A Recovery Process of Active Cathode Paste from Spent Li-Ion Batteries

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Abstract. In this work, the depleted active paste from spent lithium–ion batteries was separated from cathode by means of ultrasonic vibration. First the unit cells were discharged in brine at room temperature, for safety reasons. Then anode, separator, electrolyte and cathode were separated. Spent Li-Ion batteries were introduced into a washing container to separate electrode materials from their support substrate: active paste (lithium cobalt oxide – LiCoO₂) from cathode (Al foil) and graphite from anode (Cu foil). The Al foil and Cu foil were also recovered. A cleaning efficiency of 91% was achieved using a solution of 1.5 M acetic acid after a 6 minute time of exposure into an ultrasonic washing container with a frequency and electric power of 50 kHz and 50 W, respectively. The XRD patterns and the morphology of LiCoO₂ powder were presented.

1. Introduction
Li-ion batteries have a wider variety of materials in each cell. All Li-ion batteries pose a potential environmental hazard. The first lithium batteries were using lithium metal as the cathode and not contained toxic metals, but there is the possibility of fire if metallic lithium is exposed to moisture while the cell are corroded [1]. Lithium-ion secondary rechargeable batteries contain no metallic lithium but uses as cathode a material such as LiXMA₂ (LiCoO₂, LiNiO₂, LiNiMnCo₂) and graphite at anode [2]. These contain toxic and flammable electrolyte. Lithium-ion batteries used, partially spent and stored in dumps, can self-ignite and extinguishing these fires is particularly difficult.

On the other hand, Cobalt is a rare and precious metal, and is a relatively expensive material compared with the other constituents of lithium ion batteries. Cobalt is used in chemical production, super alloys and steels. There are few countries that possess exploitable deposits of cobalt (Congo, Canada, China and Russia). The price of cobalt is about 4.7 times more expensive than nickel, 6.6 times more expensive than titanium, 7 times more expensive than lithium [3].

A lithium-ion rechargeable battery comprises:
- A cathode consists of Al foil covered by a fine layer of powdered LiCoO₂ linked (usually) together with aluminum foil through adhesive agent such as polyvinylidene fluoride (PVDF - a highly non-reactive thermoplastic fluoropolymer) binder. PVDF could not react with most of strong acid and base, most of strong oxidant and halogen, and could not be dissolved in such organic reagents as fatty hydrocarbon, aromatic hydrocarbon or aldehyde alcohol at room temperature and could only partly be dissolved in oleum, some special ketenes and ethers [4]; NMP (N-methylpyrrolidone) is the better solvent system for PVDF, but can be tested and but can be tested and DMAC (Dimethylacetamide), DMF (Dimethylformamide), DMSO (Dimethylsulfoxide), THF (Tetrahydrofuran);...
An anode made from Cu foil covered by a line layer of powdered graphitic carbon linked together by the same adhesive agent used in the cathode;
- A toxic and flammable electrolyte, consists of an organic liquid solvent which dissolve Li salt (substances like LiClO₄, LiBF₄ and LiPF₄ [5-8]);
- Separator (polyethylene, polypropylene);
- Casing (aluminum, plastics, stainless steel).

The typical chemical composition of lithium-ion rechargeable batteries with LiCoO₂ as active cathode paste is shown in table 1.

| Component  | wt.% |
|------------|------|
| LiCoO₂     | 27.5 |
| Steel/Ni   | 24.5 |
| Cu/Al      | 14.5 |
| Carbon     | 16   |
| Electrolyte| 3.5  |
| Polymer    | 14   |

Spent lithium-ion batteries can be subjected to different recycling processes, physical process, mechanical separation, mechanochemical process, chemical process, electrochemical process etc. LiCoO₂, which is used as the cathode material for almost all lithium-ion batteries, is considered to be the most important target of this type of batteries. It is possible to recycling cobalt and other metals from the cathode, or to separate and reuse the LiCoO₂.

Contestabile et al., [9] treats the battery rolls with N-methylpyrroldione (as a solvent to dissolve PVDF) at 100°C for 1 h; LiCoO₂ was separated from their support substrate. The recycling of LiCoO₂ cathode material by ultrasonic technology was used for the first time by Jinhui Li et al., [10] develop 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.

