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# INFLUENCE OF pH VALUE OF LEACH SOLUTIONS ON EFFICIENCY OF ELECTROLYTIC DEPOSITION OF COBALT

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**ABSTRACT** – $LiCoO_2$ belongs to the first generation of cathode materials and is a component with the greatest potential for recycling. In order to recover cobalt from spent lithium-ion batteries, the cathode material was dissolved in sulfuric acid in an atmosphere of nitrogen and oxygen. As a result, a leach solution with a low pH value was obtained. In this paper, the influence of the initial pH value of leach solutions on the efficiency of electrolytic precipitation of cobalt was investigated. Recorded cyclic voltammogram indicated that the obtained leach solutions were not suitable for electrolytic precipitation of cobalt. However, 93% of cobalt was recovered by increasing the electrical conductivity and pH value of leach solutions.

**Keywords:** Lithium-ion batteries, Recycling, Leaching, Valorisation, Cobalt.

## INTRODUCTION

Cobalt is a ferromagnetic metal and, thanks to its magnetic properties, cobalt alloys are widely used [1]. About 70% of world cobalt production is based on the hydrometallurgical process, in which the last phase is the electrolytic deposition of cobalt. Sulfate solutions are most often used in the process of electrolytic deposition of cobalt [2,3].

In this paper, the influence of the initial pH value of leach solutions on the current efficiency during electrolytic deposition of cobalt was investigated. Leach solutions were obtained by dissolving $LiCoO_2$ from spent lithium-ion batteries in sulfuric acid in the presence of oxygen and nitrogen. In order to increase the quality of the obtained product, sodium sulfate and boric acid were added to the leach solution.

## EXPERIMENTAL

Electrolytic precipitation of cobalt was performed from a sulfuric acid solution. Due to the pronounced ferromagnetic properties of $LiCoO_2$, oxygen and nitrogen were used to mix the solution during the leaching of the cathode material. Leach solutions that were obtained after dissolution of the cathode material in sulfuric acid in an atmosphere of nitrogen and oxygen had almost identical composition. Because of that, these two solutions were mixed and further considered as one system (leaching system $H_2SO_4$ + $O_2$ + $N_2$). The initial pH of the leach solution was 0.9. In order to examine the possibility of

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[#] corresponding author: dmedic@tfbor.bg.ac.rs valorization of cobalt from solutions obtained after the process of leaching of the cathode material, a cyclic voltamogram was recorded. The cyclic voltamogram was recorded in the potential range of -1.0 - 0.4 V and at a potential change rate of 20 mV/s. In order to examine the efficiency of the cobalt deposition process, an apparatus for electrolytic metal deposition was assembled. Before starting the process of cobalt deposition, the copper plates were cleaned with abrasive papers, in order to remove the products of corrosion and other impurities. The samples were then degreased by immersion in 96% ethyl alcohol, washed with distilled water and dried at room temperature. After drying, the dimensions of the samples as well as their mass were measured. The copper cathode and the platinum anode were connected in an electrical circuit. During the process, the electric current was constantly controlled. After 60 minutes, the power supply was switched off, the cathode was washed with 96% ethyl alcohol and distilled water, air-dried and its mass was measured.

During the electrolytic deposition of cobalt, in addition to the basic process, secondary chemical and electrochemical processes took place, which lead to a decrease in the degree of current efficiency.

In order to calculate the current efficiency, defined by the ratio of the actual mass of metal extracted at the cathode to the theoretically possible one, the following equations were used:

$$\eta = \frac{m_s}{m_t} 100\ (\%) \tag{1}$$

$$m_t = \frac{I \cdot t \cdot k}{26.8}\ (g) \tag{2}$$

where is:

η - current efficiency (%);
$m_s$ - measured weight of the metal deposited on the cathode (g);
$m_t$ - theoretical weight of the metal deposited on the cathode (g);
I - electrical current that flows through the electrolyte (A);
t - time of the process (h);
k - electrochemical equivalent.

