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## RECYCLING LITHIUM - ION BATTERY

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**Abstract :** *Lithium-ion battery (LIB) applications in consumer electronics and hybrid and electric vehicles are rapidly growing, resulting in boosting resources demand, including cobalt and lithium. So recycling of batteries will be a necessity, not only to decline the consumption of energy, but also to relieve the shortage of rare resources and eliminate the pollution of hazardous components, toward sustainable industries related to consumer electronics and hybrid and electric vehicles. Analysing recycling processes of spent LIBs, it introduce the structure and components of the batteries, and summarize all available single contacts in batch mode operation, including pretreatment, secondary treatment, and deep recovery. Additionally, many problems and prospect of the current recycling processes will be presented and analyzed. It is hoped that this effort would stimulate further interest in spent LIBs recycling and in the appreciation of its benefits.*

**Keywords:** *lithium-ion battery, problems, prospect, recycling, waste.*

### 1. INTRODUCTION

The increase in demand for energy in electric and electronic devices as well as power hybrid and electric vehicles significantly increases battery consumption and therefore the use of materials that produce long-term increase in the amount of hazardous waste [1].

Similarly, electronic and electrical devices and lithium - ion batteries have been discarded at the stage of completion of the life cycle, passing from the global "electronic wonders of technology" to "electronic waste" in the absence of adequate policies and feasible and economically viable technology, which allows for adequate recycling of batteries. Thus, recycling and recovery of the main components of used lithium - ion batteries seems that right now is the optimal way to prevent environmental pollution and consumption of raw materials, or rather, a waste of rare and valuable raw materials [2].

Therefore, for a complete overview of the current state and future prospects in the recycling of waste lithium - ion battery, it is necessary to first examine the structure and configuration of said batteries, in order to determine the most appropriate process of separation and mechanical treatment, by analyzing the available incentives for recycling of waste lithium - ion battery, including the amount of waste lithium - ion battery, the implementation of environmental protection measures

from the aspect of the use and recycling of lithium - ion batteries, as well as the extraction and utilization of scarce materials in the construction of a lithium - ion battery, that should be separated recycling process, whereby in the first place thinking of lithium and cobalt [3], [4].

Through the description of the recycling process of waste lithium - ion batteries will be systematically introduced in the pre-treatment recycling of batteries, secondary treatment in the form of separation of the various components of the battery and the final (deep) the process of recycling of waste lithium - ion battery, with a presentation of the main problems and challenges, the current recycling technologies, as well as future prospects in the recycling of lithium - ion batteries [4].

### 2. STRUCTURE OF LITHIUM - ION BATTERY

Unlike conventional batteries, lithium-ion batteries do not use the reduction process for the creation and accumulation of electricity. Instead, the lithium ions move between the anode and cathode, forcing electrons to move with them. Basically, the lithium-ion batteries consist of: cathode, anode, electrolyte and separator. In addition, inevitably, these types of batteries and have a protective metal sheath, the protective plastic element and the electronic control unit [5], [6], [7].

For making battery anodes commonly used carbon. In

practice, this of applied carbon material has been preferably based on copper which is fixed a separate polymeric agents [8].

The basis for making battery cathodes used on aluminum, while as an active material used is usually a wider range of composite materials, that contain lithium, mostly in the form of oxides. However, in the application of the various forms of the lithium composite, for example lithium cobalt oxide ( $\text{LiCoO}_2$ ), lithium manganese oxide ( $\text{LiMn}_2\text{O}_4$ ), lithium nickel oxide ( $\text{LiNiO}_2$ ), lithium vanadium oxide ( $\text{LiV}_2\text{O}_3$ ), as well as admixtures of lithium composites of cobalt, iron and phosphorus, ie.  $\text{Li}(\text{NiCoMn})\text{O}_2$  and  $\text{LiFePO}_4$ . However, the most common material for the production of cathodes represents a lithium cobalt oxide, primarily due to its good performance, referring to the high level of capacity, which provide, as well as the short charging time, a relatively long discharge time of battery [8], [9].

