University of Belgrade
Technical Faculty in Bor

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XV International Mineral Processing & Recycling Conference

IMPRC
INTERNATIONAL MINERAL PROCESSING & RECYCLING CONFERENCE

Proceedings

Editors:
Jovica Sokolović
Milan Trumić

17-19 May 2023 | Belgrade SERBIA

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USE OF COPPER POWDER AS A REDUCING AGENT IN THE LEACHING PROCESS OF $LiCoO_2$

D. Medić[1#], I. Đorđević[2], M. Nujkić[1], A. Papludis[1], V. Nedelkovski[1], S. Alagić[1], S. Milić[1]

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ABSTRACT – In this study, the possibility of using copper powder as a reducing agent in the process of cathode material leaching from spent lithium-ion batteries (LIBs) was examined. The copper powder was obtained by grinding copper foil, which is used in LIBs as a current collector. Optimal leaching efficiency of 99.84% for lithium and 99.99% for cobalt was achieved by using 0.4 mol/L phosphoric acid with 0.2 g of copper powder, during the leaching time of 30 min, and at 80°C. Leaching results indicated that copper powder could be used as an effective reducing agent to recover lithium and cobalt.

Keywords: LIBs, Current Collector, Phosphoric Acid, Cobalt, Lithium.

INTRODUCTION

Due to the existing energy crisis and increasing environmental pollution, developing clean and sustainable energy is the biggest challenge today. Lithium-ion batteries (LIBs) have found application in many branches of industry as "green technology" [1]. However, with the popularization and development of electric cars and portable electronic devices, the amount of spent LIBs is rapidly increasing. In addition to the fact that spent LIBs represent a significant secondary source of many valuable metals, their improper disposal can seriously worsen the quality of the environment [2].

Lithium cobalt oxide ($LiCoO_2$) was the first commercialized cathode material, but it still represents the basis for the development of LIBs. For high efficiency of LIBs recycling, complete dissolution of the cathode material is necessary. In the leaching studies published so far, sulfuric acid with hydrogen peroxide as a reducing agent was most often used to dissolve the cathode material [3-5]. The advantage of using hydrogen peroxide in the reductive leaching process is that only oxygen and water are obtained by its decomposition, and thus no additional impurities are introduced into the leaching system. However, hydrogen peroxide decomposes at high temperatures in the presence of sulfuric acid, which reduces the efficiency of cathode material leaching. Considering that the standard electrode potential of $LiCoO_2$ reduction is 2.13 V, it can be concluded that iron, copper, and aluminum, which are integral parts of LIBs, can be used as reducing agents in the leaching process [6]. Ghassa *et al.* [7] investigated the possibility of using iron scrap, obtained from the metal casing of LIBs, in the leaching process of

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$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ in sulfuric acid. The results of their study indicated that the extraction rate of cobalt increased significantly by adding 6 g/L of iron scrap to the leaching system. Also, it was noted that the presence of iron scrap has no significant effect on the degree of lithium extraction, which is explained by the fact that the lithium extraction process does not require a reducing atmosphere. Porvali *et al.* [8] investigated the combined effect of Fe^{2+} ions and copper scrap on the kinetics of $LiCoO_2$ leaching in sulfuric acid and came to the conclusion that Fe^{2+} ions act as a reducing agent, whereby Fe^{3+} ions are formed, which are converted back to Fe^{2+} ions by oxidation of copper to Cu^{2+}.

In the aforementioned studies, the reduction properties of copper and iron were examined in the process of dissolving the cathode material in a sulfate medium. The aim of this work is to examine the possibility of using copper powder as a reducing agent during the leaching of $LiCoO_2$ in phosphoric acid.

EXPERIMENTAL

Preparation of cathode material and copper powder

To test the possibility of using copper powder as a reducing agent, 17 spent LIBs were collected. The spent LIBs were first disassembled into individual LIBs cells and then discharged using a 5.5 Ω resistance wire. The cathode material was obtained by separating $LiCoO_2$ from aluminum foil in a two-stage thermal treatment at 580°C and 630°C. In order to obtain the copper powder, the anode material was mechanically removed from the copper foil. The obtained copper foil was crushed in a laboratory mill.

