Academy of Romania
www.jesi.astr.ro

Journal of Engineering Sciences and Innovation
Volume 8, Issue 4 / 2023, pp. 373-382

C. Chemical Engineering, Materials Science and Engineering

Received **30 August 2023** Accepted **4 December 2023**
Received in revised form **10 October 2023**

Cobalt recovery technologies from spent Li-ion batteries

IONUT BRATOSIN, VALERIU-GABRIEL GHICA[*]

Faculty of Materials Science and Engineering, POLYTECHNIC University of Bucharest,
313 Spl. Independenței, Bucharest, Romania

Abstract. Demand for Li-ion batteries (LIBs) ramped up lately (2018-2022). Electrical vehicle (EV) industry becomes mature and conventional vehicles featuring thermal combustion engines will be gradually replaced. The evolution of Li-ion cell technology allowed decreasing manufacturing costs. Technical innovations within the sector consist in substituting liquid electrolytes with solid state ones, improving driving range, enhanced safety and faster charging times. The European Union strategy regarding batteries is focused on creating a sustainable, competitive and innovative ecosystem for reducing greenhouse gases. The European market share in Li-ion batteries worldwide production is 3% (Asia leads with 85%). In order to prevent technological dependence on fierce Asian competition and to capitalize on the economic potential that this opportunity represents, The European Union launched the "European Battery Alliance" in October 2017, with a view to stimulating cooperation between the industries of the old continent and building Li-ion battery production gigafactories. In Romania there are initiatives in the development of this sector, with investments that have mobilized public and private capital. In June 2023, the Romanian-Belgian Romvolt project was launched in Galați city, a production and recycling facility of Li-ion batteries with a total capacity of 22 GW. The paper presents the research undertaken for the recovery of cathodic paste with high content of cobalt (Co) from spent LIBs, by ultrasonography in lactic acid solution (C3H6O3). The hydrometallurgical method uses a non-polluting organic (lactic) acid. The working technique, the results obtained and the investigations carried out on the recovered materials are presented (analysis of optical and electron microscopy, EDX, X-ray diffraction).

Keywords: Li-ion batteries, recycling, cobalt, X-ray diffraction.

1. Introduction

Recycling spent Li-ion batteries is an ecological obligation and an economic necessity these days. In support of this statement there are many arguments.

---

[*] Correspondence address: gvghica@yahoo.com

The metals used in the production of Li-ion batteries are scarce and expensive (e.g. Li, Co, Ni).

Lithium is one of the critical metals inside a Li-ion battery. Due to the movement of electrically charged lithium particles (i.e. ions) between the two electrodes, a Li-ion battery either stores or releases energy. The movement of ions occurs from the anode to the cathode [1], thus: during discharge, a process in which the battery releases electricity, the cathode has a positive electrical charge (+) and a reduction reaction (loss of electrons) takes place; when charging, whilst the battery stores electricity, the cathode has a negative electrical charge (-) and an oxidation reaction (acceptance of electrons) takes place.

Lithium ores are mostly concentrated (44%) [2], in the center of Latin America, in the so-called "Lithium Triangle" (Bolivia-Chile-Argentina), but also in China, Australia, Russia and other countries (Fig.1).

