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RECYCLING OF LITHIUM BATTERIES

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ABSTRACT

During our research the possibilities of the lithium batteries recycling were examined. One process was highlighted as a potential well developed, which can be used widely for lithium and cobalt recycling. Recycling of lithium-ion batteries is more complicated and not yet developed because the batteries will need recycling for another few ten years. The paper considers one developed process, the steps, the materials what it needs, and there will be some advises which part can be more developed. However, the nowadays working industrial processes main focus is recovering the cobalt and other valuable metals because. Because of the lithium's existing low price, to recover the lithium is economically disadvantageous.

INTRODUCTION

The Morgan Stanley investment bank reported in June 2017[1] that they do not know yet that a large-scale project based on lithium recycling would take place in the next decade, and even fear that there will not be enough capacity to recycle batteries. Further improvements are needed to recover most of the materials in a closed system, furthermore to distinguish between the things we can do and the economically rewarding ones.

The claim of Francisco Carranza, Nissan's expert, confirms this, the biggest problem is that the total cost of processing the battery is 1 €/kg, the value of recovered raw materials is only a one-third part of the total cost. Therefore, Nissan has initiated a cooperation with Eaton's power management company to give priority to recycling rather than reprocessing: home energy storage should be done with used batteries removed from cars. This would allow batteries to run on 70%, because on that percentage, they have not enough capacity for vehicles, but they are ideal for energy storage at home.

TYPES OF LI-BATTERIES

Li batteries have several types, batteries on the market are Lithium cobalt oxide ($LiCoO_2$), Lithium manganese oxide ($LiMn_2O_4$), Lithium nickel manganese cobalt oxide ($LiNiMnCoO_2$ or NMC), Lithium iron phosphate ($LiFePO_4$), Lithium nickel cobalt aluminum oxide ($LiNiCoAlO_2$) and Lithium Titanate ($Li_4Ti_5O_{12}$) are the most common. Lithium Titanate disposes with the highest cycles number, has up to 7,000 times to recharge. Li-ion is harmless, but Li-ion batteries are containing a number of harmful elements. To handling these elements, need attention. One of the most valuable elements of Li-ion batteries is cobalt, which is also used to produce magnets or high-strength steel alloys. Nowadays the experience is that, recovering the Li need more money than mining that. Therefore, it would be practical to focus on the

[1] https://www.morganstanley.com/ideas/electric-car-supply-chain

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recovery of cobalt and nickel from that kind of used batteries. From Li and Li-ion batteries, it is possible to recover cobalt and nickel by hydrometallurgical methods.

SEPARATION OF NICKEL

There are basically two technological processes used to separate cobalt and nickel elements. One is the Toxco process, which essentially, in the first step cooling the batteries to -195 ° C to significantly reduce the activity of the materials contained therein. After that, batteries are shredded and treated with an alkaline solvent. The second separating process is the Sony/Sumitomo process, which process including two steps for the separation. In the first step batteries are burned at 1000 °C in Sony to open batteries and then transfer it to Sumitomo for cobalt extraction. After burning, the batteries are crushed and sieved. The residue contains iron, copper and aluminum, which can be easily separated from the crushed set. The residual material already contains $LiCoO_2$ and/or $LiCo_xNi_{(1-x)}O_2$. From these, pure Co and Ni can be separated by galvanostatic or potentiostatic methods [1].

The cryogenic process is more suitable for recycling because it is easier to separate the batteries for elements: the cathode, the anode, the separator, the vessel and the electronics.

The lithium-ion battery consists several of cells. Each cell built up from four basic components:

- cathode: lithium metal oxide (electrode)
- anode: graphite (electrode)
- separator, which separating the two poles
- an anhydrous, liquid ions are conducted by electrolyte (organic solution).

The battery is covered with an aluminum or aluminum plastic housing (vessel), which filled with organic electrolyte solvents and lithium salts between the two electrodes.

The anode consists of lithium and the cathode consists of lithium metal oxide, which are separated by the separator from each other.

The basis of each process is always cobalt and nickel solution, the cathode of the exhausted Li-ion battery must be engrafted in the solution in a proportional ratio with H_2SO_4 and H_2O_2 reagents. Solvent extraction should be used to separate Ni and Co from each other. Selective extraction was made with soap-plated 0.5 M CYANEX 272 solvent in kerosene. This solvent is a widely used solvent specifically for separating Ni and Co. The electrolytic solution of cobalt is formed by stripping the aqueous solution of H_2SO_4.[3]

SEPARATION OF COBALT

It was made by galvanostatic process, that 250 A/m^2 current density was applied and the manganese content of the electrolyte was predefined like an important pollutant element. Therefore, it is an important pollutant because the recovery of cobalt is facilitated by the presence of manganese, as the final product will be typically more homogeneous. In small manganese-containing electrolytes, cobalt is organized rather spherical than other cases. Partly the temperature and the concentration of added products were studied, these were manganese and nitric acid. As the temperature rises, the separation efficiency is slightly reduced [5,6].

