

# Cobalt recovery from spent lithium-ion batteries by leaching in H<sub>2</sub>SO<sub>4</sub>-N<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>-O<sub>2</sub> systems followed by electrochemical deposition

Dragana V. Medić<sup>1</sup>, Žaklina Z. Tasić<sup>1</sup>, Maja M. Nujkić<sup>1</sup>, Silvana B. Dimitrijević<sup>2</sup>, Stefan S. Đorđević<sup>2</sup>, Slađana Č. Alagić<sup>1</sup> and Snežana M. Milić<sup>1</sup>

<sup>1</sup>University of Belgrade, Technical Faculty in Bor, Bor, Serbia

<sup>2</sup>Mining and Metallurgy Institute, Bor, Serbia

## Abstract

This paper is focused on cobalt valorization from the cathode material of spent lithium-ion batteries (LIBs) by using leaching and electrochemical deposition methods. During the leaching experiments, the degrees of cathode material dissolution in H<sub>2</sub>SO<sub>4</sub>-N<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>-O<sub>2</sub> systems were compared. Maximal degrees of cobalt extraction were 40 % in the former and 47 % in the latter system under following experimental conditions: H<sub>2</sub>SO<sub>4</sub> concentration of 2 mol dm<sup>-3</sup>, nitrogen/oxygen volumetric flow of 2 L min<sup>-1</sup>, solid phase concentration of 33 g L<sup>-1</sup>, and temperature of 85 °C. The rate of cobalt extraction from the cathode material in both investigated systems was the most favorable in the first 15 min, after which there was a sudden decrease in the reaction rate. Cobalt from the leaching solution was deposited on a copper substrate by galvanostatic electrochemical deposition with a current efficiency of 84 %. The energy consumption was 5.8 kWh kg<sup>-1</sup> of deposited Co. The cyclic voltammetry (CV) method was used to determine the potential of cobalt deposition, as well as side reactions taking place in the system. Scanning electron microscopy with energy dispersive spectrometry has shown that during the process of electrochemical deposition agglomeration of cobalt particles occurred (in the shape of cauliflower), while the metal was deposited in its elemental state, which was also confirmed by the results of X-ray diffraction analysis.

**Keywords:** Cathode material; acid leaching; lithium-cobalt oxide; recycling; metal coating.

Available on-line at the Journal web address: <http://www.ache.org.rs/HI/>

ORIGINAL SCIENTIFIC PAPER

UDC: (669.884+621.352):669.253

Hem. Ind. 00(0) 000-000 (2023)

## 1. INTRODUCTION

Valorization of metals from spent lithium-ion batteries (LIBs) can be performed by employing the following methods: pyrometallurgical, biometallurgical and hydrometallurgical [1-3]. Among these processes, the hydrometallurgical method is most frequently used in treating spent LIBs due to low electricity consumption, low emission of pollutants, as well as high process efficiency [4]. This process can be divided into several operations such as: discharging LIBs, their disassembling into individual components, separation of the cathode material from the current collector (aluminum), leaching of the cathode material and valorization of the metal from the leach solution. The latter process is most commonly performed by the use of one of the following methods: chemical deposition, extraction with organic solvents and electrochemical deposition [5,6]. The first method is not economically viable due to low yields of the deposited metals (< 50 %) [6]. The solvent extraction method is, on the other hand, economically viable and applicable in industrial conditions, but has a number of disadvantages such as: high solvent consumption, fire hazard caused by the solvent low flash point, environmental issues associated with the volatility of the solvents and possibility of their entering the environment. Unlike these methods, the electrochemical deposition method is acceptable from the environmental standpoint and easy to implement and control [7]. During the last three decades, 70 % of the world cobalt production has been based on the hydrometallurgical process, where the electrochemical deposition method is used as the final step in cobalt valorization [8]. This method enables production of cobalt coatings, as well as cobalt alloy coatings, with a precise control of the structure and morphology of the final product [9]. Electrochemically deposited cobalt is widely used in industry due to its favorable magnetic and electrical properties [10]. In a large number of studies *e.g.* [8,11,12],

Corresponding authors: Dragana V. Medić, University of Belgrade, Technical Faculty in Bor, Vojske Jugoslavije 12, 19210 Bor, Serbia

Paper received: 21 May 2023; Paper accepted: 23 October 2023; Paper published: 16 November 2023.

<https://doi.org/10.2298/HEMIND230521027M>



electrochemical deposition of cobalt is carried out from sulfate solutions to which boric acid is added, which acts as a Lewis acid ( $pK_a = 9.237$ ), in order to control the micro and nanostructure of the deposited cobalt [11]. Still, the role of boric acid in the process of electrochemical reduction of cobalt ions has not been fully elucidated yet [13-14], but many authors [15-17] consider boric acid acting as a buffer preventing formation of  $\text{OH}^-$  ions in the immediate vicinity of the electrode surface.

In the present study, hydrometallurgical treatment was applied for cobalt extraction from spent LIBs followed by electrochemical deposition to obtain cobalt coating on a copper substrate. Due to ferromagnetic properties of cobalt, it was not suitable to use a classical leaching apparatus, in which a magnet is used for the purpose of stirring the leach solution. Also, due to high cobalt concentrations in the leach solutions it is more suitable to use ultraviolet-visible spectrophotometry (UV-VIS) for monitoring the cobalt extraction degree compared to the inductively coupled plasma optical emission spectroscopy (ICP-OES), which is a predominantly used method in this type of investigation. For this reason in this leaching study, a new apparatus was designed and placed in an UV-VIS spectrophotometer to carry out the experiments. The newly created apparatus enabled continuous monitoring of the change of cobalt concentration in leach solutions, where nitrogen and oxygen were used for the purpose of stirring the solution.

Cyclic voltammetry (CV) was used for investigation of electrochemical processes taking place on the electrodes, whereas structural characterization of electrochemically deposited cobalt was performed by employing scanning electron microscopy with energy dispersive spectrometry (SEM-EDS) and X-ray diffraction analysis (XRD).

