

A Study on the Recovery of Li_2CO_3 from Cathode Active Material NCM(LiNiCoMnO_2) of Spent Lithium Ion Batteries

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(Received August 16, 2018; Revised August 18, 2018; Accepted August 20, 2018)

Abstract In this study, an experiment is performed to recover the Li in Li_2CO_3 phase from the cathode active material NMC (LiNiCoMnO_2) in waste lithium ion batteries. Firstly, carbonation is performed to convert the LiNiO , LiCoO , and Li_2MnO_3 phases within the powder to Li_2CO_3 and NiO , CoO , and MnO . The carbonation for phase separation proceeds at a temperature range of 600°C – 800°C in a CO_2 gas (300 cc/min) atmosphere. At 600 – 700°C , Li_2CO_3 and NiO , CoO , and MnO are not completely separated, while Li and other metallic compounds remain. At 800°C , we can confirm that LiNiO , LiCoO , and Li_2MnO_3 phases are separated into Li_2CO_3 and NiO , CoO , and MnO phases. After completing the phase separation, by using the solubility difference of Li_2CO_3 and NiO , CoO , and MnO , we set the ratio of solution (distilled water) to powder after carbonation as 30:1. Subsequently, water leaching is carried out. Then, the Li_2CO_3 within the solution melts and concentrates, while NiO , MnO , and CoO phases remain after filtering. Thus, Li_2CO_3 can be recovered.

Keywords: NCM(LiNiCoMnO_2), Carbonation, Li_2CO_3 , Water leaching

1. Introduction

The cathode active material NMC(LiNiCoMnO_2) of waste lithium ion batteries is one of the compounds of the cathode active materials of various lithium secondary batteries. The materials of the ternary system have the same structure as LiCoO_2 and capacity per volume and the operating voltage is similar to LiCoO_2 and has low content of Co, so the price benefit is good and a stable cycle is possible inside the high voltage domain [1].

Small home appliances and mobile phones mainly use LiCoO_2 (LCO), but this is unsuitable to be used in medium/large batteries, which require a large output, due to the price rise of cobalt and danger of explosion. So, ternary cathode active material, which is a cathode material to replace LCO, which uses a lot of high-priced cobalt, has been highlighted. It mainly consists of three metals, nickel, cobalt, and manganese. Currently, $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ (NCM)

has been applied as a high capacity cathode material for hybrid electric vehicles (HEV). For the cathode material of the NCM system for electric cars, which is expected to be produced in earnest, the necessity for recycling and reprocessing scrap is on the rise [2-5].

Many studies on how to recover the valuable metals from the cathode of waste lithium ion batteries have been performed.

In research at the beginning of the 2000s, Lee and Kim studied the leaching behavior of nitric acid or sulfuric acid to recover lithium and cobalt from LiCoO_2 , which is the cathode material separated from waste lithium ion batteries, and how to improve the leaching rate. They used reducing agents such as $\text{Na}_2\text{S}_2\text{O}_3$ and H_2O_2 and investigated the optimal leaching conditions of LiCoO_2 [10]. In addition, in 2001, Lee and Kim studied the behavior of reduction leaching of LiCoO_2 in sulfuric acid solution in detail and established conditions for the con-

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centration of sulfuric acid, leaching temperature, density of the beginning pulp, dosage of hydrogen peroxide and reaction temperature [9].

In 2005, Swalin et al. leached LiCoO_2 into sulfuric acid and used a solvent extraction method and did research to recover more than 99.99% of the cobalt solution from sulfuric acid. In 2010, Lee and Chung [5] leached LiCoO_2 into sulfuric acid, separated and refined it for solvent extraction, used an alkaline reagent, and produced more than 99.98% of cobalt trioxide through cobalt hydroxide and heat treatment. They also performed research to manufacture lithium by using sodium carbonate [7]. Also, for the NCM system, Kim et al. produced a precursor of cathode active material of nickel, cobalt, and manganese through physical/chemical treatment of waste lithium ion battery packs of electric cars. Using a coprecipitated filtrate, they performed a study to make lithium carbonate [17]. However, for the recycling method of cathode active material of the original secondary battery, valuable metals such as cobalt, nickel, and manganese are recovered and lithium is recovered in the form of lithium carbonate by using sodium carbonate. In this case, sodium is an impurity and the fact that many washing processes are required is a disadvantage.

