Researches on the recovery of useful metals from spent Li-Ion batteries

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Abstract. The present and future importance of Li-Ion batteries is immeasurable; this is evidenced by the awarding of the Nobel Prize in chemistry in 2019, to the team of John Goodenough - director, M Stanley Whittingham and Akita Yashino, who developed the technology to make this type of rechargeable battery. Used at the beginning (1990-2000) in applications such as portable electronic equipments (mobile phones, laptops, electric tools, energy storage systems, etc.), these batteries are considered the most suitable battery for powering electric vehicles. Today the number of electric cars in the world has exceeded 4 million units and the future estimates are among the most optimistic. Recycling of Li-Ion batteries is mainly done in China and South Korea, countries that have a large share in their production, but things can change. Intense research for the recovery and reuse of useful metals contained in these batteries is carried out in many research laboratories. The paper presents the current state of the research undertaken for the recovery of the cathodic paste with high content of Co of waste LIBs, by ultrasonography in lactic acid solution. 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). The paper also includes data regarding the optimization of the separation process of the active cathode paste from the aluminium foil using the orthogonal central-compositional programming of the second order.

1. Introduction
For the development of lithium-ion batteries a class of materials of interest is lithium nickel manganese cobalt oxides - NMC (abbreviated Li-NMC, LNMC, NMC or NCM) which are mixed oxides of Li, Ni, Mn and Co (LiNiₓMnᵧCoₜO₂). The most important representatives have a composition with x + y + z = 1 and are closely related to lithium cobalt (III) oxide (LiCoO₂) and have a layered structure like these [1].

The most used combination is 1-1-1 (1/3Ni-1 / 3Mn-1/3Co) but there are also 5-3-2 (5 parts Ni - 3 parts Co - 2 parts Mn) and others.

This type of battery was born from the attempt to use as little cobalt (expensive and deficient metal) as possible at the cathode of Li-Ion batteries. Nickel cathodes have a lower price, higher energy density, longer life, even if they have a lower voltage.

The success of this type of battery is due to the nickel / manganese combination: manganese has a high specific energy but por stability while manganese forms a spinel type structure (low internal resistance) with low specific energy.
NMC batteries are used as Energy Cells or Power Cells (Battery storing electricity) for: electric cars (Audi e-tron, Renault ZOE, BMW i3, VW e-Golf), e-bikes, power tools, mobile electronics such as mobile phones / smartphones, laptops etc. The cell voltage of lithium-ion batteries with NMC is 3.6 - 3.7 V [2].

In Figure 1 is presented Lithium-ion batteries available for recycling by chemistry (tonnes) [3].

![Figure 1. Lithium-ion batteries available for recycling by chemistry (tonnes) [3].](image)

It can be seen that the market share for these batteries is increasing.

2. Materials and Methods

The experiments were performed at the Hydrometallurgy Laboratory from the Department of Engineering and Management of Metallic Materials Elaboration, Faculty of Materials Science and Engineering - University “Politehnica” of Bucharest.

In the experiments we used spent NMC Lithium-ion batteries from mobile phones which were dismantled manually in order to reach out the cathode material. The spent NMC Lithium-ion batteries were completely discharged in a salt solution for 1h. The cathode materials were manually dismantled and removed from the aluminum foil (immersed in acidic solution - lactic acid and subjected for ultrasonic cleaning) [4].

We used the ultrasonic cleaning machine (Emmi12-HC) with the following technical specifications: housing – stainless steel, cleaning frequency = 45 kHz; cleaning time = 1 - 60 min; volume = 1.2 l; heating temperature = 20 - 80°C; bath dimension 200x100x65 mm; ultrasonic power = 50/75/100W.

The samples were analyzed by SEM (Scanning Electron Microscopy) using a Quanta Inspect F50, with a Field Emission Gun (FEG) with resolution of 1.2 nm, and an EDX (Energy Dispersive X-ray) analyzer having a resolution of 133 eV at MnK. Also, the powder sample was characterized by XRD (X-ray Diffraction) using the PANalytical X’Pert PRO MRD diffractometer (wave length of $\lambda_{Cu} = 1.544$).
3. Results and discussions

The optimal parameters for the ultrasonic process and obtaining a high separation efficiency of the active paste were [5, 6]:

- Concentration of lactic acid solution: 1.7 M;
- Temperature of the ultrasonic bath: 50°C;
- The power of ultrasonic bath: 80 W;
- Time range between 1.5 to 2.5 minutes.

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

The SEM-EDX analyses, performed on the samples are captured in Figures 3 and 4.
The XRD analysis of the sample is presented in Figure 5.
Figure 5. XRD sample investigation.

After the analysis, it was highlighted the main compounds – LiCoO₂ or LiNiO₂ (nickel dioxide is formed during the charging process), forming the solid solution LiCoxNi₁−xO₂ in which cobalt ions are substituted for nickel ions.

The crystallographic parameters are presented in Table 1 and in Table 2 the comparative indexing sheets of the compounds determined by XRD.
Table 1. Crystallographic parameters of Li_{0.65}Co_{0.2}Ni_{0.8}O_2 compared to Li_{0.61}CoO_2.

| Crystal system | Li_{0.65}Co_{0.2}Ni_{0.8}O_2 | Li_{0.61}CoO_2 |
|----------------|-------------------------------|---------------|
| Space group    | R-3m                          |               |
| Space group number | 166                         | 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                      |               |
| Volume of cell (10^6 pm^3) | 100.29 | 97.03 |
| Z             | 3.00                          |               |
| RIR           | 4.50                          | 5.29          |

Table 2. The X-ray diffraction indexation sheet in Figure 5.

Peak list

| 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  |
| 17  | 0   | 1   | 8   | 1.44720 | 64.318       | 11.9  |
| 18  | 0   | 1   | 8   | 1.43450 | 64.957       | 9.7   |
| 19  | 1   | 1   | 0   | 1.42260 | 65.568       | 12.1  |
| 20  | 1   | 1   | 0   | 1.40380 | 66.559       | 10.0  |
| 21  | 1   | 1   | 3   | 1.36330 | 68.808       | 7.7   |
| 22  | 1   | 1   | 3   | 1.34600 | 69.820       | 7.6   |
4. Conclusions
Cobalt is a rare and expensive metal, so any way to replace it in the cathode composition of Li-ion batteries is welcome. The recovery of cobalt and other metals present in used Li-ion batteries (Ni, Mn, and Li) is an economic necessity and an ecological responsibility.

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

The solution used, i.e. lactic acid - C3H6O3, was used to completely detach the cathode material from Al-foil without degrading the material. The results obtained have shown that the technique gave good results at the established parameters.

Analyzing by SEM-EDX the samples of recovered paste, its structure and morphology were highlighted. X-ray diffraction analyzes confirmed the structural proximity of the active paste components.

5. References
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