The electrolyte in batteries provides the movement of electrons between the electrodes, while showing an environment in which chemical energy has been converted into electrical energy. Basically, the electrolyte is an organic liquid with a touch of the dedicated and in the application of the following electrolyte salt  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiCF}_3\text{SO}_3$  or  $\text{Li}(\text{SO}_2\text{CF}_3)_2$ , with the most common  $\text{LiPF}_6$  as the electrolyte. Because the voltage of the lithium ion battery ( $\sim 3.6$  V) is higher than the standard voltage electrolysis of water (1.23 V at  $25^\circ\text{C}$ ), it is necessary that the application elements do not contain water [10]. Figure 1 shows a schematic representation of components of various forms of lithium - ion batteries.

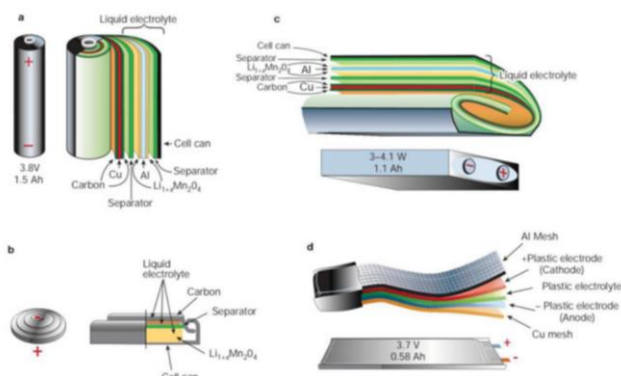


Figure 1 - Schematic representation of the components of various forms of lithium - ion battery, a - cylindrical, b - flat, c - prismatic, d - thin and flat [11]

The separator provides the interface between the anode and the cathode, and prevents the occurrence of a short circuit by direct contact between the electrodes and constitutes the microfilm usually made of polymers, such as polyethylene or polypropylene.

### 3. GENERAL ON THE PROCESS OF RECYCLING LITHIUM - ION BATTERY

In light of the increasing use of lithium - ion batteries,

growing awareness of environmental protection, the use of very valuable raw materials (elements) for the production of batteries and the limited resources of raw materials applied in this type of battery, inevitably, the need for application of highly profitable, in every respect, the process recycling of lithium - ion batteries.

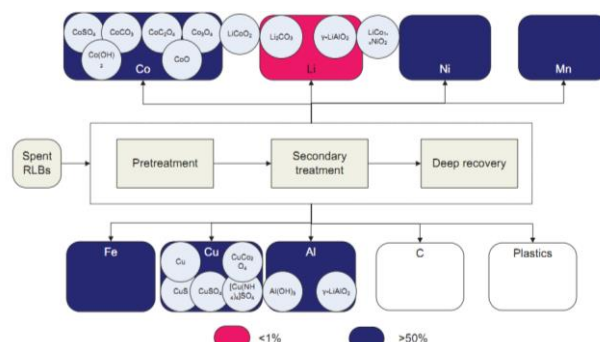


Figure 2 – The complete process of recycling of waste lithium - ion battery

In Figure 2 is shown schematically one of the possible methods of recycling lithium - ion battery, with a clearly defined three basic stages of the recycling process.

Phase pretreatment of recycling batteries has been directed to the removal of certain hazardous materials and separation of individual components of the battery, to the greatest extent possible. During the second phase of recycling takes place the main process for the separation of materials from the battery charger and the process of decomposition. At the end of the final (deep) recycling process is focused on the extraction of valuable and very rare material (eg. the elements manganese and nickel), which can be used in making new batteries, and other products that contain these valuable materials. After carrying out the three phases of recycling a lithium - ion batteries have been obtained mainly metals, but also to metals and copper, aluminum, iron, cobalt, lithium, nickel, manganese, carbon, and various plastics. Generally, metals such as iron, aluminum and copper obtained in a pure, elemental form, whereas cobalt, nickel, lithium and manganese have been usually obtained in the form of different compounds, e.  $\text{CoSO}_4$ ,  $\text{CoCO}_3$ ,  $\text{CoC}_2\text{O}_4$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{LiCoO}_2$ ,  $\text{LiCoO}_2$  and  $\text{Li}_2\text{CO}_3$  [12] [13] [14] [15].

