



POLYTECHNIC UNIVERSITY OF BUCHAREST
DOCTORAL SCHOOL OF MATERIALS SCIENCE AND ENGINEERING
DEPARTMENT OF ENGINEERING AND MANAGEMENT OF OBTAINING METALLIC
MATERIALS



SUMMARY OF THE DOCTORAL THESIS
STUDIES AND EXPERIMENTAL RESEARCH REGARDING THE
RECOVERY FOR THE PURPOSE OF CAPITALIZATION OF METALS
CONTAINED IN THE CATHODIC PASTE OF SPENT LI-ION
BATTERIES

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Keywords: *recovery, used Li-ion batteries, active cathode paste, ultrasound, leaching, lactic acid, cobalt blue.*

DOCTORAL THESIS STRUCTURE

The doctoral thesis is divided into ten chapters and organized into three parts:

- i. analysis of the specialized literature regarding the situation of capitalization of spent Li-ion batteries;
- ii. experimental research on the recovery of useful metals contained in the cathodic paste of spent Li-ion batteries and,
- iii. conclusions, genuine contributions and leads to further scientific research.

INTRODUCTION

The objectives of the research are:

- identifying ways to completely discharge spent Li-ion batteries;
- establishing an active paste recovery technology for useful and deficient metal content on the aluminum cathode, using ultrasound in lactic acid environment ($C_3H_6O_3$);
- process optimization (determining the optimal conditions for carrying out the process of separation and recovery of useful metals from the cathode of spent Li-ion batteries);
- characterization of the active paste recovered by the ultrasonic process in lactic acid environment, in order to identify the metallic compounds obtained, to establishing the recovery methods.

JUSTIFICATION FOR CHOOSING THE THESIS RESEARCH TOPIC

- (a) The proposed theme addresses an acute and important topic: environmental protection and resource conservation during the cycle of replacement of spent Li-ion batteries;
- (b) There are intense concerns in this area in the European Union, thus in October 2017 the European Commission launched the European Battery Alliance (EBA) cooperation platform to capitalize on a battery market of up to 250 billion euros a year, starting in 2025, and the creation of a complete value chain of batteries, necessary for a clean energy transition and industrial competitiveness;

(c) In Romania, Decision no. 478/2020 (July 5, 2020) for the amendment of Governmental Decision no. 1132/2008 on the regime of batteries, accumulators and waste batteries and accumulators, which has as objectives: a) the improvement of waste management practices; b) stimulating innovation in recycling; c) limiting the use of landfills and d) creating incentives to change consumer behavior;

(d) On 30 September 2020, the EU launched the European Raw Materials Alliance (ERMA), which aims for strategic autonomy over critical raw materials, focusing on rare metals and rare earths that are used in the production of batteries and electrical and electronic devices. The aim is to enable the EU to become independent in the supply of raw materials (Li, Co) for the production of Li-ion batteries by 2025.

THE RESEARCH PROGRAMME

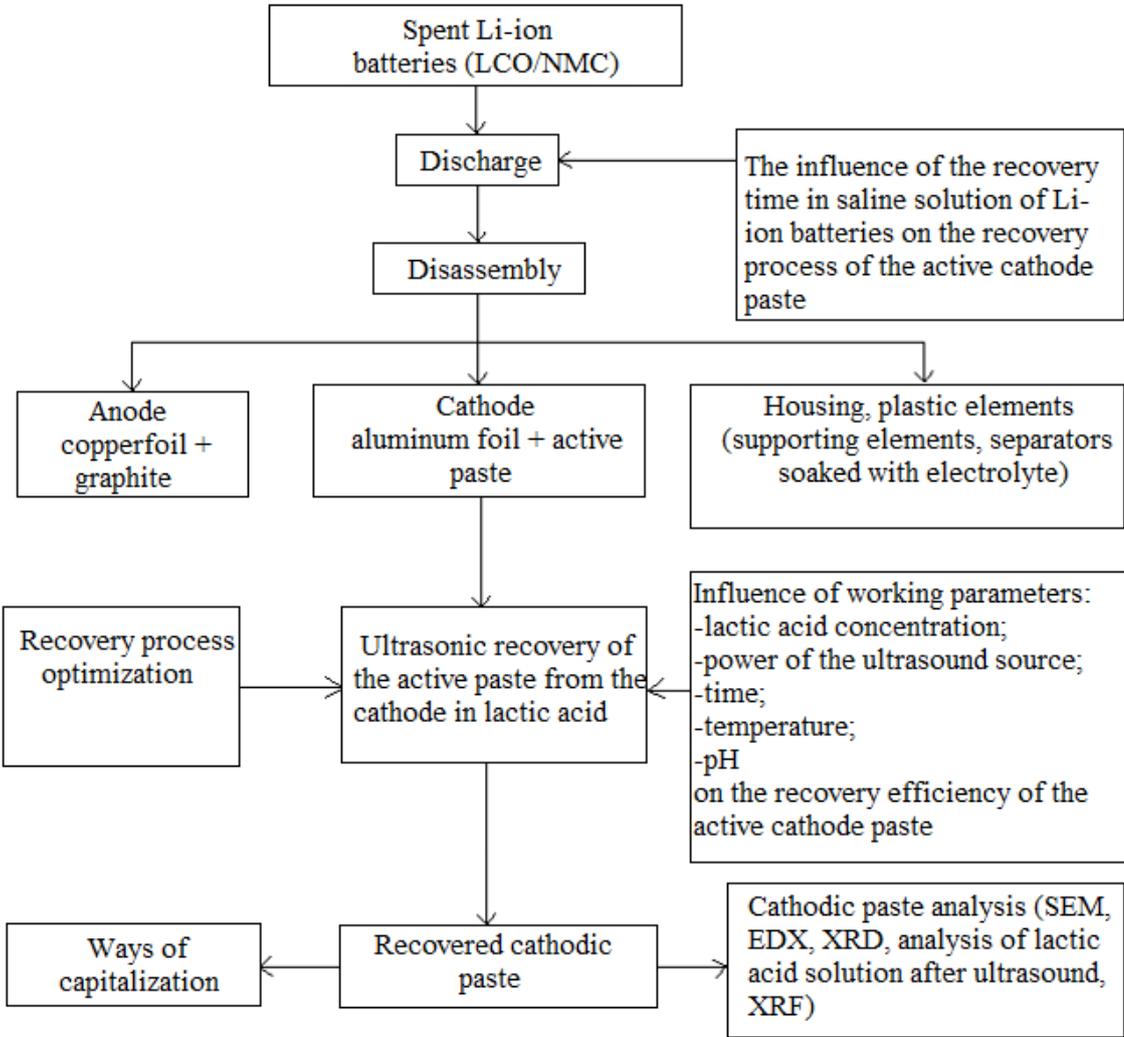


Fig.1. The research programme scheme

PART I

ANALYSIS OF THE SPECIFIC LITERATURE ON THE STATUS FOR CAPITALIZATION PURPOSES OF SPENT LI-ION BATTERIES

Chapter 1 – includes definitions, history of Li-ion batteries, compositions, operating principles, classification.

The main types of Li-ion batteries in use are presented:

- (a) **LCO** – abbreviation of the chemical compound LiCoO_2 (lithium cobalt oxide), applicability in mobile phones, laptops or digital cameras;
- (b) **LMO** – the name comes from LiMn_2O_4 (lithium-manganese oxide), intended for medical devices, power tools or propulsion electric vehicles;
- (c) **LFP** – the composition of the cathodic paste is LiFePO_4 (lithium-iron phosphate), mainly used in the propulsion of electric buses;
- (d) **LTO** – the composition of the cathodic active material is Li_2TiO_3 (titanate of lithium), used in UPS and street lighting systems, based on conversion of photovoltaic energy into electricity;
- (e) **NCA** – battery whose cathodic active material is LiNiCoAlO_2 (oxide lithium-nickel-cobalt-aluminum), used in powering devices medical and industrial, but also in the fully powered vehicle industry electric (Tesla);
- (f) **NMC** – the most successful Li-ion battery on the market due to high energy performance, increased safety and durability using LiNiMnCoO_2 (lithium-nickel oxide-manganese-cobalt) as a cathodic chemical compound.

There are several ways to classify Li-ion batteries. A classification of Li-ion battery types can be based on their specific energy. Thus, the LCO, NCA and NMC type batteries are distinguished, which record the highest values of specific energy ($\geq 200 \text{Wh / kg}$). Another important feature that Li-ion batteries can be ranked on is the lifespan, or the maximum charging / discharging cycles supported. The performers of this chapter are LTO type batteries, which is why they are mainly used in uninterruptible power supply (UPS) systems. The standings of the important parameters in the classification of Li-ion batteries is completed by their thermal stability. Improving safety is one of the most important issues that battery manufacturers are constantly working on. There have been many cases in which the batteries have self-ignited during operation and not only (e.g. Samsung phone batteries; Tesla cars). LTO type batteries stand out, performing at temperatures well below 0°C . Overall, Li-ion batteries have a good performance index compared to conventional batteries, highlighting LTO, LCO, NMC and NCA batteries. But there is room for improvement, and the future looks bright when it comes to solid state batteries.

Chapter 2. European Union strategy on batteries: creating an ecosystem sustainable,
competitive and innovative

The European Commission's economic concerns predict (by 2050) an accelerated transition to a sustainable, secure, competitive and climate-neutral economy, under the motto "a clean planet for all".

In order to reduce carbon dioxide emissions, the production of Li-ion batteries is a key factor; The EU's goal is to build a "battery ecosystem in Europe" to increase its autonomy from Asia. This can be achieved by taking coherent and comprehensive measures along the entire strategic battery chain: extraction - procurement - refining of raw materials - production - reuse - recycling.

Globally, the demand for Lithium-ion batteries will increase dramatically from 77 GWh in 2018 to around 4,000 GWh in 2040. It is estimated that the EU will develop a capacity of 207 GWh by 2023 at a demand of 400 GWh by 2028, only for electric vehicles.

Chapter 3. Processes and technologies for recycling used Li-ion batteries

Li-ion battery recycling technologies are based on the following types of processes:

- i) physical recycling procedures;
- ii) chemical recycling processes;
- iii) combined processes.

The class of physical recycling processes of used Li-ion batteries includes: mechanical separation, heat treatment, mechanical-chemical separation and various dissolution methods.

The category of chemical recycling processes includes: acid leaching, bio-leaching, solvent extraction, chemical precipitation and electrochemical methods.

There are combined methods for recharging Li-ion batteries. Among the ten combined recycling processes analyzed, we mention: crushing-leaching in acidic environment - heat treatment - chemical precipitation; manual separation - heat treatment - hydrometallurgical stage - gel solution; disassembly - leaching in acid medium - solvent extraction - chemical precipitation; selective dissolution - chemical precipitation.

PART II

THE EXPERIMENTAL RESEARCH ON THE RECOVERY OF USEFUL METALS CONTAINED IN THE CATHODIC PASTE OF SPENT LI-ION BATTERIES

Part II comprises six chapters (chapters 4 ÷ 9) and presents its own research carried out in the hydrometallurgy laboratory within the Department of Engineering and Management of Obtaining Metallic Materials of the Faculty of Materials Science and Engineering.

Chapter 4. Experimental research on the recovery of metals contained in the cathodic paste of used Li-ion batteries, for the purpose of recovery

Chapter 4.1. Working methodology

Of the six types of Li-ion batteries on the market (LCO, LMO, NMC, LFP, NCA and LTO), we initially turned our attention to spent LiCoO_2 / LCO batteries, but research continued with LiNiMnCoO_2 / NMC batteries. The NMC battery type was born from the attempt to use as little cobalt (expensive and deficient metal) as possible at the cathode of Li-ion batteries.

The experimental research started with the recovery technologies of the useful metals contained in the cathodic paste of used Li-ion batteries, presented in Table 1.

