



Innovative Electrochemistry Technique for Leaching Cobalt from Spent Lithium Ion Batteries

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This work intends to investigate the possibilities of cobalt leaching from spent lithium ion batteries by electrochemistry technique. A new method was put forward and a self-designed leaching apparatus was made. The series experiments demonstrate that the ferrous ion can improve cobalt leaching from spent lithium ion batteries and the circle of $\text{Fe}^{3+}/\text{Fe}^{2+}$ is possible. Higher voltage and appropriate amount of ferric sulfate can get better cobalt leached percentage.

Keywords: Spent lithium ion batteries, Electrochemical, Cobalt leaching, Iron cycle.

INTRODUCTION

Lithium-ion batteries have been widely used in many areas, such as mobile telephones, personal computers, video cameras and other modern-life appliances¹. Meanwhile, the environmental problem was also brought out since the spent lithium-ion batteries contain many toxic metals. If these hazardous materials were not treated properly, environment will be polluted^{2,3}. Besides, the spent LiCoO_2 contains many valuable metals such as Co and Li, so that recycling of the used batteries is also of importance for efficient utilization of these rare source⁴. Therefore, it is highly desirable to develop proper strategy to treat these hazardous materials in spent lithium-ion batteries to avoid possible pollution issues.

The methods of high-temperature calcinations, acid leaching and electrochemical treatment have been used to recycle the used lithium ion batteries. Nonetheless their application is limited by problems such as high energy consumption, high cost, low efficiency and serious second pollution. There is still no efficient recycling method up to now⁵⁻⁷. For example, the use of a substantial amount of chemicals during the hydrometallurgical process is not eco-friendly. Due to these drawbacks, bioleaching processes are developed. Bioleaching shows competitive advantages owing to environment friendly and low cost process. However, due to its slow kinetics, the commercial application of bioleaching in metal extraction is limited relatively⁸⁻⁹. To improve the efficiency of bioleaching, researchers looked into aspects such as improvement of bacterial culture, accession of metal ions and addition of surfactants¹⁰⁻¹³.

Influences of pH and redox potential on the bioleaching process have been reported in some literatures. Olson *et al.*¹⁴ reported that the key factor is redox potential during bioleaching by *Thiobacillus ferrooxidans*, where the microbial oxidation of ferrous iron increased the solution redox potential and enhanced bacterial growth rate. Modak *et al.*¹⁵ also reported that ferrous iron oxidation provided energy for the bacteria growth and an oxidation-reduction potential (ORP) couple $\text{Fe}^{3+}/\text{Fe}^{2+}$ has been monitored and considered as a criterion for bacterial activity or the bioleaching effectiveness. Solution redox potential was also found to be the key factor on the bioleaching process of LiCoO_2 and bioleaching efficiency would be improved with the increasing of solution potential¹⁶⁻¹⁸.

To the best of our knowledge, there is no report on the use of electrochemistry technique for leaching of cobalt from used lithium ion batteries. This paper is to investigate the leaching feasibility of lithium cobalt oxide from used lithium ion batteries by electrochemical and the influences of electric field on the leaching efficiencies with different initial pH and Fe^{2+} addition. The results are helpful to improve the recovery of cobalt from LiCoO_2 and find appropriate method to solve the problem of slow kinetics.

EXPERIMENTAL

The spent lithium ion batteries were obtained from Youteli Co. Ltd., Jiangxi, China. The batteries were manually separated into plastic shell, LiCoO_2 cathode material, anode material and aluminum foil. The cathode material was ground and sieved to 0.075 mm; the oversize portion was also included

after being pulverized. The powder was subject to EDX analysis and its chemical composition was as follows (%): Li, 3.37; Co, 48.5; Mn, 23.9; Ni, 24.1; Fe, 0.14.

Cobalt leaching with Fe³⁺ or Fe²⁺ added and without electric field: Two grams of LiCoO₂ powder was added into 250 mL 10 % H₂SO₄ with 300 rpm stirring speed at room temperature. The conditions of the other two experimental were carried out same as above, but 3.36 g/L Fe³⁺ as analytical reagent Fe₂(SO₄)₃ or 3.22 g/L Fe²⁺ as analytical reagent FeSO₄·6H₂O was added into the solutions simultaneously. The concentration of dissolved Co²⁺ and pH were determined by sampling at given time intervals. The concentration of Co²⁺ was determined by atomic absorption spectroscopy (Heraeus, model Varian AA-400, Germany).