## 2. EXPERIMENTAL

### 2. 1. Materials and reagents

Spent LIBs with cathodes composed of lithium-cobalt oxide ( $\text{LiCoO}_2$ ) were disassembled from laptops and used for the purpose of this research. Sulfuric acid (Merck, Darmstadt, Germany) was used as a leaching agent, whereas nitrogen and oxygen of purity 99.999 vol.% (Messer Tehnogas AD, Belgrade, Serbia) were used for stirring the leach solutions and providing an inert, that is, oxidizing atmosphere. In the process of electrolytic deposition of cobalt, the pH value of the leach solution was regulated with a saturated solution of sodium hydroxide (Merck, Darmstadt) and concentrated sulfuric acid (Merck, Darmstadt, Germany). The pH value of the solution was maintained by using boric acid (Zorka Pharma, Šabac) as a buffer. All chemical reagents were of *p.a.* quality.

### 2. 2. Experimental procedure

#### 2. 2. 1. Preparation of the cathode material and chemical analysis

Used sets of LIBs were manually disassembled into separate cells. After discharging the LIB cells, they were disassembled into their basic components: the cathode, anode, and the separator. The cathode material was separated from the aluminum foil in a two-stage thermal treatment at 580 and 630 °C. The resulting cathode material was dried at room temperature for 24 h followed by crushing in an agate mortar with a pestle. A detailed explanation of each step in the pretreatment of LIBs was described previously [18].

To prepare a sample for chemical analysis, microwave digestion of the cathode material was performed by using a mixture of nitric and hydrochloric acid ((1:3 v/v) Merck, Darmstadt, Germany). The total metal content in the cathode material was determined by using inductively coupled plasma/optical emission spectrometer (ICP/OES Optima 8300; Perkin Elmer, USA).

#### 2. 2. 2. Leaching tests

The leaching procedure included the following steps: 60 mL of sulfuric acid of a predefined concentration was poured into the reaction vessel and thermostated to the desired temperature (except for the experiments carried out at room temperature) with nitrogen or oxygen being blown at a constant flow of  $2 \text{ L min}^{-1}$ . Upon reaching the desired temperature, a previously measured mass of the cathode material was added. Absorption spectra were read every 3 min by using an UV-VIS spectrophotometer (UV-VIS, Beckman DU-65) with stirring being stopped 10 s prior to each

reading. The UV-VIS cuvette was directly connected to the reaction vessel, which was equipped with a thermistor, polytetrafluoroethylene (PTFE) gas introduction hose, and a heater. A detailed description and the scheme of the apparatus are reported previously [19].

### 2. 2. 3. Electrowinning and polarization

Electrolytic deposition of cobalt was carried out from a solution containing sulfuric acid. Due to almost identical chemical composition of the solutions obtained after cathode material dissolution in the  $\text{H}_2\text{SO}_4\text{-N}_2$  and  $\text{H}_2\text{SO}_4\text{-O}_2$  systems, these two solutions were mixed and thereafter considered as one system.

Due to a low initial pH value of the leach solution obtained under the optimal conditions of leaching the cathode material, the pH value of the leach solution was adjusted to 4.5 using saturated sodium hydroxide solution and concentrated sulfuric acid. To prevent the pH value in the cathode area from changing, boric acid was added to the solution, whose presence should inhibit the formation of hydroxyl-ions.

Cobalt electrochemical deposition was carried out galvanostatically at room temperature and at a current density of  $200 \text{ A m}^{-2}$  for 15 min. Copper sheet and platinum wire were used as cathode and anode, respectively. A constant current was obtained from a regulated power supply system (0 to 15 V, 10 A, DC, Veb Mlw Labortechnik Ilmenau, Germany). The difference in the cathode mass after and before the process of electrolysis was used to calculate the current efficiency.

Cyclic voltammogram was recorded on the IVIUM Xre potentiostat, IVIUM Technologies, (Netherlands), with the accompanying software. The measurements were performed in a three-electrode electrochemical system, with the copper electrode being used as a working electrode. The saturated calomel electrode (SCE) was used as a reference electrode, whereas a platinum wire was used as an auxiliary electrode. Prior to each experiment, surface of the copper electrode was polished with abrasive papers (1200, 2400 and 4000). Subsequent to polishing, the surface of the working electrode was rinsed with water and dried. Cyclic voltammogram was recorded in a potential range of -1.0 - 0.4 V and at a potential change rate of  $20 \text{ mV s}^{-1}$ .

### 2. 2. 4. Structural characterization

The crystal structure of the cathode deposit was investigated using an X-ray diffractometer (XRD Rigaku MiniFlex 600, Japan) equipped with a Cu X-ray source (40 kV and 15 mA operation for X-ray generation). The surface morphology of the deposit was investigated using a scanning electron microscope (SEM, model: JOEL JSM-IT300LV, Japan) operated at 20 keV. Energy-dispersive X-ray spectroscopy (EDS) was utilized to determine the chemical composition of the sample. The X-ray spectrometer was connected to the scanning electron microscope, whereas the recording was performed using the Aztec software (Oxford Instruments, United Kingdom).

## 3. RESULTS AND DISCUSSION

### 3. 1. Chemical composition of the cathode material

The results of the ICP-OES analysis of the cathode material indicated the presence of cobalt (49.81 %), lithium (5.98 %), and aluminum (0.01 %). The presence and low percentage of aluminum in the cathode material might be the result of thermal separation of the cathode material from the aluminum foil [19].

### 3. 2. Leaching of the cathode material in $\text{H}_2\text{SO}_4\text{-N}_2$ and $\text{H}_2\text{SO}_4\text{-O}_2$ leaching systems

#### 3. 2. 1. The effect of $\text{H}_2\text{SO}_4$ concentration

The effect of the initial  $\text{H}_2\text{SO}_4$  concentration (0.5 to  $3.0 \text{ mol L}^{-1}$ ) on the degree of cobalt extraction from the cathode material of spent LIBs was investigated under the following conditions: the temperature of the leach solution of  $35 \text{ }^\circ\text{C}$ , solid phase concentration of  $33 \text{ g L}^{-1}$ , a nitrogen/oxygen volumetric flow of  $2 \text{ L min}^{-1}$ , and leaching time of 100 min. Results of the investigation with the given parameters are shown in Figure 1.