Table 1. Comparison of the separation efficiency of cathodic materials and Al foil by different methods

Reference	Separation methods	Operating conditions	Phases	Efficiency (%)
L-P He et al. (2015) [1]	Disolution PVDF*	Ultrasonic cleaning, T=70°C, stirred 90min	3	~99
Hanish et al. (2011) [2]	Disolution NMP**	T=90°C, stirred 15min	6	90
Song et al. (2013) [3]	Disolution DMF***	T=70°C, stirred 2h	2	88.6
Li et al. (2009) [4]	Mechanical treatment	Crushing, ultrasonic cleaning, T=25°C, stirred 15min	1	92
Ferreira et al. (2009) [5]	Al disolution with alkaline solution	T=30°C, 10 M NaOH, S/L ratio 1:3 g ml ⁻¹	2	Selective leaching Al 80
Chen et al. (2011) [6]	Thermal treatment	T=150÷200°C, t=2÷3h	1	No data

* PVDF – Polyvinylidene fluoride - (C₂H₂F₂)_n-

**NMP – N-methyl-2-pyrrolidone (C₅H₉NO)

***DMF – Dimethylformamide

Based on the analysis of the articles published by the predecessors, the following were observed:

- the use of ultrasound as a method of cleaning the active paste of Al foil of the cathode of spent Li-ion batteries (LCO), was preceded by an attack with different solvents (NMP, DMF);

- the ultrasound was initially performed in an acidic or alkaline environment using polluting solvents (HCl, H₂SO₄, NaOH);

- the use of organic acids, environmentally friendly (citric acid, lactic acid, acetic acid, malic acid) is recent and the working parameters are not encouraging (long ultrasound time, high temperature, high power of the ultrasound source);

- although not specified, the studied articles considered the recycling of LCO-type Li-ion batteries, because at the time of the experiments, only they had exhausted the resources; in the meantime, the composition of the batteries has changed (the cobalt content has decreased, being replaced by Ni, Mn, Ti). It should not be neglected that the research is carried out on batteries whose chemical composition is not public, being confidential information.

In all experimental studies, used Li-ion batteries from mobile phones in the two categories, LCO and NMC, were used. The first step was to insert the Li-ion batteries into a saline solution of NaCl (200 g / l) for one hour, in order to completely discharge them.

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

The method used to recover the active paste from the cathode of Li-ion batteries is ultrasound in acid medium.

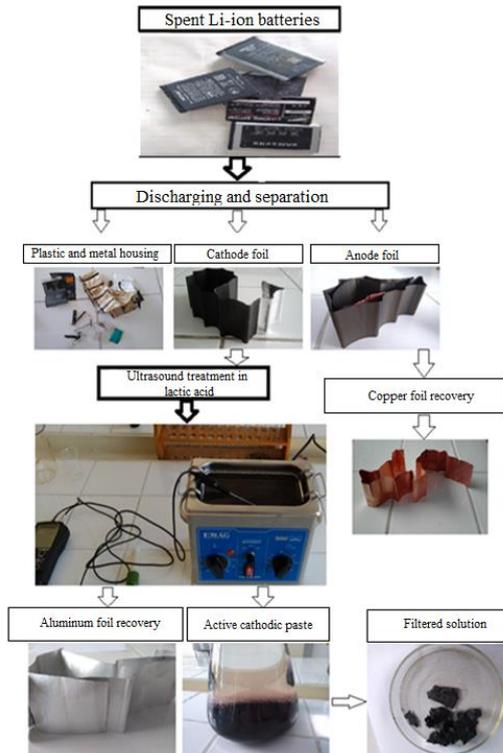


Fig.5. The method for recovering the active paste from the cathodes of spent Li-ion batteries by ultrasound in acid medium [7]

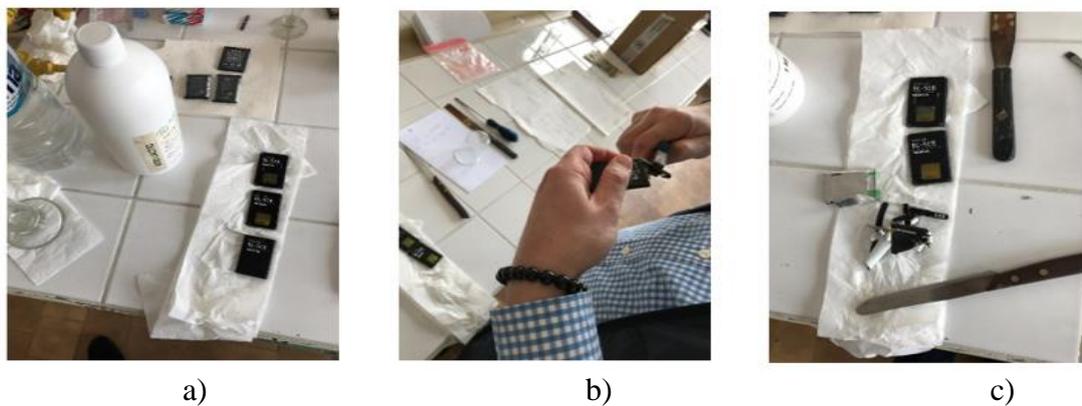


Fig.6. Manual dismantling of spent Li-ion batteries (a, b, c) [9]

Chapter 4.2. Recovery efficiency calculation

The recovery efficiency of the active paste containing useful metals (cleaning efficiency) will be calculated using the following formula:

$$\eta = \frac{m_o - m_f}{m_o} \times 100 \quad 4.1.$$

where:

m_o = initial mass of cathodic foil (aluminum foil + paste)

m_f = final mass - aluminum foil after ultrasound in lactic acid medium

Chapter 4.3. Materials used in research

In our experiments we used spent Lithium-ion batteries, from mobile phones type BL-4S (LCO) and type BL-5CB (NMC).

BL-4S batteries are 860 mAh rechargeable Li-ion batteries, 3.7 V voltage, dimensions: 50mm x 38mm x 4.8mm (H, L, L), weight ~ 28g. This type of battery was produced between 1997 - 2009 and then from 2017 until now (type I batteries).

BL-5CB batteries are rechargeable batteries that provide a high power density in a flat and light format. The production of these batteries started after 2011 (newer than type I), being still produced and used as a power supply for mobile phones. As technical specifications, the batteries are Li-ion type, charging time 1h 35 min., with a capacity of 800 mAh, voltage 3.7 V, dimensions: 53mm x 34mm x 5.8mm (L, l, h), weight 21 ÷ 24g (type II batteries).



Fig.4.3.1. Battery BL-4S (type I)[8]



Fig.4.3.2. Battery BL-5CB (type II)[9]

Chapter 4.4. Research equipment used

The experiments were performed both in the Hydrometallurgy Laboratory of the Department of Engineering and Management of Obtaining Metallic Materials, Faculty of Materials Science and Engineering – Polytechnic University of Bucharest, and in other laboratories of the Polytechnic University of Bucharest. For conducting research experiments in the hydrometallurgy laboratory, the following were used: electronic balance type EMB 200-3, Kern; ultrasonic bath type Emmi-12HC; phmeter HI 8314. Calcination of the recovered paste mixture with alumina (corundum), to obtain the cobalt blue pigment, was performed in a NABERTHERM N17/HR type furnace.

The structural and microstructural analysis of the materials was performed in the laboratories of the Polytechnic University of Bucharest, using: X-ray diffraction system, model: X'Pert PRO MPD; scanning electron microscope (SEM), model: QUANTA 450 FEG.

The analysis of the lactic acid solution after ultrasound, in order to identify the metallic elements, was performed by inductively coupled plasma optical emission spectrometry (ICP-OES), model ICAP 6300 DUO.

X-ray fluorescence spectroscopy (XRF) analyzes were determined with the XRF Oxford X-MET 5000 Handheld Analyzer.

Chapter 5. Research on the recovery of active paste containing cobalt on the aluminum cathode, using an ultrasonic bath and lactic acid as leaching environment

Chapter 5.1. Ultrasonic cleaning mechanism

Ultrasound (waves with frequency $> 16\text{kHz}$), by the peculiarities manifested due to the high frequency [transport energies higher than sounds, particle acceleration is higher ($106g$), can be amplified in the desired direction], are ideal for creating the cavitation phenomenon.

Cavitation is a phenomenon that consists in the rupture of a liquid in certain areas and the immediate recovery under the action of high stresses that occur as a result of successive expansions and compressions of the environment under the effect of wave propagation.

The cathodic paste is compact and attached to the aluminum foil with the help of PVDF (polyvinylidene difluoride – $\text{C}_2\text{H}_2\text{F}_2$), a very non-reactive thermoplastic polymer, obtained by polymerizing vinylidene difluoride, with remarkable properties (use up to $T=157^\circ\text{C}$, good insulator withstands heat transfer, heat, cold, electrical conductivity, very good resistance to oxidizing acids, solvents, halogens, alcohols, salts and weak bases);

Ultrasonids are generated by a transducer connected to a generator. When ultrasonic waves reach high frequencies, the cavitation phenomenon occurs: ultrasound performs a compression, followed by a sudden expansion of the molecules that make up the liquid (environment). Ultrasound accelerates and amplifies the convective motion of the solvent, leading to an increase in the dissolution rate of PVDF;

The mechanism of detachment of the active paste from the aluminum foil through shock waves is explained by the appearance of very high pressure peaks ($104\text{-}105\text{ atm}$), which act on very small surfaces (about 1 mm^2) for a very short time (microseconds). Ultrasonic cavitation also generates high frictional forces, which break up agglomerated particles into fine, dispersed particles

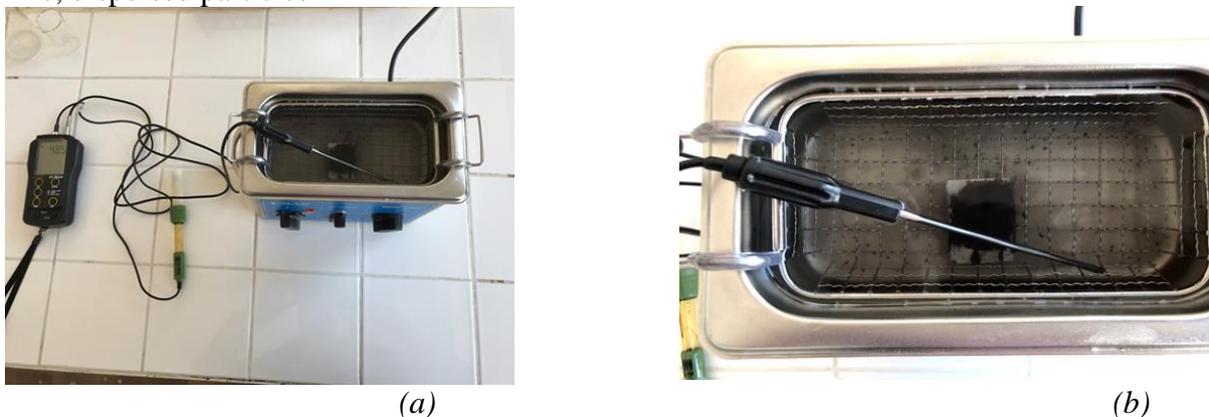


Fig.8. The mechanism of detachment of the active paste from the aluminum foil by ultrasound in lactic acid environment (a), (b) [9]

Chapter 5.2. Experimental procedure

The batteries were completely discharged by keeping them in a NaCl saline solution (200g/l) for one hour, dried and dismantled. The cathode made of aluminum foil on which the cobalt-containing paste is fixed was cut into $10 \div 12$ sections, with which the first tests were performed, and the entire cathode was finally used. The Emmi-12HC type ultrasonic bath with a capacity of 1.2 l and a maximum ultrasonic power of 80W was used; worked with power sequences of 50/75/100%. The experiments were performed at room temperature ($T=20^{\circ}\text{C}$), without the need for additional heat sources. The ultrasonic bath basket with the cathodic section was positioned and maintained at a height of 1.5 cm by the ultrasonic generator on the bottom of the tub. It was intended that the cathodic paste be completely detached from the aluminum foil in the shortest possible time and with the lowest possible energy consumption. If at the beginning a section of the cathode foil (1/10 or 1/12) was inserted in the ultrasonic bath, in the end it was worked with whole cathodes. Several concentrations of lactic acid ($\text{C}_3\text{H}_6\text{O}_3$ – a weak organic acid) were used, aiming for a recovery of the active paste as high as possible, in a short time and with as little power as possible; lactic acid concentrations between 1.35 M and 1.6 M were used.

