RECOVERY OF ACTIVE CATHODE MATERIAL CONTAINING Co AND Li FROM WASTE Li-ION BATTERIES

Gabriel Valeriu GHICA[1,*], Cristina-Madalina TOMA[2], Mihai BUZATU[3], Mircea-Ionut PETRESCU[4], Gheorghe IACOB[5], Iulian Vasile ANTONIAC[6], Eugenia VASILE [7], Francesco VEGLIO[8]

Lithium-ion batteries are used as a power source for many electronic devices and a higher number of spent batteries will need to be recycled in the future. In waste lithium-ion batteries can be found metals such as Co, Li, Cu, Al, Fe and Ni. In this work we developed an optimal process to separate active paste (containing $LiCoO_2$ compound) from the aluminum cathode. For this purpose, we used an ultrasonic bath where we have introduced a solution of citric acid and hydrogen peroxide, as a leaching agent. It was analyzed the effect of citric acid concentration ($C_6H_8O_7$ concentration was between 0.5M and 2M) and the volume of H_2O_2 (H_2O_2 volume was between 0.5 and 2%) on leaching efficiency. The experiments were performed at room temperature. The ultrasonic bath has been set at an ultrasonic power of 50 W and a frequency of 45 kHz. The ultrasound treatment time of cathodic foils in the leaching solution was between 10-60 minutes. Position of the cathode foil (loaded with pulp waste) from the ultrasonic surface was adjusted between 1 cm and 4 cm. Leaching efficiency was determined by weight measurements using a precision balance. The surface of active freed paste was investigated using a Phillips electron microscope XL-30-ESEM and a X-ray diffractometer RIGAKU.

Keywords: waste Li-ion batteries, active cathode material, citric acid, ultrasonic bath, leaching.

1. Introduction

[1] Prof., Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: gvghica@yahoo.com, * - corresponding author
[2] PhD student, Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania
[3] Prof., Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: mbuzaturo@yahoo.com
[4] Prof., Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: ipetrescu@yahoo.com
[5] Lecturer, Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: iacob_gh@yahoo.com
[6] Prof., Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: antoniac.iulian@gmail.com
[7] PhD student, Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania
[8] Prof., Departament of Industrial Engineering, Information and Economy, University of AQUILA, Italy, e-mail: francesco.veglio@univaq.it

In a society hungry of technology, in which every single electronic device has become a piece of the person who owns it thus forming one big entity, we are surrounded by technology and we cannot live without it, we identify with the new devices and merge our identities with them. Hence, the electronic equipments that interconnect each other must keep up with our activities, jobs, requirements. In order to make that possible, these batteries must be cheap, have a long life cycle and infinite energy and operate in all exterior condition, no matter the temperature [1]. But until that moment arrives and we will be able to enjoy the "ideal" batteries, we must return to our currently available batteries.

Lithium-ion batteries are an important source of energy for the majority of electronics we use in our daily routine. Due to the increased demand of these devices on the market, their recycling is imperative for the environmental protection and for their valuable metals that are containing in Li-ion batteries.

A Li-ion battery is composed from a cathode, an anode, an electrolyte and a separator. The cathode contains an active cathodic material composed from cobalt and lithium in different proportion. The recovery of this active material is vital for the contained metals, Co and Li, since Co is the most expensive metal included in Li-ion batteries, and Li is used very often in industrial processes. Cobalt is a hard metal used in chemicals production, superalloys and steels. The main producers of cobalt are Congo, Canada, China and Russia [2]. The price of cobalt is very high because there are only few resources of Co in the world. Fig.1 illustrates the price fluctuation of cobalt in the last six years [3].

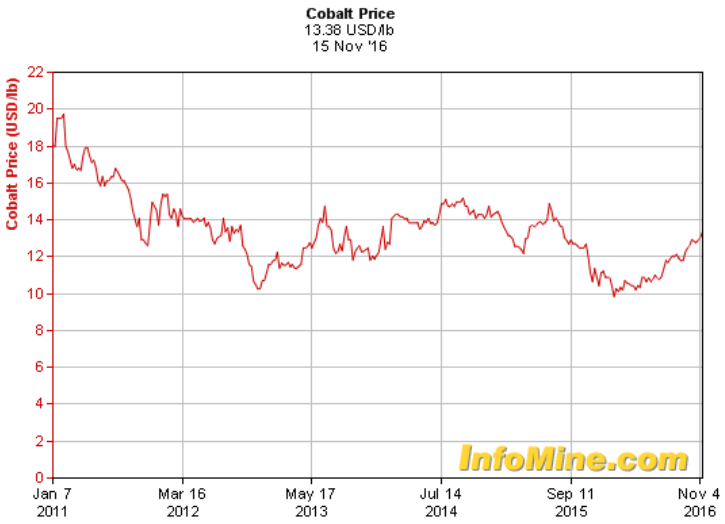


Fig.1. The fluctuation of Cobalt price [USD/lb] in the last six years [3]