Leaching tests

Cathode material leaching experiments were performed in a 600 ml glass laboratory beaker with a double bottom. The leaching apparatus was equipped with a condenser to prevent evaporation of the leach solution and a thermometer to control the temperature. 200 ml of leaching solution of a certain concentration is first thermostated to the desired temperature.

When the desired temperature was reached, 2.0 g of cathode material (with and without the addition of 0.2 g of copper powder) was added to the reactor and the mixer was turned on with a controlled number of revolutions. Leach solutions (1.0 ml of solution) were sampled at precisely determined time intervals (5, 15, 30, 45, and 60 min), filtered, and diluted to 50 ml in volumetric flasks.

An optical emission spectrometer with inductively coupled plasma (ICP-OES) Optima 8300, Perkin Elmer, USA was used to determine the content of Li and Co in the initial cathode material, as well as to monitor the content of the mentioned metals in leach solutions.

RESULTS AND DISCUSSION

The contents of cobalt and lithium in the initial cathode material determined by ICP-OES were 47.91% and 6.97%, respectively.

Leaching of the cathode material in H_3PO_4

The influence of copper powder on the degree of extraction of Co and Li

In order to examine the influence of copper powder on the degree of extraction of Li and Co, leaching experiments were performed in a solution of 0.4 mol/dm^3 H_3PO_4 with and without the addition of 0.2 g of copper powder, at a temperature of 80°C, at a stirring speed of 600 rpm and process duration of 30 min. The obtained results are shown in Figures 1a and 1b.

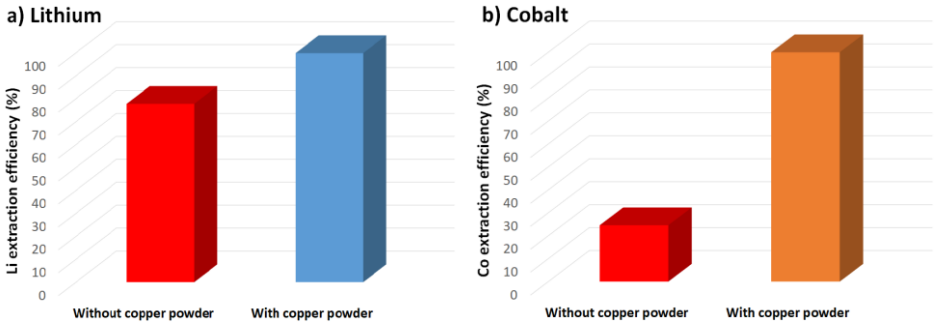

Figure 1 Effect of copper powder on Li and Co extraction

From Figures 1a and 1b, it can be seen that in the absence of copper powder, the degrees of Li and Co leaching were 77.73% and 24.58%, respectively. However, when the copper powder was added to H_3PO_4, the degree of Li leaching increased from 77.73% to 99.84%, while the degree of Co leaching increased from 24.58% to 99.99%. In this study, H_3PO_4 probably acted as a chelating agent, whereby Li and Co were extracted from the cathode material through a complexation process. The low level of Co extraction in the absence of copper powder is probably due to the fact that Co in $LiCoO_2$ is in the form of Co^{3+}, which is poorly soluble in an acidic medium, and for its dissolution, the presence of a reducing agent [9], i.e. copper powder, is necessary. Namely, in an acidic environment, Cu can be oxidized with oxygen from the air according to the following reaction [8]:

$$2\mathrm{Cu} + 4H^+ + O_2 \rightarrow 2\mathrm{Cu}^{2+} + 2H_2O \quad (1)$$

Taking into account the values for the electrode potentials of Cu of 0.34 V and $LiCoO_2$ of 2.13 V, it can be assumed that the dissolution of Cu in an acidic environment can also be a result of galvanic corrosion, where electrical contact between Cu and $LiCoO_2$ is necessary [6,8]. Since it is a complex system, for a more detailed analysis of the role of Cu powder in the process of extracting Li and Co from the cathode material, it is necessary to conduct additional experiments, which will be the subject of research in our next paper.