Chapter 5.3. The influence of technological parameters (temperature, time, pH, concentration, power of ultrasonic bath) on the recovery efficiency

The influence of lactic acid concentration, the addition of hydrogen peroxide (H_2O_2), the power of the ultrasound source, the temperature and the duration of the ultrasound on the recovery efficiency of the active paste containing useful metals (cobalt, nickel) were studied. from the cathode of spent Li-ion batteries; five samples (cathode-coated foil) were used for each concentration considered. The concentration of lactic acid was between 1.35 M and 1.6 M, and the ultrasound interval was between 4 and 12 minutes. The power of the ultrasound source was kept constant $P = 40\text{W}$, the working temperature was maintained at $T=20^{\circ}\text{C}$, and the S/L ratio was 0.60g/l.

Table 2. Centralizer on the evolution of the recovery efficiency of the active cathode paste according to the ultrasound time at lactic acid concentrations between 1.35 ÷ 1.6 M (S/L ratio: 0.60 g/l; power of the ultrasonic source $P = 40\text{W}$; process temperature $T = 20^{\circ}\text{C}$)

Lactic acid concentrations 1,35÷1,6 M		
Sample	Time [min]	Efficiency [%]
P1	11.4	50
P2	7.2	58.8
P3	5.4	89.6
P4	8.6	63

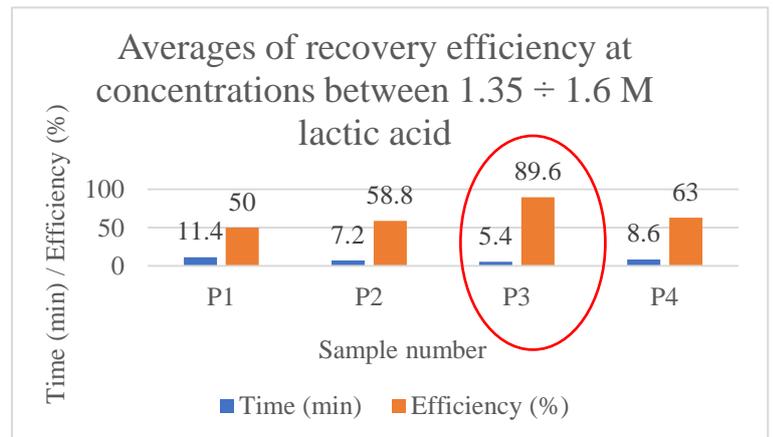


Fig.9. Centralized graph regarding the evolution of the recovery efficiency of the active cathodic paste as a function of the ultrasound time at the lactic acid concentration between 1.35 ÷ 1.6 M (S/L ratio: 0.60 g/l; power of the ultrasonic source $P=40\text{W}$ process temperature $T = 20^{\circ}\text{C}$)

The experimental analysis found that:

- the maximum recovery value of the cathodic paste was obtained for a lactic acid concentration of 1.5 M, when a recovery efficiency of about 91% was reached in a very short time of ultrasound (t = 6 minutes), in conditions constant working flow: S/L ratio: 0.60 g/l; power of ultrasonic source P=40W; process temperature T=20°C;
 - in order to improve the recovery efficiency of the active paste on the cathode foil of used Li-ion batteries, by ultrasound in lactic acid environment, hydrogen peroxide (H₂O₂) was introduced into the working environment, but the addition of hydrogen peroxide increases very little the efficiency of recovering the cathodic paste from the aluminum foil and therefore its use is not justified, unnecessarily increasing the costs.
- ❖ Table 3 and Figure 10 illustrate the effect of the recovery efficiency of the active cathodic paste, **depending on the ultrasonic power** at 1.5 M lactic acid concentration (without the addition of 5% hydrogen peroxide; S/L ratio: 0.60 g/l; process temperature T=20°C);
 - ❖ It was expected that as the power of the ultrasonic bath increases, the efficiency of separating the active paste from the aluminum foil will increase due to the amplification of the cavitation effect. It was noticed that the cleaning efficiency increased with the power of the ultrasonic bath from 20W to 40÷50W, after which it started to decrease;
 - ❖ This decrease in cleaning efficiency is explained by the fact that increasing the power of the source, the cavitation will generate large amounts of invalid bubbles, which can form a sonic barrier that attenuates the dispersion of ultrasound and causes a decrease in cleaning efficiency of the active paste on the aluminum foil;
 - ❖ Thus, the optimal ultrasonic power was established to be between P=40÷50W.

Table 3. Evolution of the recovery efficiency of the active cathode paste according to the ultrasonic power at 1.5 M lactic acid concentration (without 5% hydrogen peroxide concentration; S/L ratio: 0.60 g/l; process temperature T=20°C)

Time: 6÷12 min		
Sample	Power [W]	Efficiency [%]
P1	20	51
P2	30	56
P3	40	85
P4	50	90
P5	60	76

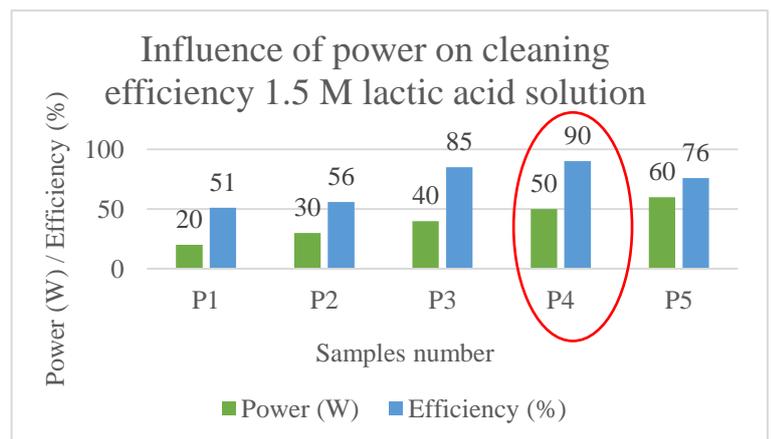


Fig.10. Graph on the evolution of the recovery efficiency of the active cathodic paste as a function of the ultrasonic power at 1.5 M lactic acid concentration (without the addition of 5% hydrogen peroxide; S/L ratio: 0.60 g/l; process temperature T=20°C)

- ❖ Table 4 and Figure 11 show the effect of the recovery efficiency of the active cathodic paste, **as a function of the ultrasound temperature** at 1.5 M lactic acid concentration (without the

addition of 5% hydrogen peroxide; S/L ratio: 0.60 g/l; power of the ultrasonic source P=40W; process temperature between T=20÷60°C);

- ❖ Recovery efficiency increases with temperature in the studied range – increases the solubility of PVDF in lactic acid solution and stirring the solution by ultrasound. Up to T=50°C, the increase in efficiency is significant, after which the increase in the temperature of the ultrasonic bath from T=50°C to T=60°C causes an insignificant increase in efficiency (from 92% to 93%);
- ❖ In addition, although the boiling point of lactic acid is T= 22°C, it was observed that the volatilization of lactic acid becomes more pronounced at a higher temperature, because the evaporation rate increases with increasing temperature;
- ❖ Therefore, in order to obtain a relatively high efficiency of useful cathodic materials and low volatilization of C₃H₆O₃, the optimum temperature was considered reached at T=50°C.

Table 4. Evolution of the recovery efficiency of the active cathodic paste as a function of the ultrasound temperature at 1.5 M lactic acid concentration (without the addition of 5% hydrogen peroxide; S/L ratio: 0.60 g/l; power of the ultrasonic source P=40W; process temperature T=20÷60°C)

Time: 6÷12 min		
Sample	Temp [°C]	Efficiency [%]
P1	20	57
P2	30	61
P3	40	71
P4	50	92
P5	60	93

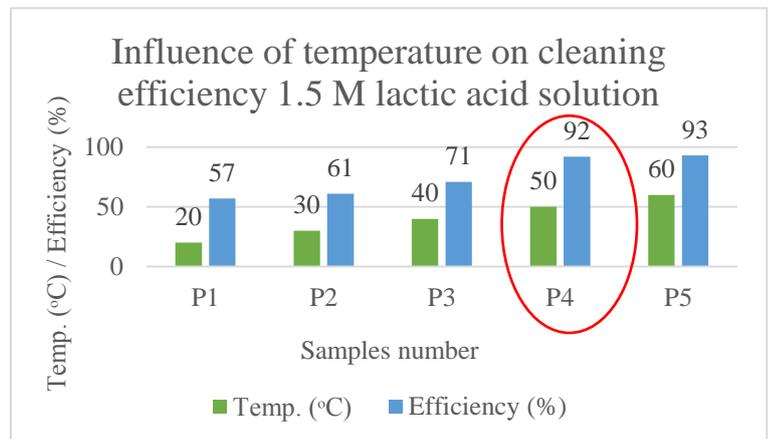


Fig.11. Graph on the evolution of the recovery efficiency of the active cathode paste as a function of the ultrasonic bath temperature at 1.5 M lactic acid concentration with hydrogen peroxide (S/L ratio: 0.60 g/l; power of the ultrasonic source P=40W; temperature process T=20÷60°C)

- ❖ The effect of **the ultrasonic duration** on the cleaning efficiency of the cathode paste on the aluminum foil is presented in Table 5 and Figure 12;
- ❖ The detachment efficiency of the cathode paste increases with the ultrasound duration of the bath, reaching a percentage of 90÷91%, when the time was t=4 minutes;
- ❖ However, an additional prolongation of the ultrasound time no longer contributes to the increase of the cleaning efficiency, instead it results in the attack of the aluminum foil (detachment of aluminum particles from the foil), which contaminates the cobalt-containing paste, making the process more difficult. to capitalize on it;
- ❖ Therefore, the optimal time was set at t=4 minutes.

Table 5. Evolution of the recovery efficiency of the active cathodic paste as a function of the ultrasound time at 1.5 M lactic acid concentration (without the addition of 5% hydrogen peroxide; S/L ratio: 0.60 g/l; power of the ultrasonic source P=40W; process temperature T=20°C)

Power: 40÷50W		
Sample	Time [min]	Efficiency [%]
P1	1	20
P2	2	40
P3	3	88
P4	4	91
P5	6	90

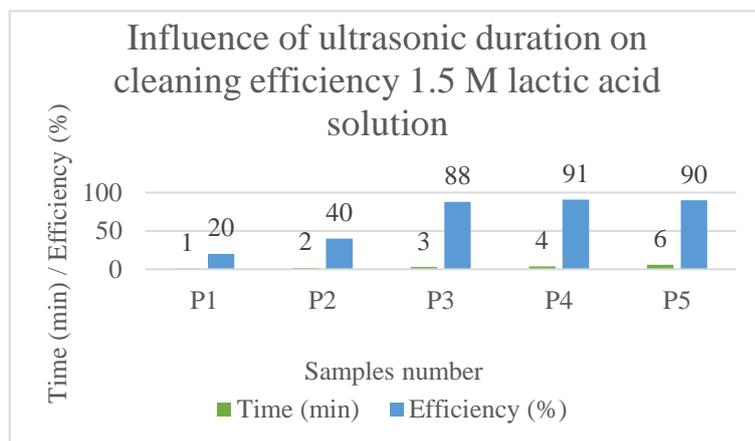


Fig.12. Graph on the evolution of the recovery efficiency of the active cathode paste as a function of the ultrasonic time at a lactic acid concentration of 1.5 M (without hydrogen peroxide; S/L ratio: 0.60 g/l; power of the ultrasonic source $P=40W$; temperature process $T=20^{\circ}C$)

Conclusions regarding the process of separation / recovery of the active paste from the cathode from aluminum foil, in lactic acid medium:

- ❖ The maximum yield, above 90%, was achieved using a 1.5 M acid solution after exposure to ultrasound under the following conditions: volume $V=1.2$ l; cleaning frequency $f=45$ kHz; heating temperature $T=50^{\circ}C$; ultrasonic power $P=40\div50$ W; cleaning time $t=4\div5$ min;
- ❖ The chemical compositions of the two types of batteries were determined by X-ray fluorescence spectroscopy.