The recycling of $LiCoO_2$ cathode material by ultrasonic technology was used for the first time by Jinhui Li et al., 2009 [4], who developed a combined

process that used among other methods, the ultrasonic washing and agitation to reduce costs and pollution. They have determined that by using both agitation and ultrasonic washing, a good percentage of electrode materials have been separated from Al foils. Jinhui et al. also studied the influence of temperature on recovering efficiency. The result was that with the increase of temperature, the removal ratio decrease. But they also observed an interesting fact, that under room temperature the removal ratio was higher than 90%.

Li et al. [5] used an ultrasonic-assisted leaching process to remove the metals from spent Li-ion batteries. They investigate the effect of ultrasonic power, leaching time and temperature on active materials, in order to obtain the optimal parameters of this process. In order to achieve the best result, they use different acidic reagents and came to the conclusion that citric acid was more efficient and eco-friendly than the others two acids that were analyzed. They also have shown that ultrasonic agitation plays an important role in leaching efficiency of the process.

The ultrasonic cleaning was explored in detail by Li-Po He et al. [6], who also proposed an environmentally process for the recycling of cathode materials from spent Li-ion batteries. They analyzed the mechanism of ultrasonic cleaning and explained it using different solvents in order to have a high peel-off efficiency, which depends of the dissolution of PVDF (polyvinylidene fluoride) provoked by ultrasounds. The environmentally process that was proposed by Li-Po He et al. in the end, based on the conducted experiments uses manual dismantling, ultrasonic cleaning with NMP (N-Methyl-2-Pyrrolidone) and pickling, as main steps of the process.

In this paper, we propose a recycling method of active cathode material based on ultrasonic leaching with citric acid, who uses manual dismantling and ultrasonic cleaning as main steps, we does not calcinations in order to not degrade the material, and the most important fact is that we can work with this active materials at room temperature, a heat contribution not being necessary.

The advantages of a Li-ion battery are: low auto-discharging, high capacity and specific energy (indicates the amount of energy a cell contains in weight Wh/kg), long life-cycle (number of cycles a battery can deliver; end of battery life for portable devices is commonly set to 80%) and high charging capacity [7].

When Li-ion batteries are discussed, automatically we think of LiCoO2/LCO batteries. But apart from those, there are five more types of Li-ion batteries, as follow: $LiMn_2O_4$/LMO, $LiNiMnCoO_2$ or NMC, $LiFePO_4$/LFP, $LiNiCoAlO_2$/NCA and $Li_4Ti_5O_{12}$/LTO [7].

LCO batteries have a high specific energy, a quick charging capacity and can be combined with other battery system in order to improve their characteristics.

LMO is defined by a good specific energy, but low performance and life cycle. Batteries only on Li-Mn are not used anymore in the usual applications; the majority of LMO are combined with NMC to increase their specific energy.

NMC also has a high specific energy, a low auto-heating rate and a good life cycle.

LFP batteries are cells with the following characteristics: a low specific energy, a high auto-discharging capacity and even if it is charged completely the battery is very stable.

NCA is the battery with the highest specific energy compared with other Li-ion batteries, having a good specific power and high costs.

LTO based batteries are characterized by a high life cycle, a low specific energy and the highest cost compared with other systems [7].

Fig. 2 illustrates that LCO, NMC and NCA batteries have the highest specific energy, compared with others, and a good performance, but not a long life cycle.

But each domain in which the battery is used, has his own requirements, and even if LTO has a long life cycle compared with LCO, specific energy is far more important for electronic devices.

