characterized by Rigaku-T III X-ray diffractometer (XRD, $\text{Cu K}\alpha$ radiation). The pyrolysis products collected from cold trap were determined by Fourier transform infrared spectrometer (FT-IR, Thermo Scientific, Nicolet 6700).

2.4. Metal leaching

Leaching the peeled cobalt lithium oxide from aluminum foils in H_2SO_4 solution was tested in a reactor, which was placed in a water bath to control the reaction temperature within $\pm 1.0^\circ\text{C}$; the system was maintained under constant magnetic agitation. The factors influencing the leaching effect of lithium cobalt oxide were studied under different experimental conditions including H_2SO_4 concentration (0.5–4 M), H_2O_2 concentration (0–20 vol.%), temperature (50 – 90°C), duration (15–75 min), and solid/liquid ratio (25 – 150 g L^{-1}). To increase the leaching efficiency, reductive leaching was carried out with H_2O_2 as the reducing agent. After leaching, the leaching solution and insoluble residue were separated by filtration. The aluminum foils were pickled with the optimum leaching solution to increase the recovery efficiencies of valuable metals, because a little cobalt lithium oxide still covered on them during metal leaching. After pickling operation, aluminum foils were washed with distilled water and dried in the oven. Aqua regia ($\text{HCl}:\text{HNO}_3$ equal to 3:1, volume ratio) was used to resolve and characterize residue after filtration. The concentrations of different metals including leaching solution and residue dissolved by aqua regia were measured with an inductive coupled plasma atomic emission spectrometer (ICP-AES, Perkin Elmer, Optima 5300DV). Fluorine concentration was measured by the fluorine ion selective electrode method (Changsha 743 ordnance factory in China, PF-1).

3. Results and discussion

3.1. Dismantling and vacuum pyrolysis

Spent LIBs were dismantled and separated manually into different parts during a safe process. Cathode materials were placed into the vacuum furnace directly without crushing or sieving procedures to decrease the material loss and the pollution of electrolyte LiPF_6 exposed in the air. After exiting the reactor, most of the cathode active material (cobalt lithium oxide) was peeled or scraped