This research studied the pyrometallurgical recovery process of waste lithium battery cathode material in the NCM system that is eco-friendly and can obtain the recovery of material with high purity with simple processing for Li metal to be recovered in the waste lithium battery powder in the NCM system. Following heat treatment in a reducing atmosphere (mixed atmosphere of CO and CO_2 or independent atmosphere of CO_2), after isolating the phases of Li, Ni, Mn, and Co, the recovery of lithium was performed through water leaching by using the solubility difference of Ni, Co, and Mn.

2. Experimental

2.1. Experiment Materials

Cathode active material NMC(LiNiCoMnO_2) powder of waste lithium ion batteries was used in the experiment. The chemical composition of the experiment materials was analyzed with X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDS) and three phases in the forms of LiNiO , LiCoO , and Li_2MnO_3 were

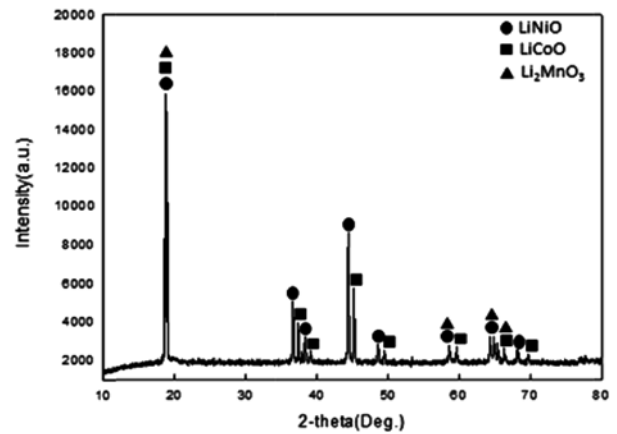


Fig. 1. XRD pattern of waste lithium-ion battery powder in this study.

Table 1. Chemical composition of waste lithium-ion battery powder (wt. %)

Element	EDS(Weight%)	ICP(Weight%)
Li	-	6.521
C	18.60	-
O	28.15	-
Al	0.81	-
Mn	8.21	-
Co	27.56	-
Ni	16.67	-

composed. The XRD results are shown in Fig. 1, and the EDS results are shown in Table 1. The lithium content of experiment materials was measured with ICP analysis, and we confirmed that it was composed of 6.521% lithium. The results are shown in Table 1.

2.2. Carbonation

To extract Li from the cathode active material NMC (LiNiCoMnO_2) powder of waste lithium ion batteries, carbonation was performed to separate Li and Ni, Mn, and Co. An electric furnace was used for the experiment apparatus, and the scheme for that is shown in Fig. 2. Using an SUS crucible, a white lubricated release agent was spread to prevent the sample from being absorbed into the crucible. A 30g sample was used.

For the experiment temperature, the heating rate was set as $10^\circ\text{C}/\text{min}$ and it was maintained for 2 hours at 600°C , 700°C , and 800°C and then reduced by $10^\circ\text{C}/\text{min}$. An Ar atmosphere was used during heat rising and CO_2 atmosphere in the maintenance step after heat rising, and

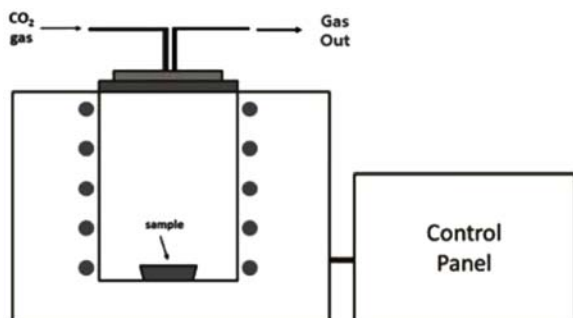


Fig. 2. Schematic diagram of experimental apparatus for carbonation of NCM system waste Li-ion battery powder.

