Recovery of LiCoO$_2$ compound from cathodic paste of waste LIBs, by ultrasonography in lactic acid solution

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Abstract. Lithium-ion batteries (LIBs) are used in electric devices such as phones, cameras, laptops, etc. and also for electric automotive propulsion. More consumption means more amount of scrap. The wastes of LIBs contain rare and high value metals: Co (32 $$/kg), Li, Ni, Cu, Al. Many recycling processes were developed with the purpose of recovering metals contained in used batteries. This paper presents a method for separation active cathodic paste (containing LiCoO$_2$ compound) from the aluminum cathode using a solution of lactic acid and an ultrasonic bath. Cathodic paste has been detached from aluminum foils and analyzed by scanning electron microscopy (SEM) and X-ray diffractometry. The effects of the lactic acid concentration and the power of ultrasonic bath on separation efficiency were investigated.

1. Introduction

The applications of Li-ion batteries as electrochemical power sources are known to each of us: mobile phones, camcorders, laptops and more. The evolution of the electric vehicle market will give a new impetus to the Li-ion battery market [1, 2].

The more numerous, the greater the amount of waste generated. Li-ion batteries contain metals such as iron, copper, aluminum, cobalt, and nickel, metals less toxic than lead or cadmium contained in Pb-acid batteries. Some lead compounds are extremely toxic. Lithium-ion batteries can be a safety hazard: they contain a flammable electrolyte and it easily catches fire if they become damaged. Stored at the landfill can cause fires that are difficult to extinguish [3, 4].

There are several types of Li-ion batteries depending on cathode chemistry: lithium iron phosphate (LFP), lithium cobalt oxide (LCO), manganese spinel oxide (LMO) and composites oxides (LCN, NCM and NCA) (meaning nickel (N), cobalt (C), aluminum (A) or manganese (M). The anode material is in the most cases composed of graphite, but it can be also of lithium salt of titanium oxide, silicone-graphite or lithium-metal [5].

In the following we will deal with the recycling of LiCoO$_2$ (LCO) batteries [6-9]. A lithium-ion battery contains three important components: a cathode consists of Al foil covered by a lithium metal oxide (LiCoO$_2$ with ~60% Co), an anode made of a copper coated with a graphite film and a toxic and flammable electrolyte consisting of a solution of a lithium salt (LiPF$_6$). The LiCoO$_2$ powder is bonded to the aluminum foil by means of a binder (typically PVDF-polyvinylidene fluoride); the same binder also attaches the graphite powder to the copper foil (anode). The chemical composition of a lithium-
ion rechargeable batteries with LiCoO$_2$ active cathode contains (wt.%): LiCoO$_2$ = 27.5; Steel/Ni = 24.5; Cu/Al = 14.5; Carbon = 16; Electrolyte = 3.5; Polymer = 14 [10].

The most expensive metal involved in the construction of the cell is cobalt, much of which is mined in Congo (64,000 t with estimated reserves at 7,100,000 t). It follows, but far away: Russia – 5,600 t / 250,000 t reserves; Australia – 5,000 t / 1,200,000 t reserves; Canada – 4,300 t / 250,000 t reserves; Cuba 4,200 t / 500,000 t reserves; Philippines – 4,000 t / 280,000 t reserves [11].

The Democratic Republic of the Congo (DRC) currently produces 63% of the world’s cobalt, but this market share may reach 73% by 2025.

For 2030, global demand could be 47 times more than it was in 2017; Bloomberg New Energy Finance has estimated [12].

The price of cobalt is currently $32 / kg [13] but can have very high fluctuations (Figure 1).

![Figure 1. Evolution of cobalt price (2005-2019) [13].](image)
discharge, disassembly, and ultimately the application of some convenient physical and chemical processing methods. Numerous technologies are known to recover the metals contained in used Li-ion batteries: hydrometallurgical, pyrometallurgical and combination of the two processes.

2. Materials and methods

The experiments aimed at establishing a recovery technology of the cathode (Co-containing) paste from the aluminum foil. We used ultrasounds in a weak acid environment [22].

Ultrasounds have found numerous technological applications due to their specific properties: short wavelength, high particle acceleration (can reach values higher than $10^5$ times the acceleration of gravity), the possibility of targeting and focusing of acoustic energy in inaccessible areas). Figure 2 presents some of the technological applications [23] of ultrasounds in liquid medium.

The technological applications of the ultrasounds in liquid media [23].

The spent Lithium-ion batteries used in this study come from mobile phones and were dismantled manually in order to reach out the cathode material [24].

The spent LIBs were discharged completely in a salt solution for 1h and dismantled manually to separate the cathode materials coated on the aluminum foil. The Al-foil was cut into small pieces initially (keep intact for final experiments) and immersed in acidic solution (lactic acid) and subjected for ultrasonic cleaning.