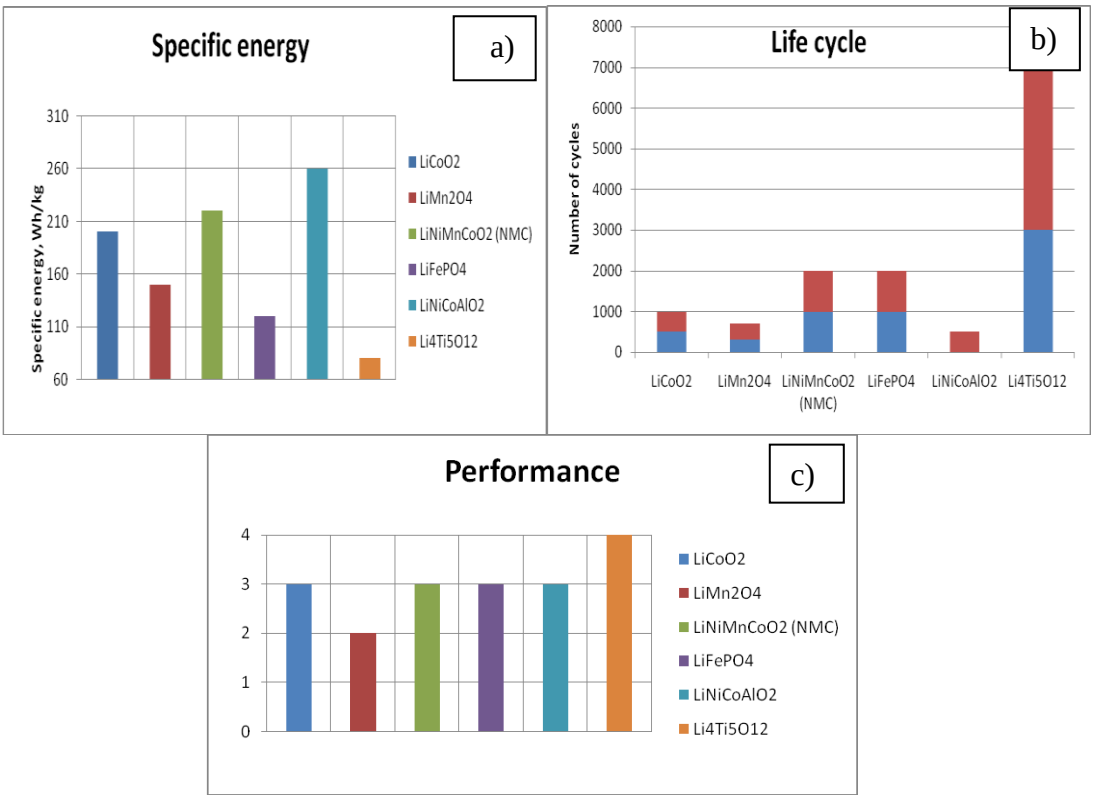


Fig.2. Specific energy (a), life cycle (b) and performance (c) of the main types of Li-ion batteries

The recovery of valuable metals (Co, Li) is necessary for many reasons:

- Co and Li are rare and expensive metals (see Fig. 1 the evolution of cobalt price being more expensive than lithium);
- The disposal of spent Li-ion batteries in garbage dumps presents the risk of self-ignitions;
- Spent Li-ion batteries contain noxious substances for the environment and any measure that we take in order to separate, neutralize and reuse these substances is a step forward in the environment protection and to have a green planet.

2. Materials and methods

For the recovery of Co and Li we used ultrasonic agitation, a method that has not been explored in detail in case of metals extraction from Li-ion batteries.

An ultrasonic cleaning machine (Emmi 12-HC, frequency 45 kHz) was used to obtain ultrasounds waves. The cleaning machine has the following technical specification: housing – stainless steel, cleaning frequency = 45 kHz; cleaning time = 1- 60 min; volume = 1.2 l; heating temperature = 20 – 80 ºC; bath dimension 200x100x65 mm; maxim power = 100 W; ultrasonic power = 50/75/100 W.

