The 6th International Symposium on East Asian Resources Recycling Technology
October 23 - 25, 2001, Gyeongju (慶州), Korea
ISBN: 89-952527-0-7 93530

The Current Situation for Recycling of Lithium Ion Batteries

Hiroshi Okamoto[1], Sang-Hoon Lee[2]
1) Seishin Enterprise Co., Ltd., Japan
2) Technology & Research Institute of KORES, Korea

The rapid development of communication equipment and information processing technology has led to a constant improvement in cordless communication. Lithium ion batteries used in cellular phones and laptop computers, in particular, have been in the forefront of the above revolution. These batteries use high value added raw materials and have a high and stable energy output and are increasingly coming into common use. The development of the material for the negative terminal has led to an improvement in the quality and efficiency of the batteries, whereas a reduction in the cost of the battery by researching new materials for the positive anode has become a research theme by itself. These long life batteries, it is being increasingly realized, can have value added to them by recycling. Research is increasingly being done on recycling the aluminum case and the load casing for the negative diode. This paper aims to introduce the current situation of recycling of lithium ion batteries.

1. Introduction

Environment friendly and clean electrical energy is used among other things in Calculators, Wrist watches, VTR's, Laptop computers, Cellular phones etc. With the development of micron size anodes and diodes the Lithium ion secondary cell has contributed enormously to this revolution because of it's very light weight and strong and stable current, which has resulted in long operational time of portable electrical appliances. Notebook computers and Cellular phones, especially, have seen their markets increase considerably because of the improvements in the Lithium ion secondary cells.

Recently there has been considerable research and development on resource extraction from and recycling of used Lithium Ion secondary cells.

Here we will introduce technology for the recycling of Cobalt products, which is connected to powder technology, and which is efficient and also adds value. This technology is not only a reality but can be used and maintained normally.

This presentation is based on the experiences and references of the plant of Asaka Riken Kogyo Company (Japan).

2. The situation and the various points of recycling of batteries

The recycling of batteries is promoted in the various countries of Europe, North America and Japan from the point of view of reuse of resources, and it being Eco- friendly.

A traditional example of the recycling of batteries would have to include that of the nickel

cadmium battery, which was powdered, heat-treated, and the Ferro – nickel and cadmium were reused.

In case of the Lithium Ion secondary cell, after heat treatment and grinding they are melted and acid treated for the recovery of cobalt as a cobalt salt.

On the other hand, dry Manganese batteries and dry alkali batteries are used for extracting ferrite's. However the reuse process, apart from recycling of resources, is not very economical and cannot be used commercially. There are various issues related to the recycling of batteries, these are-

1) Whether there is use of recycling or not
2) Whether the recovery route can be validated over and above the recycling
3) Whether the recycling is economical
4) Whether there is an assurance that the recycled product has purity, which is acceptable.
5) Whether the recycled material has close to or the same level, of properties of the virgin material.
6) Whether gas etc can be recovered safely during the recycle process.

For an environmentally friendly recycle society it is necessary to legally regulate the achievement of recycling. In recent years in Japan, the home appliances recycle law and other laws have been enacted, making recycling the norm rather than the exception. The industry has started promoting recycling of batteries through it's own volition.

3. Example of the recovery of cobalt from waste Lithium Ion secondary cell.

3-1) Flow Chart of Lithium Ion secondary cell.

Figure 1 illustrates the recycle process of non-standard products of waste Lithium Ion secondary cell. Low grade Cobalt is recovered from recovered batteries after the pulverizing process, electric discharge stabilization process, again pulverizing, grinding process, magnetic separation process, fine grinding process, classification and sieving process. Moreover using gas furnace high-grade cobalt can be made. As a recycled product, cobalt metal, cobalt carbonate, and lithium carbonate are recovered.

3-2) Materials that make up the Lithium Ion secondary cell.