Effect of Fe²⁺ amount on cobalt leaching without electric field: Two grams of LiCoO₂ powder was added into 250 mL 10 % H₂SO₄ with 300 rpm stirring speed at room temperature, then 2, 4, 6, and 10 g/L FeSO₄·6H₂O was added to the solutions respectively.

Cyclic experiment of Fe³⁺/Fe²⁺: This work put forward an innovative electrochemistry technique for enhancement leaching of cobalt from LiCoO₂ powder by using the properties that salt bridge can transfer electrons. The test was conducted by using a self-designed leaching apparatus suitable for this method, which includes reactor, conductance cell, salt bridge, constant voltage power supply and stirrer. The construction of the leaching device for leaching valuable metals from spent lithium ion batteries is illustrated in Fig. 1. Good conductivity material was added into the conductance cell and the agitation speed was controlled with 300-400 rpm. When the leached percentage of Co was above 80 %, sulphuric acid should be added once again and the LiCoO₂ powder can be leached continually.

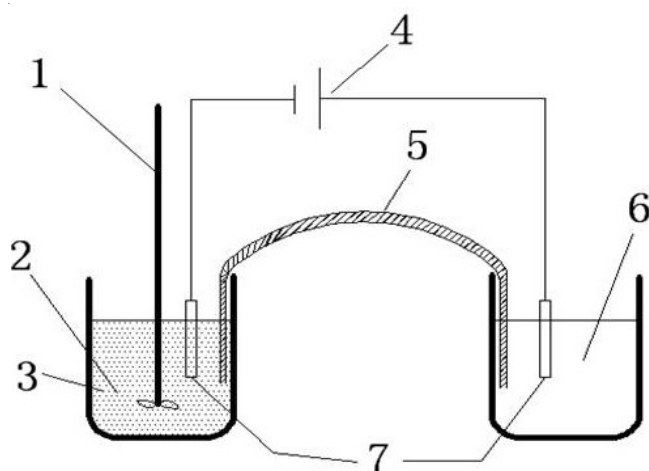


Fig. 1. Construction of the self-designed leaching apparatus, 1-stirrer; 2-LiCoO₂ powder; 3-sulphuric acid; 4- constant voltage power supply; 5- KCl salt bridge; 6-conducting solution; 7-graphite electrode

The mechanism of the apparatus is as below. With the principle that salt bridge can transfer electron, Fe³⁺ gets the electrons and converts into Fe²⁺ in cathode. Fe²⁺ reacts with LiCoO₂ and Fe³⁺ and Co²⁺ are generated. The newly formed Fe³⁺ gets the electronic and is reduced to Fe²⁺ in cathode. In the leaching process, Fe³⁺ can be used repeatable. Lithium

cobalt oxides convertes into Co²⁺ and consumes H⁺ in the whole process. A certain amount of acid should be added into the reactor to ensure the reaction continually.

Feasibility experimental: Two grams of LiCoO₂ powder was added into 250 mL 10 % H₂SO₄ with 300 rpm stirring speed at room temperature and 2V of external control voltage was performed. The other experiment was carried out at the same condition as above and 3 g ferric sulfate hydrate in the 250 mL H₂SO₄ which volume fraction is 10 % with graphite negative electrode. The other experiment is KCl solution and insert graphite positive pole with the stirring speed 300 rpm and the external control voltage 12 V.

Then, the effect of voltage of 3, 5, 7, 10 and 12 V and the amount of ferric sulfate of 1, 2, 3, 4, 5, 7 g on the cobalt leaching was studied.