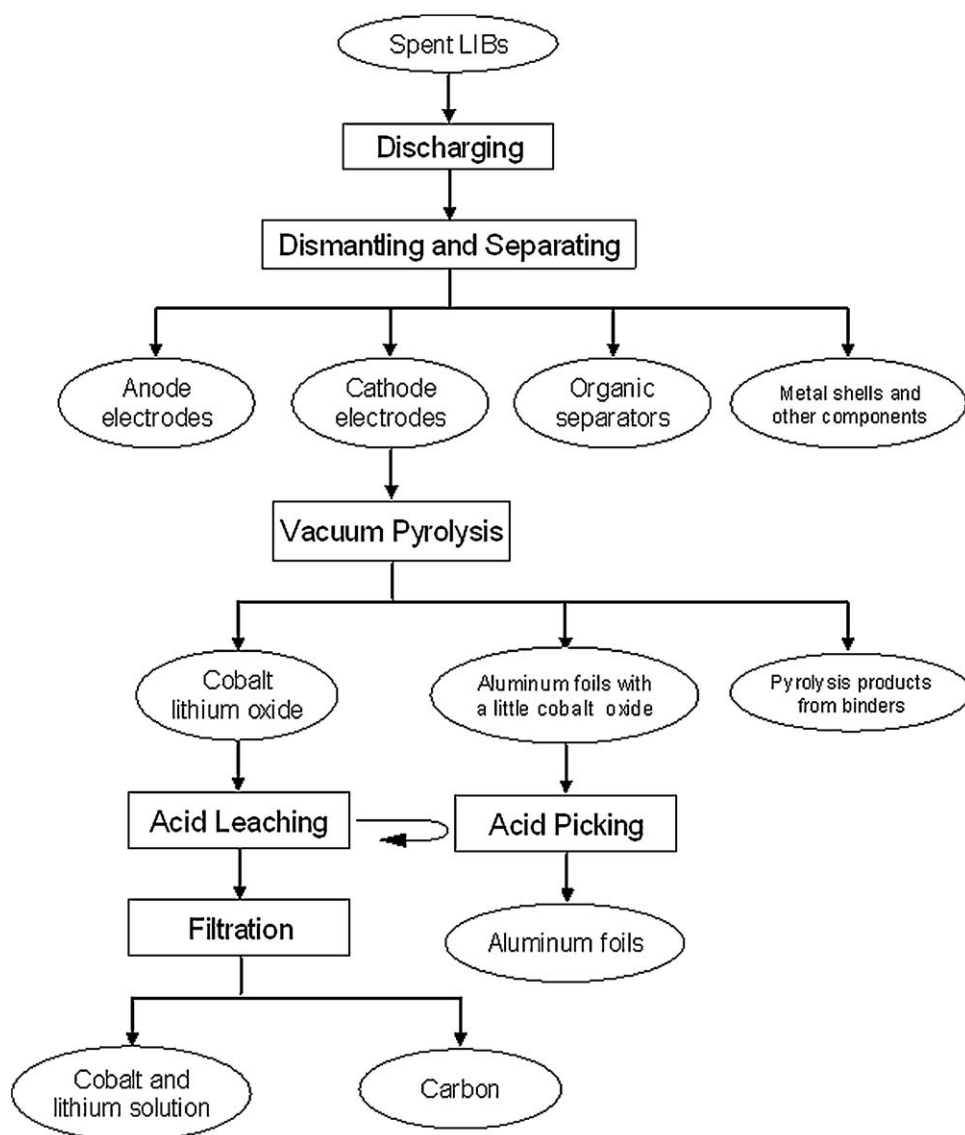


Fig. 1. Illustrations of the flowsheet of the recovery process.

from aluminum foils as shown in Fig. 3. It was observed that only little cathode material left on the aluminum foil, and the aluminum foil was excellent without damage.

During the battery manufacturing process, organic binder like PVDF was used to paste cathode active material LiCoO_2 onto alu-

minum foils. After use for a long period, part of the cathode active material did not bind the foils firmly due to the multiple charge–discharge processes. After pyrolysis, the organic materials (including electrolyte and binder) were evaporated or decomposed to low molecular weight products, liquids or gases, while

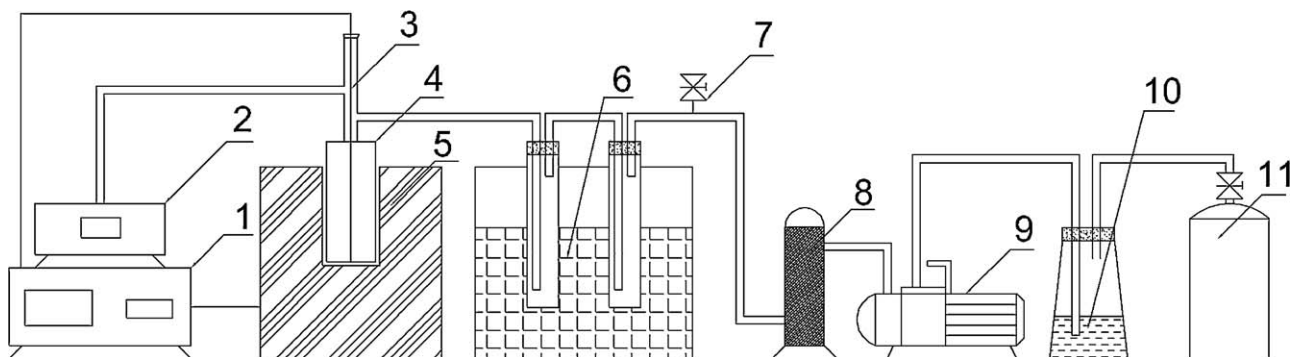


Fig. 2. The schematic illustration of the lab-scale pyrolysis system: 1, intelligent temperature control instrument; 2, vacuumeter; 3, thermocouple; 4, reactor; 5, temperature controlled furnace; 6, cold trap; 7, valve; 8, drying tube; 9, vacuum pump; 10, alkali solution; 11, gas collector.

