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THE RECOVERY OF COBALT FROM THE CATHODE-RAY PASTE OF USED Li-ION BATTERIES IN THE FORM OF COBALT BLUE

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Abstract

Used Li-ion batteries through recycling allow the recovery of deficient and expensive elements such as cobalt, nickel and lithium. The work presents the possibilities of recovering cobalt from the cathodic paste of worn Li-ion batteries. The method applied for the recovery of cathode paste is the one with ultrasonication in acidic medium. Citric acid was used as a fainting medium. The method is viable and environmentally friendly. The cathode paste obtained by processing in the oven mixed with alumina leads to the obtaining of a blue cobalt pigment.

Keywords*:* *batteries, recycling, cobalt, cathode, ecology*

Introduction

The battery consists of one or more separate electrochemical cells being a device that stores chemical energy and converts it into electrical energy and is used by individual and industrial consumers. Currently, there is a number of researches [1-8] undertaken in order to improve the characteristics of the batteries as well as in terms of their recycling after their end of use.

A battery is a device that stores chemical energy and converts it into electricity. Chemical reactions in a battery produce a flow of electrons through an electrical circuit, generating an electrical current that can be used to power devices. Batteries are widely used from individual to industrial consumers. The most widely used type of battery is lithium-ion in various equipment. The performance of the battery can be assessed according to: Voltage, current, power, capacity, volumetric energy density, specific energy density, life cycle and charging rate [4,5]. Li-ion battery components: Anode, cathode, organic electrolyte, separator, housing and closures. Lithium-ion batteries contain: metals (Co, Ni, Li), plastics, organic chemicals. The cathode material is the most expensive component of a Li-ion battery, the cost of which represents about 40% of the total cost of producing a battery [6]. The choice of cathode material is directly correlated with the safety and stability of Li-ion batteries.

Types of Li-ion batteries: $LiCoO_2$, $LiMn_2O_4$, $LiNiMnCoO_2$, $LiFePO_4$, $LiNiCoAlO_2$ and $Li_4Ti_5O_{12}$ [4,6,9]. The advantages of a Li-ion battery are: low automatic discharge, high capacity and high specific energy, long life cycle and a high charging capacity.

More and more companies are dealing with the industrial recycling of these batteries. Currently, hydrometallurgical and pyrometallurgical processes are the most widely used. Most focus on the recovery of cobalt, lithium and nickel, as these are the most economically performing elements [9, 10]. Proper end-of-life battery management (Fig. 1) through the use of recycled

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materials in battery production contributes to reducing energy and material consumption throughout the production process. Battery recycling aims at reusing the materials that make up the batteries to promote both sustainable production and the circular economy and a reduction in the negative impact of waste on the environment. Circularity and recycling of raw materials is an integral part of the transition to a climate-neutral economy. Increasing product life and the use of secondary raw materials will help meet an increasing proportion of demand for raw materials. To encourage the recovery of materials from the increasing quantities of batteries placed on the market, the new regulations address, among other aspects, the end-of-life stage, specifically the second life cycle (reuse and reorientation), collection rates, recycling efficiency and material recovery, recycled content and extended producer responsibility. Recycling batteries and recovering multiple minerals has been shown to maximize both energy savings and reducing emissions during material production. Studies [11-13] have shown that recycling and reusing materials from used batteries could reduce primary energy consumption and lead to up to 50% reductions in greenhouse emissions during the battery manufacturing process.

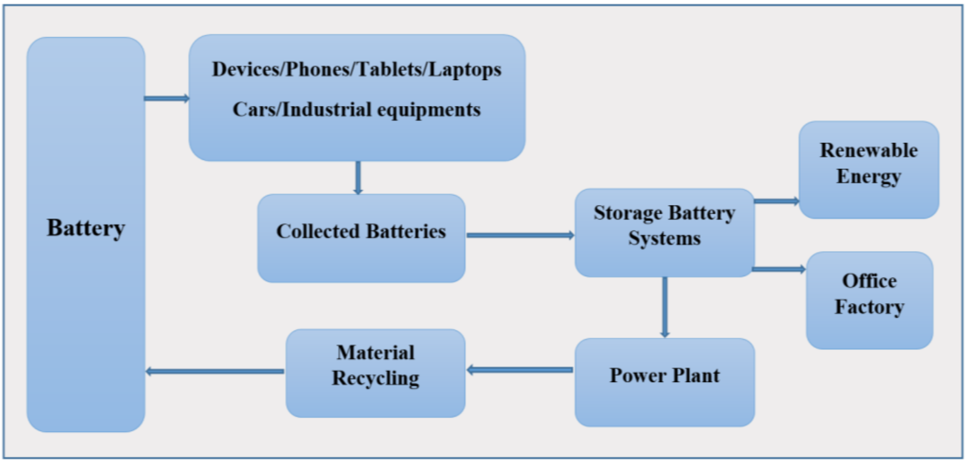

Fig. 1. End of life, options for batteries

Currently, in addition to Li-ion batteries, the following are used: Lithium-air batteries, lithium-sulfur batteries, sodium ion batteries, aluminum-ion batteries, lithium-ion batteries with solid state electrolyte, etc.