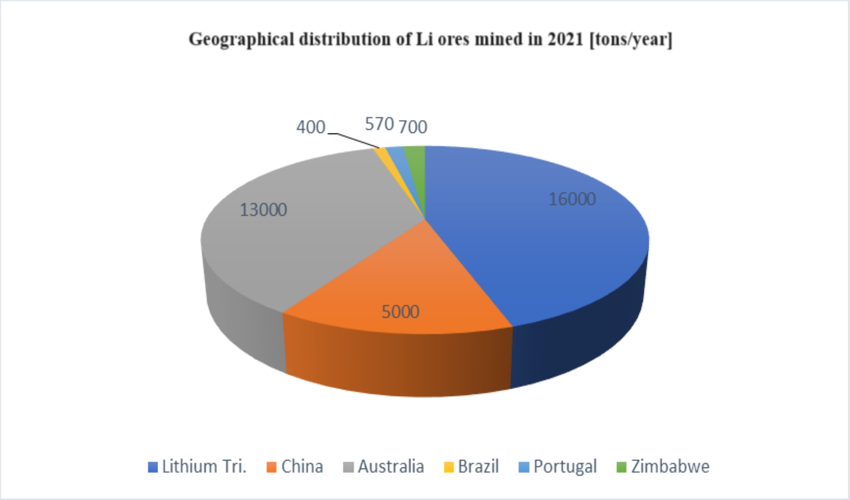

Fig. 1. The geographical distribution of Li ores mined in 2021 [3].

In Argentina, Chile and China, lithium is mined as brine (lithium carbonate - Li_2CO_3), while in Australia, for example, lithium is mined as spodumene (lithium aluminum inosilicate – $LiAl(SiO_3)_2$ from hard rock ore, being exported to China and other Asian countries [4].

China processes 70% of the world's lithium production, produces 77% of cell capacities and 60% of Li-ion battery component production. The current situation is about to change as Germany is catching up in these segments.

1.1. World lithium resources

Global lithium production was 85,000 metric tons (mt) in 2018 and is set to double by 2024 in response to increased demand for applications using Li-ion batteries.

Following the exploration campaigns carried out in recent years, lithium resources identified worldwide have increased significantly in 2022, totaling approximately 75 mil. metric tons (Table 1).

Table 1. The situation of world lithium production and resources in 2022 [5]

COUNTRY	MINING PROD. 2022 (mt)	RESOURCES (mil. mt)
Argentina	6,200	20
Australia	61,000	7,9
Brazil	2,200	0,73
Canada	500	2,9
Chile	39,000	11
Bolivia	-	21
China	19,000	6,8
Portugal	600	0,27
Zimbabwe	800	0,69
Other countries	-	3,3
TOTAL	**129,300+**	**74,59**

1.2. Li-ion battery production

Li-ion battery production is largely concentrated in Asia (84%), with 79% of capacity in China, 2.5% in South Korea and 2.4% in Japan [6].

As for the market share in the production of Li-ion batteries, the status is set to change in the near future, with Europe adopting a series of programs to support this sector, for instance the European Battery Alliance and the Strategic Action Plan on Batteries [7], in order to promote clean mobility, storing energy from renewable sources and achieving energy independence.

Fig. 2 indicates the market shares in Li-ion battery production in the world and their equivalent in Giga-Watt hours (GWh) [8].

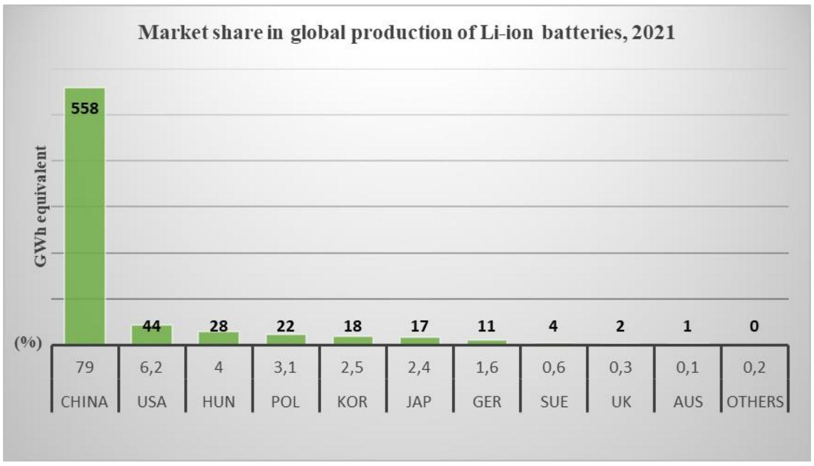

Fig. 2. Market shares in Li-ion battery production in the world and their equivalent in Giga-Watt hours (GWh), 2021.