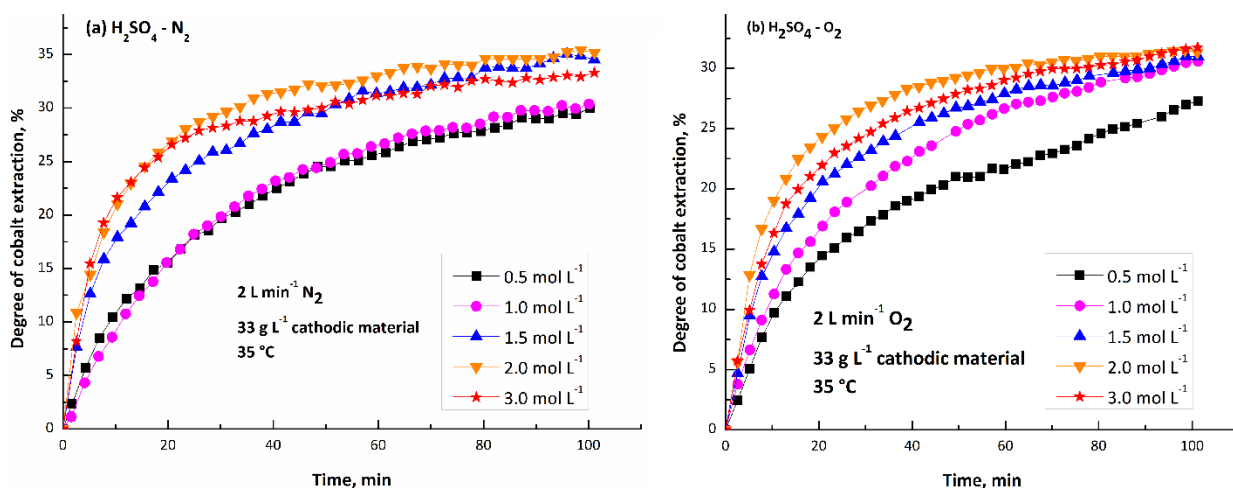


Figure 1. Effects of  $H_2SO_4$  concentration on the degree of cobalt extraction: (a) in the system  $H_2SO_4-N_2$ , (b) in the system  $H_2SO_4-O_2$

The obtained results (Fig. 1) show that the cobalt extraction degree increases with the increasing sulfuric acid concentration from 0.5 mol L<sup>-1</sup> to 2.0 mol L<sup>-1</sup>. However, a further increase in the sulfuric acid concentration to 3 mol L<sup>-1</sup> leads to a decrease in the extraction degree in both investigated leaching systems. In a previous study [20], the authors stated that an increase in sulfuric acid concentration (from 2.0 mol L<sup>-1</sup> to 4.0 mol L<sup>-1</sup>) had a negligible effect on the cobalt extraction degree, while in another study [21] it was pointed out that a higher extraction degree is achieved when using 3 mol L<sup>-1</sup> sulfuric acid compared to a lower concentration of 2 mol L<sup>-1</sup>, but only in the first 20 min of the cathode material leaching. The latter result is in accordance with the results obtained in the present study for the H<sub>2</sub>SO<sub>4</sub>-N<sub>2</sub> leaching system (Fig. 1a). Considering that in the investigated sulfuric acid concentration range, the cobalt extraction degree ranged from 30-35 % for the H<sub>2</sub>SO<sub>4</sub>-N<sub>2</sub> system and 27-31 % for the H<sub>2</sub>SO<sub>4</sub>-O<sub>2</sub> system, it can be concluded that in both investigated systems the initial sulfuric acid concentration had a minor effect on the cobalt extraction degree, particularly when higher acid concentrations are used. Further analyses were performed with using 2 mol L<sup>-1</sup> sulfuric acid for both investigated systems, which was considered as the optimal acid concentration during the leaching process.

### 3. 2. 2. The effect of solid phase concentration

To determine the effect of solid phase concentration on the cobalt extraction degree, a series of experiments was conducted at a solid phase concentration ranging from 10 to 67 g L<sup>-1</sup>, sulfuric acid concentration of 2 mol L<sup>-1</sup>, temperature of 35 °C, nitrogen/oxygen volumetric flow of 2 L min<sup>-1</sup>, and leaching time of 100 min and the results are presented in Figure 2.

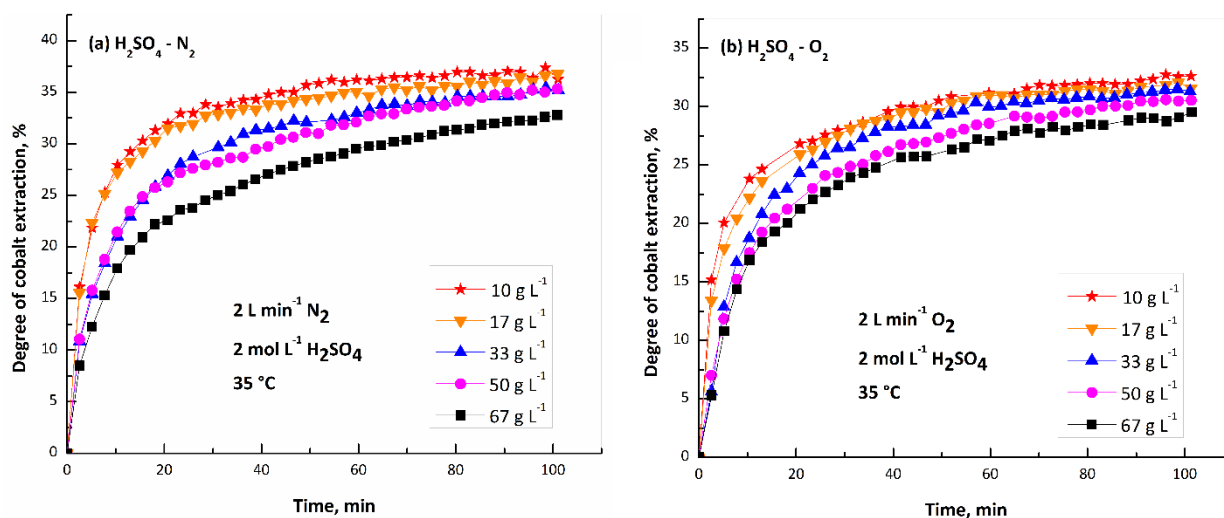


Figure 2. The effect of solid phase concentration on the degree of cobalt extraction: (a) in the system  $H_2SO_4-N_2$ , (b) in the system  $H_2SO_4-O_2$

Based on the obtained results, it can be concluded that the cobalt extraction degree in both investigated systems decreases with increasing the solid phase concentration. The highest degrees of cobalt leaching amounting to 36 % for the  $\text{H}_2\text{SO}_4\text{-N}_2$  system and 32 % for the  $\text{H}_2\text{SO}_4\text{-O}_2$  system were recorded at a solid phase concentration of  $10 \text{ g L}^{-1}$ . A decrease in the cobalt leaching degree with increasing the solid phase concentration was probably caused by thickening of the suspension, which led to the increase in mass transfer resistance. Also, the increase in the solid-liquid phase ratio requires additional consumption of the leaching agent [22]. However, leaching of the cathode material in sulfuric acid at a low solid-liquid phase ratio is not economically justified [23]. Therefore, a solid phase concentration of  $33 \text{ g L}^{-1}$  in both investigated systems can be considered the optimal value and was used in further experimental research.

