Study on separation of cobalt and lithium salts from waste mobile-phone batteries

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Abstract

The metals in waste mobile-phone batteries may cause environmental pollution. In this paper, leaching with $\text{H}_2\text{SO}_4+\text{H}_2\text{O}_2$, P507 extraction, and sedimentation with oxalic acid and carbonic acid were used to deal with waste batteries and obtain cobalt and lithium salts by separation, which shows an easy and feasible method with less waste water disposal. The effects of sulphuric acid concentration, pH value, and lithium ions on the recovery were investigated. When the sulphuric acid concentration was over 0.4 mol/L, the loss of cobalt increased significantly. If pH value of 3.5 was used, it was easy for cobalt and lithium separation with a low cobalt loss. Over several recycles, the recovery of lithium could reach the maximum with the lithium ion concentration of 27.3 g/L. The recovery efficiencies for cobalt and lithium were 90.02\% and 86.04\%, respectively.

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Keywords: waste mobile-phone battery; separation and recovery; cobaltous oxalate; lithium carbonate

1. Introduction

With the advantages of light weight, large capacity, long service life, etc, lithium-ion secondary battery has become an extensively used portable power [1]. Benefiting form the popularity of mobile phones, laptops, digital cameras, the production and consumption of the lithium battery straight to soar. In 2008, cell phone production in China was about 300 million, which means if each cell phone matches 1.5 batteries on average, then the amount of Li-ion battery production reached 450 million. After hundreds of times of charging and discharging, batteries expansion and capacity decline till scrapped. So the service

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life is 2 to 3 years [2]. Accordingly, the huge battery consumption also brings a startling quantity of waste batteries. However, lithium battery recovery rate is very low due to some technical and economic issues. A large number of waste batteries have been abandoned, which not only cause harmlessness to the environment, but also a waste of resources [3].

A small cell phone battery may become a "killer" of the environment and human health after scrapped. For instance, the dose of cadmium in one battery could contaminate the water of three standard pool, while copper, aluminum, electrolyte and other non-ferrous metals also cause great pollution to the environment-contaminate groundwater and soil. Accordingly, people long time exposure to these metal ions may lead to nervous system and respiratory system diseases [3].

Currently, the methods of separation and recovery lithium in batteries are adding precipitant after treatment, which converts lithium-ion into the precipitation. Then we could calcinate it and absorb the lithium-ion steaming out in form of lithia vapor. D. S. Kim [4] studied on separation of LiCoO$_2$ and manufactured stainless steel pressure boiler with two Teflon chambers. Then put LiCoO$_2$, conductive carbon, binder and diaphragm in this device and separate LiCoO$_2$ at 200° C by hydrothermal method. This method is mainly based on the mechanism of "dissolution - precipitation". Yong-xun JING[5] recovers lithium and cobalt oxide from waste lithium-ion batteries by flotation. The electrode material is heated at 500° C in muffle furnace after pretreatment (organic binder would volatilize and the surface of lithium cobalt oxide would change from hydrophobic to hydrophilic), then separate lithium cobalt oxide from graphite via flotation. In the optimum flotation conditions (kerosene=0.2 kg/t, MIBC=0.14 kg/t, concentration of slurry solids = 10%), lithium and cobalt content is more than 93% and cobalt recovery rate reaches 90% by this method. The above method has simple step and higher recovery characteristics, but the high facility cost and demanding operation request are not suitable for industrialization[6].

2. Experimental

2.1. Raw material and reagents

The specification of lithium battery is 1020 mA/h. Lithium-ion secondary battery is composed of shell and internal battery cell. Specifically, shell is nickel plated steel and battery cell is spiral structure which mainly consists of cathode, anode, isolating membrane and electrolyte. Batteries' cathode material consists of about 90% activated lithium cobalt oxide, 7～8% conductive acetylene black and 3～4% organic binder. The isolation membrane is the polypropylene membrane while electrolyte is organic carbonate solution of lithium hexafluorophosphate[7]. The chemical reagents contain NaOH, Al(OH)$_3$, H$_2$SO$_4$, H$_2$O$_2$, TBP, sulphonating kerosene, oxalic acid, saturated sodium carbonate solution, etc.