Europe will register a market share increase in the production of Li-ion batteries, especially due to the commissioning of several giga-factories. Germany will rise to the top of the producers to 11.3%, starting from 2025.

1.3. Li-ion battery manufacturers in the world

As expected, the main companies involved in the production of Li-ion cells and batteries come from China (e.g. CATL), South Korea (e.g. LG Energy Solution, SK Innovation, Samsung SDI) and Japan (e.g. Panasonic). These companies register a combined market value of approx. 200 billion USD and mainly serve the electric vehicle and consumer electronics markets [9].

As an example, CATL (Contemporary Amperex Technology Co. Limited) is the largest manufacturer of medium and large Li-ion batteries for electric vehicles, with new production facilities in Hungary (Debrecen) and Germany (Arnstadt). This manufacturer supplies Li-ion batteries for Tesla, Toyota, Hyundai, Honda, BMW, Volvo or VW and has a market share of 34% (Fig.3) [10].

Fig. 3. Geographical distribution of the main Li-ion battery manufacturers in the world [11].

1.4. Li-ion batteries in Romania

There are local concerns in the development of this sector, with investments that have mobilized public and private capital. In June 2023, the Romanian-Belgian Romvolt project was launched in Galati, a Li-ion battery production and recycling plant with a total capacity of 22 GWh.

Starting in 2018, the well-known Romanian company ROMBAT, a member of the METAIR group headquartered in South Africa, started an investment of approx. 12 mil. Euros for a new production capacity of Li-ion cells and batteries. The factory is located near Bucharest, at Cernica, and started production in February 2020 with a monthly capacity of 100 MWh [12].

The batteries produced within this facility are type LFP, with an active cathode paste composition based on $LiFePO_4$ (lithium iron phosphate). These batteries are intended to replace conventional lead-acid batteries, which provide high starting power, being used predominantly in the propulsion of electric buses.

The completion of a new investment worth 400 million Euros is foreseen in 2024, in order to produce raw materials/components (lithium hydroxide - LiOH) for Li-ion batteries, intended for the automotive industry. The investment will create 700 new jobs and was announced by the German-Canadian company Rock Tech Lithium, which has a similar project under development in Germany, at Guben (Brandenburg), 60 kilometers away from Tesla’s factory in Grünheide [13].

2. Materials and methods - technologies for recovery of cobalt from spent Li-ion batteries

In all experimental studies carried out, spent Li-ion batteries from mobile phones were used. The first step consisted of placing the Li-ion batteries in a saline solution of NaCl (200 g/l) for one hour in order to fully discharge them.

The Li-ion batteries were then disassembled manually, and the contents were separated into components (anode – copper foil covered with graphite, respectively cathode – aluminum foil covered with active paste containing cobalt).

The method used to recover the active paste from the cathode of Li-ion batteries is ultrasonication in acid medium [14], as it can be seen in Fig. 4.

The recovery efficiency of the active paste containing useful metals (cleaning efficiency) was calculated with the following formula [15]:

$$\eta = \frac{m_o - m_f}{m_o} \times 100$$

where:

m_0 = initial mass of the cathode foil (aluminum foil + paste)

m_f = final mass of aluminum foil after ultrasonication in lactic acid medium

To carry out the experimental research at the laboratory level for recovering the active paste from spent Li-ion batteries cathodes, an ultrasonic bath type Emmi-12HC [16] was used - ideal device for chemical cleaning operations in laboratories, workshops and medical offices, having the following characteristics:

- Case material – stainless steel;
- Cleaning frequency = 45 kHz;
- Cleaning time = 1÷ 60 min;
- Bath volume = 1.2 l;
- Heating temperature = 20°C ÷ 80°C;
- Maximum ultrasonic power = 80 W;
- Ultrasonic power regulator = 50/75/100%;
- Dimensions 260x140x180 mm (L, W, H);

- Bath size 200x100x65 mm (L, W, H).