### 3. 2. 3. The effect of temperature and leaching time

The effect of temperature and leaching time on the degree of cobalt extraction in the presence of nitrogen and oxygen was investigated in the temperature range of  $35\text{-}85 \text{ }^\circ\text{C}$  and in the time interval of  $0\text{-}100 \text{ min}$ , at a sulfuric acid concentration of  $2 \text{ mol L}^{-1}$ , solid phase concentration of  $33 \text{ g L}^{-1}$ , and nitrogen/oxygen volumetric flow of  $2 \text{ L min}^{-1}$ . The experimental results shown in Figure 3 indicate that the cobalt extraction degree increases with increasing both temperature and leaching time for both investigated leaching systems.

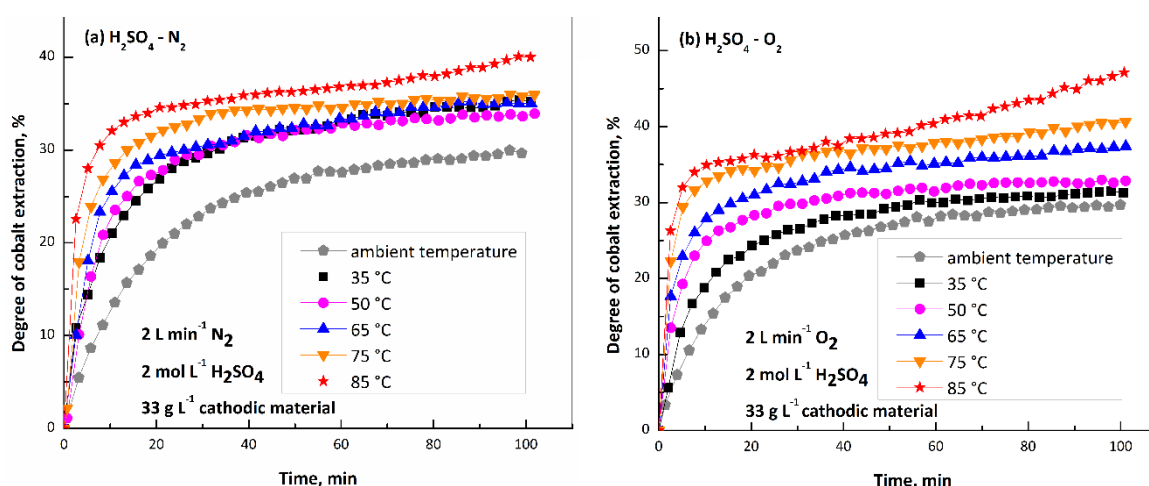


Figure 3. The effect of temperature and leaching time on the degree of cobalt extraction: (a) in the system  $\text{H}_2\text{SO}_4\text{-N}_2$ , (b) in the system  $\text{H}_2\text{SO}_4\text{-O}_2$

The maximum cobalt extraction degrees of 40 % in the  $\text{H}_2\text{SO}_4\text{-N}_2$  leaching system and 47 % in the  $\text{H}_2\text{SO}_4\text{-O}_2$  system were achieved at the temperature of  $85 \text{ }^\circ\text{C}$  and for the leaching time of 100 min. The shape of the obtained experimental curves shown in Figure 3 indicated that the rate of cobalt extraction from the cathode material in both investigated systems is most favorable in the first 15 min, after which there is a sudden decrease in the extraction rate. However, at a temperature of  $85 \text{ }^\circ\text{C}$ , after 60 min from the start of the leaching process, an increase in the cobalt leaching degree can be observed. The cathode material leaching is an endothermic reaction that is favored at high temperatures [24]. A sudden decrease in the leaching reaction rate in the investigated systems indicates the possibility of the formation of leaching products, which slow down diffusion of the leaching agents to the cathode material surface.

Considering all obtained experimental results, it can be concluded that among the investigated parameters, temperature and leaching time have the greatest effect on the process of cathode material leaching in the presence of nitrogen and oxygen. Furthermore, the shapes of the kinetic curves of the cathode material leaching (Fig. 1 and Fig. 2) indicate that the acid concentration, as well as the solid phase concentration slightly affect cobalt extraction in both investigated leaching systems. The observed similar cobalt extraction behavior in  $\text{H}_2\text{SO}_4\text{-N}_2$  and  $\text{H}_2\text{SO}_4\text{-O}_2$  systems is probably the result of the poor solubility of oxygen in the leaching solution [25]. The experimental data obtained in the present leaching study indicated that neither the oxidizing oxygen atmosphere nor the inert nitrogen atmosphere provided conditions for a satisfactory cobalt extraction degree. Achieving a high degree of cobalt extraction from the cathode material requires a reducing atmosphere which may favor the reduction of  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  [26].

### 3. 3. Electrowinning and polarization

The electrowinning test resulted in a cobalt coating obtained with a current efficiency of 84 % and energy consumption of 5.8 kWh kg<sup>-1</sup>. During the experiments, it was observed that only 5 min after the start of electrolytic cobalt deposition, cloudiness of the solution occurred throughout its entire volume as well as formation of a black coating on the platinum anode. These observations are shown in Figure 4.