### 4. PRETREATMENT OF RECYCLING LITHIUM - ION BATTERY

Lithium - ion batteries are generally so complex and sensitive structures to direct implementation pyrometallurgy and hydrometallurgy procedures were extremely inefficient, that have been first applied pretreatment battery to prevent damage to the loss of very valuable materials. In order to prevent short-circuit the batteries, these must be completely discharge. Pretreatment battery has been carried out by mechanical, and manual (manual) separation of the individual components and materials. Manual separation of the

components generally and more frequently used for the separation of plastic and metal material, generally the battery housing, that is shown schematically in Figure 3, [16], [17], [18].

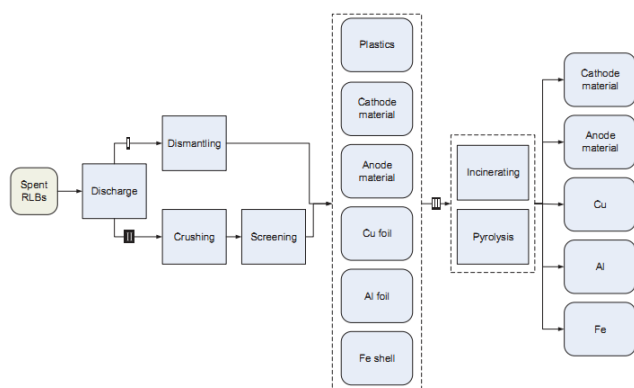


Figure 3 - Schematic representation of pretreatment of recycling lithium - ion batteries [3]

The anode and cathode can be manually separated after removal of the protective shell (casing) of the terminals, followed by the same drying for 24 hours at a temperature of 60 °C. All actions in the pretreatment have been performed by trained personnel, with the mandatory use of protective equipment (goggles, gloves, protective breathing masks) [19]. For example, during this process, the largest amount of copper provides in fractions of a size greater than 0,59mm, and copper is separated from the battery in an amount up to 93.1%. In order to increase the efficiency of the process, mechanical separation combined with crushing and reviewing obtained fragments battery. During the final step of pre-treatment with the help of thermal processes, such as pyrolysis and incinerating stand out unwanted materials, in order to obtain the highest possible purity substances entering the secondary treatment of recycling lithium - ion battery, where for example, first cathode parts are heated up to 150-500 °C for a period of 1 hour to burn off the binder of materials and organic impurities, and then to 700-900 °C for a period of 1 hour, to remove primarily of carbon [20].

Especially in recent years developed an advanced procedure that involves vacuum pyrolysis combined with hydrometallurgical technique to separate the cobalt and lithium from batteries as much as possible, and what percentage of higher purity [21]

## 5. SECONDARY TREATMENT OF RECYCLING LITHIUM - ION BATTERY

After completion of the pretreatment recycling of lithium - ion batteries are still a certain amount of anode and cathode material haven't been separated from Al and Cu foils. Figure 4 shows schematically secondary treatment recycling of used lithium - ion batteries that principally distinguished Cu, Cu solution, Al, Al solution, cobalt and carbon solution [10].

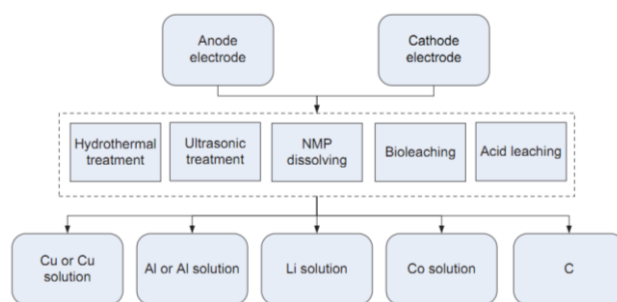


Figure 4 - Secondary treatment recycling of used lithium - ion battery

Through a very controlled and progressive hydrothermal process can be consolidated LiCoO<sub>2</sub> separation of waste batteries and regeneration of valuable compounds for the production of new batteries. During this procedure, using concentrated LiOH, at a temperature of 200 °C with a gradual increase of temperature of 3 °C / min [22].

Ultrasonic treatment has been mostly used for the separation of cathode materials of the Al film [23].

NMP represents a five-layered chemical composite material that codes for lithium - ion batteries used for power increase adhesion of Al and Cu foils. In the secondary treatment process of battery recycling this composite has been separated by heating to 100 °C, with simultaneous separation of Al and Cu [24].