## RESULTS AND DISCUSSION

On the cyclic voltammogram shown in Fig. 1, it can be noticed that during the electrolytic precipitation of cobalt from the obtained solution, the following reactions took place [3,4,5]:

**On the cathode:**

$Co^{2+}_{(aq)} + 2e^- \rightarrow Co_{(s)}$ E° = - 0.227 V (3)
$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$ E° = 0.000 V (4)

**On the anode:**

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ E° = 1.229 V (5)

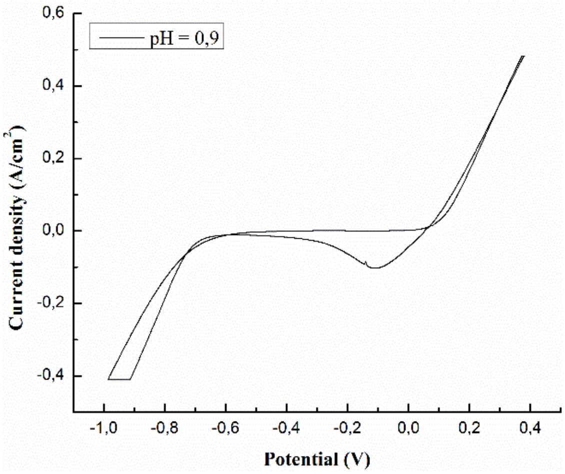

**Figure 1** Cyclic voltammogram of cobalt deposition from leaching system $H_2SO_4$+$N_2$+$O_2$

In the cathode part of the voltamogram, the cobalt reduction reaction is observed at a potential of -0.68 V. The shift of the cobalt separation potential to more negative values, as well as the sudden increase in the cathode current density is probably a consequence of the side reaction of hydrogen ion reduction [3,6]. In addition to the side reaction of hydrogen ion reduction, the reaction of water oxidation is also noticeable in the system during electrolytic precipitation of cobalt. The present side reactions during the electrolytic deposition of cobalt cause a decrease in the current efficiency and can lead to a change in the morphological and structural properties of the electrolysis product [7].

The cyclic voltamogram in Fig. 1 indicates that the leach solutions obtained under optimal conditions of dissolution of the cathode material in sulfuric acid (2 mol/dm$^3$ $H_2SO_4$, solid phase concentration 33 g/dm$^3$, gas volume flow 2 dm$^3$/min, temperature 85 °C and time 100 min) are not suitable for electrolytic precipitation of cobalt, and that for a higher degree of process efficiency it is necessary to increase the pH and electrical conductivity of the solution.

Table 1 shows the operating conditions for electrolytic precipitation of cobalt from solutions obtained under optimal conditions of leaching of cathode material in the tested leaching systems. Due to the low initial pH of the leach solutions, the pH of the solution was adjusted to 4.5 using saturated NaOH solution and concentrated sulfuric acid. In addition to the already present components in the bath for electrolytic precipitation of cobalt ($CoSO_4$ and $Li_2SO_4$), sodium sulfate and boric acid were added to the acid-sulfate bath. The introduction of sodium sulfate into the acid sulfate bath was necessary to ensure an increase in the electrical conductivity of the solution. The presence of boric acid should inhibit the formation of hydroxyl ions. Santos *et al.* [8] also reported about the phenomenon of adding boric acid to a leach solution and its buffering role in the process of electrolytic precipitation of cobalt.

The dependence of the current efficiency on the pH value of leach solutions and the time of cobalt deposition is shown in Fig. 2. The results of experimental studies given in Fig. 2 show that with increasing duration of the electrolysis process there is a sharp decrease in pH value of the solution. After 15 minutes from the beginning of the process of cobalt deposition on copper electrodes, the pH of the solution decreased to 2.89. The sharp drop in the initial pH value of the solution is probably a consequence of the mixing of the catholyte and anolyte solutions due to the absence of an ion-exchange membrane. Also, during the process of cobalt deposition, electrolyte depletion by cobalt ions occurs. If only reactions 3, 4 and 5 are present in the system for electrolytic precipitation of cobalt from leach solutions, then the decrease in the pH value of the solution is directly proportional to the amount of precipitated cobalt [3].

**Table 1** Operating conditions for electrolytic precipitation of cobalt from leach solutions

| **Leaching system $H_2SO_4 + O_2 + N_2$** | | | | | | |
|---|---|---|---|---|---|---|
| Cathode | Anode | Electrolyte composition (mol/dm$^3$) | Current density (A/m$^2$) | Temp. (°C) | pH value | Stirring rate (rpm) |
| Cu (plate) | Pt (spyral wire) | $CoSO_4$ (0.037)<br>$Li_2SO_4$ (0.068)<br>$Na_2SO_4$ (0.018)<br>$H_3BO_3$ (0.018) | 200 | 25 | 4.5 | 200 |