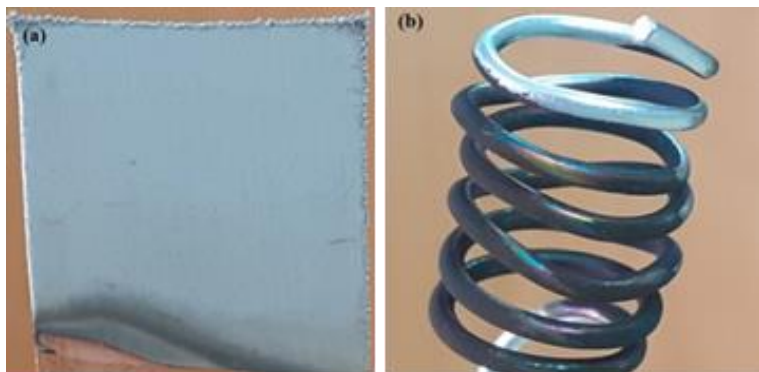


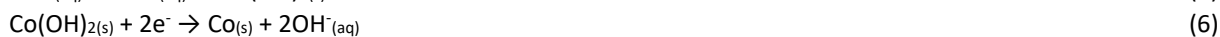
Figure 4. Appearance of the cathode (a) and the anode (b) after electrolytic deposition of cobalt from the leach solution

The layer formed on the platinum electrode probably represents cobalt oxide occurring because of Co<sup>2+</sup> oxidation on the anode.

In a literature study [9] it was assumed that at pH values of the solution below 4, cobalt reduction is accompanied with simultaneous hydrogen evolution. During the process of electrolytic deposition of cobalt, H<sup>+</sup> ions are adsorbed on the surface of the deposited cobalt according to the following reactions:



At a solution pH above 4, it was assumed that cobalt electrolysis proceeds with the formation of Co(OH)<sub>2</sub> according to the following reactions [9]:



The polarization behavior of the cathode during cobalt electrochemical deposition from a solution obtained by mixing two leaching solutions H<sub>2</sub>SO<sub>4</sub>-N<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>-O<sub>2</sub> at pH 4.5 is shown in Figure 5.

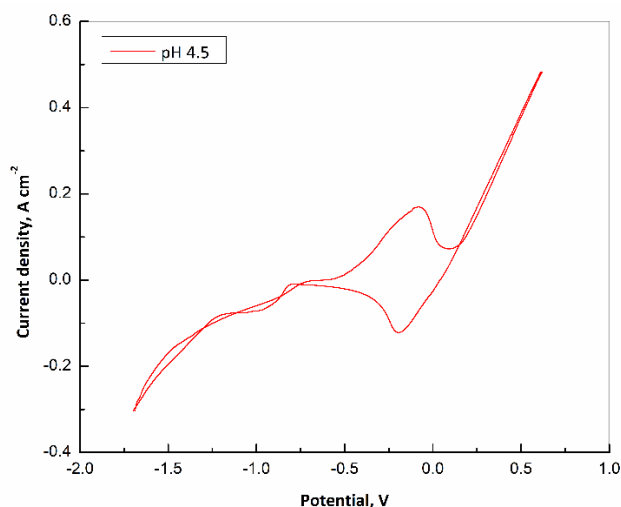


Figure 5. Polarization behavior of the cathode during cobalt electrochemical deposition from the leaching solution obtained in H<sub>2</sub>SO<sub>4</sub>-N<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>-O<sub>2</sub> systems

According to the Nernst equation, the deposition potential for cobalt is  $-0.51$  V. Cyclic voltammogram shown in Figure 5 indicates a shift of the cobalt extraction potential to a more negative region. More specifically, in the presence of boric acid, the process of  $\text{Co}^{2+}$  reduction starts at a potential of  $-0.81$  V, which could be the result of boric acid adsorption on the electrode surface. Boric acid probably acts as a surfactant, inhibiting direct cobalt ion reduction and resulting in an increase in the cathode potential of cobalt deposition [11]. Similar observations were reported in literature [27] during an investigation of the effect of boric acid in the process of electrolytic deposition of nickel. In the anodic part of the voltammogram at  $-0.07$  V a peak can be observed, which may be a consequence of cobalt oxidation [28], while in the cathodic part of the voltammogram at  $-0.19$  V there is a peak that can be attributed to the reduction of the passive film. Within the given potential range, lithium ions do not affect the process of electrochemical deposition of cobalt since the cathode potential for lithium deposition is  $-3.02$  V. Similar observations were reported in literature [9].

### 3. 4. Structural characterization

Morphology of electrochemically deposited cobalt from the leach solution at an initial pH value of 4.5 is shown in Figure 6. The SEM microphotographs indicate that agglomeration of cobalt particles occurred in the form of cauliflower (Fig. 6a), which can be seen more clearly at a higher magnification (Fig. 6b).