DEVELOPED TECHNOLOGIES FOR RECYCLING OF LI

During the research, hydrometallurgical process was used for recovering Li and Co elements from batteries.
During the tests, the most commonly found metals were Al, Cu, Co, Fe and Li. These metals were found in the cathode and anode of the battery. The anode was typically built up to cover the carbon anode with a thin foil, while the cathode contained Al, Co and Li. This was partly an interesting discovery, as the elements in the cathode represent 41% of the weight or represent 48.8% of the cathode price.

Table 1.

Element	Price [USD/kg]
Al	1,58
Cu	5,3
Ni	10,57
Co	27,5
Li	9,5

The experiments completed here also examined the pyro-hydrometallurgical separations, but it was found that these methods were expensive and consumed a lot of energy.
The following steps were followed during the testing:

- disassemble,
- physical separation of each element,
- manual separation of anode and cathode,
- cathode acid washing,
- crystallization of Co.

Lithium-ion batteries are among the most modern battery types. During discharge, these lithium ions move from the negative electrode towards the positive electrode, while during charge they move in the opposite direction. They have more advantageous properties compared to other batteries: high energy density (more energy can be stored in the same volume), more charge cycles and less memory effect. This memory effect is related to the previous use of the battery, for example, if it is not fully recharged several times, it will be the maximum level charging level for subsequent charges, and the previous charge status cannot be reached again.
As it is a fairly new technical solution, it has some disadvantages against other types, like greater weight, high price and charging capacity. However, the modern automotive application make them unavoidable in electric cars. As these electric vehicles gain more space in the near future, more and more lithium and cobalt raw materials will be required, and it will be important to recycle these important materials from used batteries. In addition to automotive batteries, it can also provide power to other household appliances such as mobile phones or DIY devices.
All in all, there are several factors that make recycling of lithium-ion batteries much more complicated than recycling lead-acid or Ni-MH batteries. Each cell of the Li-ion batteries contains much many different materials. These active materials are in powder form coated with a metal foil. These materials must be separated from each

other during recycling. Compared to a conventional lead-acid car battery that contains a small number of large lead plates in a single plastic housing, a Li-ion unit is usually assembled with hundreds of individual cells (nearly 5000 cells in Tesla electric vehicle) into a package with a control circuit. In this case, a temperature control system is also required. Within individual cells, the composition of the active materials (especially the cathode) varies depending on the manufacturer, it is non-standardized, making more complicating the recycling possibilities.

Lead-acid batteries are small and can be easily removed from their place, while the size and shape of a larger Li-ion unit also depends on the position in the vehicle, so the removal requires more time and expertise [1,2].

When taking the battery structure, the device consists essentially of four main parts: the anode, the cathode, the electrolyte, and the separator. These are complemented by a protective metal cover, an outer plastic cover and a control unit. Anode, cathode, and electrode account for 40 percent of device weight. It also includes aluminum and copper foil (7 and 9%), steel and plastic sheath (11 and 22%). The remaining weight are provided by the electrolyte, the solvent and the electrical circuit.

The structure of the cathode plate shows a greater difference than the structure of the anode. The lithium-containing material is generally an oxide, for example, $LiCoO_2$, $LiMn_2O_4$, $LiNiO_2$, or in other cases, some complex oxides such as $LiMn_xNi_yCo_zO_2$. The newest developments are based on iron phosphate material ($LiFePO_4$). The binder is most often made of polyvinylidene fluoride (PVDF) polymer due to it has good chemical, heat and electrical resistance. As a solvent, should be used a non-water-based, high dielectric constant material, since the voltage of Li-ion cell (~ 3.6V) is greater than the potential difference for electrolysis of water, which is 1.23V at 25 °C. The electrolyte contains high quality lithium salt dissolved in a dipolar solvent and made electrically conductive [3,4]. On the other hand, this electrolyte acts as a lithium tank. In these devices, the most commonly used cathode material is the nickel-cobalt-aluminum matrix (NCA), in which this lithium salt is dispersed. In this case, the anode is made of graphite. This thin graphite layer is built on a copper foil. This kind of designed rechargeable battery are converting with extremely efficiency the chemically stored energy into electrical energy. Because lithium is 100% recyclable, should be not dispose the used batteries in the wasteland. In addition to lithium, batteries contain in high percentages aluminum, copper, cobalt and iron, reusing of these materials also solvable task. In the other case, the cathode is made of lithium iron phosphate ($LiFePO_4$), in this case the anode structure does not change.

HYDROMETALLURGICAL PROCEDURE

There are several hydrometallurgical and pyrometallurgical procedures for metal recycling. The steps of the hydrometallurgical process are the follows: first, the battery parts must be physically separated; then separating the anode and cathode, then washing the cathode with hydrochloric acid and sulfuric acid, and finally carrying out a crystallization assay to recover the cobalt. The steps of the hydrometallurgical process are shown in Figure 1.