Recycling is an important step in mitigating waste management and environmental concerns about the recovery and return to the economic circuit of materials used in Li-ion batteries. Recycling enables lower production costs by recovering valuable raw materials such as cobalt, nickel and lithium from end-of-life batteries. The recovery of raw materials is essential for expanding the raw material base and recovering natural capital components. Current recycling technologies require high energy and capital consumption and must become sustainable in the long term [10,14-20]. Thus, worldwide efforts are made to optimize current technologies and investments are made in innovative applications that lead to the obtaining of recovered materials at the lowest possible costs and with the lowest possible environmental effects.

Methodology of Production

The paper presents the laboratory phase experiments regarding the possibilities of recovering cobalt from the cathode-like paste resulting from the recycling process of used Li-ion batteries. The method used is direct recycling using used $LiCoO_2$/LCO batteries from mobile phones.

A $LiCoO_2$/LCO battery contains the following components: cathode, anode, electrolyte, separators, carcass and contacts. The cathode consists of an aluminum foil covered with an active paste - an oxide compound ($LiCoO_2$ with about 60% Co). The cathode-like paste (active paste) is glued to the aluminum foil with a PVDF glue. The anode consists of a copper foil covered with a graphite film, a film glued with a PVDF adhesive and $LiPF_6$ is the electrolyte.

For the recovery of cobalt, the active cathodic paste must be separated at first. For separation, the aluminum foil coated with the cathode-ray paste is inserted into a solution of citric acid, therefore an ecological solution, using an ultrasonication method [21]. The cathode paste resulting from the ultrasonication process is further subjected to the cobalt extraction process in the form of cobalt blue.

In this research, in order to obtain the cobalt blue going through the following steps [4]:

$$\text{At temperature of 400°C: } LiCoO_2 \rightarrow Co_3O_4 \quad (1)$$

$$\text{At temperature of 900°C: } 2Co_3O4 \rightarrow 6CoO + O_2 \quad (2)$$

$$\text{At temperature of 1200°C: } CoO + Al_2O_3 \rightarrow CoAl_2O_4 \quad (3)$$

For the laboratory phase experiments, the technological flow shown in Fig. 2 was used.

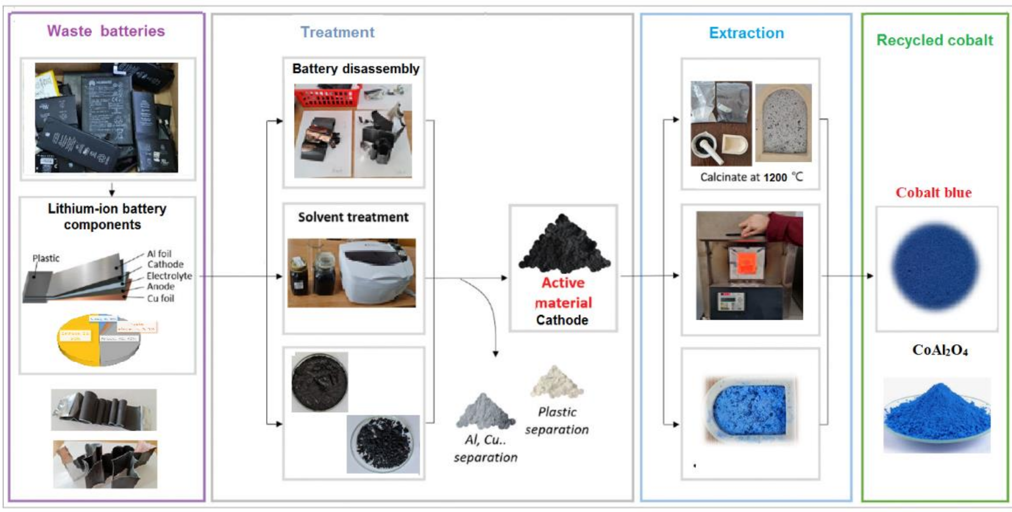

Fig. 2. Technological flow to obtain cobalt blue from used Li-ion batteries

Pigments containing cobalt have been used since ancient times as enamel on porcelain. They are currently used in fine paints for artists, both in oil and watercolor, and in industrial applications (ceramics, porcelain, sandstone and glass) as well as in military camouflage paints.