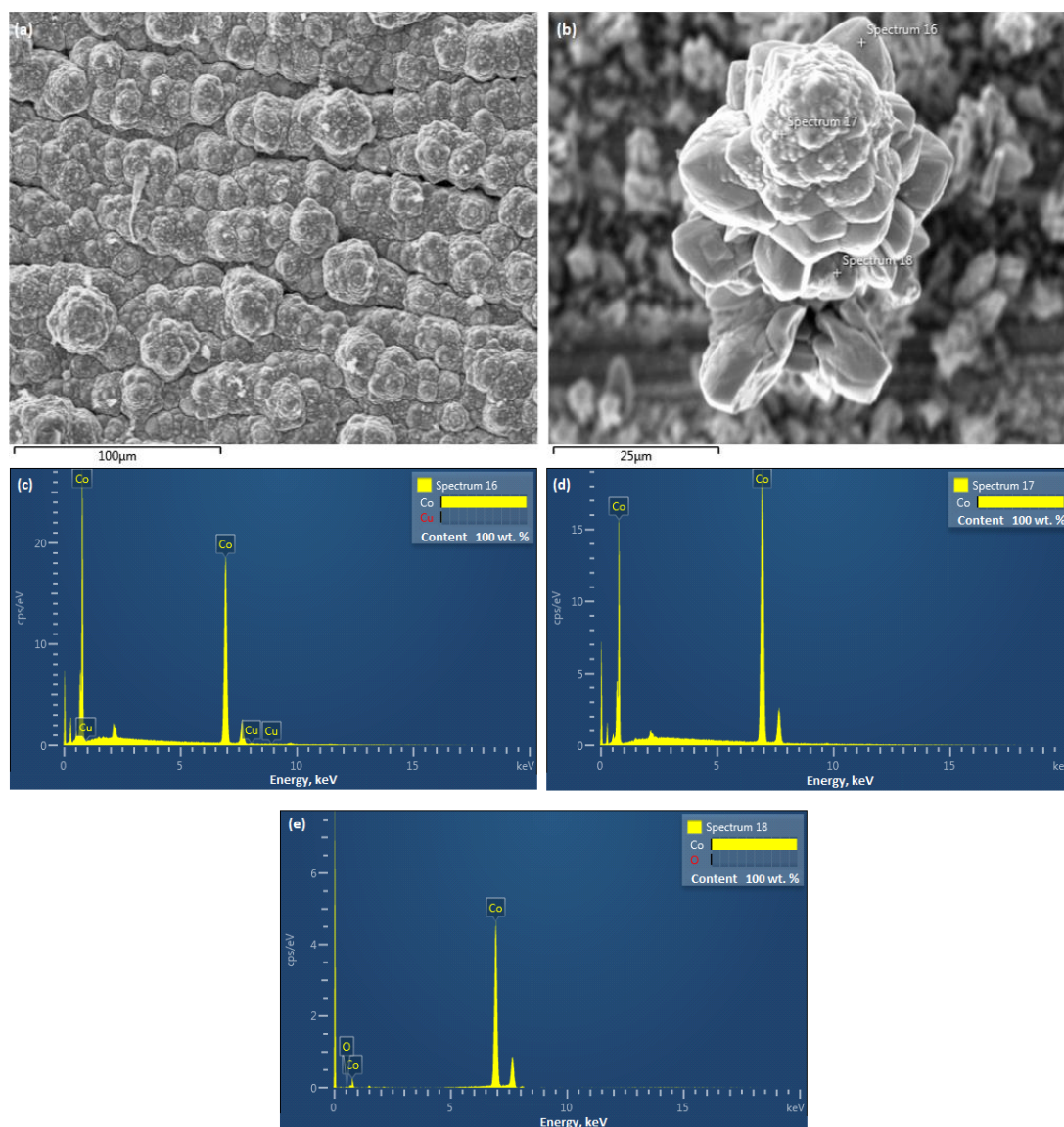


Figure 6. SEM micrographs (a: scale bar =  $100 \mu\text{m}$ ; b: scale bar =  $25 \mu\text{m}$ ) and EDS analyses results (c,d,e) of cobalt deposits obtained by electrochemical deposition from the leaching solution obtained in  $\text{H}_2\text{SO}_4\text{-N}_2$  and  $\text{H}_2\text{SO}_4\text{-O}_2$  systems

The presented agglomerates of a cauliflower shape, were formed under conditions of a side reaction of hydrogen ion reduction [29], which is characteristic of electrolytic deposition of cobalt. The energy spectra recorded at three different positions of the formed aggregates indicate a dominant presence of cobalt, whereas oxygen recorded in spectrum 18 is present in a small amount. A low copper content is observed in spectrum 16, which can be interpreted as the result of using a copper electrode as the cathode in the course of electrolytic deposition of cobalt from the leach solution.

Cobalt is deposited in its elemental state, which is confirmed by the XRD analysis (Fig. 7).

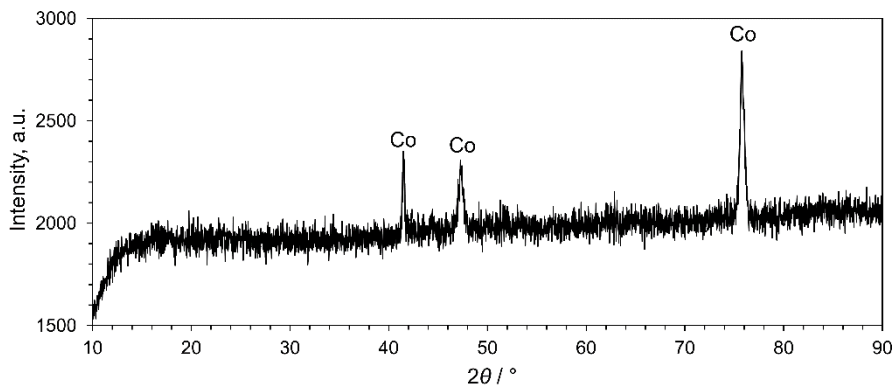


Figure 7. Diffractogram of cobalt particles obtained in the process of electrochemical deposition of cobalt from the leaching solution obtained in  $H_2SO_4-N_2$  and  $H_2SO_4-O_2$  systems

The recorded diffractogram of cobalt particles obtained in the process of electrochemical deposition confirms the assumption reported in literature [15-17] that boric acid acts as a buffer in the investigated system, preventing formation of  $OH^-$  ions, which enables deposition of elemental cobalt on a copper cathode.

#### 4. CONCLUSION

The treatment of spent LIBs presented in this study enabled valorization of cobalt in the form of a metal coating on a copper substrate. The apparatus constructed for leaching the cathode material proved to be an effective solution for continuous monitoring of the changes in cobalt concentration in the leach solutions. The similar appearance of the leaching curves in the  $H_2SO_4-N_2$  and  $H_2SO_4-O_2$  systems is probably the result of poor solubility of oxygen in the leach solution. The presented results of electrochemical deposition indicate that boric acid has a dual role in the process of cobalt electrochemical deposition. In specific, boric acid in the leach solution acts as a buffer, preventing formation of  $OH^-$  ions and simultaneously affecting the morphology of deposited cobalt. Future research should be focused on increasing the efficiency of the process by introducing a reducing agent (*e.g.* copper powder, hydrogen peroxide, sulfur dioxide) into the leaching system. Also, processes for obtaining metallic cobalt coatings on different metal substrates should be developed and optimized.