Table 6. (a) The composition of the cathode paste of a used BL-4S Li-ion battery

Element	%	STD
Ti	ND	0,0527
Cr	0,071	0,0200
Co	78,114	0,1997
Ni	ND	0,0166
Cu	ND	0,0305
Zn	ND	0,0246
Zr	0,022	0,0043
Nb	ND	0,0080
Mo	ND	0,0083
Ag	ND	0,0166
Cd	ND	0,0245
W	ND	0,0564
Pt	ND	0,0230
Au	ND	0,0101
Hg	ND	0,0204
Fe	ND	0,0032
Ca	0,174	0,0051
V	ND	0,0532
Mn	ND	0,0316
Pb	ND	0,0103

(a)

Element	%	STD
Ti	ND	0,0551
Cr	0,071	0,0367
Co	54,174	0,1856
Ni	12,936	0,855
Cu	ND	0,0374
Zn	ND	0,0249
Zr	ND	0,0068
Nb	ND	0,0073
Mo	ND	0,0074
Ag	ND	0,0200
Cd	0,020	0,0109
W	ND	0,0596
Pt	ND	0,0208
Au	ND	0,0256
Mn	7,569	0,0690

(b)

Table 6. (b) Cathode paste composition of a used BL-5CB Li-ion battery [10]

Chapter 6. Mathematical modeling of the recovery process, by ultrasonic process in lactic acid, of spent Li-ion batteries

- o Mathematical modeling was performed in order to optimize the recovery process of the active cathode paste;
- o The optimization was performed under the following conditions: lactic acid environment at a constant pH of 1.5 M; the ultrasound duration was kept constant $t=4$ minutes.
- o The aim was to obtain the optimal values of temperature and power of the ultrasonic bath in order to streamline the operation of separating the paste from the cathode foil;
- o The initial model (linear model) was calculated using a factorial matrix, but not in accordance with the analyzed process (i.e. low efficiency) and a nonlinear model was determined, completing the factorial matrix with the following experiments performed (no. 5÷9), necessary for the central-compositional-orthogonal programming of the second order PCCO;
- o The nonlinear model checked the calculated Fisher Criterion, and in order to optimize it, the model was brought to the canonical form or the standard form;
- o Determining the optimal regime was done by the method of Ridge analysis (linear regression), based on the method of Lagrange multipliers;
- o The optimal values found were: **T=59.86°C**; **P=46W** and, taking into account the error of calculation of the process performance, the lower limit of the efficiency has the value **$\eta=80,15$** .

Chapter 7. Analyzing the active paste recovered by ultrasonic process in lactic acid of spent Li-ion / LCO batteries

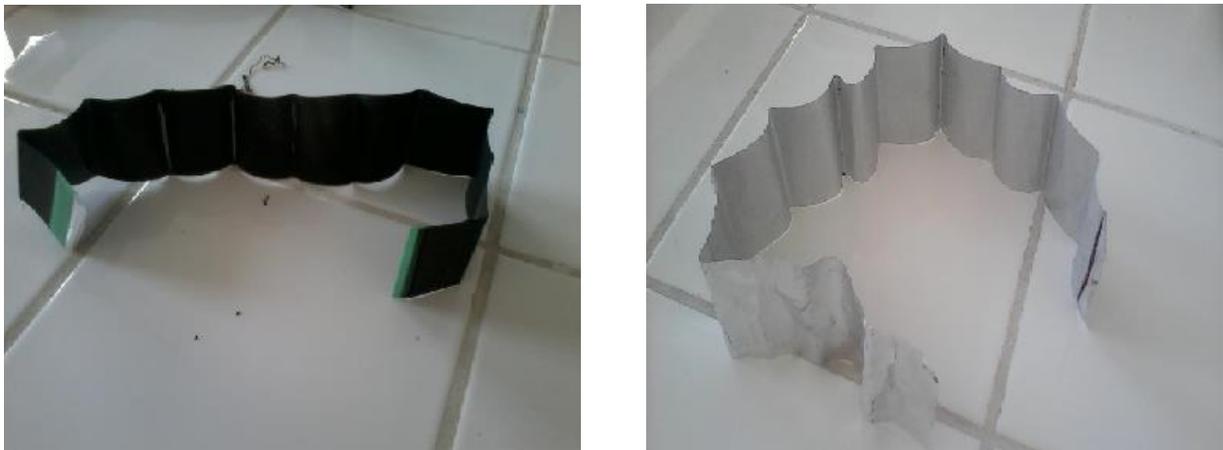


Fig.13. Waste battery cathode: (a) aluminum foil coated with active paste $MnO_2 + LiCoO_2$; (b) aluminum foil cleaned following ultrasonic process in 1.5 M lactic acid – high purity aluminum foil is obtained (cathode foil width = 4.5 cm)

Prior to the ultrasonic process, an X-ray diffraction analysis was performed on the cathode of the used LCO batteries [Fig. 13 (a)] to identify the compounds present. X-ray diffraction allowed to obtain the interplanar distances - Fig.14. (a) and, based on them, it was possible to identify the compounds present Fig.14. (b).

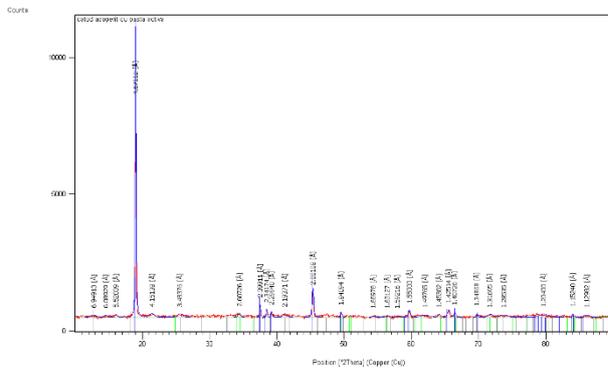


Fig.14. (a) X-ray diffraction analysis performed before the start of the ultrasonic process (a – interplanetary distances)

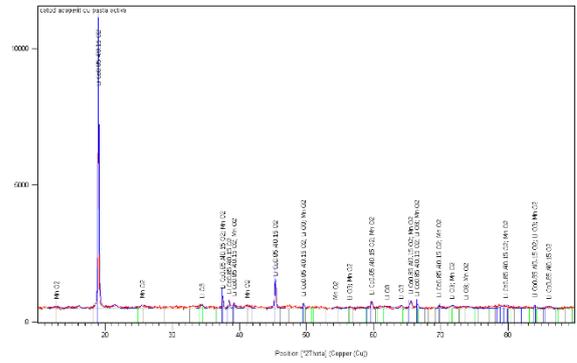


Fig.14. (b) X-ray diffraction analysis performed before the start of the ultrasonic process (b – identified compounds)



Fig.15. Active paste cleaned and recovered from the process 1.5 M lactic acid ultrasound

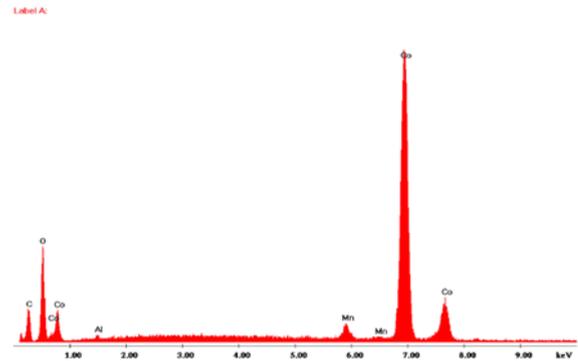
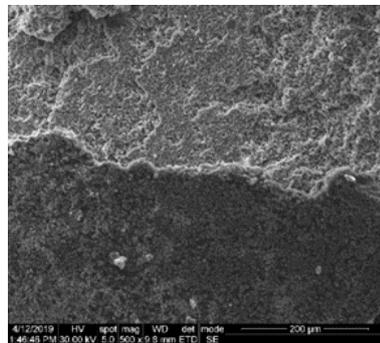
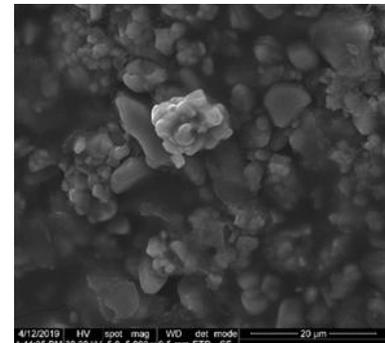


Fig.16. EDX analysis; Co and Mn is well outlined

- From the EXD analysis (Fig.16.) Performed on the recovered paste (Fig.15.), It is observed that the matrix of the active paste is based on cobalt. The identified manganese, deposited at the interface of the active paste / aluminum foil, aims to increase the electrical conductivity of the electrochemical system; after disintegration, the high purity aluminum foil was recovered, perfectly cleaned of the cathodic paste. The recovered cathodic paste was dried and subsequently analyzed to identify cobalt compounds for recovery.rom the EXD analysis (Fig.16.) it is observed that the matrix of the active paste is based on cobalt. The identified manganese is deposited at the interface of the active paste/aluminum foil in order to increase the electrical conductivity of the electrochemical system



a)



b)

Fig.17. Morphological appearance of the surface of the cathode paste after the cleaning operation: (a) SEM image (x500); (b) SEM image (x5,000)

- From the SEM electron microscopy image [Fig.17. (a) and (b)], the surface morphology indicates that the active paste is easily detached from the aluminum foil, the ultrasound conditions in lactic acid medium being correctly identified;
- Investigations by X-ray diffraction performed on the recovered paste, allowed the identification of the compound LiCoO_2 (Fig.18).

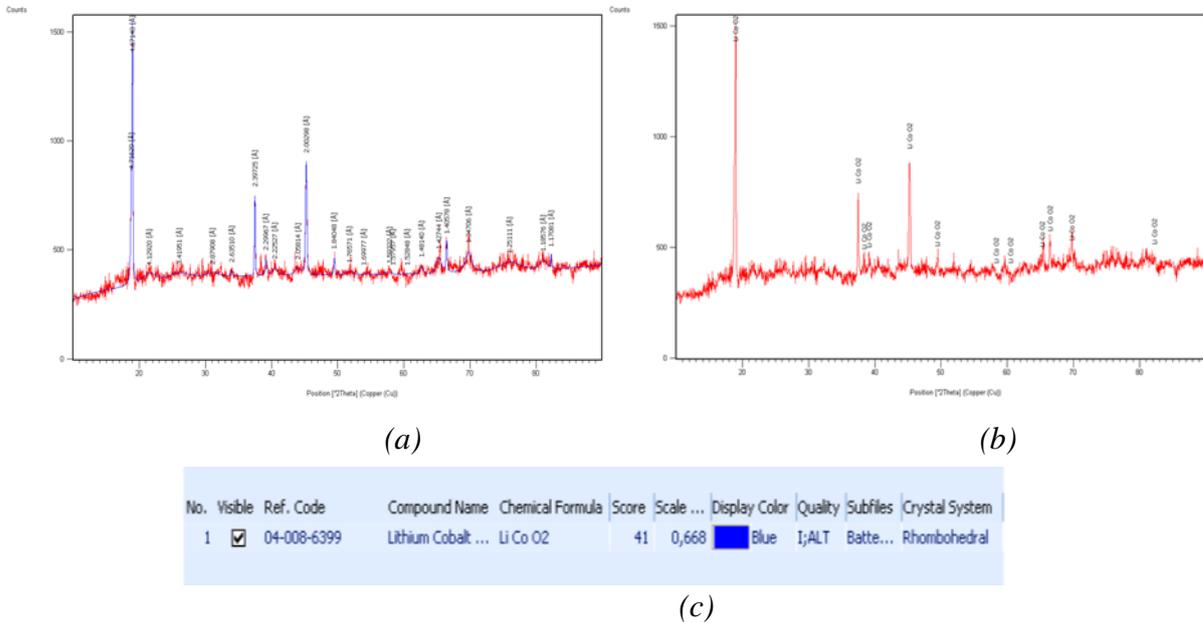


Fig.18. Results of X-ray diffraction investigation on recovered cathode paste: (a) interplanetary distances; (b) characteristic compounds; (c) the database file

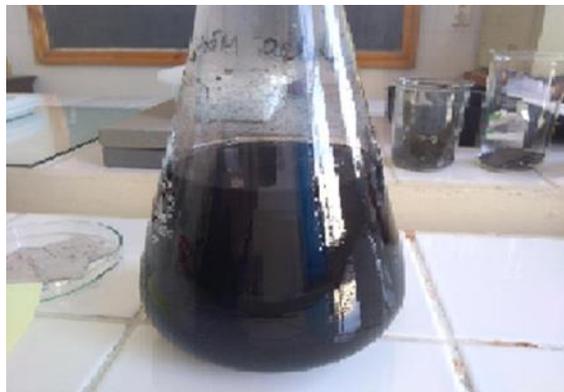


Fig.19. The resulting solution after ultrasonic cleaning treatment

- The solution resulting from the ultrasonic process in lactic acid environment was analyzed using inductively coupled plasma optical emission spectroscopy, following which the below results are obtained:

Nr. crt.	Analyzed element	Detection limit (DL)	Quantification limit (QL)	Results $\mu\text{g/g}$
1	Lithium	0,015	0,050	42,72
2	Manganese	0,003	0,010	1,308
3	Cobalt	0,750	2,500	323,68

Chapter 8. Analyzing the active paste recovered by ultrasonic process in lactic acid of spent Li-ion / NMC batteries

- The cathodic paste was recovered and analyzed all during the disintegration process, as well as at the end of this process. The disintegration process begins with the detachment from the aluminum foil of quite large sections (Fig.20.);
- The electron microscopy image from Fig.20. SEM (100) indicates that due to the ultrasonic conditions and the chosen leaching environment, the active paste is easily detached from the aluminum foil;
- Electron microscopy (SEM) images Fig.21. (a)÷(d) capture at different resolutions (x500÷x5.000) a fragment of active paste detached from the aluminum foil;
- It can be seen that the particles have been homogenized, compacted and stabilized with a binder (PVDF).

