

S.M. SHIN*, G.J. JUNG**, WOO-JIN LEE***, C.Y. KANG***, J.P. WANG***,†

RECOVERY OF ELECTRODIC POWDER FROM SPENT LITHIUM ION BATTERIES (LIBs)

ODZYSK PROSZKU ELEKTRODOWEGO Z ZUŻYTYCH AKUMULATORÓW LITOWO-JONOWYCH

This study was focused on recycling process newly proposed to recover electrodic powder enriched in cobalt (Co) and lithium (Li) from spent lithium ion battery. In addition, this new process was designed to prevent explosion of batteries during thermal treatment under inert atmosphere. Spent lithium ion batteries (LIBs) were heated over the range of 300°C to 600°C for 2 hours and each component was completely separated inside reactor after experiment. Electrodic powder was successfully recovered from bulk components containing several pieces of metals through sieving operation. The electrodic powder obtained was examined by X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS), and atomic absorption spectroscopy (AA) and furthermore image of the powder was taken by scanning electron microscopy (SEM). It was finally found that cobalt and lithium were mainly recovered to about 49 wt.% and 4 wt.% in electrodic powder, respectively.

Keywords: Lithium ion battery, Electrodic powder, Cobalt, Lithium, Thermal treatment

1. Introduction

Lithium ion batteries (LIBs) are a kind of secondary batteries where lithium ions move from cathode to anode in the discharge process. Upon recharging, lithium ions move from anode to cathode again to recover the original places. The lithium ion battery is different from the lithium primary battery where recharging and reuse are impossible, and also from lithium ion polymer battery using solid polymer as the electrolyte. Lithium ion battery may be largely divided into 3 parts of anode, cathode and electrolyte, where a variety of materials may be used. The most widely used anode material commercially is a graphite (C). For cathode materials such as layer-structured lithium cobalt oxide (LiCoO₂), lithium iron phosphate (LiFePO₄) and lithium manganese oxide (LiMnO₂) are in use and titanium disulfide (TiS₂) was also used initially. Depending on what materials are used for cathode, anode, electrolyte, voltage, life, capacity and stability of LIBs may vary greatly. Recently, production with application of nanotechnology is enhancing the battery performance.

Lithium ion batteries (LIBs) are widely used as electrochemical sources in portable electronic applications including mobile phones, personal computers and video-cameras due to their favorable performance of electrochemical properties; they are also likely to play an important role providing power for electric automobiles in the future [1]. The main reason for such increase can be summarized as follows [2]:

1. Very good electrochemical properties of LIBs such as high energy density (120W h/kg), high voltage (up to 3~6 V), longevity (500~1000 cycles), wide temperature range (-20 to 60°C), and minimum memory effect.
2. LIBs do not contain hazardous heavy metals such as cadmium and lead.
3. Soaring price of oil and gas in recent year increasing the interest renewable energy, HV, and EV which in turn increased the demand for secondary batteries in general as an effective energy storage device.

With the increasing of electronic equipments and vehicles nowadays, the generation of spent LIBs increases significantly in the parallel way. Recycling LIBs has increasingly become important because their safe disposal may become a serious problem due to the presence of flammable and toxic elements or compounds although spent LIBs are not generally classified as dangerous waste [3-5], and at the same time, some economic benefits could be achieved in recovery of major components from LIBs [6-7].

Therefore, an objective of the present study is to develop new recycling process for recovering valuable metals from spent lithium ion batteries, which is eco-friendly and cost-saving process with thermal treatment as well as classification unlike previously developed leaching operations to dissolve all materials from the electrodic powders. Owing to newly proposed thermal treatment technique, it is possible

* EXTRACTIVE METALLURGY GROUP, KOREA INSTITUTE OF GEOSCIENCE AND MINERAL RESOURCES, DEAJEON 305-350, KOREA

** DEPARTMENT OF ARCHITECTURAL ENGINEERING, PUKYONG NATIONAL UNIVERSITY, BUSAN 608-737, KOREA

*** DEPARTMENT OF METALLURGICAL ENGINEERING, PUKYONG NATIONAL UNIVERSITY, BUSAN 608-739, KOREA

† Corresponding author: jeipil.wang@gmail.com

safely to handle the spent lithium ion batteries and efficiently concentrate the valuable metals in the electrodic powders.