**Acknowledgements:** *The research presented in this paper was performed with the financial support of the Ministry of Science, Technological Development, and Innovation of the Republic of Serbia, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor, according to the contract number 451-03-47/2023-01/ 200131, and within the funding of the scientific research work at the Mining and Metallurgy Institute Bor, according to the contract number 451-03-47/2023-01/ 200052.*

#### REFERENCES

- [1] Guo Y, Zhao YL, Lou X, Zhou T, Wang Z, Fang C, Guan J, Chen S, Xu X, Zhang RQ. Efficient degradation of industrial pollutants with sulfur (IV) mediated by  $LiCoO_2$  cathode powders of spent lithium ion batteries: A “treating waste with waste” strategy. *J Hazard Mater.* 2020; 399: 123090. <https://doi.org/10.1016/j.jhazmat.2020.123090>
- [2] Chen X, Ma H, Luo C, Zhou T. Recovery of valuable metals from waste cathode materials of spent lithium-ion batteries using mild phosphoric acid. *J Hazard Mater.* 2017; 326: 77–86. <https://doi.org/10.1016/j.jhazmat.2016.12.021>



- [3] Wang MM, Zhang CC, Zhang FS. Recycling of spent lithium-ion battery with polyvinyl chloride by mechano chemical process. *Waste Manage.* 2017; 67: 232–239. <https://doi.org/10.1016/j.wasman.2017.05.013>
- [4] Meng Q, Zhang Y, Dong P, Liang F. A novel process for leaching of metals from  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  material of spent lithium ion batteries: Process optimization and kinetics aspects. *J Ind Eng Chem.* 2018; 61: 133–141. <https://doi.org/10.1016/j.jiec.2017.12.010>
- [5] Yang Y, Sun W, Bu Y, Zhang C, Song S, Hu Y. Recovering metal values from spent lithium ion battery via a combination of reduction thermal treatment and facile acid leaching. *ACS Sustain Chem Eng.* 2018; 6: 10445–10453. <https://doi.org/10.1021/acssuschemeng.8b01805>
- [6] Othman EA, Van der Ham AGJ, Miedema H, Kersten SRA. Recovery of metals from spent lithium-ion batteries using ionic liquid [ $\text{P}_{8888}$ ][Oleate]. *Sep Purif Technol.* 2020; 252: 117435. <https://doi.org/10.1016/j.seppur.2020.117435>
- [7] Prabakaran G, Barik SP, Kumar N, Kumar L. Electrochemical process for electrode material of spent lithium ion batteries. *Waste Manage.* 2017; 68: 527–533. <https://doi.org/10.1016/j.wasman.2017.07.007>
- [8] Patnaik P, Padhy SK, Tripathy BC, Bhattacharya IN, Paramguru RK. Electrodeposition of cobalt from aqueous sulfate solutions in the presence of tetra ethyl ammonium bromide. *Trans Nonferrous Met Soc of China* 2015; 25: 2047–2053. [https://doi.org/10.1016/S1003-6326\(15\)63814-6](https://doi.org/10.1016/S1003-6326(15)63814-6)
- [9] Garcia EM, Santos JS, Pereira EC, Freitas MJB. Electrodeposition of cobalt from spent Li-ion battery cathodes by the electrochemistry quartz crystal microbalance technique. *J Power Sources* 2008; 185: 549–553. <https://doi.org/10.1016/j.jpowsour.2008.07.011>
- [10] Bhuiyan MS, Taylor BJ, Paranthaman M, Thompson JR, Sinclair JW. Microstructure and magnetic properties of electrodeposited cobalt films. *J Mater Sci.* 2008; 43: 1644–1649. <https://doi.org/10.1007/s10853-007-2383-2>
- [11] Rafsanjani-Abbasi A, Rahimi E, Shalchian H, Vahdati-Khaki J, Babakhani A, Hosseinpour S, Davoodi A. Recycled Cobalt from Spent Li-ion Batteries as a Superhydrophobic Coating for Corrosion Protection of Plain Carbon Steel. *Materials* 2018; 12: 90. <https://doi.org/10.3390/ma12010090>
- [12] Rigsby MA, Spurlin TA, Reid JD. The Multi-Functional Role of Boric Acid in Cobalt Electrodeposition and Superfill. *J Electrochem Soc.* 2020; 167: 112507. <https://doi.org/10.1149/1945-7111/aba640>
- [13] Santos JS, Trivinho-Strixino F, Pereira EC. Investigation of  $\text{Co}(\text{OH})_2$  formation during cobalt electrodeposition using a chemometric procedure. *Surf Coat Technol.* 2010; 205: 2585–2589. <https://doi.org/10.1016/j.surfcoat.2010.10.005>
- [14] Zhou J, Wang SF, Song XS. Electrodeposition of cobalt in double-membrane three-compartment electrolytic reactor. *Trans Nonferrous Met Soc of China* 2016; 26: 1706–1713. [https://doi.org/10.1016/S1003-6326\(16\)64279-6](https://doi.org/10.1016/S1003-6326(16)64279-6)
- [15] Zech N, Landolt D. The influence of boric acid and sulfate ions on the hydrogen formation in Ni-Fe plating electrolytes. *Electrochim Acta* 2000; 45: 3461–3471. [https://doi.org/10.1016/S0013-4686\(00\)00415-1](https://doi.org/10.1016/S0013-4686(00)00415-1)
- [16] Ho HY, Chen WB, Fu TY, Chen SJ. On the Electrodepositing of Cobalt Nanoparticles on ITO in the Presence of Boric Acid. *IEEE Trans Magn.* 2014; 50: 2100304. <https://doi.org/10.1109/TMAG.2013.2277758>
- [17] Altamari P, Schiavi PG, Rubino A, Pagnanelli F. Electrodeposition of cobalt nanoparticles: An analysis of the mechanisms behind the deviation from three-dimensional diffusion-control. *J Electroanal Chem.* 2019; 851: 113413. <https://doi.org/10.1016/j.jelechem.2019.113413>
- [18] Medić D, Milić S, Alagić S, Đorđević I, Dimitrijević S. Classification of spent Li-ion batteries based on ICP-OES/X-ray characterization of the cathode materials. *Hem Ind.* 2020; 74: 221–230. <https://doi.org/10.2298/HEMIND200114012M>
- [19] Medić VD, Sokić MD, Nujkić MM, Đorđević SS, Milić SM, Alagić ČS, Antonijević MA. Cobalt extraction from spent lithium-ion battery cathode material using a sulfuric acid solution containing  $\text{SO}_2$ . *J Mater Cycles Waste Manage.* 2023; 25: 1008–1018. <https://doi.org/10.1007/s10163-022-01580-w>
- [20] Nayl AA, Elkhashab RA, Badawy SM, El-Khateeb MA. Acid leaching of mixed spent Li-ion batteries. *Arab J Chem.* 2017; 10: S3632–S3639. <https://doi.org/10.1016/j.arabjc.2014.04.001>
- [21] Jha MK, Kumari A, Jha AK, Kumar V, Hait J, Pandey BD. Recovery of lithium and cobalt from waste lithium ion batteries of mobile phone. *Waste Manage.* 2013; 33: 1890–1897. <https://doi.org/10.1016/j.wasman.2013.05.008>
- [22] Jiang F, Chen Y, Ju S, Zhu Q, Zhang L, Peng J, Wang X, Miller JD. Ultrasound-assisted Leaching of Cobalt and Lithium from Spent Lithium-ion Batteries. *Ultrason Sonochem.* 2018; 48: 88–95. <https://doi.org/10.1016/j.ultsonch.2018.05.019>
- [23] Gao W, Zhang X, Zheng X, Lin X, Cao H, Zhang Y, Sun ZHI. Lithium Carbonate, Recovery from Cathode Scrap of Spent Lithium-ion Battery - a Closed-loop Process. *Environ Sci Technol.* 2017; 51: 1662–1669. <https://doi.org/10.1021/acs.est.6b03320>
- [24] Zhu SG, He WZ, Li GM, Zhou X, Zhang XJ, Huang JW. Recovery of Co and Li from spent lithium-ion batteries by combination method of acid leaching and chemical precipitation. *Trans Nonferrous Met Soc of China* 2012; 22: 2274–2281. [https://doi.org/10.1016/S1003-6326\(11\)61460-X](https://doi.org/10.1016/S1003-6326(11)61460-X)
- [25] Kaskiala T. Determination of oxygen solubility in aqueous sulfuric acid media. *Miner Eng.* 2002; 15: 853–857. [https://doi.org/10.1016/S0892-6875\(02\)00089-4](https://doi.org/10.1016/S0892-6875(02)00089-4)
- [26] Ndalama J, Mulaba-Bafubandi AF, Mamba BB. UV/visible spectroscopic analysis of  $\text{CO}^{3+}$  and  $\text{CO}^{2+}$  during the dissolution of cobalt from mixed Co-Cu oxidized ores. *Int J Min Met and Mater.* 2011; 18: 260–269. <https://doi.org/10.1007/s12613-011-0432-y>