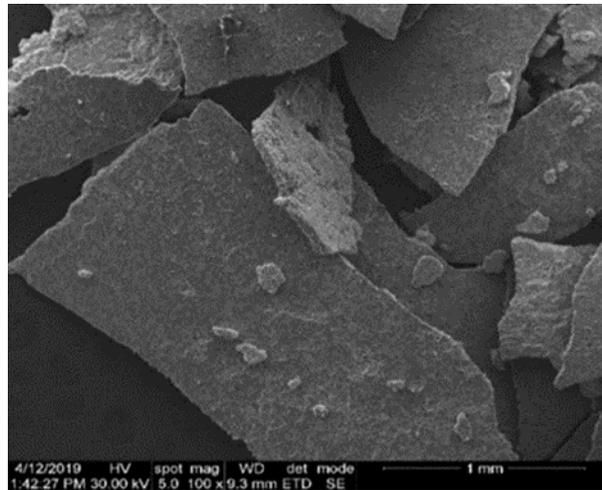
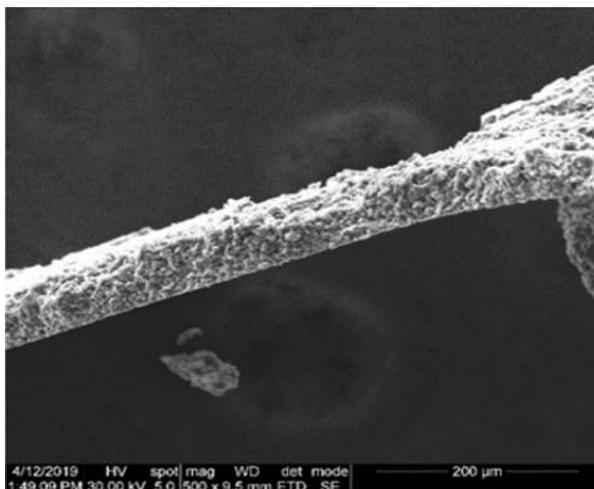
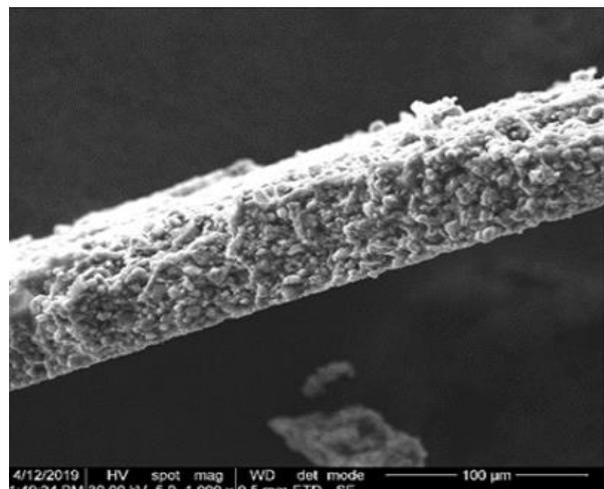


Fig.20. SEM image (x100) – the beginning of the disaggregation process



(a)



(b)

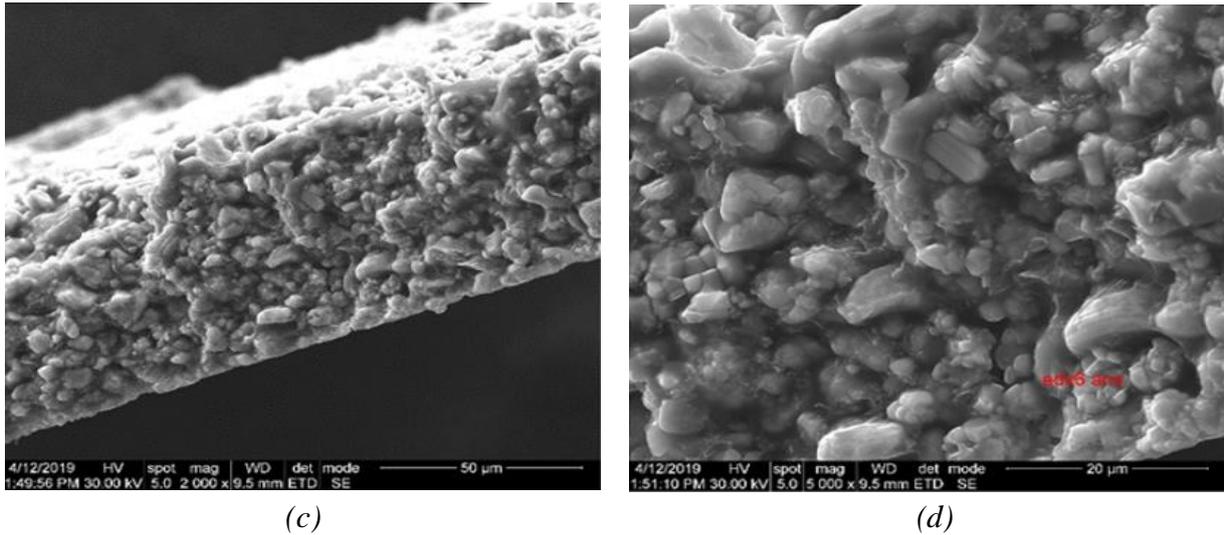


Fig.21. Morphological appearance of the cathode paste after the cleaning process: (a) Imag. SEM (x500); (b) Imag. SEM (x1.000); (c) Imag. SEM (x2.000); (d) Imag. SEM (x5.000)

- From the EDX analysis on the recovered paste, the presence of cobalt, nickel and manganese was identified (Fig.22).

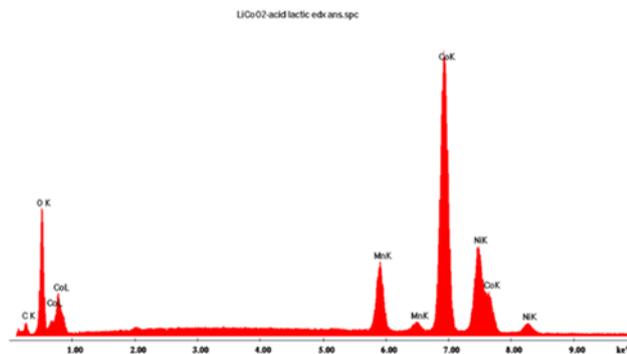


Fig.22. EDX analysis; the presence of Co, Ni and Mn is well defined

- EDX analysis (energy dispersive X-ray spectroscopy) performed on the fragment section (Fig.22.), Indicates the presence of manganese, nickel and cobalt; the particles have variable dimensions;
- From the analysis of the images presented in Fig.23. and Fig.24. it is observed that the cobalt particles have dimensions between $6 \div 8 \mu\text{m}$, and the nickel and manganese particles have smaller dimensions, between $0.5 \div 1 \mu\text{m}$ [edx1: Co = 17.23; Ni = 36.75; Mn = 15.18; edx2: Co = 23.83; Ni = 36.56; Mn = 14.6; edx3: Co = 72.67; Ni = 1.58; Mn = 0.94 (Wt% - mass percentage)].

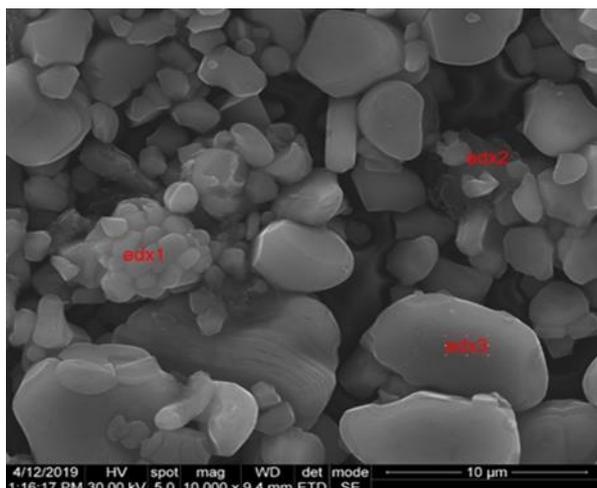


Fig.23. SEM image (x10.000)

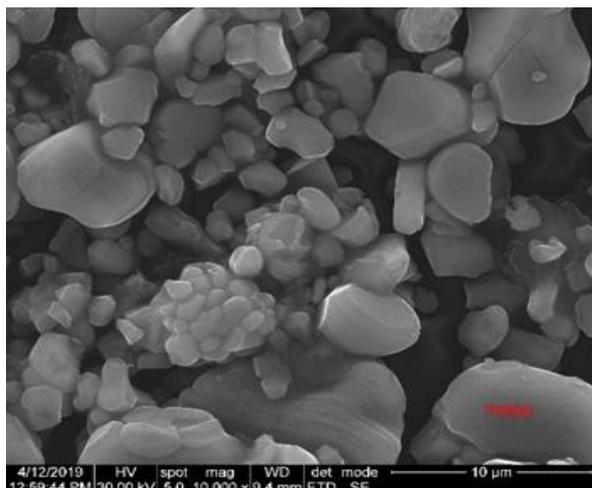


Fig.24. SEM image (x10.000)

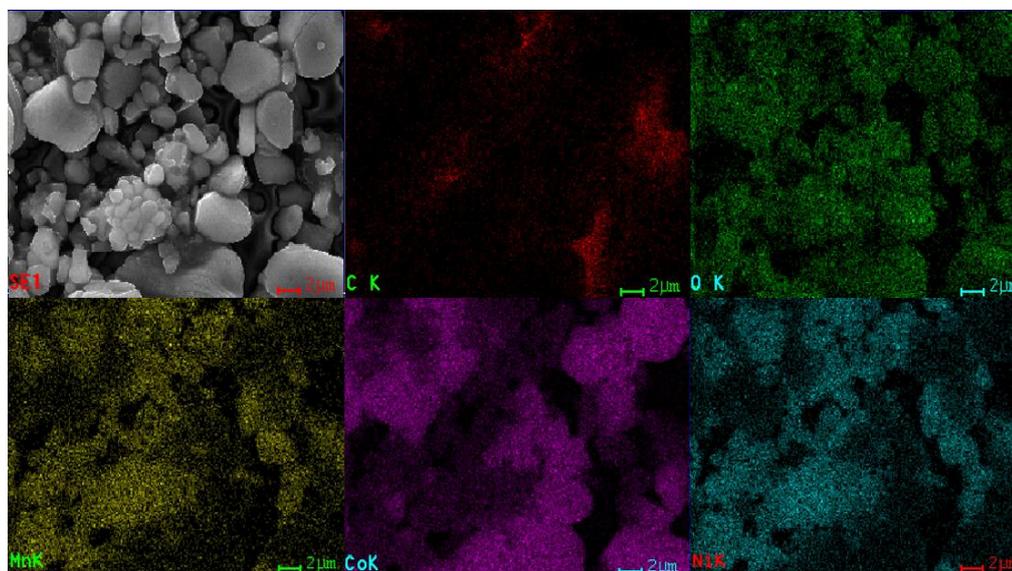


Fig.25. Distribution on the analyzed surface of the elements Mn, Co, Ni

Following the distribution of the elements (Fig.25), it is found that the nickel and manganese fingerprints overlap; cobalt covers the spaces not occupied by Ni and Mn.