2. Materials and methods

Spent lithium ion batteries were used in this study, and especially same brand batteries have been used to maintain the reproducibility of experiments. The conventional structure of lithium ion battery mainly consists of cathode, electrolyte, separator, anode, gasket, gas release valve, and sealing plate shown in Fig. 1 [8]. The cathode is the positive electrode of the battery, which means it is the source of positive ions (Li^+) and accepts negative ions (e^-). In layered cathodes, the composition is denoted by LiMO_2 , where M corresponds to Co, Ni, Mn or V [8]. LiCoO_2 is currently the most popular option, despite the high cost of cobalt, as it is relatively easy to prepare an electrode with a layered structure of extremely high quality. The anode is the negative electrode of the Li ion battery, which consists of layered graphitic carbon. The separator provides a barrier which prevents short circuiting of the cathode and anode. It should be sufficiently porous to allow the electrolyte to freely connect the two electrodes. Most commonly, separator are made of polytetrafluoroethylene (PTFE) and other inert polymer membranes with defined porosity and ionic conductivity. Commonly used electrolyte for LIBs include propylene carbonate and mixtures of these solvents [9-11].

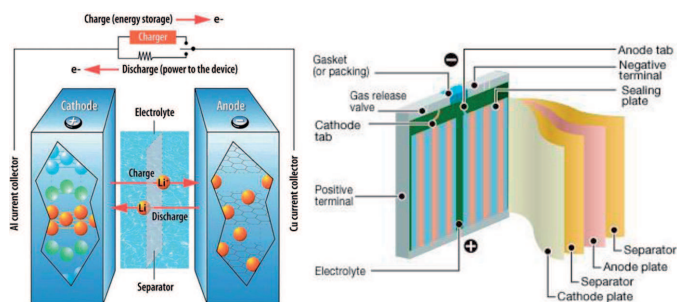
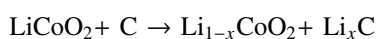


Fig. 1. Structure and principle of operation of a Li-ion battery

Battery charging and discharging occur through the migration of lithium ions between the cathodes and anodes and the exchange of electrons through doping and dedoping. More specifically, during charging lithium is dedoped from cathodes consisting of a lithium-containing compound, and the interlayers of carbon in anodes are doped with lithium. Conversely, during discharge lithium is dedoped from between the carbon layers in anodes, and the compound layers in cathodes are doped with lithium. Reactions occurring in lithium ion rechargeable batteries employing LiCoO_2 (lithium cobaltate) in cathodes and carbon in anodes are shown in Fig. 1. By means of the initial charging, which takes place during battery manufacture, lithium ions migrate from the lithium compound of the cathode to the carbon material of the anode [12-14].

initial charge



Subsequent discharge reactions occur through the migration of lithium ions from the anode to the cathode.

discharge



charge

Experimental device newly designed for thermal treatment to concentrate valuable metals is shown in Fig. 2. It illustrates a side view of the main reactor and a top view of the cover for thermal treatment furnace employed for the present process. The electric furnace(1) has been devised to treat mixed spent batteries in a stable manner and to efficiently treat the electrolyte and its gas produced in the closed system. Since the reactor should be able to withstand explosiveness generated in the thermal treatment process and requires a material with high heat- and corrosion- resistance. The reactor was made of SUS 3103S, since it has an excellent heat- and corrosion- resistance as well as concentrated acetic acid resistance along with good formability and weldability. In particular, it has an excellent resistance to high-temperature oxidation and strength due to its high Ni-Cr contents. Heating element(2) is made of SiC material, which enables the temperature to be raised up to 1500°C . The cover for the electric furnace is also made of SUS 310S material, consisting of 3ea of gas outlet(5), thermocouple(4), gas inlet(6), vacuum tube(11), water cooler tube(7). And to prevent inflow and outflow of inside and outside gas to and from the reaction furnace and the cover, O-ring(8) is installed, while water cooler tube(7) was placed above and below so that the O-ring may withstand high temperatures during the experiment.