2.2. Separation principle

Under the consideration of environmental protection and security of the leaching process, a brand-new proposal of low liquid-to-solid ratio using H$_2$SO$_4$+H$_2$O$_2$ system as extraction solution has been chosen. Leaching solution from experiment contains very minor amount of iron and the PH endpoint of leaching is 3.5, which avoid removing iron in traditional high-liquid-solid ratio leaching process. It achieves the purpose of selective leaching of cobalt and lithium [8, 9].

Using Organophosphorus P507 as an extractant, TBP as a modifier and Sulfonated kerosene as a diluent, cobalt extraction from solution will reach a high rate by twice extraction while lithium extraction rate is very low. Then, the coextraction lithium in organic phase can be removed by dilute sulfuric acid, which achieves the separation of cobalt and lithium. After adding sulfuric acid, P507 extraction experiment raffinate can be recycled as leaching solution. This process makes the lithium ions increase
gradually in the leaching-extraction system. Thus, we should precipitate lithium by using saturated sodium carbonate when lithium ion concentration reaches a certain level in raffinate[10-12].

2.3. Process flow diagram of valuable metal recovery from waste lithium batteries

![Diagram of valuable metal recovery process](image)

**Fig. 1.** Process flow diagram of valuable metal recovery from waste lithium batteries

3. Results and Discussion

3.1. Effect of acid type on cobalt leaching rate

Leaching experiments were carried out of hydrochloric acid, nitric acid and sulfuric acid, respectively. The results are shown in Table 1. The most efficient acid is hydrochloric acid, followed by nitric acid and sulfuric acid is lowest. However, due to the use of HCl and HNO₃ in leaching process of the mixed powder causing harmful chlorine and nitrogen oxides which will pollute the environment, the cost must be increased by using exhaust gas treatment device. Consequently, using sulfuric acid as the leaching solution is both environmentally friendly and safe.
3.2. Effect of acid concentration on leaching cobalt loss

As it can be seen from Fig. 1, the Co-loss rate rises with the increase of sulfuric acid concentration. In particular, the Co-loss rate shoots up when sulfuric acid concentration exceeded 0.4mol / L. As a result, sulfuric acid concentration close to 0.4mol/L is used in Sulfuric acid-hydrogen peroxide system, which reduced Co-loss effectively.

Table 1. Effect of types of acid on cobalt leaching rate

<table>
<thead>
<tr>
<th>Time/h</th>
<th>Hydrochloric acid leaching rate /%</th>
<th>Time/h</th>
<th>Nitric acid leaching rate /%</th>
<th>Time/h</th>
<th>Sulfuric acid leaching rate /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>40.0</td>
<td>1.0</td>
<td>60.3</td>
<td>1.0</td>
<td>30.8</td>
</tr>
<tr>
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<td>70.1</td>
<td>1.5</td>
<td>80.5</td>
<td>2.0</td>
<td>49.2</td>
</tr>
<tr>
<td>1.5</td>
<td>99.2</td>
<td>2.5</td>
<td>90.4</td>
<td>3.0</td>
<td>79.7</td>
</tr>
</tbody>
</table>

3.3. Effect of pH on separation factor of leaching of cobalt and lithium

The effect of pH on the separation factor of leaching of cobalt and lithium is shown in Fig. 2. As the pH increasing, the separation factor of cobalt and lithium is greater and the change becomes flat after reaching pH=4.0. Under the consideration of the impact on Co-loss by different acid concentration, pH=3.5 has been chosen, which not only achieves a greater degree of separation but also reduces the loss of cobalt.

3.4. Lithium-ion concentration on the precipitation of lithium

Only when lithium-ion concentration exceeding 25g/L can, we achieve a higher rate of precipitation. Therefore, precipitation of lithium has to been carried out after seven leaching-extraction cycles. Then the lithium-ion concentrations in raffinate phase reaches 27.3g/L and the recovery of lithium-ion could reach a higher rate.

4. Conclusions
Experimental results show that leaching batteries with H$_2$SO$_4$+H$_2$O$_2$ system will not generate harmful gases, and will not threaten the environment; the end of leaching pH=3.5 avoids iron removal step in traditional high-liquid-solid ratio leaching process. Leaching with H$_2$SO$_4$+H$_2$O$_2$, P507 extraction, and sedimentation with oxalic acid and carbonic acid were used to deal with waste batteries and obtain cobalt and lithium salts by separation, which showed an easy and feasible method with less waste water disposal. The recovery rates for cobalt and lithium were 90.02% and 86.04%, respectively.

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References