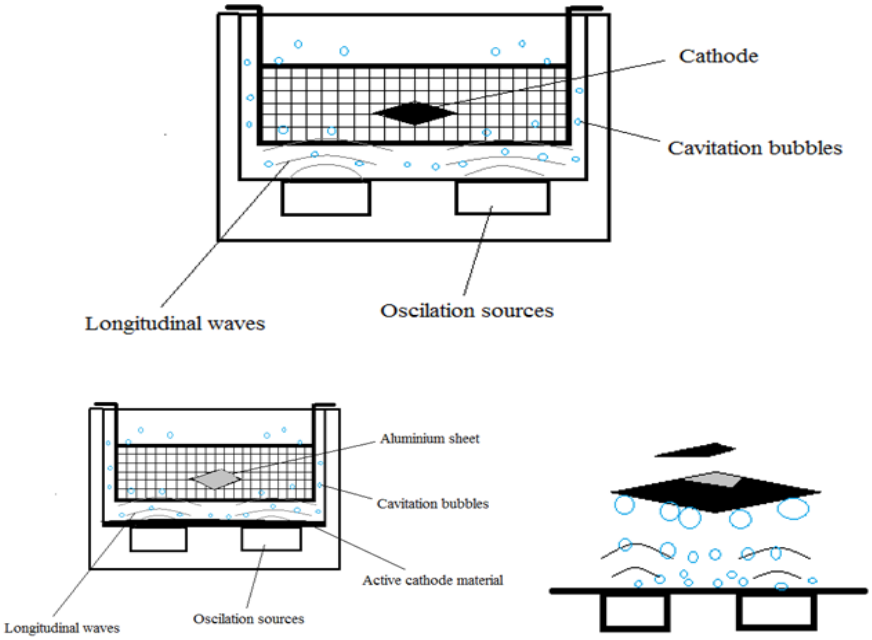


Fig.3. Visualization of cavitations effect on cathodic foils

In Fig.3 can observe that ultrasonic technology plays a major part in the detachment of active cathode material from the aluminum sheet. Ultrasonic

cleaning method is used because of the quality of the realized operation and for low working time. In the bottom area, where pressure and density is low enough, little cavitation bubbles are formed. If the waves are generating high pressure, then the bubbles can increase in dimension, till a critic dimension of the bubble, where take place the bubbles implosion. Cavitations bubbles implosion sends ultrasonic impulse to the material, which helps the cleaning process [8].

The spent Li-ion batteries were discharged and dismantled manually. After that, the cases were removed from the cells for extracting the cathodes and anodes. The cathodes were cut into pieces of 3x4.3 cm dimensions and immersed in an acidic solution (with different concentrations) for different times. In Fig.4 is presented the flow sheet of this process.

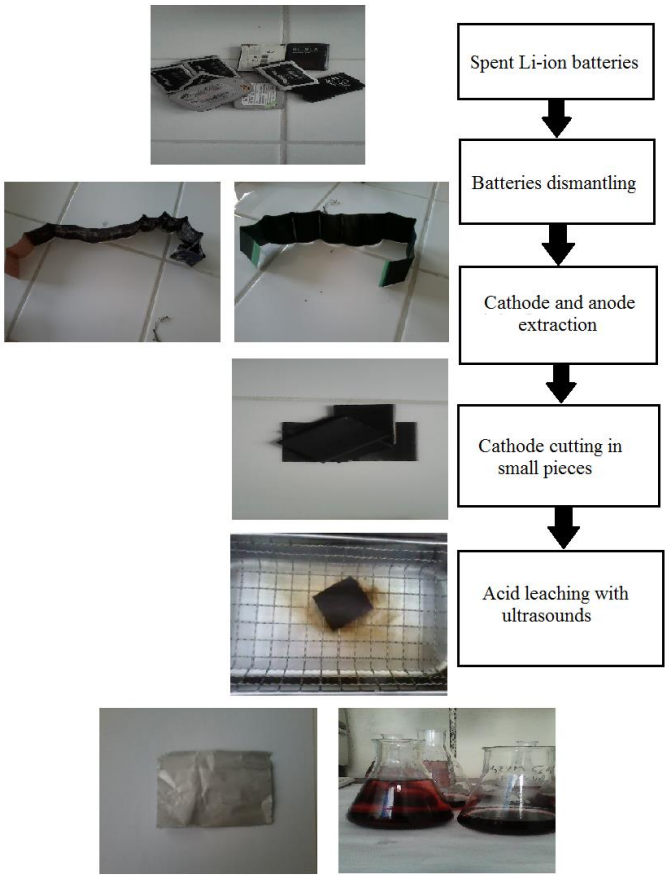


Fig.4. Flow sheet of cathode material recovery process in an ultrasonic bath

Each cathodic piece from the spent Li-ion batteries was combined with citric acid of different concentration and placed in the ultrasounds bath. The detachments were run at different time (1-20 min) and citric acid concentration

(1.20 – 1.25M). The obtained data was used to calculate the recovering efficiency. For this, we weight the cathodic piece before and after putting it in the ultrasonic bath. For weighing, we used an analytical balance with two decimals. Cleaning efficiency was calculated using the following equation:

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

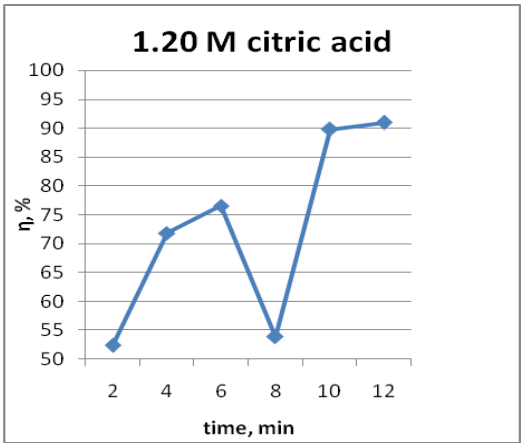
η - cleaning efficiency;
m_i - initial weight of cathodic piece, g;
m_f - final weight of cathodic piece, g.