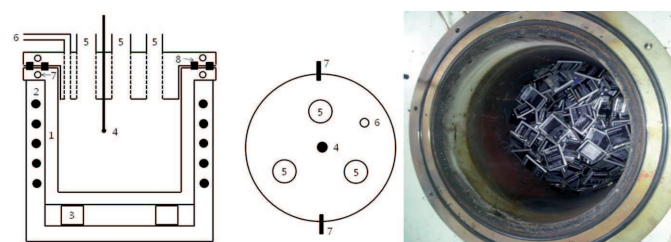


Fig. 2. A schematic diagram for thermal treatment furnace newly proposed

Newly proposed recycling process to recovery of electrodic powder enriched in various metal values was shown in Fig. 3. This process mainly focused on preventing explosion of batteries by thermal treatment under inert atmosphere, since the oxidation of metallic compositions in a presence of air during thermal treatment might result in dramatic reaction able to produce dangerous explosion. End-of-life spent batteries were collected and charged in steel vessel as a container. Thermal treatment in this work was performed at different temperatures from 300°C to 600°C for 2 hours in electric furnace with SiC heater. Spent batteries were placed inside the reactor which was completely sealed and ultra high-purity argon was injected at a rate of 3 liter/min to maintain inert atmosphere inside the furnace during experiments. Temperature was raised at $10^\circ\text{C}/\text{min}$ and maintained for 2 hours once the target temperature was obtained. After thermal treatment, temperature was lowering at a rate of $10^\circ\text{C}/\text{min}$ up to room temperature. A sieving operation was carried out to separate fine powders (electrodic powder) less than $105\ \mu\text{m}$ (75 mesh) from bulk components containing several pieces of metals. The collected powders was sent to have further extracting process by

chemical leaching, while the larger fractions were sent to further separating operations where ferrous metals, non-ferrous metals, and non-metals were separated by an Eddy Current Separator. To remove organic solvents present in the powders, another heat treatment was conducted to remove them completed by maintaining the temperature at 200°C for 2 hours using a muffle furnace.

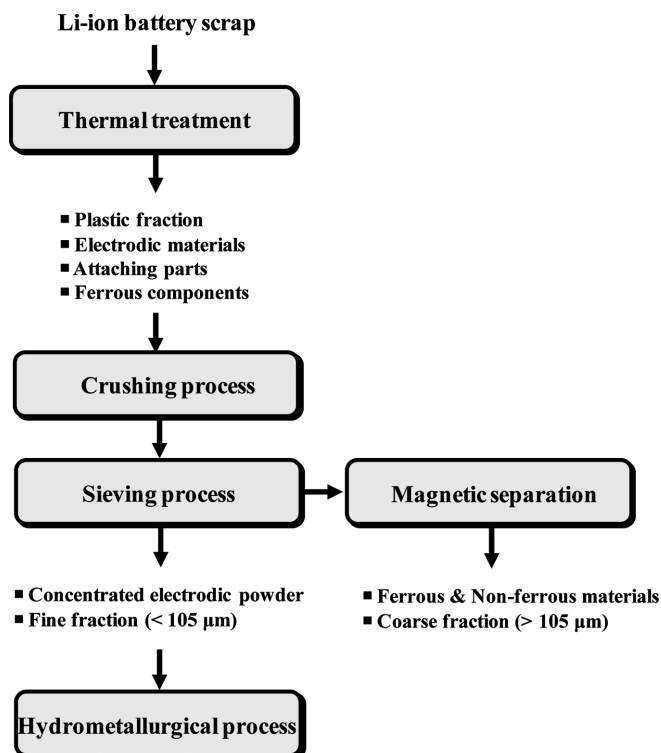


Fig. 3. Proposed flowsheet for recycling spent LIBs using thermal treatment process

3. Results and Discussion

Spent lithium ion batteries from the same brand manufacturer were heated at different temperatures from 300°C to 600°C shown in Fig. 4. As a result of thermal treatment for 2 hours at each temperature, it was found that electrodic powder, copper electrode foil, separator as well as metal case were completely separated each other inside reactor after experiment. The sheath and label of batteries were completely removed during thermal treatment, and electrodic powders were found to be erupted out of the torn battery case. Regardless of an increase of temperature, spent batteries were easily disintegrated and battery's components were found to

be separated each other above 300°C, which might be enough temperature for thermal treatment stage.

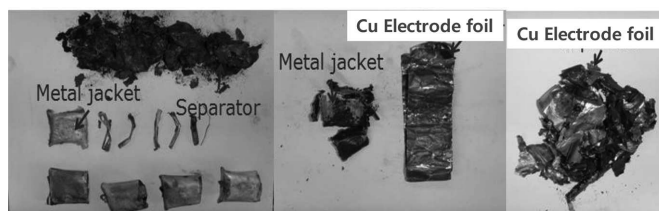


Fig. 4. Component and electrodic powder obtained after thermal treatment

Overall recycling process to separate electrodic powder from components of spent batteries was shown in Fig. 5. Spent LIBs were fed into the electric furnace and thermal treatment was conducted at 500°C for 2 hours. Explosion was taken place inside reactor during test and then samples including battery component were taken out of the furnace. The samples that underwent crushing processes became small pieces of materials including fine electrodic powder. Continually, the classification process was carried out to screen concentrated powders from various components of spent batteries using sieving machine. The electrodic powders less than 75 μm were recovered using a sieve with 105 mesh, while for other batteries' components such as metal cases, caps, bottoms, separator, and electrode foil were left behind on the sieve due to oversize.