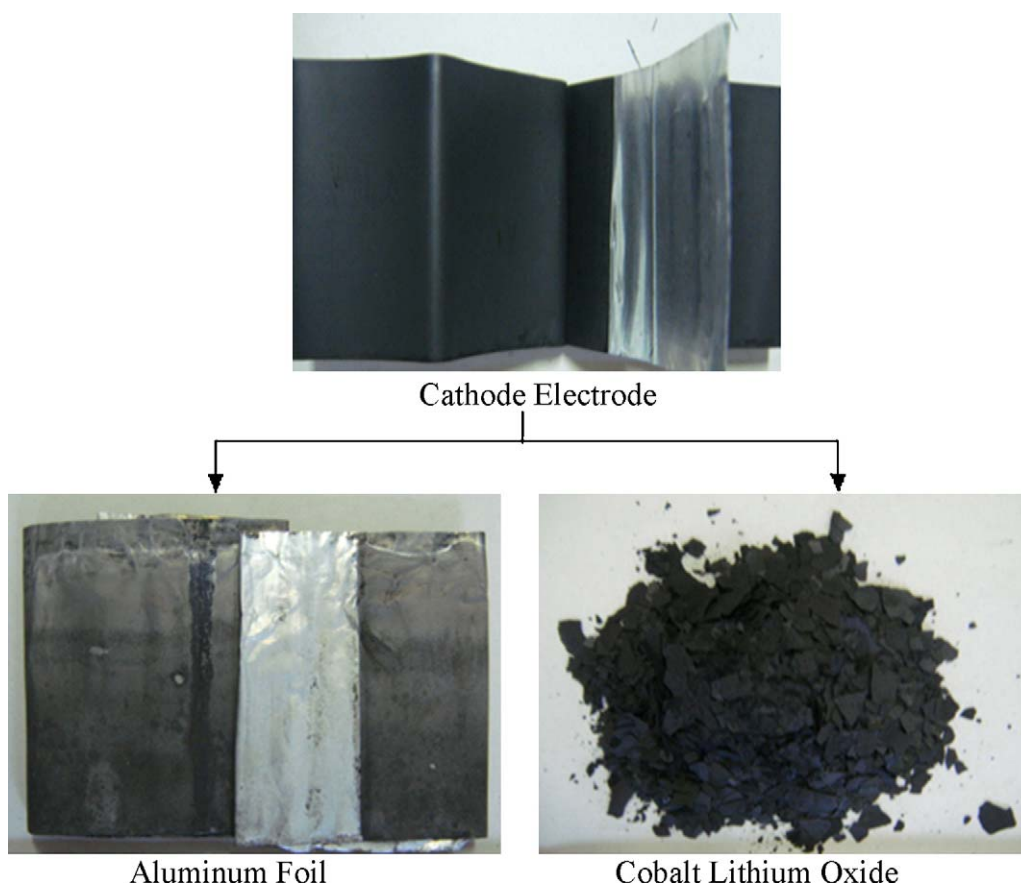


Fig. 3. Illustrations of the cathode electrode after vacuum pyrolysis.

the inorganic components (mainly metal oxides) remained as solid residues. Most of the low molecular weight products were transferred from reactor to gas collectors by vacuum pump. Therefore, the cathode active materials can easily be separated from the aluminum foils due to the disappearance of binder. The metals and decomposed products were collected from the reactor and cold trap, respectively.