3. Experimental results and discussion

In the experiments performed at the Hydrometallurgy Laboratory from the Department of Engineering and Management of Metallic Materials Elaboration were obtained the following results:

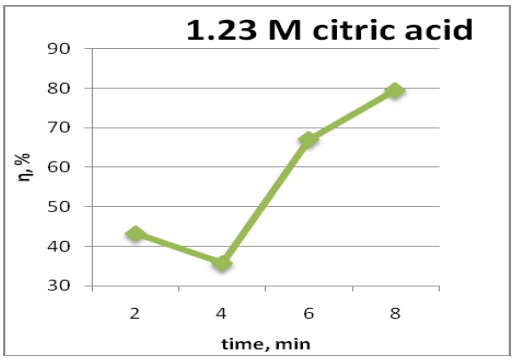
- ✓ all experiments were performed at room temperature, with no need for additional heat sources;
- ✓ the position of the cathode foil in the basket of ultrasonic bath was maintained at 1.5 cm from the source of ultrasonic oscillations;
- ✓ cathodic paste (containing $LiCoO_2$ compound) has been detached entirely from aluminum foil (battery cathode);
- ✓ maximum yield of over 90% was achieved using a solution of 1.25M citric acid after exposure to ultrasounds in the following conditions: cleaning frequency = 45 kHz; cleaning time = 8 min; volume = 1.2 l; heating temperature = 20º C; ultrasonic power = 50 W.

Fig.5 shows that the optimal value of citric acid concentration is 1.25M. At 1.25M citric acid we obtain low recovery time and high recovery efficiency compared with the others investigated concentrations.



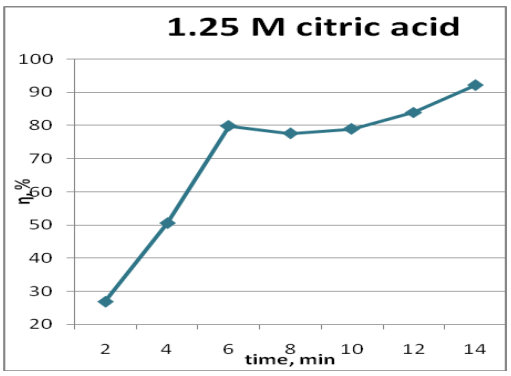
Initial weight,g	Final weight,g	η, %	Time, min
0,403	0,192	52,35732	2
0,522	0,147	71,83908	4
0,525	0,123	76,57143	6
0,512	0,236	53,90625	8
0,489	0,05	89,77505	10
0,49	0,044	91,02041	12

a)



(b)

Initial weight,g	Final weight,g	η, %	Time, min
0,499	0,283	43,28657	2
0,551	0,354	35,75318	4
0,549	0,181	67,03097	6
0,523	0,107	79,54111	8



(c)

Initial weight,g	Final weight,g	η, %	Time, min
0,547	0,4	26,87386	2
0,528	0,261	50,56818	4
0,466	0,094	79,82833	6
0,572	0,128	77,62238	8
0,57	0,12	78,94737	10
0,573	0,092	83,94415	12
0,511	0,04	92,17221	14

Fig.5. Effect of recovery time (2, 4, 6, 8, 10, 12, 14 min) and of citric acid concentration (1.20M (a), 1.23M (b) and 1.25M (c)) on spent cathode;

In Fig.6 we can observe the polynomial trend line of recovery time at different citric acid concentration and the best recovery time being obtained at 1.25M citric acid.

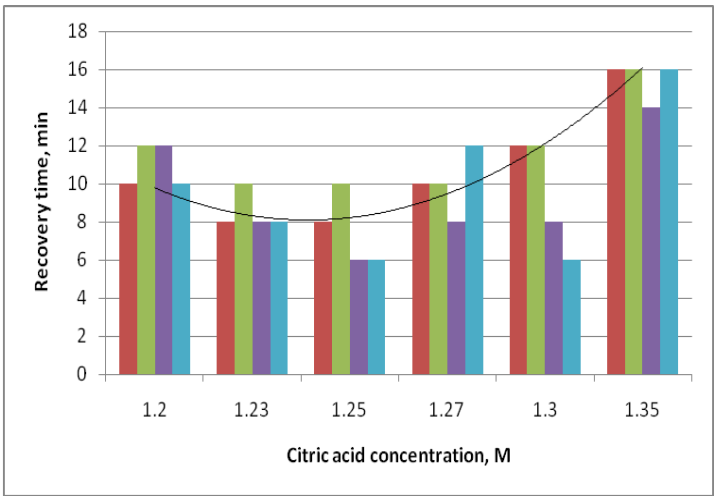


Fig.6. The polynomial trend line of recovery time at different citric acid concentration.