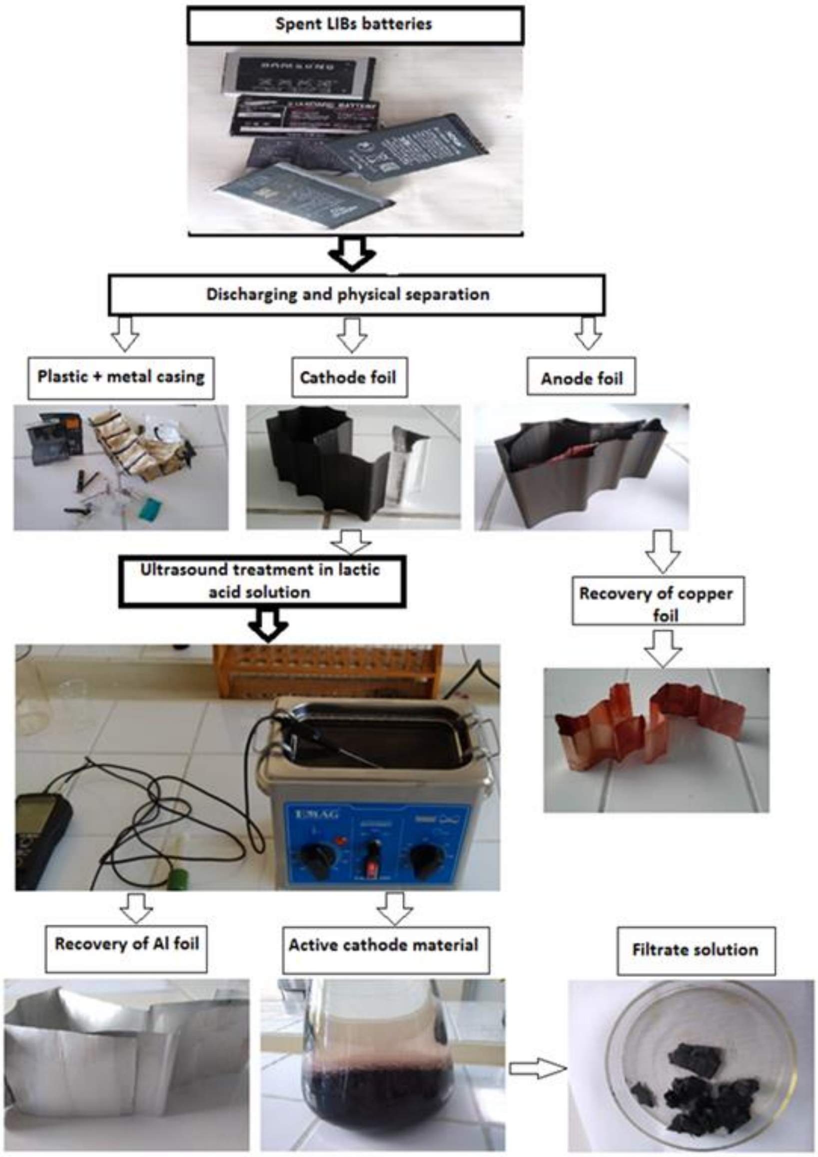

Fig. 4. The method of recovering the active paste from the cathode of spent Li-ion batteries, by ultrasonication in an acidic environment [17].

The maximum yield, over 90%, was achieved using a 1.5 M acid solution after exposing the samples to ultrasounds, under the following conditions: volume V=1.2 l; cleaning frequency f=45 kHz; heating temperature T=50^{o}C; ultrasonic power P= 20÷100 W; cleaning time t= 4÷5 min.

3. Results and discussions - obtaining cobalt blue pigment ($CoAl_2O_4$)

Cobalt blue ($CoAl_2O_4$) or cobalt aluminate is part of the complex oxides with spinel type structure (AB_2O_4), which can be found in many applications – ceramic materials, pigments or magnetic materials.

