

RASTVARANJE KATODNOG MATERIJALA IZ LIB U SUMPORNOJ KISELINI U PRISUSTVU AZOTA

DISSOLUTION OF LIBs CATHODE MATERIAL IN SULFURIC ACID IN THE PRESENCE OF NITROGEN

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Dobro je poznato da litijum-jonske baterije (LIB), sa kratkim životnim vekom (od 1 do 3 godine), čine veliki udeo u elektronskom otpadu. Pored opasnih materija (uglavnom soli litijuma rastvorene u organskim rastvaračima), LIB sadrže i značajnu količinu vrednih metala (pre svega Co i Li), čija valorizacija u velikoj meri doprinosi konceptu održivog razvoja. Postupci reciklaže LIB odnose se na fizičke, hemijske i biološke procese i mogu se generalno podeliti na: hidrometalurške, pirometalurške i biološke procese. U cilju smanjenja emisije štetnih gasova i optimizacije procesa, u novijim istraživanjima prednost se daje hidrometalurškom pristupu. U ovom radu ispitana je mogućnost izluženja kobalta iz katodnog materijala istrošenih LIB u sumpornoj kiselini u prisustvu azota. Postupku luženja prethodio je specifičan višefazni tretman pripreme pojedinačnih ćelija. Kako bi se odredili optimalni uslova luženja, ispitan je uticaj različitih procesnih parametara, i to: koncentracija kiseline, odnos čvrsto/tečno, temperatura i vreme trajanja procesa. Pri optimalnim uslovima luženja (2M H₂SO₄, 33 g/L, 85°C i 100 min) postignuta je efikasnost izluženja Co od oko 40%. Niska efikasnost izluženja Co može se objasniti jakom hemijskom vezom između Co i O₂, te se može zaključiti da je za potpuno rastvaranje LiCoO₂ u H₂SO₄ potrebno prisustvo redukujućeg sredstva.

Ključne reči: kiselinsko luženje; kobalt; LIB; reciklaža; azot

It is well known that the short-lasting (1-3 years) lithium-ion batteries (LIBs) represent a large part of electronic waste. Except hazardous materials (mainly Li-salts in organic solvents), LIBs contain a significant quantity of valuable metals such as Li and cobalt (Co); namely, their valorization contributes to the concept of sustainable development. Recycling LIBs procedures refer to physical, chemical and biological processes, so that, they can be divided into the hydrometallurgical, pyrometallurgical, and biological processes. In order to reduce waste gases emissions and to enhance the optimization of the process, the novel researches force the hydrometallurgical approach. In this work, the possibilities for Co leaching from the cathode material of spent LIBs were investigated using sulfuric acid in nitrogen presence. Before the leaching, a specific multi-stage preparation treatment was applied to each cell. In order to determine the optimum leaching conditions, different influential parameters were investigated such as: acid concentration, solid to liquid (S/L) ratio, temperature, and the process duration. Under the optimal leaching conditions (2M H₂SO₄, 33 g/L, 85°C and 100 min), the leaching efficiency of Co was about 40%. Low leaching efficiency of Co can be explained by the strong chemical bond between Co and O₂, which leads to a conclusion that the total dissolving of LiCoO₂ in H₂SO₄ requires the presence of a reducing agent.

Key words: acid leaching; cobalt; LIBs; recycling; nitrogen

1 Introduction

Lithium-ion batteries (LIBs) have a key role in the further development of electric vehicles, energy storage and the renewable sources of energy. It is considered that LIBs are going to contribute to the reduction of global carbon-dioxide emission. Higher demand for this specific type of batteries in the fields of portable electronics and transportation has sparked the interest for the recycling process of LIBs [1].

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LIBs are composed of battery cylindrical case, anode, cathode and separator. Main components of anode are the graphite and binder, while the cathode is composed of carbon and lithium-transition metal oxides, such as: LiCoO_2 , LiNiO_2 , LiMn_2O_4 , and $\text{LiCo}_x\text{Mn}_y\text{Ni}_z\text{O}_2$. Content of Co, Ni and Li in cathode material varies and reaches from 5% up to 15% for Co, 2-7% for Ni, and 0.5-2% for Li; with other elements (Au, Al, Fe, etc.) that are present in lower concentrations [2].

Most commonly used cathode material is LiCoO_2 . The content of Li and Co in spent LIBs remains around 10-20 wt.%, which in some cases exceeds the content of said elements in the ores found in nature [3].

According to the European Union, certain components of LIBs, such as Co, P and graphite are classified as „Critical Raw Materials“, because of their economic significance and high supply risk [1].

Generally, for the valorization procedure of valuable metals from expired LIBs, it is necessary to include and comprehend two main processes: Separation of active cathode material from the current collector, and the extraction of precious metals [4].

Taking into consideration the structural composition of cathode material, separation of aluminum foil from the active cathode material represents the decisive step in the recycling process [5].

Three methods are used for the separation of aluminum foil from the active cathode material: mechanical separation, dissolution of current collector and the removal of the binder [4].