For the electrodic powders concentrated in the classification process, an analysis of chemical composition was conducted with atomic absorption spectroscopy (AA) and energy dispersive X-ray spectroscopy (EDS) and the results were stated in Fig. 6. According to the AA analysis result, it may be seen that cobalt accounted for about 50 wt.% of the total amount and Li was also contained by 1.2~1.5 wt.% and about 2.0 wt.% of Al regardless of temperatures. These are considered to have been concentrated from anode and cathode materials as well as copper/aluminum electrode foil. The EDS mapping was conducted for concentrated powder, and Co, Al, Fe, P and gas phases of oxygen (O) and fluorine (F) were observed as the major composition. The fact that cobalt composition shows the largest amount is considered to reflect the lithium cobalt oxide (LiCoO₂) as the cathode material being contained in the concentrated powders. Aluminum might be considered to be contained in the powders during pulverizing process as the case for the lithium ion battery, which is made of an aluminum plate. Substances such as oxygen and fluorine are considered to have been concentrated into powder forms from organic solvents used for the electrolyte of LIBs.

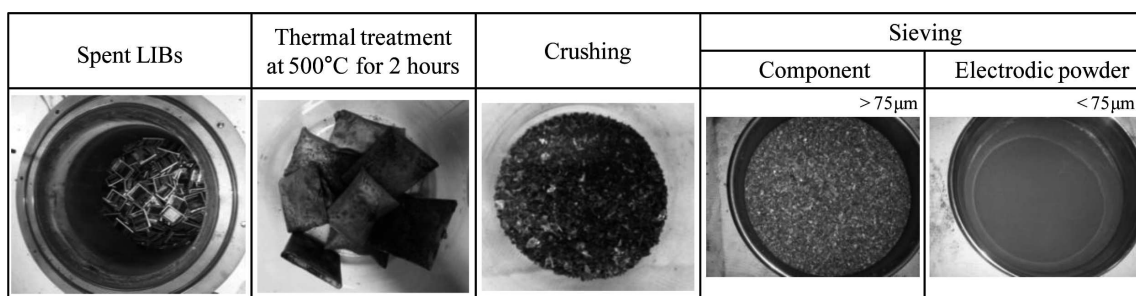


Fig. 5. Overall process to obtain electrodic powder using thermal treatment method