RESULTS AND DISCUSSION

Cobalt leaching with Fe³⁺ or Fe²⁺ added and without electric field: Fig. 2 is the leached Co percentage *versus* time with Fe³⁺ or Fe²⁺ added and without electric field. It can be seen that the leaching efficiency has no different obviously between Fe³⁺ added and acid leaching directly, but it enhances remarkably when Fe²⁺ was added. This is because LiCoO₂ shows oxidability in acidic condition and Fe²⁺ shows reducibility, in this way redox reaction is happened, which can be expressed by

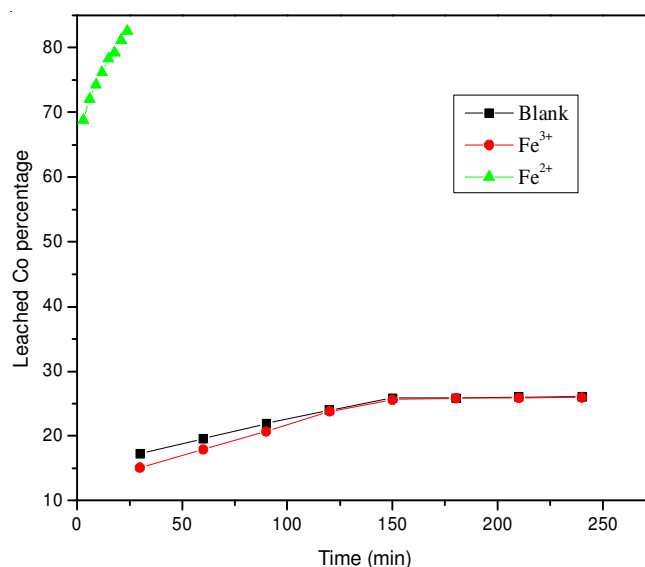
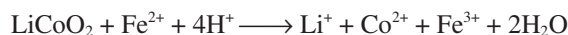


Fig. 2. Leached Co percentage *versus* time with Fe³⁺ or Fe²⁺ added and without electric field

Effect of Fe²⁺ amount on the leaching of Co without electric field: The effect of Fe²⁺ amount on the leaching efficiency of Co and the pH of solutions without electric field are shown in Figs. 3 and 4. From Fig. 3, it is noticed the leaching efficiency increases with the more Fe²⁺ added. From Fig. 4, pH is still increasing. In the process of leaching, the oxidation of Fe²⁺ and lithium cobalt oxide are accompanied with the process of acid consumption. pH will increase with the increase of the amount of consumption in solution.

The reactions in the overall process involved in the leaching of LiCoO_2 can be divided into acid consumption (eqns. 1 and 2), acid generation (eqns. 3 and 4). pH is the combined action result of acid consumption and generation in the process of leaching. The total reaction can be classified as Eqn. (5).

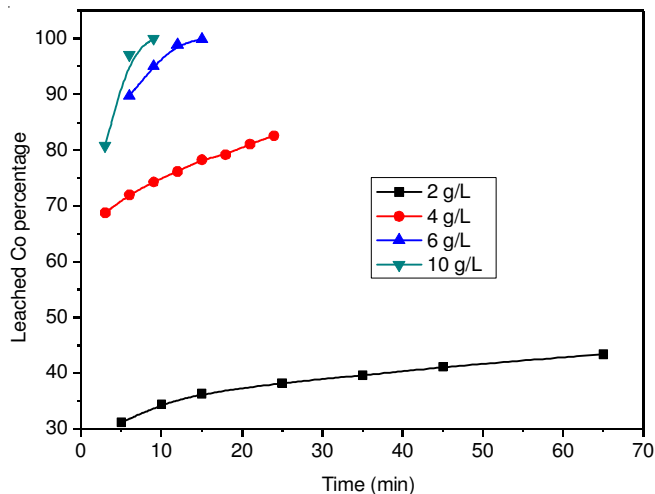
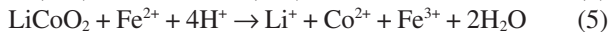
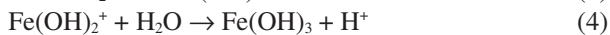
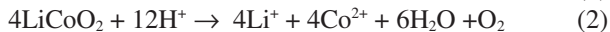
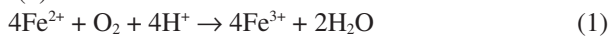