Material and Methodology of Research

The methodology of the research consists in the manual dismantling of batteries. Previously, the used batteries are discharged and immersed in a saline solution for 1 h. After dismebration, the resulting materials are separated. Huawei Li-ion batteries were dismantled from mobile phones and the fainting medium used was 1.25M citric acid. The batteries were weighed before and after dismantling, on the components. The data obtained on the battery components resulting from the dismantling, expressed in % are shown in Fig. 3.

The cathode film was inserted into an ultrasonic bath shown in Fig. 4. The ecological environment used for leaching is citric acid. Removal of the cathode-ray paste from the aluminum foil was performed at room temperature. The duration of the treatment was 5-8 minutes. The cathode paste was removed during treatment from the aluminum foil in samples undergoing leaching treatment.

The recovery yield of the active paste is calculated as follows [4]:

$$\eta = \frac{m_0 - m_f}{m_0} \times 100 \tag{4}$$

where: m_0 is the initial mass of the cathode film (Al+paste foil);
m_f is the final mass (Al foil), after ultrasonication in acidic medium (citric acid).

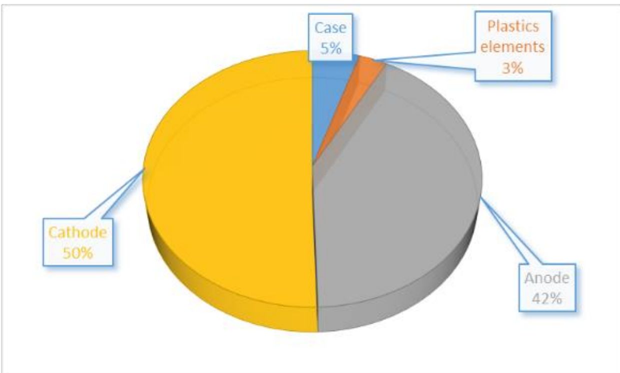

Fig. 3. Dismantled battery components

Fig. 4. Aspects of the cathodic paste recovery process

With the obtained experimental data, the recovery yield of the active paste was calculated, it varied within the range of 65-85%.

The active cathode paste recovered after drying was ground and subjected to analysis. The presence of cobalt has been recorded in the analyses carried out for the samples taken, and an average chemical composition of these samples is shown in Fig. 5.

The recovered cathode paste was homogenized with alumina, loaded in ceramic crucibles and heat treated in an oven 5 recipes have been made for obtaining cobalt blue. Experimental recipes are shown in Fig. 6.