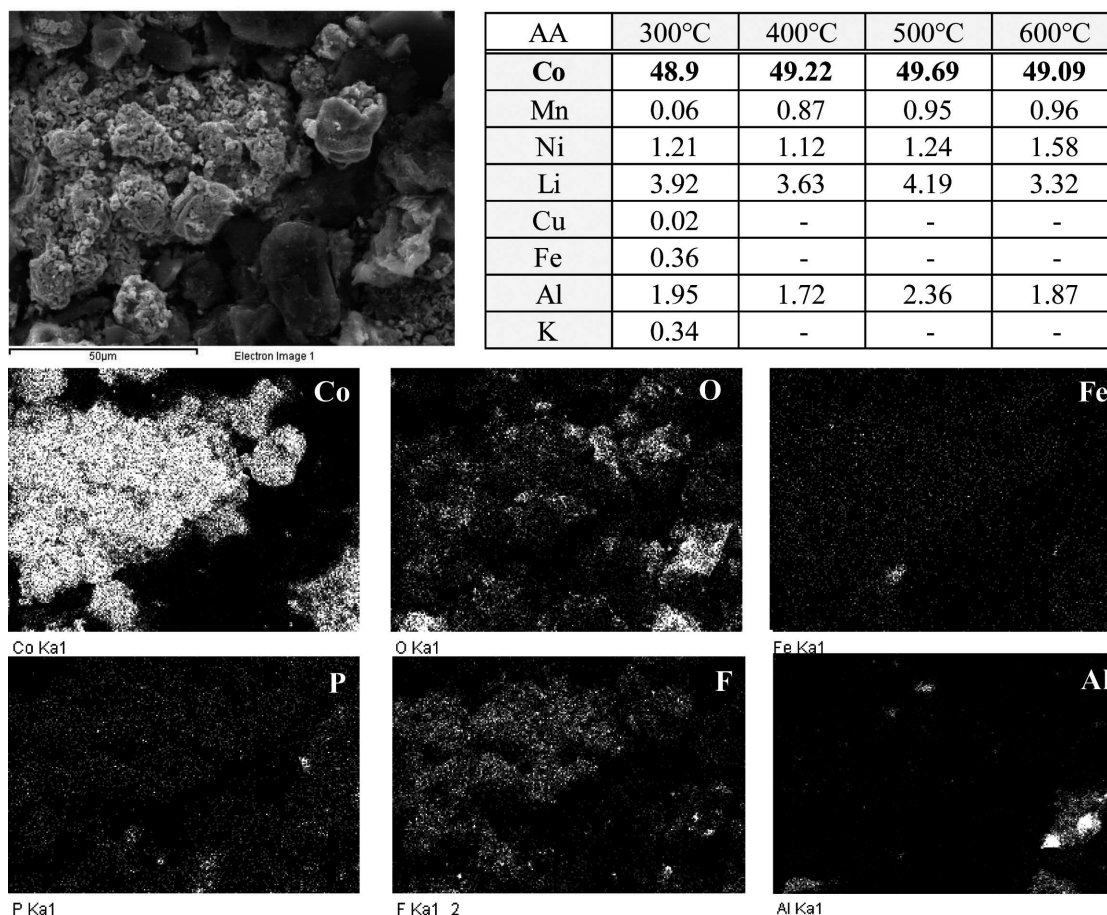


Fig. 6. Chemical composition of electrodic powder analyzed by AA and EDS

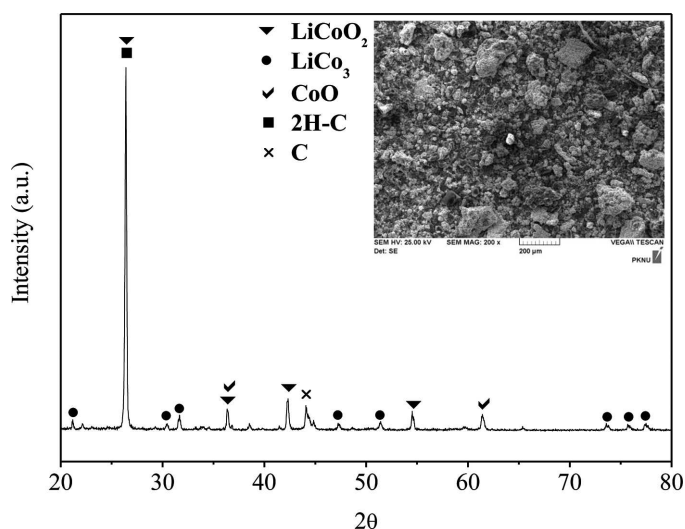


Fig. 7. XRD patterns and SEM image of electrodic powder obtained at 500°C

The electrodic powder obtained after thermal treatment at 500°C for 2 hours was examined by X-ray diffraction (XRD) and the image of powder was taken by scanning electron microscopy (SEM) shown in Fig. 7. It was found that major peak is observed to be lithium cobalt oxide (LiCoO_2) and lithium cobalt (LiCo_3), which would be resulted from metallic lithium and cobalt used as cathode materials as well as a salt of lithium dissolved in an organic solvent of the most common type of lithium ion cell. Other patterns of XRD observed in

Fig. 7 could be expected that their compositions are considered as an anode material of graphite (C) and liquid electrolytes in lithium-ion batteries, which consist of lithium salts, such as LiPF_6 , LiBF_4 or LiClO_4 in an organic solvent, such as ethylene carbonate, dimethyl carbonate, and diethyl carbonate contained in the concentrated powders.

4. Conclusions

Newly proposed recycling process to recover valuable metals in the electrodic powder from the spent lithium ion batteries (LIBs) has been conducted by thermal treatment method at different temperatures under inert atmosphere. Finally, metal values such as cobalt of about 49 wt.% and lithium of about 4 wt.% were concentrated in the electrodic powder. With thermal treatment process, the end-of-life lithium ion batteries could be treated in a stable manner, and explosion risks and environment problems could be resolved effectively as well.

Acknowledgements

This study was supported by the R&D Center for Valuable Recycling (Global-Top Environmental Technology Development Program) funded by the Ministry of Environment.(Project No.:GT-11-C-01-060-0).

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Received: 20 November 2014.