In the extraction process of valuable metals, they are firstly dissolved via leaching process; then the separation, purification and the preparation of the final product follows. Among all of these steps, the leaching process is the most accountable one [4].

A common leaching processes used in this case are: leaching via inorganic and organic acids, alkaline leaching and bioleaching. Some experiments have confirmed that the use of inorganic acids provides better results in the term of leaching efficiency, unlike the use of organic acids. Inorganic acids can also effectively dissolve all the metals present in the cathode material, however, the organic acids dissolve metals selectively, and the leaching efficiency of Co extraction is relatively low [6,7].

In this paper, optimal conditions for the extraction process of Co from the cathode material via leaching process are discussed. Experiments were conducted in sulfuric acid in the presence of nitrogen. Raw material for the leaching process is obtained after multiphase treatment of individual cells.

2 Experimental

2.1 Materials and methods

Cathode material collected from 40 LIBs, was treated thermally, via procedure explained in previous work/paper of Medić et al. (2020) [8]. Chemical composition of examined material was determined using inductively coupled plasma optical emission spectrometry (ICP-OES). For the dissolution of cathode material, 65% HNO_3 and 36% HCl (Merck, Darmstadt, Germany) in ratio 1:3, were used. All reagents were of analytical purity and the solutions were prepared by deionized water. For the continuous assessment of Co concentration, UV-VIS spectrophotometry was used (Beckman DU-65).

2.2 Leaching tests

Leaching experiments were carried out in a reactor with measuring tube (diameter of 1 cm), which was used to determine absorbance. The apparatus was placed inside the spectrometer. Spectrometer working conditions, gas flow and temperature were controlled via device based on the microcontroller STM32F103. The obtained data was processed and given in a form of Python scripts.

Before the leaching process, mass of the material was determined and precisely measured. In the reactor was added 60 ml H_2SO_4 of known concentration and thermostated until desired temperature was reached, with constant gas flow rate of 2 L/min. Upon reaching this temperature, predetermined amount of cathode material was added. Spectra were recorded every 3 minutes, with 10 s pause of mechanical mixing before every reading/recording. Cobalt concentration was determined by calibration curve method, previously obtained by reading standard of known concentration CoSO_4 in

H₂SO₄. Because of light dissipation on the material used in leaching, slight corrections were conducted.

Leaching efficiencies were calculated using eq 1 [9]:

$$\text{Leaching efficiency} = \frac{\text{Metal content in leachate}}{\text{Total amount of metal in cathodic materials}} \times 100\% \quad (1)$$

3 Results and discussion

3.1 Chemical Composition of the Cathode Active Material before leaching

Chemical analysis results of examined cathode material are shown in Table 1. According to the obtained results, it can be concluded that the cathode material is composed mainly of LiCoO₂, while the presence of Al can be explained via pretreatment of the batteries. In the analyzed sample, it has been determined high content of Li and Co, which has led to the consideration of these batteries as an important source of said metals.

Table 1 Metal contents found in the obtained cathode active material

Metal element	Li	Co	Al
Content [wt. %]	5.98	49.81	0.01

3.2 Leaching of waste cathode material

3.2.1 Effect of acid concentration on leaching

The effect of the initial concentration of sulfuric acid (0.5–3M) on leaching efficiency of cobalt from cathode material was investigated at constant conditions: temperature 35°C, solid-liquid ratio 33 g/L, nitrogen flow rate 2 L/min, total time of the experiment 100 min. From the obtained results and according to the Fig. 1, it can be concluded that the leaching efficiency of Co was increasing with the increase of H₂SO₄ concentration until 2M. At this specific concentration, leaching efficiency of cobalt was around 35%.

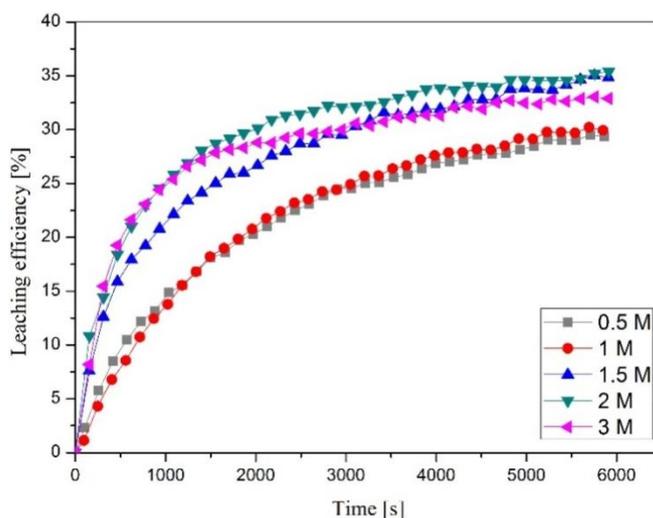


Fig.1 Effect of H₂SO₄ concentration on the leaching of waste LiCoO₂

However, a continued increase in concentration resulted in the decrease of leaching efficiency (from 35% to 33 %). As described by Swain et al. (2007) [10], the lower concentration of H₂SO₄ results in the better leaching efficiency of LiCoO₂ as Co(II), while the strong acid solution causes the lower leaching efficiency of cobalt - Co(III) is more unstable than Co(II). Taking into account the obtained results, 2M sulfuric acid solution was selected as the optimum concentration for the leaching of Co.