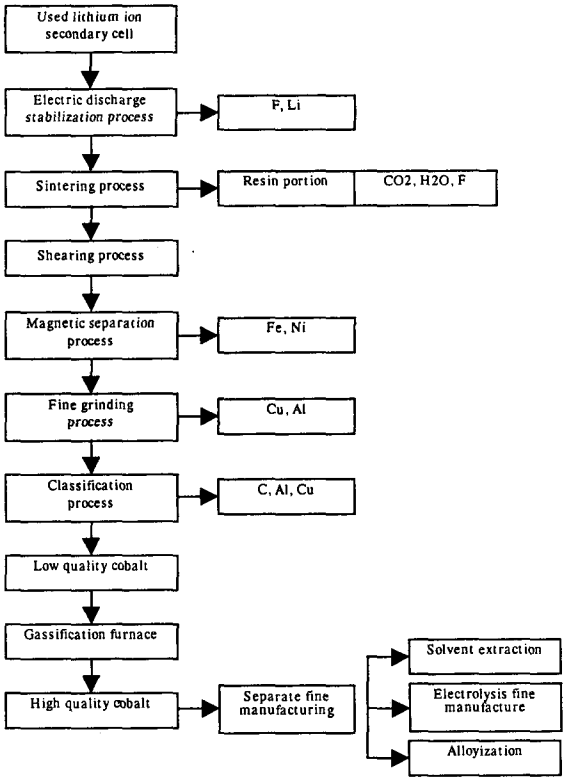

Fig.1 The recycle process of non-standard products of waste Lithium Ion secondary cell

The main materials the Lithium Ion secondary cell is composed of are the following.

Positive anode ------- Lithium compounds
(Cobalt acid Lithium)
Other examples of anodes
LiNiO2, LiMnO4, LiMn2O4

Negative diode ------ Hard Carbon, cokes related
Natural and artificial black
Lead Carbon Fiber,
Meso Carbon, Micro beads

Solution ------ Waste solution which includes organic solvent, LiPF6, Propylene carbonate, Ethylene carbonate

Separator ------ PE, PP

Body ---------- Diode (copper container for voltage enhancer, and copper container for Solution)

Anode (Aluminum container)

Binder --------

1. Lithium (Li.)	approx.2%
2. Cobalt (Co.)	approx.17%
3. Carbon (C)	approx.17%
4. Case (SS)	approx.32%
5. Copper foil +Aluminum foil	approx.19%
6. Nickel (Ni)	approx. 0.5%
7. Miscellaneous	approx. 12.5%

Fig. 2 The weight ratios per ton of the main components of the lithium ion secondary cell. (Avg.)

3-3) Electrical discharge stabilization and coarse grinding of waste Lithium ion secondary cell.

When considering coarse grinding of the materials which compose of the Lithium ion secondary cell it is necessary to consider methods and processes which take into consideration and negate the propensity of the materials to ignite and does not raise the temperature.

Coarse grinding is therefore preferable in water, steam or inert gases, however if we consider the economy point of view water is the most desirable grinding medium. In grinding with water, methods such as grinding with super high-pressure water are available but not economical as compared to mechanical grinding with water.

Our recycling plant uses a grinding system with special blades for grinding Lithium ion secondary cells, which is used in Figure 3. This continuously grinds, in the presence of water and also stabilizes the electric discharge in the Lithium ion secondary cell after coarse grinding there is electrical discharge stabilization in the stabilization water tank, this process takes approximately two hours as indicated in Figure 4. The discharged and cooled cell body is lifted out of the water tank by a mesh conveyer, and automatically the burning process is undertaken.

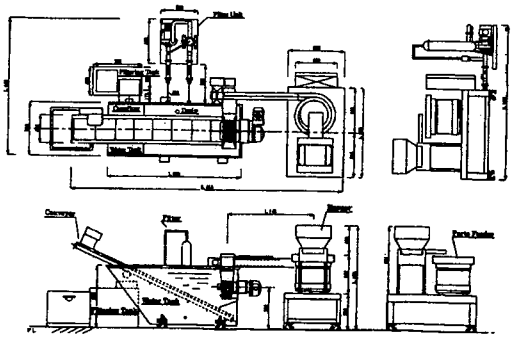

Fig. 3 A grinding system with special blades for grinding Lithium ion secondary cells

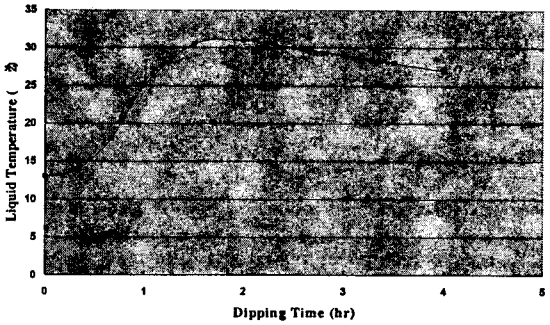

Fig. 4 Time of electrical discharge stabilization in the stabilization water tank

3-4) Burning

The lithium battery is discharge stabilized in the stabilization tank and then fed into a revolving type burning furnace, where at 600 degrees centigrade all organic matter is burnt.