The effect of vacuum pyrolysis temperature was investigated in the range from 450 °C to 700 °C. The experimental results are summarized in Fig. 4. Contrast the cathode electrode before vacuum pyrolysis (Fig. 4a), it did not change when it was pyrolyzed at 450 °C under vacuum as shown in Fig. 4b, and the cathode active material did not peel from the aluminum foils. It was not clear enough of the separation phenomenon, indicating that the organic binder or electrolyte was not evaporated or decomposed completely at this temperature. Fig. 4c–f shows that the separation efficiency gradually increased when the pyrolysis temperature varied from 500 °C to 600 °C. When the temperature higher than 600 °C, the aluminum foils were fragile, making the cathode active material hard to be separated. This phenomenon was more serious when the temperature reached 700 °C (Fig. 4g). It is obvious that 600 °C is the optimal temperature for separating the cathode active material from aluminum foils because most of the binder could be evaporated or decomposed completely at this temperature; and the cathode active material was detached from aluminum foils, which could be separated satisfactorily. Furthermore, the aluminum foils were still intact under the optimal temperature. It was also demonstrated that the amount of cathode active material peeled from aluminum foils was different due to different adhesive agents used and making methods of cathodes, but the phenomenon of peeling was an inevitable outcome.

For the sake of contrast, the pyrolysis experiment was also carried out at 600 °C under the atmospheric pressure. As shown in Fig. 4h, part of the cathode active material could peel from aluminum foils, but the cathode electrode was out of shape and became breakable, which mean the electrode easily oxidize at high temperature. This fully demonstrates that vacuum condition is necessary for cathode active material separation.

The typical XRD patterns of cathode active materials peeled from aluminum foils are shown in Fig. 5. The results show that the main compositions of separated material are LiCoO_2 and CoO . In general case, the Co_3O_4 present in the cathode materials results from the transformation of LiCoO_2 , and can be identified as the existence of the PVDF binder, due to its release of HF at high temperature [25–27]. The appearance of the CoO present in the peeled powder may come from the decomposition of HCoO_2 during vacuum pyrolysis process. Compared with Co_3O_4 , it is much easier to leach Co in acid solution without adding extra reductant.

The appearance of pyrolysis products collected by the condenser was similar to liquid. These pyrolysis products were analyzed for their composition by FT-IR. As shown in Fig. 6, a large peak between 3300 and 3000 cm^{-1} can be assigned to O–H stretching vibration, and the peak at 1967 cm^{-1} is associated with vinyl hydrocarbon compounds. The bands between 1805 and 1770 cm^{-1} are present when C=C stretching vibration is being analyzed from $\text{H}_2\text{C}=\text{CF}-\text{R}$ group. The peak around 1076 cm^{-1} can be ascribed to C–F stretching vibration from aliphatic difluorinated compounds. All band assignments of the pyrolysis products are shown in Table 1. The FT-IR analysis indicated that the main components of pyrolysis products are fluorocarbon organic compounds. Most of the fluorinated compounds can be enriched and recovered to prevent environmental pollution and resource