Li et al. [11] 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 investigate in detail by Li-Po He et al. [12], who also proposed an environmentally process for the recycling of cathode materials from spent Li-ion batteries.

In this paper, we propose a recycling method of recover cathode material based on ultrasonic leaching with acetic acid, at room temperature.

2. Materials and methods
Spent Li-ion batteries Li-ion batteries from telephones were used in this study. The recovery process of active paste, graphite, and films of Al and Cu is shown in figure 1.

For the first, the batteries were put into a 10 wt. % NaCl solution to discharge for 30 minutes. Then, Li-ion batteries were manually dismantled and physically separated into their different parts:
cathode, anode, steel, separators, and current collectors. Cathodes and anodes were treated in an ultrasonic cleaning machine (Emmi 12-HC).

**Figure 1.** Flow sheet of the metal recovery process.

The technical specifications of the cleaning machine were as follows: housing – stainless steel, cleaning frequency = 45 kHz; cleaning time = 1 - 60 min; volume = 1.2 l; heating temperature = 20 - 80ºC; bath dimension 200x100x65 mm; maxim power = 100 W; ultrasonic power = 50/75/100 W. The position of cathode foils in the basket of ultrasonic bath was maintained at 15 mm from the ultrasonic generator.

This process was aimed at separating LiCoO$_2$ from the Al foils, and separating carbon powder from Cu foil. Figure 2 shows the mechanism by which the ultrasonic help dislodge active paste (or graphite powder) of the carrier foil.

**Figure 2.** Flow sheet of the metal processing and recovery.

Ultrasonic cleaning uses cavitations bubbles induced by high frequency pressure (sound) waves to agitate a liquid. The cavitations bubbles can increase in dimension, till a critic dimension, when are taking place the bubbles implosion. Stirring produce large forces that help the detachment of active paste from the metallic foil substrate.
The ultrasound can be used with just water, but using a solution of acetic acid as solvent the cleaning efficiency grows.

We have conducted the experimental research in order to identify the molar optimal concentration of acetic acid in the recovery of active quasi-full slurry of the cathode occurs.

Weight of pieces from cathode, before and after separation of active paste was determined using a balance with three decimal.

All experiments were performed at room temperature (no need additional heat sources). Purified water and acetic acid (technical grade) was use as the cavitations medium (figure 3) to investigate the effect of acetic acid concentration on the recovery time.

Cleaning efficiency was calculated with the following equation:

\[
\eta = \frac{m_i - m_f}{m_i} \cdot 100
\]

\(\eta\) - Cleaning efficiency;

\(m_i\) - initial weight of cathode piece, g;

\(m_f\) - final weight of cathode piece, g.

The cathode of spent Li-ion batteries was characterized by X-ray diffraction, SEM and EDAX. Also, active paste containing LiCoO\(_2\) (collected after decantation, filtered and dried) was investigated at the end of the process by X-ray diffraction, SEM and EDAX. Processing solutions is the subject of subsequent works.

![Visualization of cavitations effect on cathodic foils.](image)

**Figure 3.** Visualization of cavitations effect on cathodic foils.

### 3. Results and discussions

All the experiments were carried out in the Laboratory of Hydrometallurgy and Metal Recycling of the Department of Engineering and Management of Obtaining Metallic Materials from Faculty of Materials Science and Engineering, University Politehnica of Bucharest.

The results have been summarized below:

Discharging waste batteries before manually dismantling and physically separated into their different parts, it has an important effect in the recovery flow of the slurry active; cleaning time in acetic acid solution is halved (figure 4).
Figure 4. Discharge treatment effect on the recovery time for a different number of pieces.