This pigment can be obtained in the laboratory by heating a mixture of aluminum chloride ($AlCl_3$) and cobalt chloride (II) – ($CoCl_2 \cdot {}_6H_2O$) in a gas flame. The classic technology for obtaining cobalt blue is the calcination of cobalt oxide (CoO) mixed in well-established proportions with alumina (Al_2O_3) at T=1200°C ÷1300°C [18].

In the experiments undertaken to obtain cobalt blue, aluminum oxide (alumina) α - Al_2O_3 (corundum - mineral name) was used, employed in the production of aluminum metal.

Scanning Electron Microscopy images (SEM) Fig.5. and Fig.6., capturing at different resolutions (x100 and x5,000) the α-Al_2O_3 powder. The morphology of the particles could be observed and their size could be measured, between 11.77µm and 77.73µm.

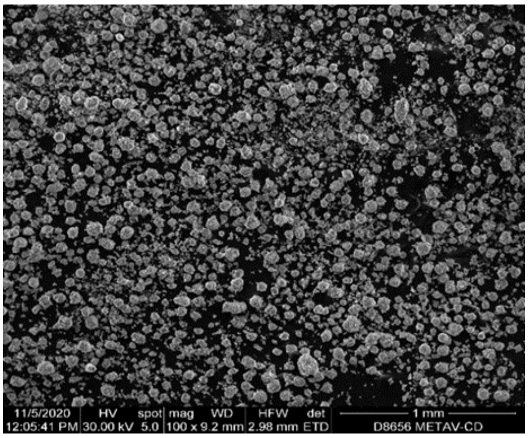

Fig. 5. SEM image (x100) of $\alpha - Al_2O_3$ powder.

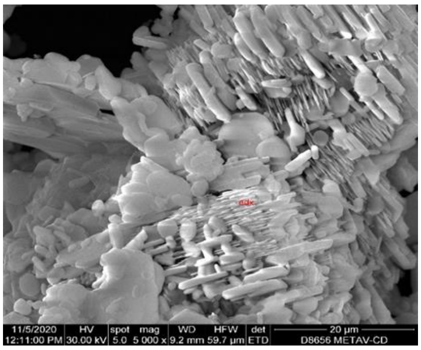

Fig. 6. Figure 6. SEM image (x5000) of $\alpha - Al_2O_3$ powder.

In the research [19], we succeeded in obtaining cobalt blue through a heating treatment, starting from the $LiCoO_2$ compound recovered from spent Li-ion/LCO batteries, going through the following steps:

- At T= 400^{o}C: $LiCoO_2 \rightarrow Co_3O_4$ (cobalt tetra oxide);
- At T= 900^{o}C: ${}_2Co_3O_4 \rightarrow {}_6CoO + O_2$;
- At T= 1200^{o}C: $CoO + Al_2O_3 \rightarrow CoAl_2O_4$ (Fig.7, cobalt blue, with a structure spinel type).

Fig. 7. Cobalt blue obtained ($CoAl_2O_4$).

Cobalt blue ($CoAl_2O_4$) was identified by X-ray diffraction analysis, alongside α – Al_2O_3 (unreacted) in Fig.8 and Fig.9 [20].