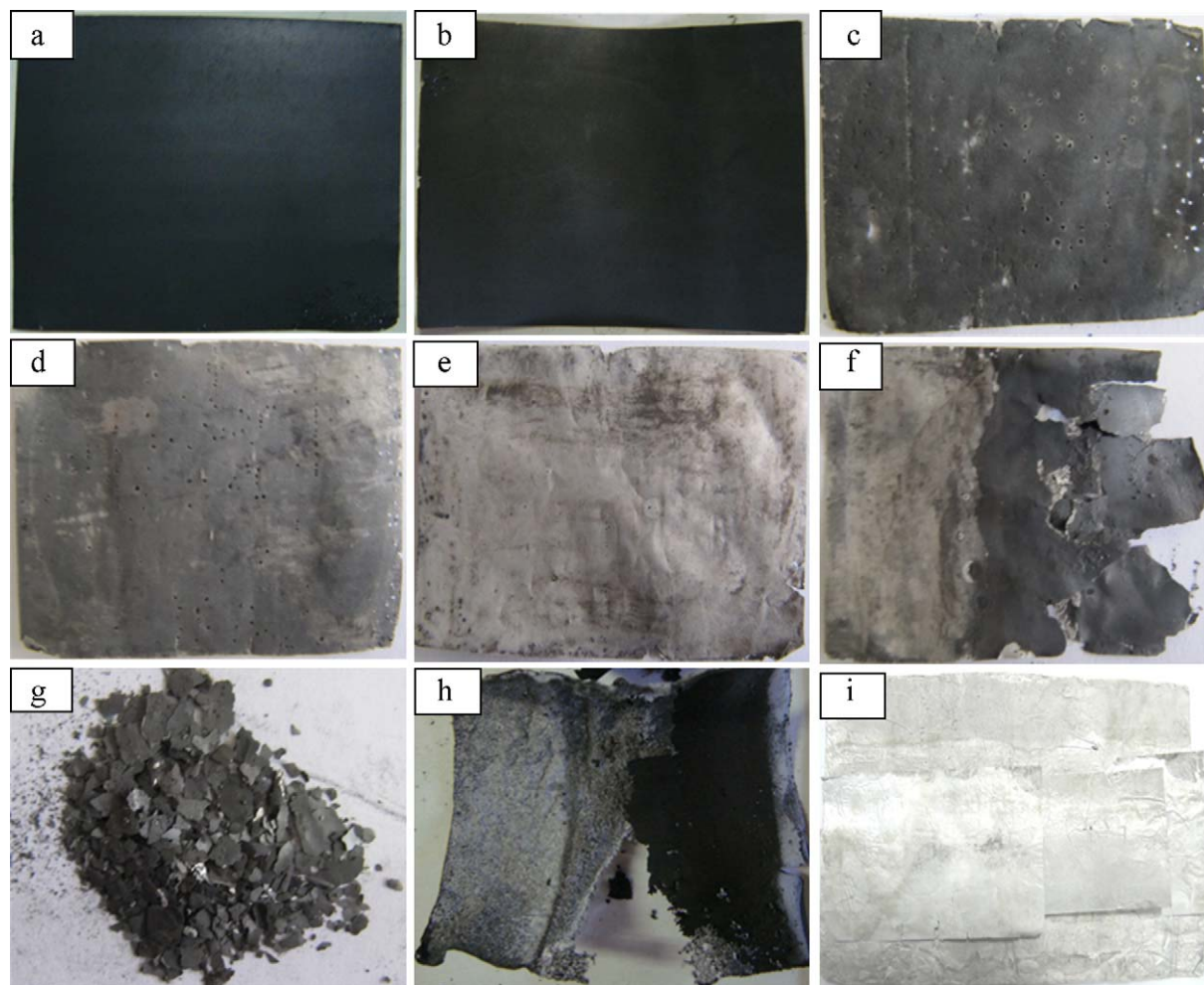


Fig. 4. Illustrations of the cathode electrode after different heating: (a) cathode electrode after battery dismantling and cutting, aluminum foil after vacuum pyrolysis (b) at 450 °C, (c) at 500 °C, (d) at 550 °C, (e) at 600 °C, (f) at 650 °C, (g) at 700 °C, (h) aluminum foil after heating in normal pressure at 600 °C, (i) aluminum foils after acid washing.

waste, and the research and reuse on the products is for further processing.