The influence of temperature on the degree of extraction of Li and Co

The influence of temperature on the degree of extraction of Li and Co was investigated in the range from 35°C to 80°C in a solution of 0.4 mol/dm^3 H_3PO_4 with the

addition of 0.2 g of copper powder, at a mixing speed of 600 rpm and duration of the process of 30 min. The test results are shown in Figure 2.

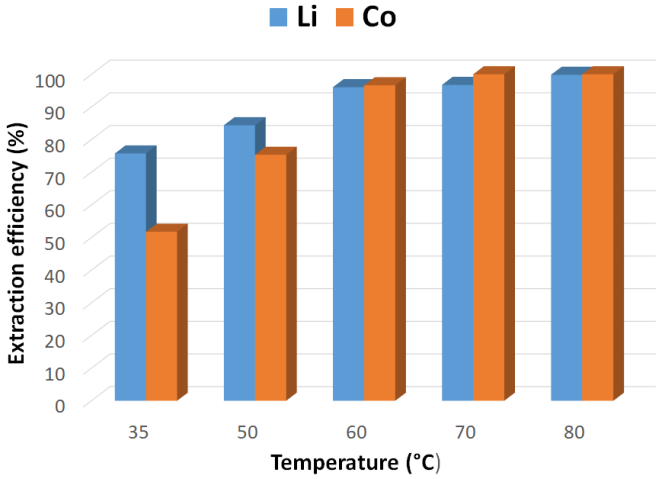

Figure 2 Effect of temperature on Li and Co extraction

From Figure 2 it can be seen that an increase in temperature leads to an increase in the degree of extraction of both tested metals. The maximum extraction values of Li and Co of 99.84% and 99.99%, respectively were achieved at a temperature of 80 °C. Similar results were obtained by Pinna *et al.* [10] when examining the effect of temperature on the degree of dissolution of $LiCoO_2$ in H_3PO_4 in the presence of H_2O_2 as a reducing agent.

The influence of time on the degree of extraction of Li and Co

The influence of time on the degree of extraction of Li and Co was investigated at a temperature of 80°C in a solution of 0.4 mol/dm^3 H_3PO_4 with the addition of 0.2 g of copper powder, at a mixing speed of 600 rpm (Figure 3).

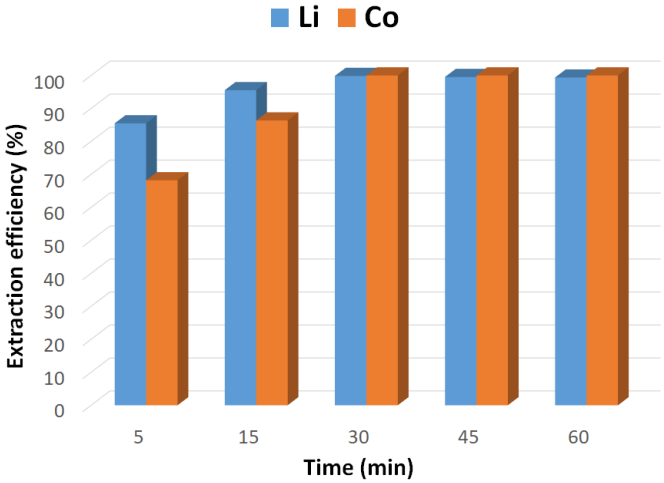

Figure 3 Effect of time on Li and Co extraction

The obtained results indicated that the degree of extraction of Li and Co increased with the increase in the duration of the leaching process, especially in the first 30 min. After 30 min, the degree of extraction of Li and Co reached a value of about 100%. For this reason, a time of 30 min can be considered the optimal time for the leaching process of the cathode material. The increase in the degree of metal extraction with an increase in the duration of the process can be related to the well-known fact that increasing the contact time between the solid and liquid phases increases the degree of dissolution of the solid phase [10].

CONCLUSION

Based on the conducted experiments, it can be concluded that copper powder is an effective reducing agent in the process of cathode material leaching in phosphoric acid. In the presence of copper powder, the degree of Li extraction increased from 77.73% to 99.84%, while the degree of Co extraction increased from 24.58% to 99.99%. The greater influence of copper powder on the Co extraction process was probably due to the fact that the Li extraction process does not require a reducing atmosphere. The obtained results were achieved at an optimal temperature of 80°C and a duration of the process of 30 min.

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