To analyze the surface morphology of spent $LiCoO_2$ we used an XL-30-ESEM Phillips electron microscope.

Fig.7. illustrates the SEM image of surface topography before the combined acid / ultrasound attack and the EDAX analysis on cathode foil coated with active paste; the diffraction peaks for Co and Mn are identified. The Al foil is underneath the active paste (the active paste thickness is about 10 μm and the EDAX analysis collects information from a depth of max. 5 μm).

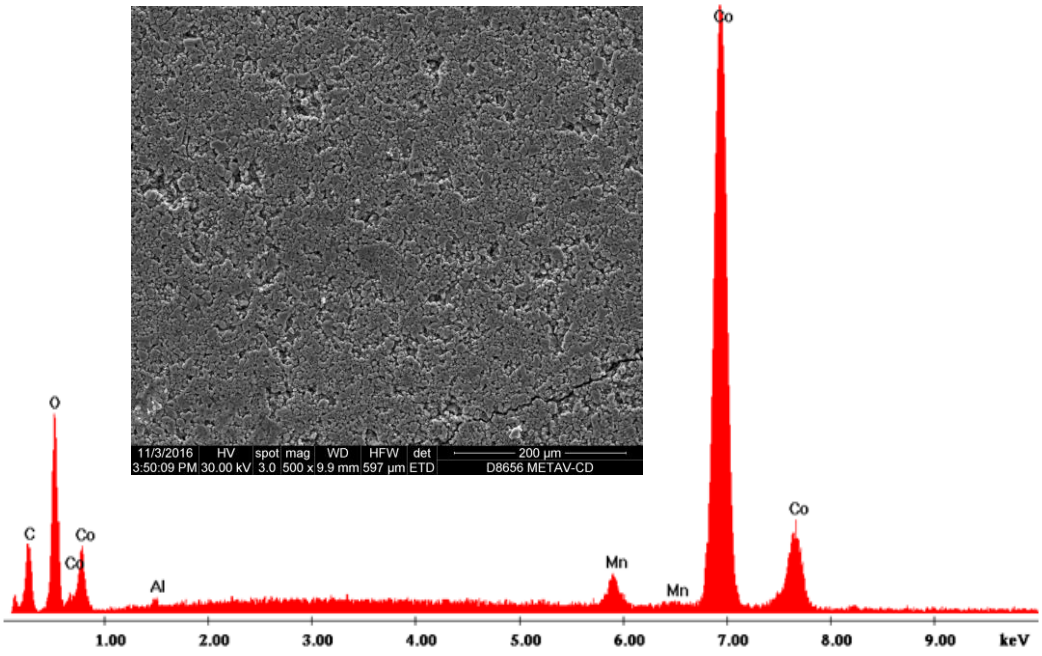


Fig.7. SEM image of surface topography before the combined acid / ultrasound attack and the EDAX analysis on cathode foil coated with active paste

Fig.8 illustrates SEM image of surface topography during the combined acid / ultrasound attack and the EDAX analysis on cathode foil; the active paste was partially removed from the foil. The relative intensity of the diffraction peaks in Mn is higher. It is surprised the moment when the combined attack of citric acid / ultrasounds reached near the final removal of the active paste.