3.2. Metal leaching

Leaching in H_2SO_4 has been widely performed to recover valuable metals from spent LIBs [9,13,14,28]. Theoretically, the leaching

reaction of the waste $LiCoO_2$ and CoO with H_2SO_4 solution can be represented as follows:

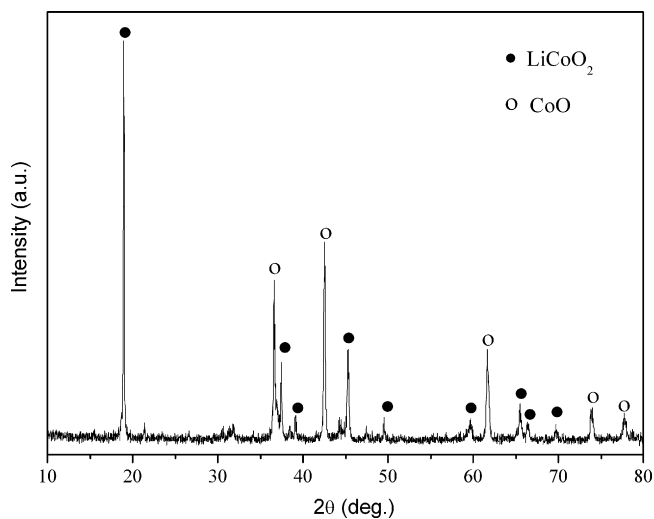


Fig. 5. XRD patterns for cobalt lithium oxide after vacuum pyrolysis.

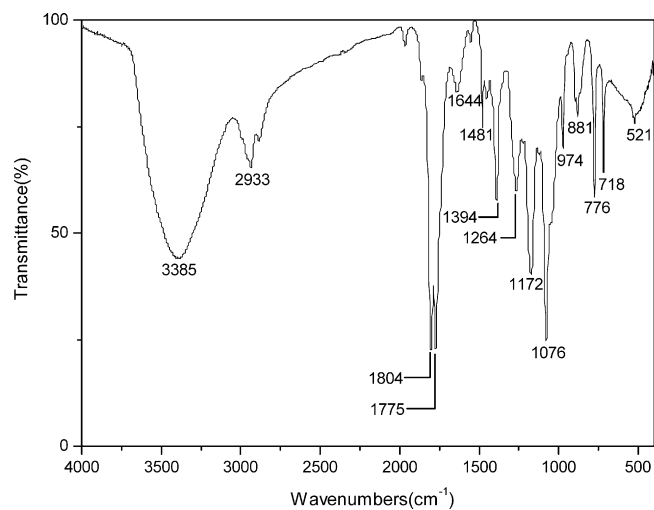


Fig. 6. FT-IR analysis of the pyrolysis products of the cathode materials from spent LIBs.