Fig. 3. Effect of Fe^{2+} amount on the cobalt leaching

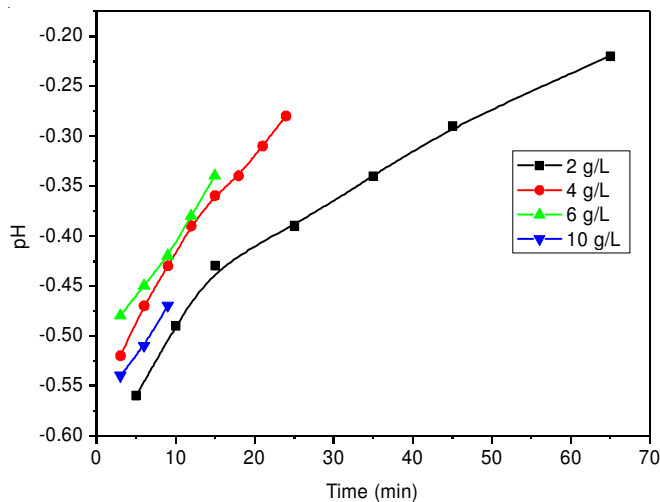


Fig. 4. pH during leaching process with different added amount of Fe^{2+}

However, pH is anomalous when the concentration of Fe^{2+} is 10 g/L. This is because a large number of Fe^{3+} can be produce acid when it hydrolysis in the solution, which made the pH reduced.

Cobalt was leached quickly and effectively with the Fe^{2+} added. If we can find a method which can make Fe^{3+} reverts to Fe^{2+} continuously, it is very significant.

Cyclic experiment of $\text{Fe}^{3+}/\text{Fe}^{2+}$: The results of feasibility experiment was shown in Fig. 5. The leaching efficiency of cobalt with electric field is higher than that of with acid leaching directly. This is because the external control voltage provides

electron to the redox reaction in the solution, which makes LiCoO_2 converts to Co^{2+} . However, due to the valence state of CoO^- is -1 and with negative charge, it can not be reduced directly in cathode, therefore the leaching percentage is low. When Fe^{3+} was added to negative zone, external voltage provide redox potential and Fe^{3+} gets electron to revert to Fe^{2+} directly in cathode. Fe^{2+} reacts with LiCoO_2 by $\text{LiCoO}_2 + \text{Fe}^{2+} + 4\text{H}^+ \rightarrow \text{Li}^+ + \text{Co}^{2+} + \text{Fe}^{3+} + 2\text{H}_2\text{O}$. So the leaching efficiency increased obviously and the circle of $\text{Fe}^{3+}/\text{Fe}^{2+}$ is possible.

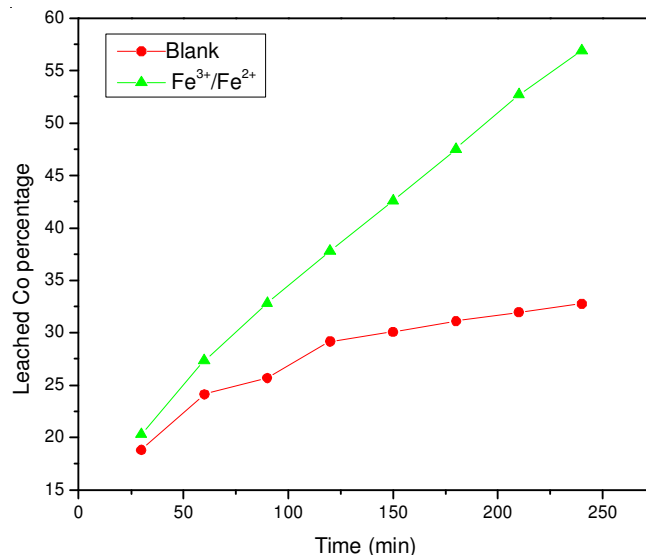


Fig. 5. Leached Co percentage versus time under electric field with and without $\text{Fe}^{3+}/\text{Fe}^{2+}$

Influence of voltage on the cobalt leched percentage:

The influence of voltage on the cobalt leching percentage was shown in Fig. 6. From Fig. 6, the leached percentage of cobalt is similar with that of acid leaching when voltage is 1 V. While voltage is 3V or above, the leached percentage increased obviously. According to electrochemistry:

$$E = E_+ - E_- + \frac{0.059}{Z} \lg \frac{\alpha_{\text{oxidant}}}{\alpha_{\text{reductant}}}$$