3.2.2 Effect of the solid-to-liquid ratio on leaching

In terms of investigating the effect of solid-liquid ratio on leaching efficiency of cobalt, an experiment has been performed at: solid-liquid ratio 10-67 g/L, acid concentration of 2 M, temperature 35°C, nitrogen gas flow 2 L/min and total time of the experiment of 100 min. Obtained results are shown in Fig. 2, where it can be seen that curves representing leaching efficiency of cobalt during a given time period indicate that the leaching efficiency of cobalt declines with the increase of solid-liquid ratio. With the increase of solid-liquid ratio of 10-67 g/L, leaching efficiency is lowered from 36% to 32%.

The lower leaching efficiency at higher solid/liquid ratio was due to the higher viscosity of the mixture, the higher resistance of diffusion mass transfer, and acid deficiency [11].

However, a large solid-liquid ratio is usually required to facilitate proper operational efficiency in practical applications and therefore solid-liquid ratio was chosen to be 33 g/L in accordance to Fig. 2 [12].

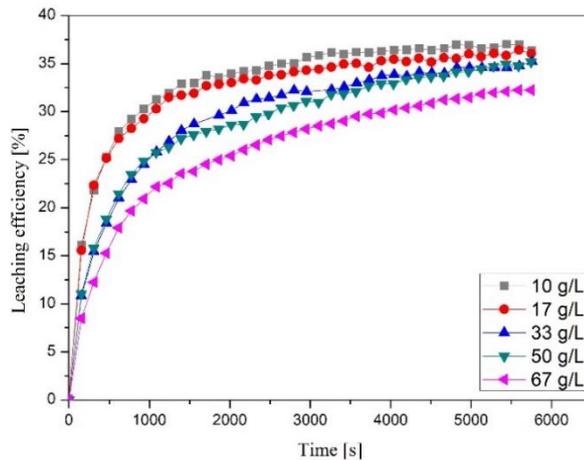


Fig. 2 Effect pulp density on the leaching of waste LiCoO_2

3.2.3. Effect of temperature on leaching

The effect of temperature on leaching efficiency, was investigated in the temperature range from standard room temperature up to 85°C in 2M sulfuric acid, at 33 g/L solid-liquid ratio, nitrogen flow rate 2 L/min and total time period of 100 min. The results of this experiment are shown on Fig. 3, where it can be seen that leaching efficiency increases from 29% to 40% with the increase of temperature from 35 to 85°C. Similar results were reported by He et al. (2017) [13].

It can also be noted that by the shape of the dissolution curves, temperature in the initial stadium of the process has a significant impact on the rate of dissolving the cathode material obtained from the expired LIBs.

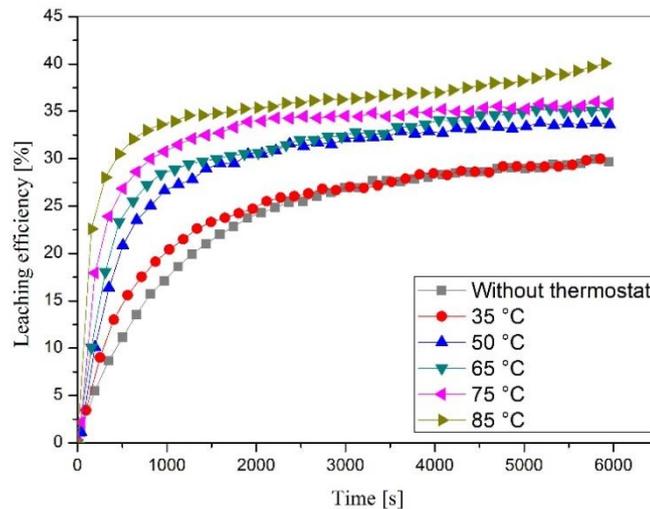


Fig. 3 Effect of leaching temperature on the leaching of waste LiCoO_2

Conclusion

Taking into consideration all of the results obtained from the conducted experiments, it can be concluded that the LIBs are deemed to be a significant source of Co. Using the H_2SO_4 in the leaching process of the cathode material obtained from the spent LIBs, low leaching efficiency of Co is achieved (around 40%). In view of the fact that a strong chemical bond between Co and O_2 in the LiCoO_2 is/can be formed, for a high leaching efficiency usage of an adequate reducing agent is necessary. Maximum cobalt leaching efficiency is achieved at the concentration of leachate being 2 M, solid-liquid ratio being 33 g/L, nitrogen flow rate being 2 L/min and at the temperature of 85°C. Obtained results have shown that with the increase of both - temperature and the solid-liquid ratio, leaching efficiency of cobalt increases. Also, based on the shape of LiCoO_2 dissolution curves, it can be noted that the leaching efficiency increases with the increase of the sulfuric acid concentration, until 2 M concentration of H_2SO_4 is reached, when the further increase of concentration leads to reduction in leaching efficiency.

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