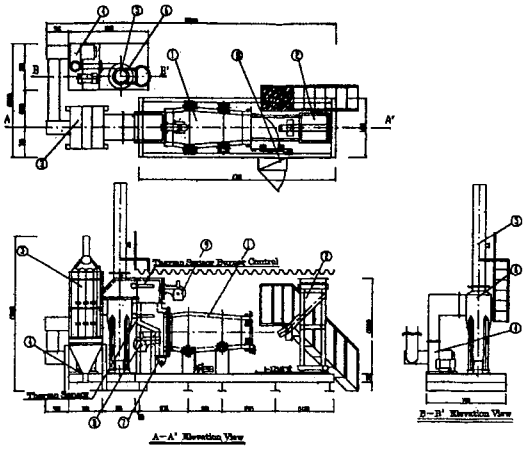

Fig. 5 Revolving Type Burning Furnace

The gases, which are generated in the furnace, are trapped in the liquid cooling tower which the furnace has for the purpose.

3-5) Grinding

After sintering there are many ways to grind batteries, In the recycling of Lithium ion batteries for the next processes of separation and classification to be effectively done grinding is necessary. After sintering the naturally cooled product is milled in a grinder using impact and compression. Inside the cell the carbon of the diode and the lithium acid cobalt of the anode are made into fine powders while being separated and exit the cell body. The ground product contains lithium cobalt and carbon.

3-6) Magnetic separation

The way of separation by using the differences of the characteristics of each material is an important process for recycles of valuable resources. Various techniques like magnetic characteristics, static electricity characteristics, shape etc are used to separate things in waste material recycling.

Separation Method	Way of separation and representative equipment.
Density separation	Air separators, Zigzag separators, Fluid bed Separators, Slant vibrating sieves, are representative of equipment inertial force for separation using sedimentation speed and acceleration of wet and dry materials.
Static separation	Separation of materials using electrostatic precipitation. Static electricity model, Corona discharge model, Drum model static electricity separator is representative of this equipment.
Spirai-current separation	Separation using spiral current differences for separation. The eddy current separator is representative of this kind of equipment.
Magnetic separation	This kind of separation equipment uses magnetic properties of materials for separation. Various kinds of magnetic separation equipment exists.
Floating separation	Separation using floatability of the material.
Physical separation	Separation using density and shape resistance of materials. Slant Sieve Separator is representative of this equipment. Zigzag type separator

After grinding the material which comes out of the cell and which includes anode and diode raw materials, cell materials, aluminum containers, copper containers, is all separated. Normally separation is done by a magnetic drum separator or using static electricity.

For precise separation, it is important not only to separate the various materials but also to send the material on the line with easy specifications. For dispersion and separation of the material, it is desirable that the material is in 3mm to 5mm size.

It is thus natural that crushing and grinding technology is important for proper separation. Figure 6 introduces typical separation technology.

3-7) Dry sieving

The metals, which could not be separated using a magnetic separator, are removed using dry sieving. Furthermore, the sieve effectively separates the cobalt and Lithium of the anode and the carbon of the diode. Normally dry sieves use vibrating sieves, recently however sieves using sonic sifting have entered the market and separate and sieve effectively, In dry sieving they can separate in three grades. In the upper grade relatively large sized metal particles and the remains of the cell are recovered, In the middle powder with cobalt as the main constituent is recovered, In the lowest sieve powder with carbon as the main constituent is recovered.

Normally all material has grinding characteristics, In the same machine under the same conditions carbon will be ground more finely than cobalt and more will be recovered under the sieve.

3-8) Dry Classification

After separation and dry sieving, dry air classification helps recover the cobalt. The density of cobalt is high as a result of which, as illustrated in Figure 7, the centrifugal force makes collection of the cobalt easy. The Classifier does not have any moving parts. In the powder that enters the classifier with the air current, the larger air particles because of their high density and weight are pushed towards the outer extremes of the air current whereas the smaller particles with a lower density are pushed to the center of the air current and are classified. The air classifier can be controlled by adjusting the airflow and the height of the classification area.