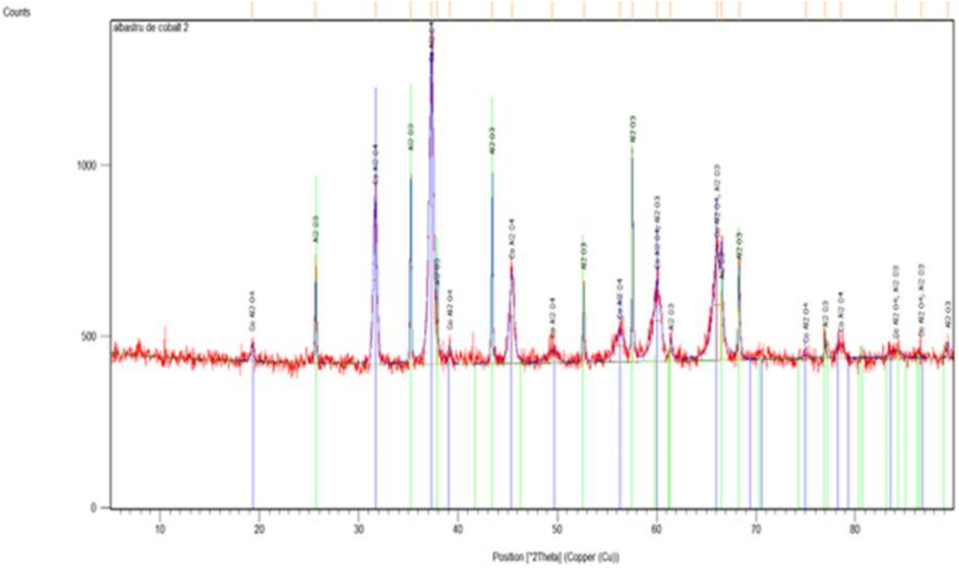

Fig. 8. X-ray diffraction investigation results of cobalt blue ($CoAl_2O_4$); interplanar spacings are marked.

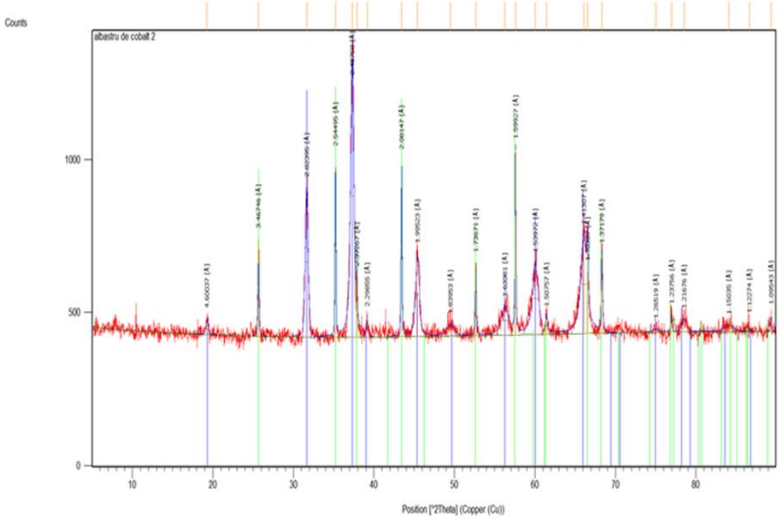

Fig. 9. X-ray diffraction investigation results of cobalt blue ($CoAl_2O_4$); identified compounds are marked.

4. Conclusions

- The cathodic paste of spent Li-ion/LCO batteries containing cobalt, can be efficiently recovered and capitalized through a salable product – cobalt blue ($CoAl_2O_4$);
- The price of cobalt is approx. USD 33,500/mt [21] on specific markets, according to the contracts for differences (CfD), increasing by 12% in comparison to the period of Covid-19 pandemic inception; cobalt blue is an expensive pigment, rated at USD 3,800/kg [22], and lithium is traded as carbonate (Li_2CO_3), at a price of approx. USD 28,000/mt;
- By recycling a spent Li-ion/LCO battery, approximately 1.4 g of cobalt blue pigment (with 50% alumina addition) is obtained; approximately 72 spent Li-ion batteries are needed to obtain 100 g of $CoAl_2O_4$ pigment.

Acknowledgements

No funding has been provided for concluding this paper.

References

---

[1] Brooke Schumm, *Battery*, Encyclopedia Britannica, Mach 2005: https://www.britannica.com/technology/battery-electronics. Accessed 30 August 2023.

[2] *A battle for supremacy in the lithium triangle*, The Economist, 15th June 2017 edition: https://www.economist.com/the-americas/2017/06/15/a-battle-for-supremacy-in-the-lithium-triangle

[3] Vincent Bos, Marie Forget, *Global production networks and the lithium industry: A Bolivian perspective*, Geoforum, **125**, 2021, p. 168-180.