X-ray diffraction analysis of a crystalline powder is characteristic of a given substance, each component of the mixture being analyzed producing its characteristic figure;

Diffraction data, systematized under the auspices of JCPDS (Joint Committee for Power Diffraction Standards (ASTM) in order to order by d_s (distance between different families of crystalline planes) and relative intensities of diffraction maxima, highlighted the main compounds - LiCoO_2 and LiCoNiO_2 (nickel-cobalt dioxide is formed during the charging process of the battery), making up the solid solution $\text{LiCo}_x\text{Ni}_{1-x}\text{O}_2$, in which cobalt ions are replaced by nickel ions (Figure 26.).

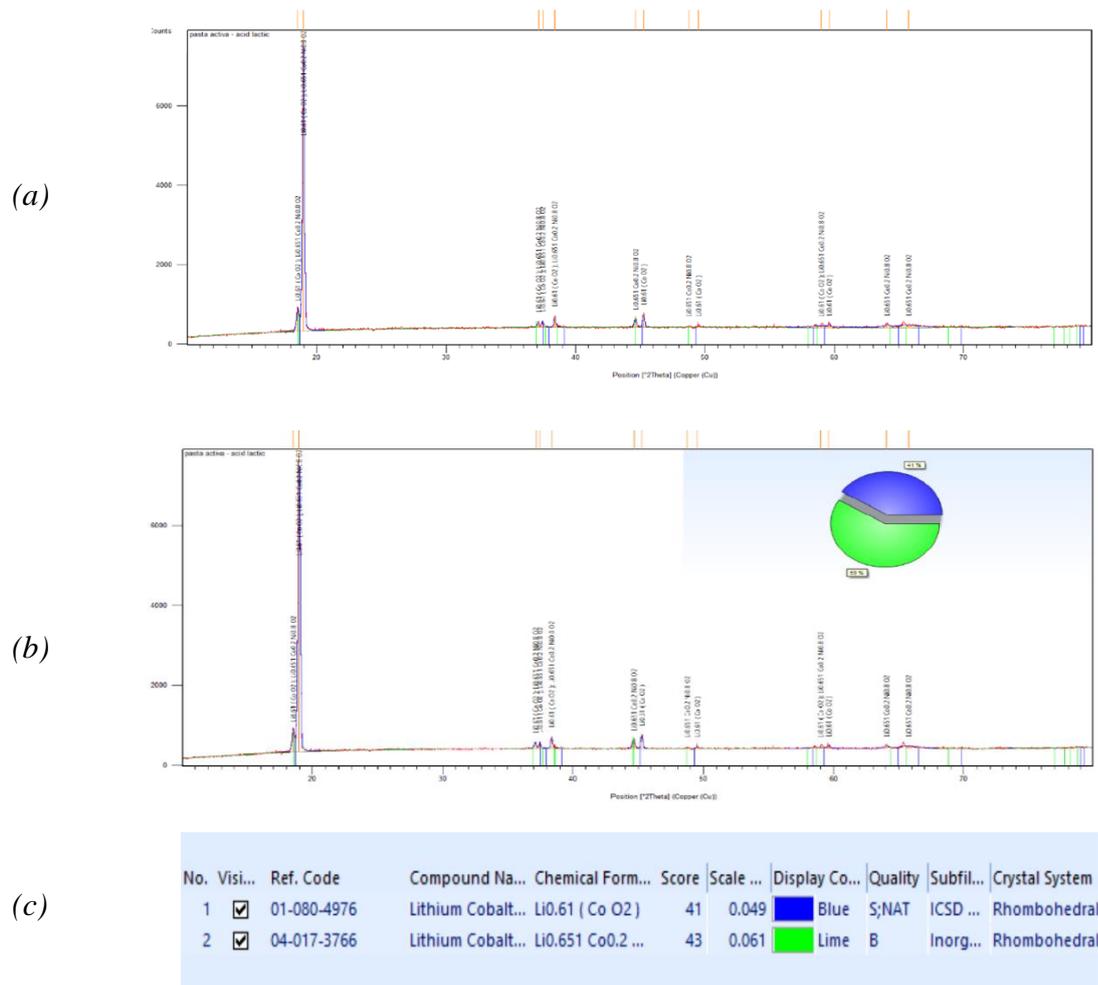


Fig.26. Results of X-ray diffraction investigation: (a) interplanetary distances; (b) characteristic compounds; (c) the database file

- The data obtained from X-ray diffraction investigations on the powder recovered from the cathode of used NMC batteries were compared with the data published by Maxime Blangero [11] in his doctoral thesis defended at the University of Bordeaux in 2008 (Fig.27.) For LiCoO_2 compound and those published by Haider, AJ and collaborators [12] for the compound LiCoNiO_2 (Fig.28.);
- The first three most important maxima (I%), highlighted in Fig.26., correspond to the planes (003), (104) and (101) both for the LiCoO_2 compound (Fig.27.) and for the LiCoNiO_2 compound (Fig.28.);
- The software also allowed a quantitative analysis, so it turned out that the presence of LiCoNiO_2 is 51% while LiCoO_2 represents 41% of the analyzed mass. This shows that this method has succeeded, to some extent, in reducing the share of cobalt in the active cathodic paste.

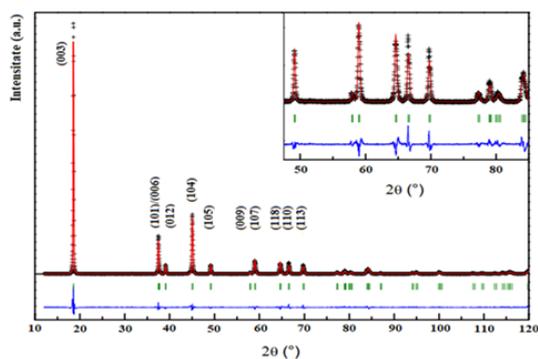


Fig.27. The result of the diffraction investigation of X-rays for the compound LiCoO_2 ($\text{Li}_{0.61}\text{CoO}_2$) identified by M. Blangero [13]

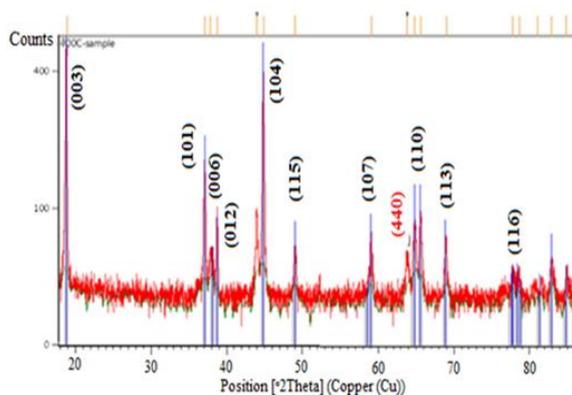


Fig.28. The result of the investigation by X-ray diffraction for the compound LiCoNiO_2 ($\text{Li}_{0.651}\text{Co}_{0.2}\text{Ni}_{0.8}\text{O}_2$) identified by Haider, A.J. et al. [14]

Table 8.7. Comparative indexation of X-ray diffraction (compared ds) for $\text{Li}_{0.651}\text{Co}_{0.2}\text{Ni}_{0.8}\text{O}_2$, reference code 04-017-3766 (marked in green), respectively of $\text{Li}_{0.61}\text{CoO}_2$, reference code 01-080-4976 (marked blue)

No.	h	k	l	d (Å)	2Theta (deg)	I (%)
1	0	0	3	4.76830	18.593	100.0
2	0	0	3	4.73760	18.715	100.0
3	1	0	1	2.42830	36.990	30.7
4	1	0	1	2.39660	37.497	29.0
5	0	0	6	2.38420	37.699	3.8
6	0	0	6	2.36880	37.954	3.7
7	0	1	2	2.32970	38.616	8.7
8	0	1	2	2.30050	39.126	7.8
9	1	0	4	2.02910	44.621	58.7
10	1	0	4	2.00660	45.149	48.2
11	0	1	5	1.86710	48.732	7.9
12	0	1	5	1.84770	49.278	7.5
13	0	0	9	1.58940	57.979	0.9
14	0	0	9	1.57920	58.389	0.9
15	1	0	7	1.57300	58.642	10.0
16	1	0	7	1.55850	59.242	10.1

Table 8.8. The crystallographic parameters of $\text{Li}_{0.651}\text{Co}_{0.2}\text{Ni}_{0.8}\text{O}_2$ reference code 04-017-3766 (marked green), compared to those of compound $\text{Li}_{0.61}\text{CoO}_2$ reference code 01-080-4976 (marked blue)

Parametrii cristalografici	$\text{Li}_{0.651}\text{Co}_{0.2}\text{Ni}_{0.8}\text{O}_2$	$\text{Li}_{0.61}\text{CoO}_2$
Sistem de cristal		Romboedric
Grup spațiu		R-3m
Număr grup spațiu		166
a (Å)	2.8453	2.8076
b (Å)	2.8453	2.8076
c (Å)	14.3050	14.2129
Alpha (°)		90.0000
Beta (°)		90.0000
Gamma (°)		120.0000
Volumul celulei (10^6pm^3)	100.29	97.03
Z		3.00
RIR	4.50	5.29

Table 8.7. presents the compared ds for $\text{Li}_{0.651}\text{Co}_{0.2}\text{Ni}_{0.8}\text{O}_2$ (green), respectively $\text{Li}_{0.61}\text{CoO}_2$ (blue), and Table 8.8. presents the crystallographic parameters for the two compounds.

It can be easily observed how much the two structures are similar.

Conclusions:

- Cobalt is a rare and expensive metal, so any way to replace it in the cathodic composition of Li-ion batteries is welcome. The recovery of cobalt and other metals present in used Li-ion batteries (e.g. Ni, Mn and Li) is an economic necessity and an ecological responsibility;
- An ecological way to recover active cathodic material from used Li-ion batteries has been investigated. The proposed ultrasound technology has the advantages of being easy to use, uses an organic acid, non-polluting, operates at room temperature, without the need for additional heat, the duration and energy consumption being reduced to a minimum by optimizing the process.
- Analyzing by SEM-EDX the samples of recovered cathodic paste, its composition and morphology were highlighted. X-ray diffraction analyzes identified the compounds present in the recovered active paste and confirmed their structural proximity.

Chapter 9. Obtaining the cobalt blue pigment (CoAl_2O_4) for capitalizing on the active paste recovered from spent Li-ion batteries

Cobalt blue (CoAl_2O_4) or cobalt aluminate is part of complex oxides with spinel structure (AB_2O_4).

The pigment is blue, many applications - ceramic materials, pigments, magnetic materials, anticorrosive.

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 1200°C .

In our own research, we managed to obtain cobalt blue starting from the LiCoO_2 compound recovered from used LI-ION/LCO batteries, going through the following steps:

- At temperature of 400°C : $\text{LiCoO}_2 \rightarrow \text{Co}_3\text{O}_4$ 1.
- At temperature of 900°C : $2\text{Co}_3\text{O}_4 \rightarrow 6\text{CoO} + \text{O}_2$ 2.
- At temperature of 1200°C : $\text{CoO} + \text{Al}_2\text{O}_3 \rightarrow \text{CoAl}_2\text{O}_4$ (spinel structure) 3.



Fig.29. Cobalt blue (CoAl_2O_4)

Cobalt blue (CoAl_2O_4) was initially identified by X-ray diffraction analysis, along with Al_2O_3 (unreacted) in Fig.30. (a) and (b), respectively Fig.31. (a) and (b).