Table 2. Cleaning efficiency for cathode paste from discharged batteries.

| Cathode                | $m_i$ (initial weight), g | $m_f$ (final weight), g | $\Delta m = m_i - m_f$ | $\eta^*$, % | Time, min. |
|------------------------|---------------------------|-------------------------|-------------------------|-------------|------------|
| 2 pieces               | 1.030                     | 0.913                   | 0.913                   | 88.64       | 5          |
| 3 pieces               | 1.696                     | 1.549                   | 1.549                   | 91.33       | 4.8        |
| 4 pieces               | 2.350                     | 2.141                   | 2.141                   | 91.10       | 4.9        |
| 16 pieces (entire cathode) | 7.756                    | 7.064                   | 7.064                   | 91.07       | 6          |

$\eta^*$, [%] - it was calculated without taking into account the amount of solubilized paste.

Figure 5. Recovery time of active paste at different acetic acid concentration.
The shortest time to remove the active pulp from cathode was achieved using a solution of 1.5M acetic acid, after exposure to ultrasounds in the following conditions: 50 W ultrasonic power; 45 kHz frequency; 20°C temperature; 8 minutes time (figure 5).

The samples were analyzed by Scanning Electron Microscopy (figure 6) using a Quanta Inspect F50, with a field emission gun (FEG) with 1.2 nm resolution and an Energy Dispersive X-ray Spectrometer (EDXS) having 133 eV resolution at MnKα.

XRD data (figure 7) were obtained using a Panalytical X’PERT MPD X-ray diffractometer with a Cu Kα radiation source (\( \lambda = 1.5418 \) Å) in the range \( 2\theta = 10–90^\circ \).

**Figure 6.** SEM image of cathode materials after treated in an ultrasonic cleaning machine (a, b, c) and Al cathode surface after removing active paste (d).

The appearance of the pulp (identified as LiCoO₂) is caught in figure 6 (a, b, c) after the ultrasonic treatment in a solution of acetic acid. LiCoO₂ particles are bonded through adhesive agent (polyvinylidene fluoride – PVDF probably).

Figure 6 (d) presents the surface topography of the aluminum foil after ultrasonic attack.
Identification of LiCoO$_2$ compound was realized by XRD.

4. Conclusions
The result obtained from present work can be summarized in the following points.

1. Our experiments indicate that this method allows to recovery of active paste from cathode by ultrasonic in acetic acid medium.
2. Even if we had obtained for the moment cathode/anode foils through manual dismantling, in the next future, when electric vehicle will dominate the automotive market, standardization and design will require a slight separation of parts.
3. Cathode active paste containing LiCoO$_2$ has been detached entirely from Al foils.
4. Optimal value of molar concentration of acetic acid for the quasi-full recovery of active paste from the cathode was situated at 1.5 M.
5. LiCoO$_2$ compound it has been identified by X-ray diffractometer.
6. The proposed method is cheap (acetic acid is cheap and biodegradable).
7. Analysis of chemical elements solubilized by sonication process of cathodes in acetic acid solution (1.5 M) will be subject to further work.
References
[1] Xu J, Thomas H R, Francis R W, Lum K R, Wang J and Liang B 2008 J. Power Sources 177 512
[2] Battery University, http://batteryuniversity.com
[3] London Metal Exchange, https://www.lme.com/metals/minor-metals/cobalt/
[4] Qin Y and Qi S 2006 Nonferr. Meetal (Part of Metallurgy) 1 13
[5] Bernardes A M, Espinoza D C R and Tenorio J A S 2004 J. Power Sources 130 291
[6] Wu Q, Lu W and Prakash J 2000 J. Power Sources 88 (2) 237
[7] Iwakura C, Fukumoto Y, Inoue H, Ohashi S, Kobayashi S, Tada H and Abe M 1997 J. Power Sources 68 (2) 301
[8] Chen J, Yao C, Sheu S, Chiou Y C and Shin H C 1997 J. Power Sources 68 (2) 242
[9] Contestabile M, Panero S and Scrosati B 2001 J. Power Sources 92 65
[10] Jinhui L, Pixing S, Zefeng W, Yao C and Chein-Chi C 2009 Chemosphere 77 1132
[11] Li L, Zhai L, Zhang X, Lu J, Chen R, Wu F and Amine K 2014 J. Power Sources 262 380
[12] Li-Po H, Shu-Ying S, Xing-Fu S and Jiang-Guo Y 2015 Waste Management 46 523