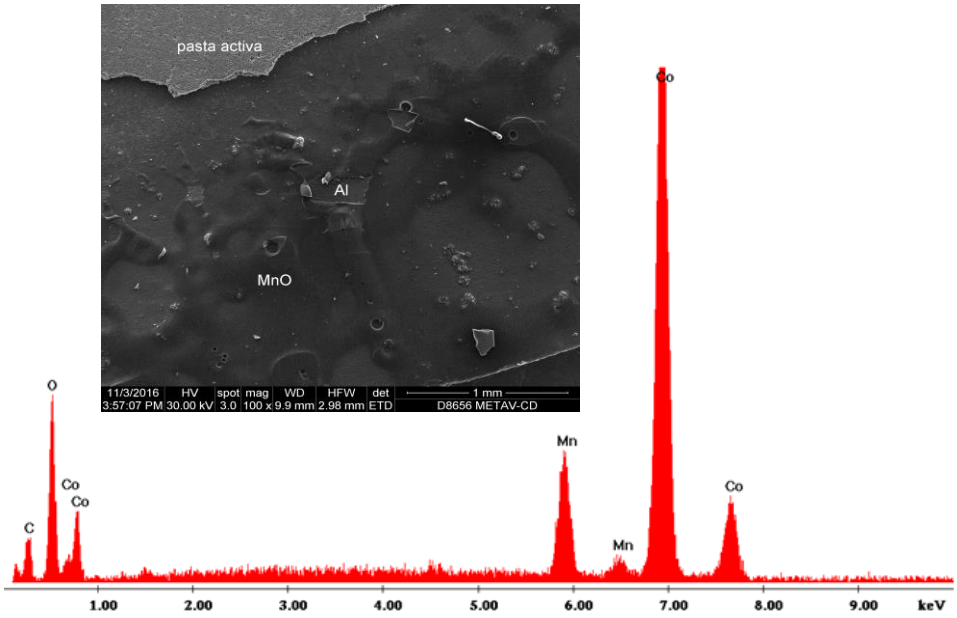


Fig.8. SEM image of surface topography before the combined acid / ultrasound attack and the EDAX analysis on cathode foil coated with active paste

Fig.9 illustrates the SEM image of the surface after the combined acid / ultrasound attack; the cavitation holes produced in the aluminum foil can be observed.

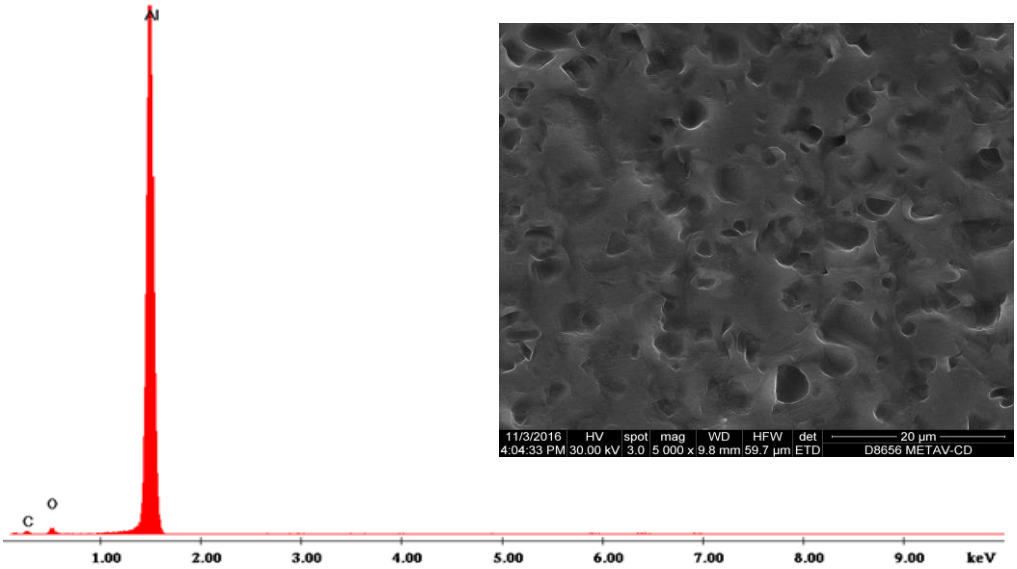


Fig.9. SEM image of the surface before the combined acid / ultrasound attack and the EDAX analysis on the aluminum cathode foil after removal of the active paste

Also, is presented the EDAX analysis performed on the aluminum cathode foil after removal of the active paste.

Identification of $LiCoO_2$ compound which was recovered after the combined acid / ultrasound attack; it was realized with an X-ray diffractometer and the characteristic peaks for this compound can be seen in Fig.10.