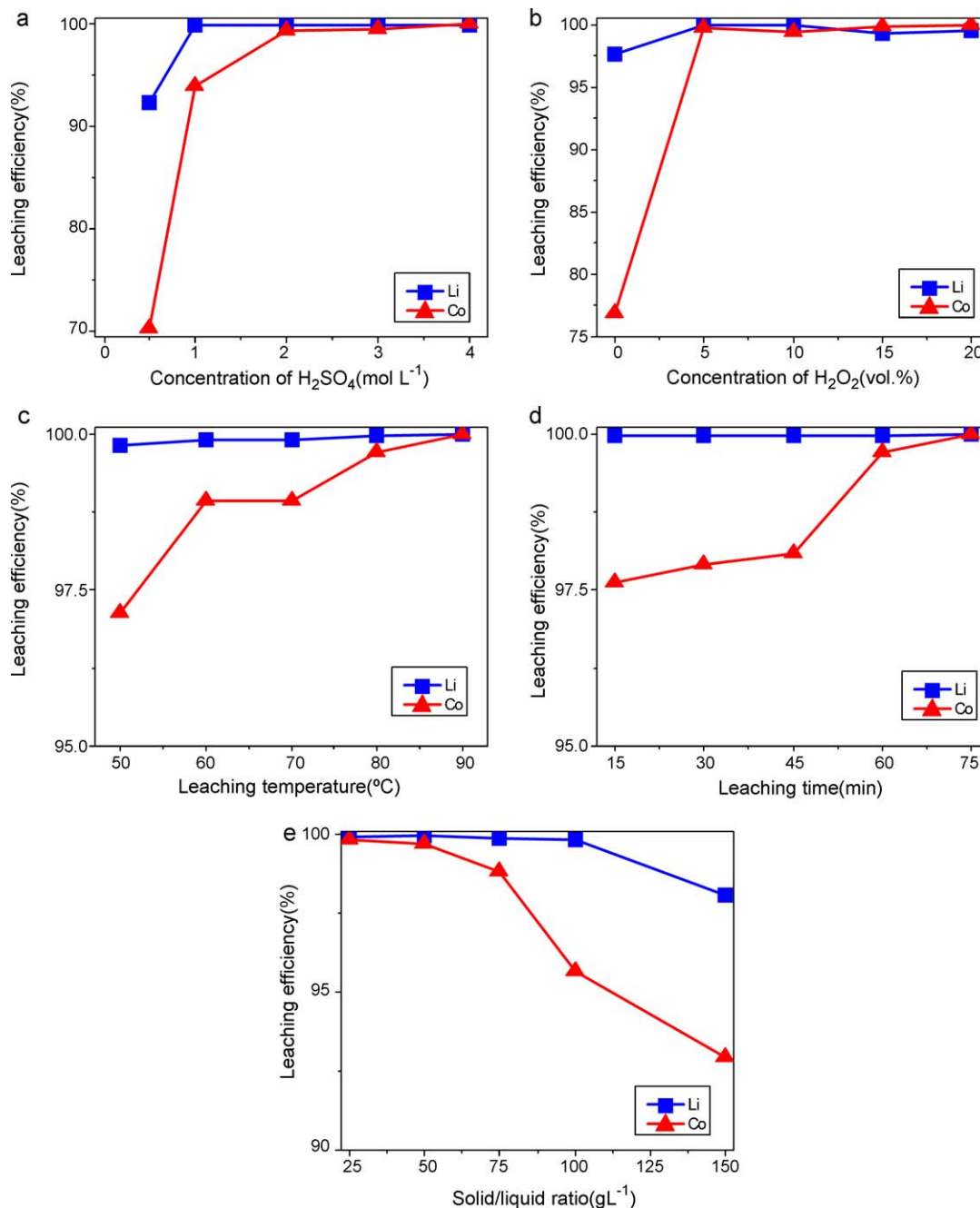
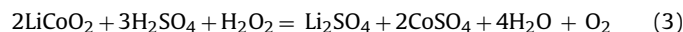


Fig. 7. Effects of (a) H₂SO₄ concentration, (b) H₂O₂ concentration, (c) leaching temperature, (d) leaching time, and (e) solid/liquid ratio on the leaching efficiency.

Table 1
FT-IR spectrum band assignments.

Band numbers (cm ⁻¹)	Assignment
3385	ν (O–H) stretching vibration
2933	ν (C–H) stretching vibration in methyl and methylene groups
1804, 1775, 1644	ν (C=C) stretching vibration in H ₂ C=CF–R groups
1481	ν (C–H) scissor vibration in methylene groups
1394	ν (C–F) stretching vibration in general range
1264, 1172	Some bands in polyfluorinated alkane groups
1076	ν (C–F) stretching vibration in aliphatic difluorinated compounds
974, 881	ν (C–H) out-of-plane deformation vibration in vinylidene groups
776, 718	ν (C–F) deformation vibration in general range
521	ν (C–F) bending vibration in C=CF ₂ groups

H₂O₂ has also been added as reductant during the metal leaching process to improve the leaching efficiency of cobalt, which can reduce Co(III) to Co(II) and thus facilitate the forward reaction [3,14,28]. The chemical reaction equation in the presence of H₂O₂ solution can be represented as:



To obtain the optimum conditions for the reductive leaching of cobalt lithium oxide, a series of experiments under different conditions were conducted. The effect of H₂SO₄ concentration on the leaching efficiency was investigated in the range from 0.5 to 4.0 M at solid/liquid ratio of 50 g L⁻¹, 80 °C, 15 vol.% H₂O₂, and 60 min. As shown in Fig. 7a, the leaching efficiency of cobalt and lithium increased with increasing H₂SO₄ concentration. The leaching efficiencies of cobalt and lithium were both 99% in the presence of 2 M

H₂SO₄. Considering the following recovery operation of extraction or chemical precipitation, further studies for leaching were carried out by using 2 M H₂SO₄.