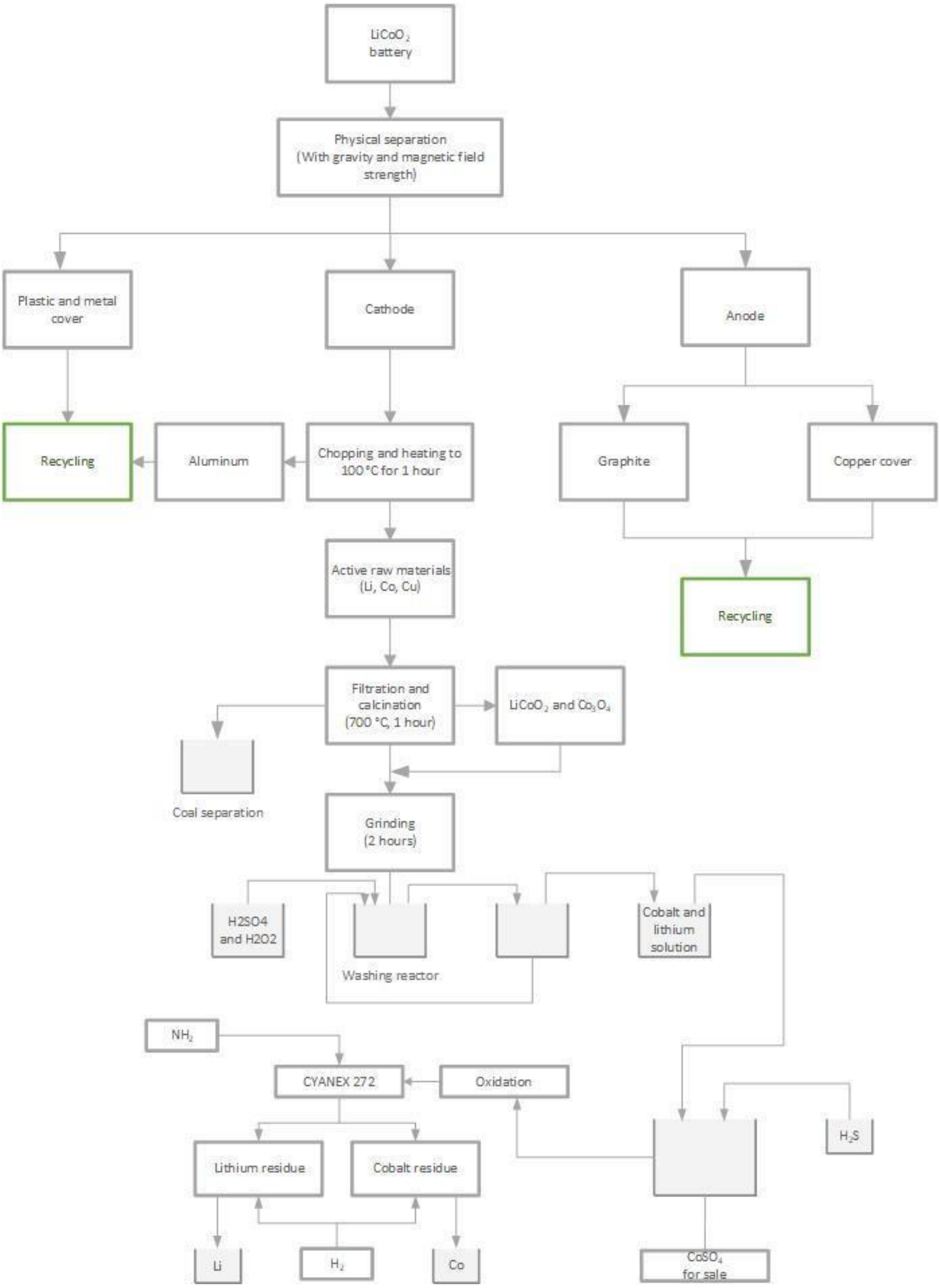

Figure 1.: Hydrometallurgical process

PHYSICAL SEPARATION

Physical separation begins with a mechanical process, whereby the plastic and metal parts of the battery are crushed and then separated by a gravitational or magnetic separation process. The plastic pieces forming the shell are separated by floating, while the metal parts are separated by magnetic field strength.

WASHOUT

The last step is to wash the cathode. This operation is a liquid-solid equilibrium material transfer where the two phases are in direct contact with each other. The electrolyte in the anode is diffused into the liquid, which causing separation of the components in the solid phase. After that process the lithium and cobalt can be captured separately from each other.

CONCLUSION

As one can see to recover the lithium and cobalt is a quite challenging process which should be more developed and more researched. The basic problem nowadays is cheaper to mine the lithium than to recover it, which led the researchers not spending so much efforts to develop and maintain processes for that purpose. The end-of-life lithium batteries now recycled for the cobalt and for other valuable materials, not for the lithium. When the demand of the lithium batteries will increase more significantly the price of the pure lithium is also increasing, maybe that time will press the researchers to develop processes for recovering the lithium from the Li-batteries.

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