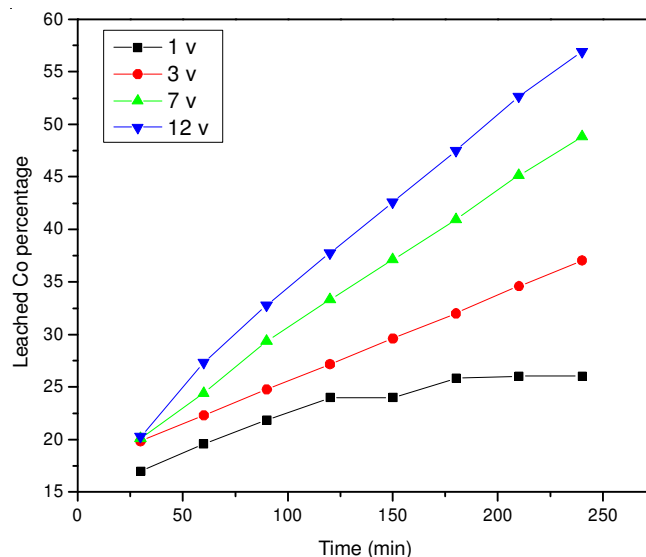


Fig. 6. Effect of voltage on the leached Co percentage versus time

the solution is not conductive if the applied voltage is less than a certain value. Under these circumstances, the whole circuit is equivalent with broken circuit. When the applied voltage is exceeding a certain value, Fe^{3+} is oxidized Fe^{2+} . With the increasing of voltage, current density increased and the conversion rate of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ increased resulted in the leached percentage increased.

Influence of the amount of added ferric sulfate: The result of the influence of the amount of added ferric sulfate was shown in Fig. 7. With the amount of iron ion increasing, the leached percentage of cobalt firstly increased and then remained constant. When the amount addition of Fe^{3+} is above 5 g/L, due to the small current density, the rate of Fe^{3+} oxidized to Fe^{2+} is constant and the leached percentage of cobalt will not increase correspondingly. Comprehensively, appropriate amount of ferric ions addition not only has better leaching efficiency, but can also save resources.

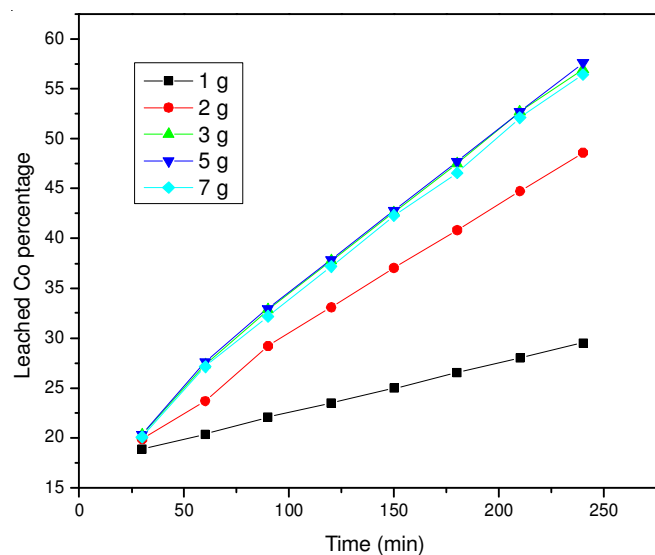


Fig. 7. Effect of ferric sulfate amount on the leached Co percentage versus time

Conclusions

• This work demonstrates that the ferrous ion can improve cobalt leaching from spent lithium ion batteries. The reaction of $\text{LiCoO}_2 + \text{Fe}^{2+} + 4\text{H}^+ \rightarrow \text{Li}^+ + \text{Co}^{2+} + \text{Fe}^{3+} + \text{H}_2\text{O}$ is spontaneous.

• Innovative electrochemistry technique for leaching of cobalt from spent lithium ion batteries by the self-designed leaching apparatus is feasible and the circle of $\text{Fe}^{3+}/\text{Fe}^{2+}$ is possible.

• Higher voltage and appropriate amount of ferric sulfate can get better cobalt leached percentage.

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