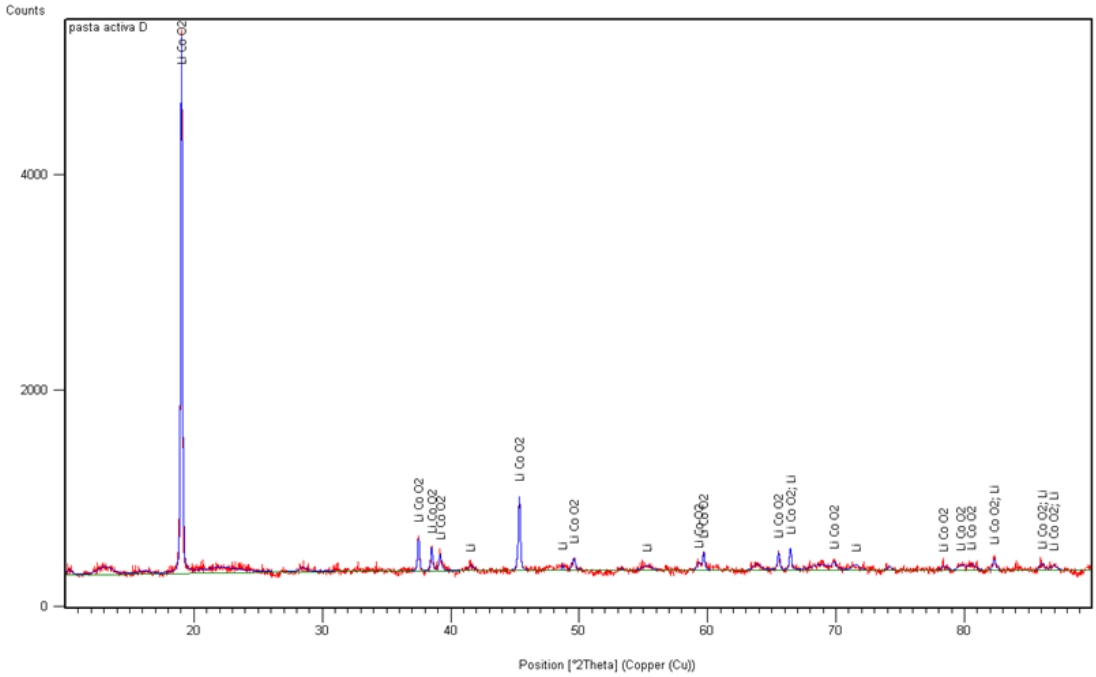


Fig.10. XRD patterns after ultrasonic method

If the combined acid / ultrasound attack process is well controlled, the entire amount of active paste containing $LiCoO_2$ can be detached from the aluminum foil cathode. The active paste is deposited on the bottom of the ultrasonic bath and then recovered, washed and dried. The organic binder is to be removed later.

The ultrasound agitation technology can bring remarkable results in spent Li-ion batteries recycling domain, if is used at proper parameters.

4. Conclusions

1. Even if we had obtained the cathodic / anodic foils through manual dismantling, this method will be replaced. When rechargeable Li-ion batteries will enter the vehicle market in mass this will force standardization of these parts, and therefore the future battery components will be dismantled in order to be replaced quickly enough and their recovery to be realize much easier.

2. Recovery of active cathode material method from spent Li-ion batteries by ultrasonic technology has proved to be reliable. Ultrasound technology combined with the use of citric acid for recovering cathodic paste from spent Li-ion batteries is a perspective method.

3. The proposed method is cheap (citric acid is cheap and most important biodegradable) and is working at room temperature.

4. Optimizing the extrication process, a high recovery efficiency of active cathode material was obtained at 1.25M citric acid.

5. In the further studies, we are looking to try another type of solution with the purpose of process efficiency.

6. In the future, we propose to process further the obtained cathodic powder of $LiCoO_2$ and to clean PVDF (polyvinylidene fluoride) material using a hydrometallurgical method in order to not degrade the active material.

R E F E R E N C E S

[1] Contributii privind estimarea in timp real a starii de incarcare si a unor parametrii caracteristici la bateriile de tip Li-ion utilizate in industria auto, Ing. Adriana Traistaru, Teza de doctorat, 2010, Ed. Politehnica-Timisoara, ISBN: 978-606-554-064-4

[2] www.tradingeconomics.com/OTC

[3] http://www.infomine.com/investment/metal-prices/cobalt/5-year/

[4] *Jinhui, L., Pixing, S., Zefeng, W., Yao, C., Chein-Chi, C.*, 2009. A combined recovery process of metals in spent lithium-ion batteries. Chemosphere 77, 1132-1136.

[5] *Li, L., Zhai, L., Zhang, X., Lu, J., Chen, R., Wu, F., Amine, K.*, 2014. Recovery of valuable metals from spent lithium-ion batteries by ultrasonic-assisted leaching process. J. Power Sources 262, 380–385.

[6] *Li-Po, H., Shu-Ying, S., Xing-Fu, S., Jiang-Guo, Y.*, 2015. Recovery of cathode materials and Al from spent lithium-ion batteries by ultrasonic cleaning. Waste Management 46, 523-528.

[7] http://batteryuniversity.com

[8] *Scheffel, M., Stiuca, P., Gr.,* Dispozitive ultraacustice si optice, vol.1, Editura Tehnica, Bucuresti 1996, ISBN 973-31-0795-6.