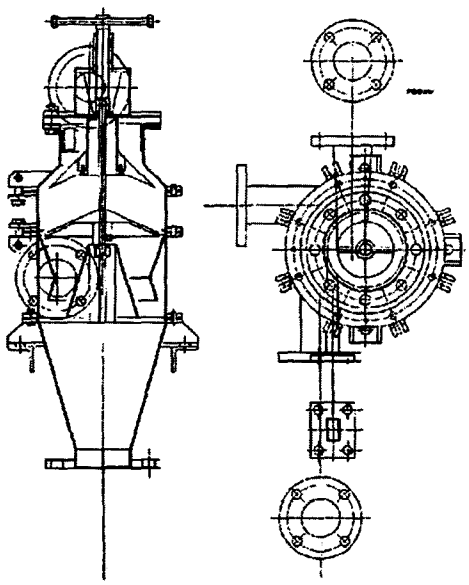

Fig. 7 Air inertia micron classifier

3-9)Composition ratio of recycled Cobalt products

After grinding, sintering, separation, the recovered Cobalt products, have a material balance as illustrated in Figure 8. The final cobalt product composition ratios are given as values in Figure 9.

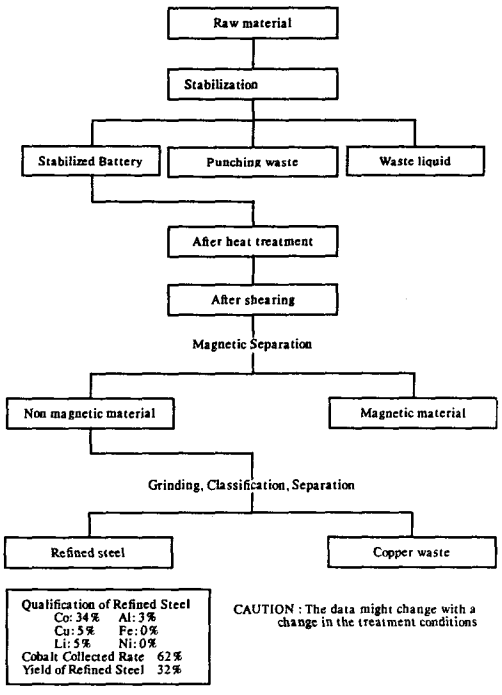

Fig. 8 Material Balance of Cobalt products

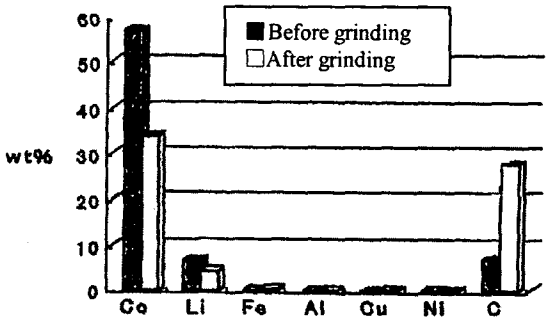

Fig. 9 Composition ratios of the final cobalt product

3-10)Summary of Line used for the recovery of Cobalt from waste Lithium ion batteries.

Using mechanical grinding, separation and classification as a base this recycling system has considerable economic feasibility. As far as is possible wet process are avoided and dry processes are used as the main. Diagram 10 introduces a real example of this lithium ion secondary cell recycle plant. The cobalt recovery ratio is shown as exceeding 62% and other metals are shown as 32%. Other metals recovered are Cu, Lie, Al, and also included at about 3 to 5 % is low-grade cobalt. Because of the use of the process for high-grade cobalt, it is possible to make a high value added recycled product.

4. Conclusion

The ways of recycling Lithium Ion secondary cell and collecting valuable resource Cobalt can be divided generally into two ways, mechanical method and chemical method. Because Cobalt itself is a limited material, it is important to reuse it by recycling. It takes a lot of cost for the processing such as separation and sintering of Cobalt. It is said that 3$/kg is usually taken for one process. By using the mechanical method that I have introduced before, 60% of cobalt can be gained at the most, but the recycling cost is very low compared to the chemical method. In addition, mechanical method can be more effective by separating Cobalt precisely. Cordless products are getting more and more popular and secondary cell is an electric energy that can be recycled. However, it has certainly a recycling life span. It is necessary to take measures soon so that many wasted Lithium Ion secondary cells will not be let alone.