In biological melting as one of the procedures that has been divided by individual scarce materials in the recycling of batteries, a key micro-organisms as iron oxide and sulfur oxide bacteria (lat. Acidithiobacillus ferrooxidans, Thiobacillus ferrooxidans) that show a remarkable tendency to allocate and preserve precious metals, a particularly cobalt and lithium. This process is aided by certain compounds, such as: (NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub>, K<sub>2</sub>HPO<sub>4</sub>, MgSO<sub>4</sub>•7H<sub>2</sub>O, CaCl<sub>2</sub>•2H<sub>2</sub>O, FeSO<sub>4</sub>•7H<sub>2</sub>O, and the purity of obtained cobalt is about 98%, while the purity of lithium is about 72% [15].

Melting using acids, compared to the previous year, the most common procedure in the allocation of materials for the cathode of lithium - ion batteries. Melting may be carried out with conventional acids, such as sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), hydrochloric acid (HCl) and nitric acid (HNO<sub>3</sub>), as well as certain organic acids, the most common of which is citric acid [25].

## 6. FINAL (DEEP) TREATMENT OF RECYCLING LITHIUM - ION BATTERY

Final (deep) treatment of recycling lithium - ion battery combines the processes of solvent extraction, precipitation, electrolysis, crystallization and kalcinazicije, to obtain the highest purity materials, as well as those most valuable materials, that have failed to obtain the previous phases of recycling batteries (manganese, nickel and cobalt) and has been shown schematically in Figure 5 [10].

Universal finishing the process of recycling lithium - ion battery, that is the largest application, reflected in a process in that first allocates manganese in liquid solution, to give a manganese oxide ( $\text{MnO}_2$ ) and manganese hydroxide. Remainder of the process has been allocated nickel, by the compounds dimethylglyoxil. At the end of the process in the universal stands, and lithium in the form of a compound of  $\text{Li}_2\text{CO}_3$ . Cleanliness of the obtained element in this process is as follows: 96.97% for lithium, manganese for 98.23%, 96.94% for cobalt and nickel 97.43% [26].

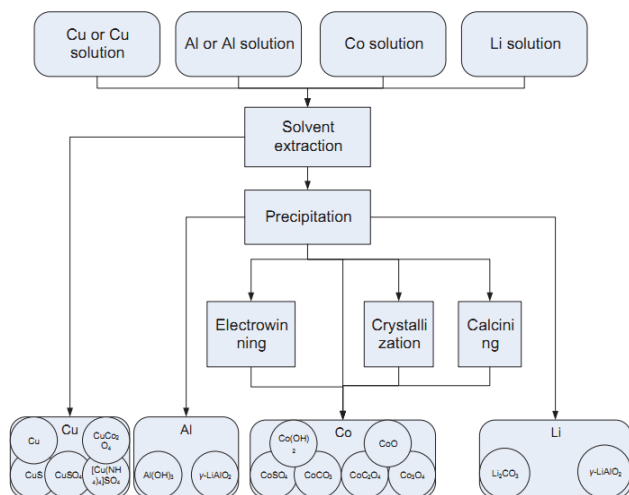


Figure 5 - Deep (final) treatment recycling of used lithium - ion battery.

Improved the final process of recycling lithium - ion battery, which has been developed in recent years is the pyrometallurgical process in which it is used and controlled electric arc, appropriate characteristics, with the aim of obtaining the finest fraction of lithium and cobalt [27].

## 7. CONCLUSION

The increasing use of electronic equipment and electrical machinery, and electric and hybrid vehicles inevitably causes the increasing requirements regarding the use of rare and expensive materials, such as cobalt, lithium, copper or aluminum, which are used in the preparation of a lithium - ion battery, that are the main source of electrical power these machines and appliances. On the other hand, used lithium - ion batteries may explode or leak and cause damage to human health or the environment pollution in case of improper disposal or further treatment, after completing the life cycle.

As the area of further research in the field of recycling of waste lithium - ion battery, could be used as follows:

- shorten battery recycling process while retaining a high percentage purity of sorted materials,
- introduction of more automated and software controlled pretreatment process of recycling lithium - ion battery,
- development of sophisticated separation techniques particularly rare materials, primarily within the secondary and final treatment recycling of batteries,

- development and improvement of the system of collecting used batteries, that are the subject of recycling, both in technical - technological point of view, and in the legal - normative aspect in terms of legal regulations and other regulations [10].

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