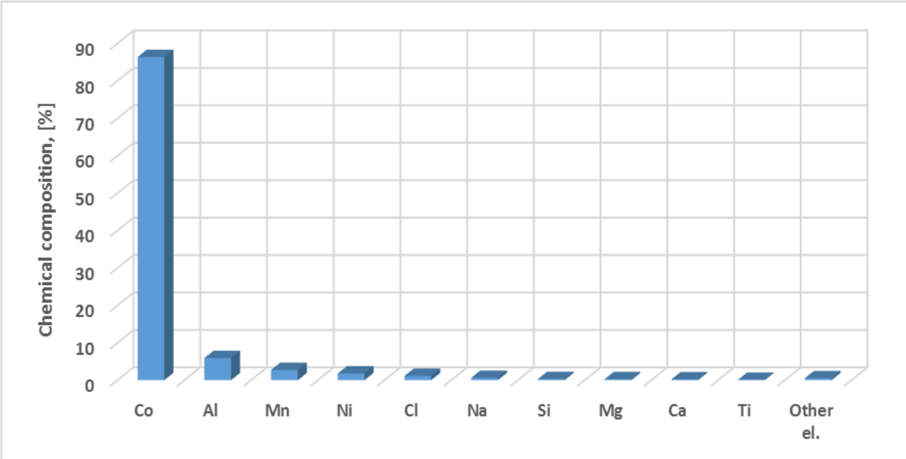

Fig. 5. Chemical composition of the recovered active paste

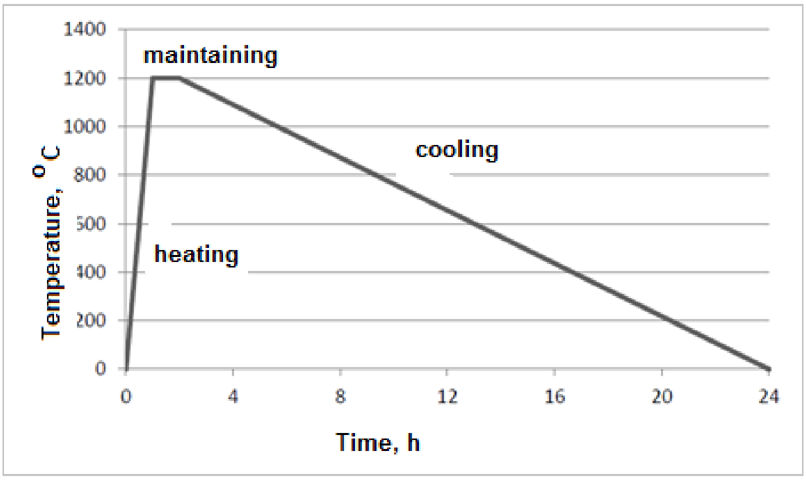

Fig. 6. Time/temperature diagram for the calcination process

The heat treatment was carried out according to the diagram shown in Fig. 7 and the aspects during the cobalt blue are shown in Fig. 8.

Depending on the alumina content used in the experimental recipes, various shades of cobalt blue were obtained, the resulting samples being presented Fig. 9.

$CoAl_2O_4$ is a double oxide with a normal spinel-type structure. Ceramic pigments are coloured oxide substances that can be dispersed in silicate melts.

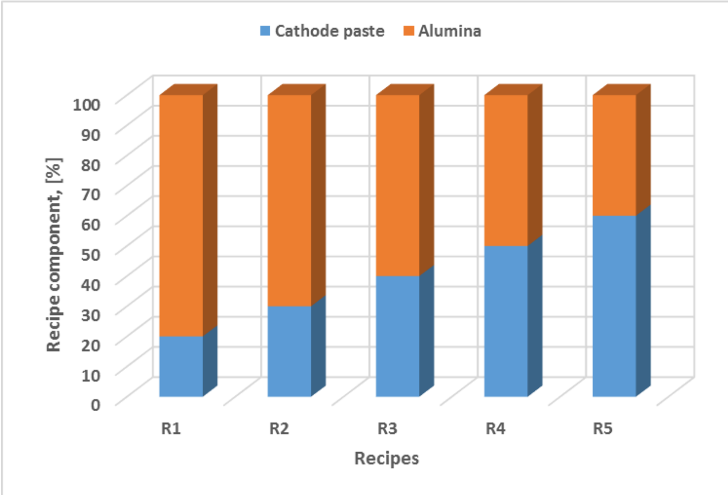

Fig. 7. Composition of experimental recipes for obtaining cobalt blue

Fig. 8. Aspects of obtaining cobalt blue pigment

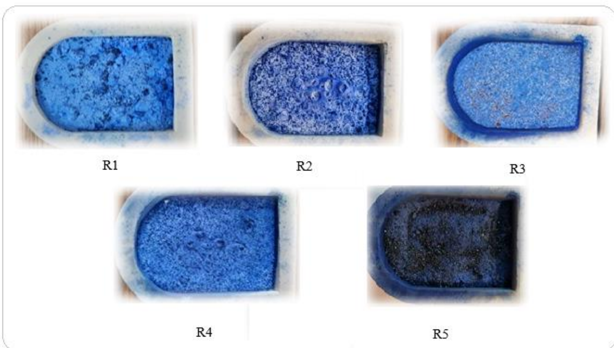

Fig. 9. Samples - cobalt blue

$CoAl_2O_4$ - is commercially well known and has been extensively used, as a pigment for the coloration of ceramics, glazes, porcelain enamels, glass, paint, fibers, paper, cement, rubber, plastics, and cosmetics.

Conclusions

Cobalt is considered a strategic and non-renewable mineral. The African continent has the largest share of cobalt resources, with about 50% of them in the Democratic Republic of the Congo. Currently, about a quarter of the world's cobalt production is used in smartphones. But while a lithium-ion battery for smartphones needs about eight grams of refined cobalt, a battery for an electric car requires nearly 1,000 times more.

The price of cobalt varies strongly, so if in 2019 it was trading at about 80,000 per ton, now the price is about 35,000 per ton. Two-thirds of the world's cobalt supplies come from the Democratic Republic of the Congo. Hundreds of companies are competing for cobalt extraction, but the strongest is China Molybdenum (CMOC), a Chinese natural resources company that controls 15% of the cobalt market after several acquisitions in the Democratic Republic of the Congo. Romania has cobalt resources, but it does not exploit them.

The recovery of the respective cathodic paste of cobalt blue cobalt using the acid ultrasonation method is a simple and environmentally friendly method. The advantages of the method: Cobalt recovery efficiency over 80%, environmentally friendly use for leaching and low energy consumption. The disadvantage of the method is how to separate the battery components (manual dismantling).

Cobalt blue is obtained by a process that is easy to apply and the resulting product can be used as a pigment in the dye industry, in painting and glassware workshops and its production cost is lower than the pigment obtained industrially.

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