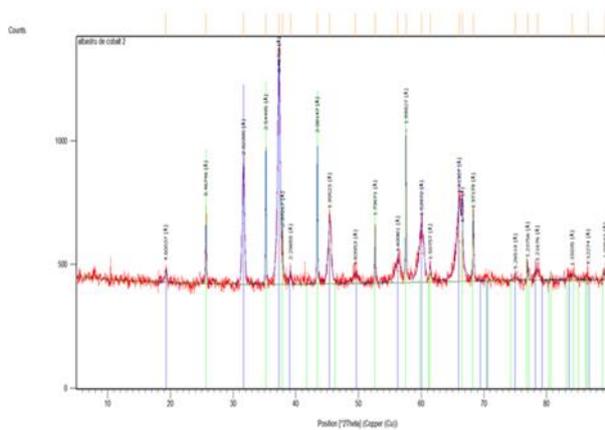


Fig.30.(a) The results of the investigation by cobalt blue X-ray diffraction; the interplanar distances are marked

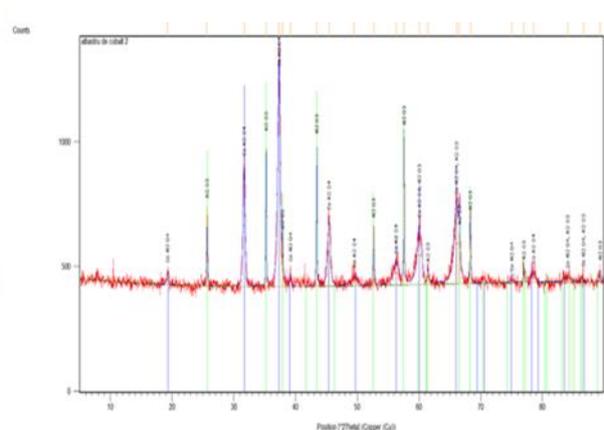
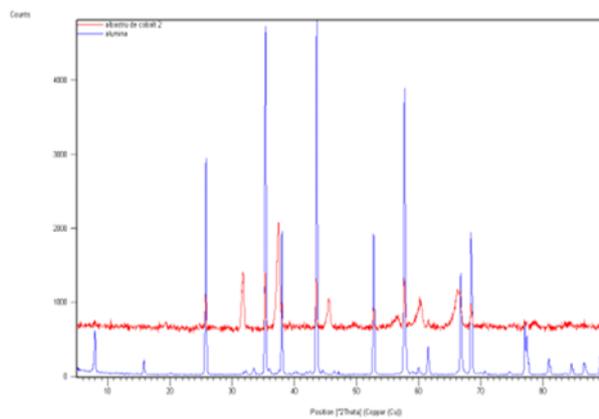
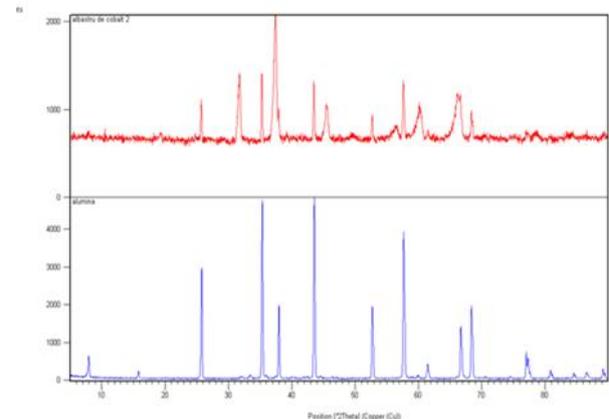


Fig.30.(b) The results of the investigation by cobalt blue X-ray diffraction; the identified compounds are marked



(a)



(b)

Fig.31. Results of X-ray diffraction investigation: (a) CoAl_2O_4 (red marking) and (b) Al_2O_3 (blue marking)

- ❖ The analysis of the reaction compounds continued by EDX analysis. This allowed the presence of Al, Co and Mn to be identified;
- ❖ The Mn concentration is much lower than the one present on the cathode of used Li-ion/LCO batteries, before ultrasound;
- ❖ Manganese was located next to cobalt, generally on small particle agglomerations. Alumina particles larger than $3\mu\text{m}$ reacted less with cobalt.

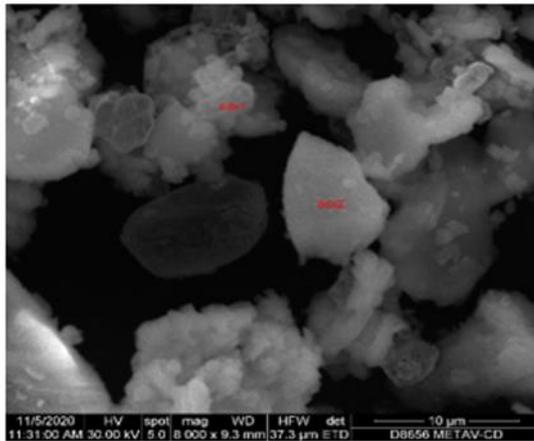


Fig.32. SEM analysis (x8,000) and location EDX-1 and EDX-2 analysis on cobalt blue

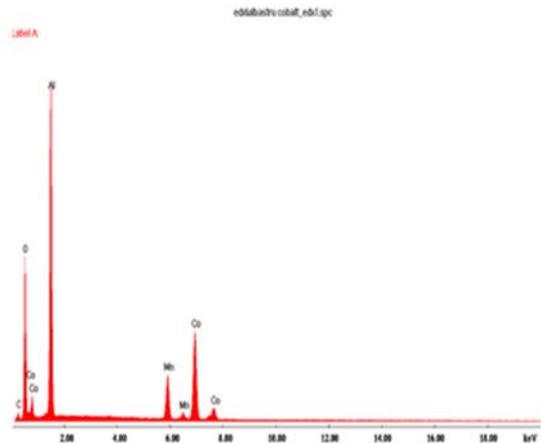


Fig.33. EDX-1 analysis; the presence of Al, Co and Mn is well defined on the particles small size ($\leq 1\mu\text{m}$)

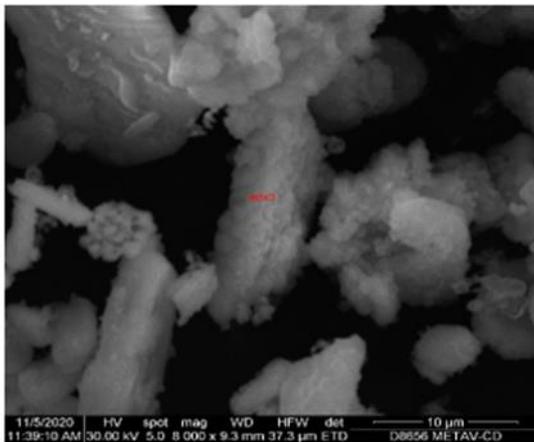


Fig.34. SEM Analysis (x8,000) and the localization of the EDX-3 on cobalt blue

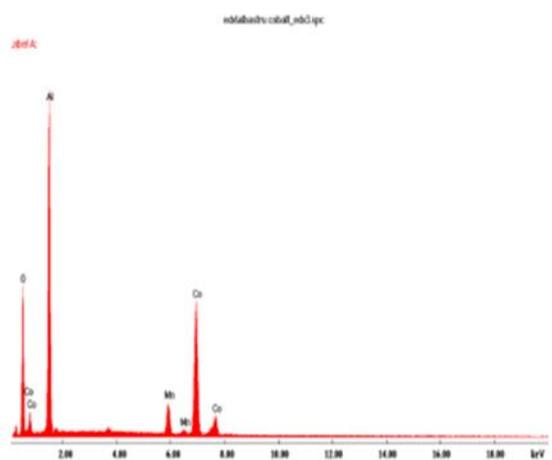


Fig.35. EDX-3 analysis; analysis the presence of Co and Mn is weakly outlined on small alumina particles ($\leq 1\mu\text{m}$)

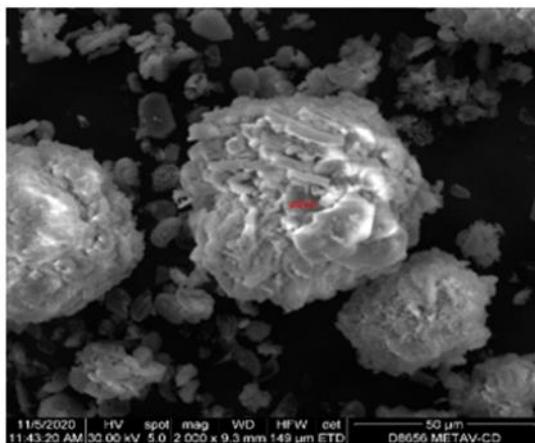


Fig.36. SEM analysis (x2,000) and the location of the EDX-4

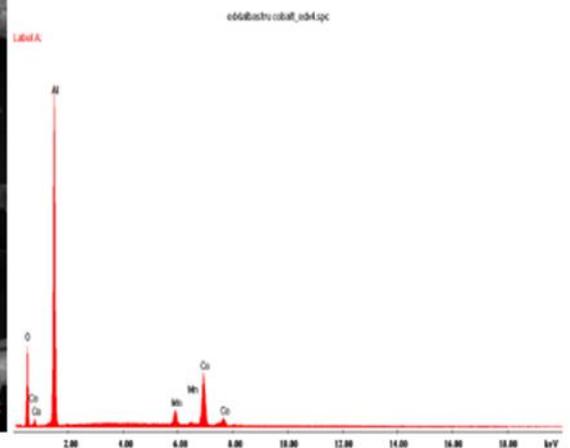


Fig.37. EDX-4 analysis; the presence of Co and Mn analysis is identified on the particles of on large cobalt blue alumina ($\leq 40\mu\text{m}$)

We can conclude:

- the paste of used Li-ion/LCO batteries, with cobalt content, can be recovered efficiently and capitalized through a salable product – cobalt blue (CoAl_2O_4);
- it was found that the LCO battery paste contains Co in high percentage (78.114%), while in the NMC battery paste, the cobalt content decreases to 54.174%, being replaced with Ni (12.936%) and Mn (7.569%);
- the price of cobalt increased on the profile markets by 24,355 USD / MT (~ 76%) since the beginning of 2021, according to trading on contracts for differences (CFD [13]);
- by recycling a spent Li-ion/LCO battery, approximately 1.4 g of cobalt blue pigment (50% alumina) are obtained, being necessary about 72 spent Li-ion batteries to obtain 100 g of CoAl_2O_4 pigment.

PART III

CONCLUSIONS, GENUINE CONTRIBUTIONS AND LEADS TO FURTHER SCIENTIFIC RESEARCH

Chapter 10.1. Final resolutions

Within this thesis we proposed a method of separating the active paste containing cobalt (mainly LiCoO_2 compound) from the cathodic aluminum foil, by ultrasound in lactic acid medium and its transformation into a marketable product - the cobalt blue pigment (CoAl_2O_4).