The experiments were conducted in the H₂O₂ concentration range from 0 to 20 vol.%, maintaining solid/liquid ratio of 50 g L⁻¹, 80 °C, 60 min, and 2 M H₂SO₄. As can be seen in Fig. 7b, the leaching efficiencies of cobalt increased with the increasing H₂O₂ addition. In the absence of reductant, the leaching efficiency of cobalt was only 76%, but it increased to 99% when 5 vol.% of H₂O₂ was added. But the leaching efficiency of lithium was little affected by the amount of H₂O₂. This is in agreement with the conclusion obtained by Ferreira et al. [14]. The result also shows that the amount of 5 vol.% H₂O₂ was sufficient for the complete dissolution of cobalt and lithium, as further increasing the concentration of H₂O₂ did not show a significant increase in the recovery efficiency of cobalt and lithium.

The effects of leaching temperature and time on the leaching efficiencies of cobalt and lithium are shown in Fig. 7c and d, respectively. It was found that both variables have little influence on the leaching efficiencies of cobalt and lithium. The behaviors with different solid/liquid ratios are presented in Fig. 7e. It was observed that the leaching efficiencies of cobalt and lithium decreased with the increasing solid/liquid ratio, especially cobalt. Nevertheless, it was shown that 92% of cobalt and 98% of lithium were leached out at the solid/liquid ratio of 150 g L⁻¹, which are still high efficiencies within the experimental range. The suitable solid/liquid ratio of 50 g L⁻¹ for leaching was obtained for further recovery processes.

The concentrations of H₂SO₄ and H₂O₂ were found to be significant for the metal leaching conditions, and increasing the amount of them was beneficial to metal dissolution. High recovery efficiencies of 99% for both of cobalt and lithium were obtained with low energy and chemical consumption when the leaching process was carried out under the optimum conditions: 2 M H₂SO₄, 5 vol.% H₂O₂, leaching time of 60 min, leaching temperature of 80 °C and solid/liquid ratio of 50 g L⁻¹. Without any fluoride removal treatments like addition of soluble calcium, the concentration of fluoride in the wastewater is measured below 3 mg L⁻¹, which meets the Chinese regulatory let out concentrations in the “Generalized Sewage let out Criterion” (GB8979-96).

Although the amount of lithium cobalt oxide peeled from aluminum foils was demonstrated to be influenced by the used binders and rolling methods of electrode, aluminum foils obtained from vacuum pyrolysis were pickled with the optimized leaching solution to increase metal leaching efficiencies in the leaching process. As verified in Fig. 4i, the cobalt lithium oxide clung infirmly to aluminum foils after vacuum pyrolysis could also be washed with leaching solution, and almost all of the electrode materials can be separated from aluminum foils.

4. Conclusions

An investigation of vacuum pyrolysis and acid leaching has been developed for the separation and extraction of cobalt and lithium from spent LIBs.

- (i) Cathode active materials could be peeled from aluminum foils by vacuum pyrolysis, and the composition of shedding was LiCoO₂ and CoO by X-ray diffraction analysis. The aluminum foils were intact without any scraping processes and could be recovered in their metallic forms.
- (ii) By the addition of H₂O₂ to H₂SO₄ used for leaching, the leaching efficiency of cobalt was increased obviously. The highest leaching efficiency of 99% of cobalt and lithium was obtained under the optimum conditions. The acid pickling of aluminum foils was also proposed to recover valuable metals and metallic aluminum.

Based on the above processes, the solution containing cobalt, lithium and little fluoride was recovered from spent LIBs.

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