Once all the active cathode material was detached from aluminum foil, it was filtered and washed with alcohol, and filtered again. In Fig. 4, it can be seen the steps of recovery process. The ultrasonic cleaning installations consist of the following elements: the casing, the washbasin, the transducer. The ultrasonic cleaning machine (Emmi12-HC) used has the following technical specifications: housing – stainless steel, cleaning frequency = 45 kHz; cleaning time = 1- 60 min; volume = 1.2 l; heating temperature = 20- 80 °C; bath dimension 200x100x65 mm; ultrasonic power= 50/75/100W.
Figure 3. The flow sheet of the cathode material separation process.

Figure 4. Visualization of cavitations effect on cathode foils.
The main advantages of the ultrasonic cleaning process are: reduced working time, low cost of the whole process, high productivity and lack of superficial microfiches [25].

The ultrasonic cleaning process is based on the phenomenon of ultrasonic cavitations [26], which can be seen in Figure 3. This process can be explained as follows: changes in pressure and fluid breakage favor the formation of cavitations bubbles, which once penetrated into the pores of the adhering layer, increase in size and produce a gradual detachment of this layer.

The samples were analyzed by Scanning Electron Microscopy using a Quanta Inspect F50, with a Field Emission Gun (FEG) with resolution of 1.2 nm, and an EDX analyzer having a resolution of 133 eV at MnK. The powder sample was also characterized by XRD using the PANalytical X’Pert PRO MRD diffractometer (wave length of λCu = 1.544).

3. Results and discussions
The ultrasonication process (in acidic environment) is very complex, and there are many factors that can influence the efficiency of the process of stripping / detaching the active paste from the aluminum foil (cathode). In all trials the ultrasound frequency was kept at 45 Hz. The temperature inside the ultrasonic bath represents the controllable variable and was increased from 20 to 50°C.

In order to obtain the proper parameters for a maximum recovery potential we have made several attempts. Since the amount of foils used for experimentation was limited, the foils were cut into equal pieces (12 pieces), being used for each preliminary experiment. Once the optimal parameters of the ultrasonic separation process have been established, whole foils were used to separate the active paste, as will be noticed later.

The first set of experiments took place at different lactic acid concentrations. Figure 5 shows the evolution of separation efficiency at different concentration (1.34…1.7 M) of lactic acid.

![Figure 5. Influence of pH on separation efficiency.](image)

Separation efficiency was calculated with the following equation:

$$\eta = \frac{m_i - m_f}{m_i} \times 1$$

Where: $\eta$ - separation efficiency; $m_i$ - initial weight of cathode, g; $m_f$ - final weight of cathode piece, g.

It can be observed that lactic acid concentration, power and temperature of the ultrasonic bath play a major role in the separation of the cathode material.

The proper concentration for a maximum efficiency (reduced ultrasonic time) was reached at a concentration of 1.7 M for lactic acid. The data shown that the ultrasonic power influence recovery
time; a higher applied ultrasonic power decreases the process efficiency (increases cleaning time). A temperature around 50°C greatly shortens the recovery time of the active paste on the cathode sheet.

The second set of experiments took place at different ultrasonic power. In Figure 6 it can be observed the effective removal of active cathode paste from Al film at different ultrasonic power.

![Figure 6. Influence of ultrasonic power on the separation efficiency.](image)

The third set of experiments took place at different temperatures. In Figure 7 it can be observed the evolution of the cleaning time during the recovery process of active paste at different temperatures.

![Figure 7. Influence of temperature on separation efficiency.](image)

The SEM images of the samples after separation are presented in Figure 8.
The XRD analysis of the selected sample after ultrasonography in lactic acid solution of the active cathodic paste (containing LiCoO$_2$ compound) is presented in Figure 9.

**Figure 9.** XRD patterns after ultrasonic method.
The main compounds are lithium-based layered oxides – LiCoO$_2$ or LiNiO$_2$ (nickel dioxide is formed during the charging process), forming the solid solution LiCo$_{1-x}$Ni$_x$O$_2$ in which cobalt ions are substituted for nickel ions.

4. Conclusions
In this paper an environmentally route for the recovery of active cathode material from spent Li-ion batteries was investigated. The ultrasound technology has the advantages to be easy to use, to work at different temperatures without the need of additional heat and to have low working times.

The solution used, lactic acid, was found to completely detach the cathode material from Al-foil without degrading the material. The results obtained have shown that the technique gave good results at the established parameters.

The optimal parameters for the ultrasonic process and obtaining a high separation efficiency of the active paste were:
- Concentration of lactic acid solution: 1.7 M;
- Temperature of the ultrasonic bath: 50°C;
- The power of ultrasonic bath: 80 W;
- Time range between 1.5 to 2.5 minutes.

After the optimal parameters have been established, we tested the process using an entire cathode foil. The result was a maximum separation efficiency of $\eta = 88.08\%$.

In the future, we propose to process further the obtained cathode powder of LiCoO$_2$ and to clean PVDF (polyvinylidene fluoride) material using a hydrometallurgical method in order to not degrade the active material.

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