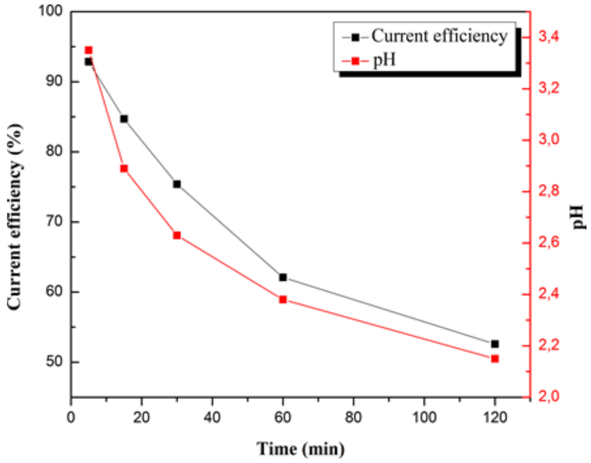

**Figure 2** Dependence of the current efficiency on the pH value of leach solutions and the duration of the process of electrolytic deposition of cobalt

During the experiments, it was noticed that after 5 minutes from the beginning of the process of electrolytic deposition of cobalt the solution becomes turbid throughout the volume, and that along with the reaction of cobalt separation on the copper electrode, the platinum anode is coated with a black coating.

SEM microphotography of electrochemically precipitated cobalt is shown in Fig. 3. The presented cauliflower-shaped agglomerates are formed under the conditions of the secondary reaction of hydrogen ion reduction [9], which is also characteristic for the process of electrolytic deposition of cobalt. The results of SEM and EDS analysis of the electrodeposited layer of the product on the platinum electrode are shown in Fig. 4.

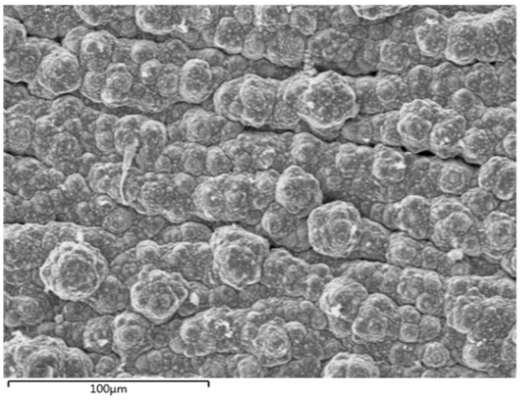

**Figure 3** Morphology of cobalt particles obtained in the process of electrochemical precipitation from leach solutions in the presence of boric acid (magnification 500 times)

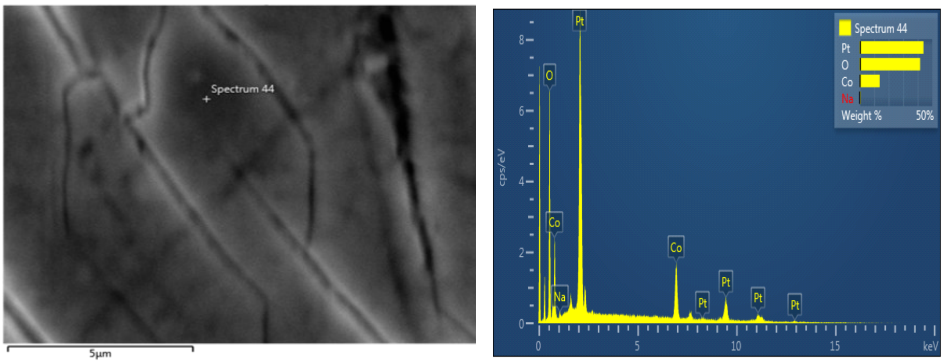

**Figure 4** SEM and EDS analysis of the electrodeposited layer of the product on the platinum electrode

The results of SEM and EDS analysis indicated that during the electrolytic deposition of cobalt at the copper cathode, the formation of cobalt oxide at the platinum anode probably also occurred. EDS analysis revealed the presence of a small amount of sodium, which probably originated from the sodium hydroxide used to adjust the pH of the leach solutions. The presence of platinum indicates that a very thin layer of product has formed, which does not cover the entire surface of the platinum electrode.

## CONCLUSION

Based on the presented results of experimental research, it can be concluded that leach solutions with a pH value of 0.9 are not suitable for electrolytic precipitation of cobalt. Also, the obtained results indicate that with the increase of the duration of the electrolysis process, there is a sharp decrease in the pH value of the solution. To achieve a high degree of process efficiency, it is necessary to maintain the pH value of the solution above 3, which can be achieved by using an ion-exchange membrane between the cathode and anode space, as well as by providing an additional source of cobalt ions.

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