- [27] Šupicová M, Rozik R, Trnková L, Oriňáková, Gálová M. Influence of boric acid on the electrochemical deposition of Ni. *J Solid State Electrochem.* 2006; 10: 61–68. <https://doi.org/10.1007/s10008-005-0656-8>
- [28] Metikoš-Huković M, Babić R. Passivation and corrosion behaviours of cobalt and cobalt–chromium–molybdenum alloy. *Corros Sci.* 2007; 49: 3570–3579. <https://doi.org/10.1016/j.corsci.2007.03.023>
- [29] Avramović Lj, Maksimović VM, Baščarević Z, Ignjatović N, Bugarin M, Marković R, Nikolić ND. Influence of the Shape of Copper Powder Particles on the Crystal Structure and Some Decisive Characteristics of the Metal Powders. *Metals* 2019; 9: 56. <https://doi.org/10.3390/met9010056>

## Valorizacija kobalta iz istrošenih litijum-jonskih baterija luženjem u sistemima H<sub>2</sub>SO<sub>4</sub>-N<sub>2</sub> i H<sub>2</sub>SO<sub>4</sub>-O<sub>2</sub> i metodom elektrohemijškog taloženja

Dragana V. Medić<sup>1</sup>, Žaklina Z. Tasić<sup>1</sup>, Maja M. Nujkić<sup>1</sup>, Silvana B. Dimitrijević<sup>2</sup>, Stefan S. Đorđević<sup>2</sup>, Slađana Č. Alagić<sup>1</sup> i Snežana M. Milić<sup>1</sup>

<sup>1</sup>Univerzitet u Beogradu, Tehnički fakultet u Boru, Bor, Srbija

<sup>2</sup>Institut za ruderstvo i metalurgiju, Bor, Srbija

(Naučni rad)

Izvod

Tema rada je valorizacija kobalta iz katodnog materijala istrošenih litijum-jonskih baterija (LIBs) primenom metoda luženja i elektrohemijškog taloženja. Tokom eksperimenata luženja upoređivani su stepeni rastvaranja katodnog materijala u sistemima H<sub>2</sub>SO<sub>4</sub>-N<sub>2</sub> i H<sub>2</sub>SO<sub>4</sub>-O<sub>2</sub>. Maksimalni stepeni ekstrakcije kobalta od 40 % u sistemu luženja H<sub>2</sub>SO<sub>4</sub>-N<sub>2</sub> i 47 % u sistemu H<sub>2</sub>SO<sub>4</sub>-O<sub>2</sub> postignuti su pod sledećim eksperimentalnim uslovima: koncentracija H<sub>2</sub>SO<sub>4</sub> 2 mol L<sup>-1</sup>, zapreminski protok azota/kiseonika 2 L min<sup>-1</sup>, koncentracija čvrste faze od 33 g L<sup>-1</sup>, i temperatura od 85 °C. Kinetika ekstrakcije kobalta iz katodnog materijala, u oba ispitivana sistema, bila je najpovoljnija u prvih 15 min, nakon čega je došlo do naglog smanjenja brzine reakcije. Kobalt je deponovan iz rastvora za luženje na bakarnu podlogu metodom galvanostatskog taloženja sa iskorišćenjem struje od 84 %. Potrošnja energije je bila 5.8 kWh kg<sup>-1</sup> deponovanog kobalta. Metoda ciklične voltametrije (CV) korišćena je za određivanje potencijala taloženja kobalta, kao i sporednih reakcija koje se odvijaju u sistemu. Metodom skenirajuće elektronske mikroskopije sa energetsko disperzivnom spektrometrijom utvrđeno je da je tokom procesa elektrohemijškog taloženja kobalta došlo do aglomeracije čestica kobalta (u obliku karfiola) i da je kobalt deponovan u njegovom elementarnom stanju, što je potvrđeno rezultatima rendgenske difrakcione analize.

*Ključne reči:* reči: katodni materijal; kiselinsko luženje; litijum kobalt oksid; reciklaža; metalna prevlaka