Numerous experiments have been carried out to determine the influence of lactic acid concentration, addition of hydrogen peroxide (H_2O_2), power of the ultrasonic source, temperature and duration of the ultrasound on the recovery efficiency of the active paste containing useful metals (cobalt, nickel) on the cathode of spent Li-ion batteries. It has been established that the optimum value of the lactic acid concentration is 1.5 M. At this concentration we obtain low recovery time and high recovery efficiency, compared to the other concentrations tested. The maximum yield, above 90%, was achieved using a 1.5 M acid solution after exposure to ultrasound samples, under the following conditions: volume $V = 1.2$ l; cleaning frequency $f = 45$ kHz; heating temperature $T = 50^\circ$ C; ultrasonic power $P = 20 \div 100$ W; cleaning time $t = 4 \div 5$ min. This was followed by the mathematical modeling of the recovery process by the process of ultrasonication in lactic acid medium of used Li-ion / LCO and Li-ion / NMC batteries, in order to optimize the process. The optimization of the operation of separating the active paste with cobalt content from the aluminum foil that constitutes the battery cathode, was performed under the following conditions: acid environment (lactic acid) at a constant pH of 1.5 M; the ultrasound duration was kept constant $t = 4$ minutes. The aim was **to obtain the optimal values of temperature and power of the ultrasonic bath** in order to streamline the operation of separating the paste from the cathode foil. Starting from the linear determination of the form: $\tilde{y}_1 = b_o + b_1x_1 + b_2x_2$. The model was calculated using the factorial matrix 2^2 . Since the linear model did not agree with the analyzed process, we proceeded to determine a nonlinear model, completing the matrix with experiments $5 \div 9$, necessary for central-compositional-orthogonal programming PCCO of ordinal II ($\alpha = 1$; $\text{no} = 1$). The nonlinear model verifies the calculated Fisher Criterion and has the form:

$\tilde{y} = 51,98 + 13,56x_1 + 17,22x_2 + 4,16x_1x_2 + 6,98x_2^2$. To optimize it, the nonlinear model is brought to the canonical form or the standard form. The equation in canonical form is: $\tilde{Y} - 70 = 7,55X_1^2 - 0,57X_2^2$. The determination of the optimal regime was done by the

method of Ridge analysis (linear regression), based on the Lagrange multiplier method. The optimal values found were: $\hat{z}_1 = z_1^0 + \hat{x}_1 \cdot \Delta z_1 = \mathbf{59,86^\circ C (T)}$; $\hat{z}_2 = z_2^0 + \hat{x}_2 \cdot \Delta z_2 = \mathbf{46W (P)}$ and, taking into account the error in calculating the performance of the process (δ_y), the lower yield limit has the value $\boldsymbol{\eta} = \mathbf{80.15}$. The research continued with a laborious analysis of the active paste recovered by the ultrasonic process in lactic acid medium of the spent batteries: Li-ion / LCO, respectively Li-ion / NMC. The chemical compositions of the two types of batteries were determined by X-ray fluorescence spectroscopy. X-ray fluorescence spectroscopy (XRF) was performed with the XRF Oxford X-MET 5000 handheld analyzer. LCO battery paste was found to contain Co (78.114%), while in the NMC battery paste, the cobalt content decreases to 54.174%, but Ni (12.936%) and Mn (7.569%) appear. These values confirm the trend agreed by Li-ion battery manufacturers to reduce the cobalt content in more recently manufactured batteries, with the aim of lowering the price and reducing the dependence on the only major manufacturer - Democratic Republic of Congo (Zaire). Starting from this analysis, the active cathodic paste from each type of battery (LCO, respectively NMC), was analyzed in detail in the following steps. The analysis was performed by X-ray diffraction, SEI / EDX electron microscopy, and the residual solution obtained after removal of the paste was analyzed by inductively coupled plasma optical emission spectroscopy. In LCO batteries, the paste collected after washing and drying consists practically of the compound LiCoO_2 . This paste can be capitalized by transforming it into the cobalt blue pigment, a finished, salable product. Regarding the NMC type Li-ion batteries (from mobile phones, type BL-5CB, more recently manufactured batteries), the characterization of the active paste recovered by the ultrasonic process in lactic acid medium revealed interesting information. It is well known that, unfortunately, the composition of Li-ion batteries is considered confidential information, which increases the difficulty of choosing recycling technology. It is only known that the cathodic paste of this new type of battery consists of a mixture of oxides of Li, Ni, Mn and Co ($\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$). The NMC battery was born from the attempt to use as little cobalt (expensive and deficient metal) as possible at the cathode of Li-ion batteries. The presence of nickel along with cobalt makes the recycling process more difficult. The main compounds - LiCoO_2 and LiCoNiO_2 (nickel-cobalt dioxide is formed during the charging process), forming the solid solution $\text{LiCo}_x\text{Ni}_{1-x}\text{O}_2$, in which cobalt ions are replaced by nickel ions. The crystallographic parameters of $\text{Li}_{0.651}\text{Co}_{0.2}\text{Ni}_{0.8}\text{O}_2$ compared to $\text{Li}_{0.61}\text{CoO}_2$ are very close, and the separation of cobalt from nickel is difficult. In Chapter 10.3., in order to continue the research, a variant of selective leaching of lithium, nickel and cobalt from the NMC battery paste is presented, in order to capitalize on Ni and Co. In order to capitalize on the LiCoO_2 compound obtained from the cathodic paste recovered from used LCO batteries, it was proposed and successfully transformed it into cobalt blue. Cobalt blue (CoAl_2O_4) or cobalt aluminate is part of complex oxides with spinel structure (AB_2O_4), which find many applications - ceramic materials, pigments, anticorrosive agent, etc. The pigment is blue, extremely stable. This pigment could be obtained by homogenizing the compound LiCoO_2 with alumina / corundum ($\alpha - \text{Al}_2\text{O}_3$) and transformed, by calcination, into cobalt blue CoAl_2O_4 . The raw materials used were analyzed. The heat treatment diagram was established and the reaction product was characterized. Given the high price of the pigment (~ 27 USD / 100g) [14], the cost of materials (alumina, lactic acid) and the working base (low power ultrasonic bath and short working time), open up favorable prospects for the recovery of cobalt from spent LCO batteries.

Chapter 10.2. Genuine contributions:

We have developed an original and environmentally friendly method of separating and recovering the active paste containing expensive and deficient metals (Co, Ni) by ultrasound

in acid medium (lactic acid) of the cathode of spent Li-ion batteries. Through an extensive research program, we established the influence of lactic acid concentration, hydrogen peroxide addition, ultrasound temperature and duration, the power of the ultrasound source, on the recovery efficiency of the active paste. We managed to optimize the process of separating the active paste, choosing the significant influencing factors - the working temperature and the power of the ultrasonic source. These factors were assigned two levels of variation (upper and lower) around which 2^k EFC (complex factorial experiment) modeling was performed. As the linear model did not match the proposed model (according to the F - Fischer-Snedecor $F_c < F_{\text{Fischer}}$ distribution), a nonlinear model was determined. The concordance hypothesis (verification of the calculated Fischer criterion) was verified on the nonlinear model, which expressed a good approximation of the analyzed process. The model was brought in canonical form in order to establish the optimal regime. The optimal regime was determined using the Ridge method, based on the Lagrange multiplier. This allowed the determination of the optimal conditions of the ultrasonic process in lactic acid medium: $T = 59.80^\circ\text{C}$; $P = 46.35\text{W}$). We performed the analysis of the recovered active paste, using a wide range of investigative methods: XRF analysis, electron microscopy analysis (SEM, EDX), X-ray diffraction and analysis of the residual solution by inductively coupled plasma optical emission spectroscopy. These analyzes identified the presence of LiCoO_2 in the paste recovered from used LCO-type Li-ion batteries and the presence of LiCoNiO_2 (51%) and LiCoO_2 (41%) in the paste recovered from used NMC Li-ion batteries. This information was appreciated by the researchers, the paper published (2021 IOP Conf. Ser. : Mater. Sci. Eng. 1037 012039; [doi:10.1088/1757-899X/1037/1/012039](https://doi.org/10.1088/1757-899X/1037/1/012039)), being quoted in Coatings 2021, 11 (7), Article Number: 744, Impact Factor: 2,881 (2020), a few months after its publication. Another element of originality was the transformation of the paste recovered from used LCO-type Li-ion batteries into a salable product - cobalt blue (CoAl_2O_4). For this purpose, we mixed in well-established proportions (experimentally) the paste recovered from the cathode of the spent Li-ion / LCO batteries with alumina (Al_2O_3) and we calcined it at $T = 1200^\circ\text{C}$. We obtained a homogeneous cobalt blue, of different shades, which can be used as a pigment in the ceramics, glass industry or for corrosion protection. In conclusion, we have proposed ways to continue the research: (a) adapting the technology of recovery of active paste containing Co, Ni, Li – from newly created Li-ion batteries (cheaper and more efficient), given the exponential development of electric vehicles and storage batteries; (b) deposition and testing of cobalt blue obtained on various metal surfaces in order to determine its anticorrosive properties.

DISSEMINATION OF RESULTS / QUOTES

- Articles published in the field of doctoral thesis:
1. (a) **Ionuț Bratosin**, Valeriu Gabriel Ghica, Mircea Ionuț Petrescu, Mihai Buzatu, Alina Daniela Necșulescu, Gheorghe Iacob - “**Recycling Li-ion batteries in eco-friendly environments**” - ICCECIP 2019 - International Conference on Central European Critical Infrastructure Protection, 18-19 November 2019. Budapest, Hungary; Quote: [Vol. 54 No. 2 \(2020\): Haditechnika 2020/2 /;](#)
 (b) **Ionuț Bratosin**, Valeriu Gabriel Ghica, Mircea Ionuț Petrescu, Mihai Buzatu, Alina Daniela Necșulescu, Gheorghe Iacob - “**Recycling Li-ion batteries in eco-friendly environments**”, HADITECHNIKA, 54 (5). pp. 8-14. ISSN 0230-6891; doi.org/10.23713/HT.54.5.02;
 2. **Ionuț Bratosin**, Valeriu-Gabriel Ghica, Mihai Buzatu, Mircea-Ionuț Petrescu, Gheorghe Iacob, Tünde Anna Kovács, Alina-Daniela Necșulescu - “**Separation process optimization of the paste from the aluminum cathode, in the process of recovery of cobalt from used batteries**”, University Politehnica of Bucharest, Scientific Bulletin Series B-Chemistry and Materials Science (WoS) - Volume 82; Issue: 3; Pages: 199-210; Published 2020; [WoS:000610098500017](#);
 3. **Ionuț Bratosin**, C.M. Toma, E Vasile, V. G. Ghica, M. Buzatu, M. I. Petrescu, T. A. Kovács, A. D. Necșulescu and G. Iacob – “**Recovery of LiCoO_2 compound from cathodic paste of waste LIBs by ultrasonography in lactic acid solution**”, International Conference on Innovative Research – ICIR EUROINVENT 2019, 16-17 May, Iași, România, IOP Conf. Series: Materials Science and Engineering – International Conference on IOP

Conf. Series: Materials Science and Engineering 572 (2019) 012053 IOP Publishing; [doi:10.1088/1757-899X/572/1/012053](https://doi.org/10.1088/1757-899X/572/1/012053);

4. **Ionuț Bratosin**, V. G. Ghica, M. I. Petrescu, M. Buzatu, G. Iacob, A.D. Necșulescu - “**Researches on the recovery of useful metals from spent Li-ion batteries**”, 24th edition of IMan EE 2020 International Conference - Innovative Manufacturing Engineering and Energy 2020, 14-15 December, Heron Polytechniou, 15780, Athens, Greece; 2021 IOP Conf. Ser. : Mater. Sci. Eng. 1037 012039; [doi:10.1088/1757-899X/1037/1/012039](https://doi.org/10.1088/1757-899X/1037/1/012039); paper quoted in “**A Comparative Review of Metal Oxide Surface Coatings on Three Families of Cathode Materials for Lithium Ion Batteries**” - Thabang Ronny Somo, Tumiso Eminence Mabokela, Daniel Malesela Teffu, Tshepo Kgokane Sekgobela, Brian Ramogayana, Mpitloane Joseph Hato and Kwena Desmond Modibane - Coatings 2021, 11 (7), Article Number: 744, Impact Factor: 2,881 (2020); 5-Year Impact Factor: 3,038 (2020); <https://doi.org/10.3390/coatings11070744>; WoS:000676408300001;
5. **Ionuț Bratosin**, Ghica Valeriu Gabriel, Cristina Madalina Toma, Petrescu Ionuț, Iacob Gheorghe, Buzatu Mihai, Alina Daniela Necșulescu - “**Obtaining the CoAl₂O₃ / Al₂O₃ pigment from used Lithium-Cobalt-Oxide (LCO) batteries**”, paper presented at the International Conference RoMAT 2020, 27 November 2020 Scientific session I.2 Obtaining, processing and characterizing materials; currently appearing at the Polytechnic University of Bucharest.
6. Valeriu-Gabriel Ghica, Gheorghe Iacob, Mircea-Ionuț Petrescu, **Ionuț Bratosin**, Ana Vasile, Irina-Gabriela Scarlat - “**Li-ion batteries - an important component in critical infrastructure protection**”, submitted and accepted as an attendee to the SATCIP 2021 conference (August 27-28, 2021); paper accepted for publication, in progress at Springer Nature B.V.

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