[4] Mineral Commodity Summaries, 2018: https://minerals.usgs.gov/minerals/pubs/mcs/2018/mcs2018.pdf (US Department of the Interior & US Geological Survey).

[5] Mineral Commodity Summaries, 2023: https://pubs.usgs.gov/periodicals/mcs2023/mcs2023-lithium.pdf. Accessed 30 August 2023.

[6] https://www.eca.europa.eu/ECAPublications/SR-2023-15/SR-2023-15_EN.pdf. Accessed 30 August 2023.

[7] European Economic and Social Committee, Strategic Action Plan on Batteries: https://www.eesc.europa.eu/en/our-work/opinions-information-reports/opinions /strategic-action-plan- batteries-report, (2019). Accessed 31 August 2023.

[8] https://www.statista.com/statistics/1249871/share-of-the-global-lithium-ion-battery-manufacturing-capacity-by-country/. Accessed 31 August 2023.

[9] https://www.dnkpower.com/top-10-lithium-ion-battery-manufacturers/. Accessed 31 August 2023.

[10] "2022 1H Global[1] EV & Battery Performance Review". SNE research.

[11] https://worldmapblank.com/blank-map-of-world/.Accessed 1 September 2023, modified by the author.

[12] https://bistritabusiness.ro/rombat-a-finalizat-fabrica-de-baterii-li-ion-de-langa-bucuresti-si-demareaza-productia/. Accessed 1 September 2023.

[13] https://economedia.ro/breaking-canadienii-de-la-rocktech-lithium-vor-investi-400-de-milioane-de-euro-in-romania-intr-o-fabrica-de-componente-pentru-bateriile-masinilor-electrice.html. Accessed 1 September 2023.

[14] Toma C.M., Ghica G.V., Buzatu M., Petrescu M.I., Vasile E., Iacob G., *A recovery process of active cathode paste from spent Li-Ion batteries*, IOP Conf. Ser., Mater. Sci. Eng., 2017, 209 012034.

[15] Bratosin I., Ghica V., Petrescu G., Mircea I., Buzatu M., Necșulescu A. D., Iacob Gh., *Recycling Li-ion batteries in eco-friendly environments*, HADITECHNIKA, **54**, 5, 2020, p. 8-14. ISSN 0230-6891.

[16] Technical data sheet, source: https://www.emmi-dent.com/discover/ultrasonic-cleaning-devices/535/12-hc-stainless-steel-ultrasonic. Accessed on 1 September 2023.

[17] Bratosin I. N., Toma C.M., Vasile E., Ghica V.G., Buzatu M., Petrescu I.M., Kovács T.A., Necșulescu A.D., Iacob G., *Recovery of* $LiCoO_2$ *compound from cathodic paste of spent LIBs by ultrasonography in lactic acid solution*, International Conference on Innovative Research, 2019, IOP Conf. Ser.: Mater. Sci. Eng. 572 012053, p. 1-9.

[18] Mika Yoneda, Kuniaki Gotoh, Makoto Nakanishi, Tatsuo Fujii, Toshiyuki Nomura, *Influence of aluminum source on the color tone of cobalt blue pigment*, Powder Technology, 323, 2018, p. 574–580.

[19] Bratosin I., Ghica V. G., Petrescu M. I., Buzatu M., Iacob G., Necșulescu A.D., *Researches on the recovery of useful metals from spent Li-ion batteries*, IOP Conf. Ser.: Mater. Sci. Eng., 2021, 1037 012039.

[20] Bratosin I., Doctoral Thesis *Studies and experimental research regarding the recovery, for the purpose of capitalization, of the metals contained in the cathode paste of spent Li-ion batteries*, 2022, Polytechnic University of Bucharest.

[21] Trading Economics, Cobalt (USD/T), 2021: https://tradingeconomics.com/commodity/cobalt. Accessed 1 September 2023.

[22] Cobalt Blue Dark synthetic mineral pigment 100g (jar) price, source: https://shop.kremerpigments.com/us/shop/pigments/45700-cobalt-blue-dark.html. Accessed 1 September 2023.