CO₂ gas was blown in at 300cc per minute. At the stage of heat reduction after maintenance, the Ar atmosphere was maintained again.

2.3. Water Leaching

After heat treatment with CO₂, the experiment was performed by pulverizing the battery powder of waste lithium batteries in the NCM system, which was sintered. By using the solubility difference of Li₂CO₃ and metallic oxides (NiO, MnO, CoO), an experiment to separate Li₂CO₃ and metallic oxides (NiO, MnO, CoO) through water leaching was performed. For experiment apparatus, a mixer and beaker were used. Distilled water was used as the solvent for water leaching, and the ratio of distilled water to NMC(LiNiCoMn) powder of the cathode active material of waste lithium ion batteries was set to be 30:1. The time for water leaching was 5 hours.

3. Result and Discussion

3.1. Carbonation

First, the thermal behavior of cathode active material NMC(LiNiMnCoO₂) of waste lithium batteries was confirmed with a thermogravimetric apparatus (TGA) and the heat rising temperature was 995°C/min and heat rising speed was 5°C/min, and they were measured in a CO₂ atmosphere. The results are shown in Fig. 3.

As a result of TGA analysis, a big weight change was observed between 650°C and 800°C and the phase change occurred in this temperature range.

In the TGA experiment results, the battery powder of the NCM system carbonated at 600°C, 700°C, and 800°C and to see the phase change during the process, XRD

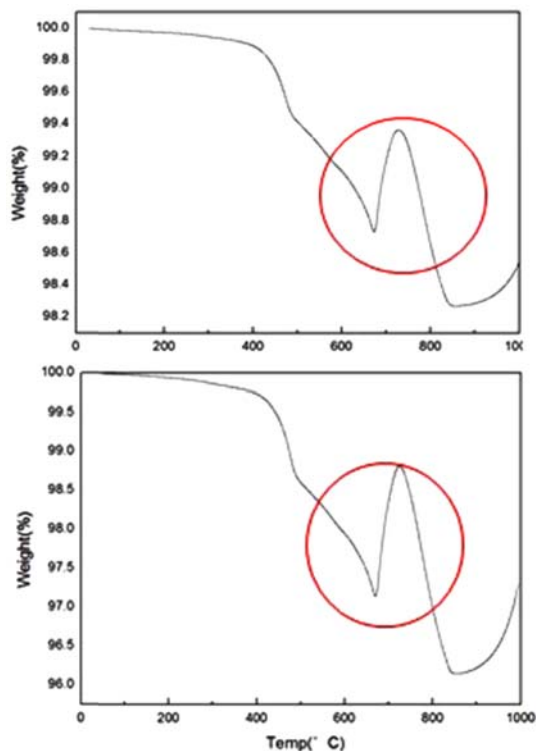


Fig. 3. TGA curve of NMC waste Li-ion battery powder.

analysis was performed. The XRD analysis results are shown in Fig. 4. Looking at the XRD analysis results, when carbonation was performed at 600°C and 700°C, Li₂CO₃ and NiO, CoO, and MnO were not completely separated, and Li and the compounds of other metals remained. It was confirmed that the phase of the raw sample, which was LiNiO, LiCoO, and Li₂MnO₃, was completely separated into NiO, CoO, and Li₂CO₃ phases by carbonation at 800°C. The Chemical composition after Carbonation is shown in Table 2. It was observed that lithium content was not changed during thermal treatment.

3.2. Water Leaching

After pulverizing the sintered sample after carbonation, water leaching was performed by using the solubility difference of Li₂CO₃ and Ni, CoO phases. Table 3. shows the solubility difference according to the temperature of Li₂CO₃ and Ni, CoO phases.

In Table 3, in the case of Ni and CoO, they do not melt in water, and in the case of Li₂O₃, because solubility decreases as temperature rises, flushing at a lower temperature is more favorable.

If we consider that Li content in the raw sample is

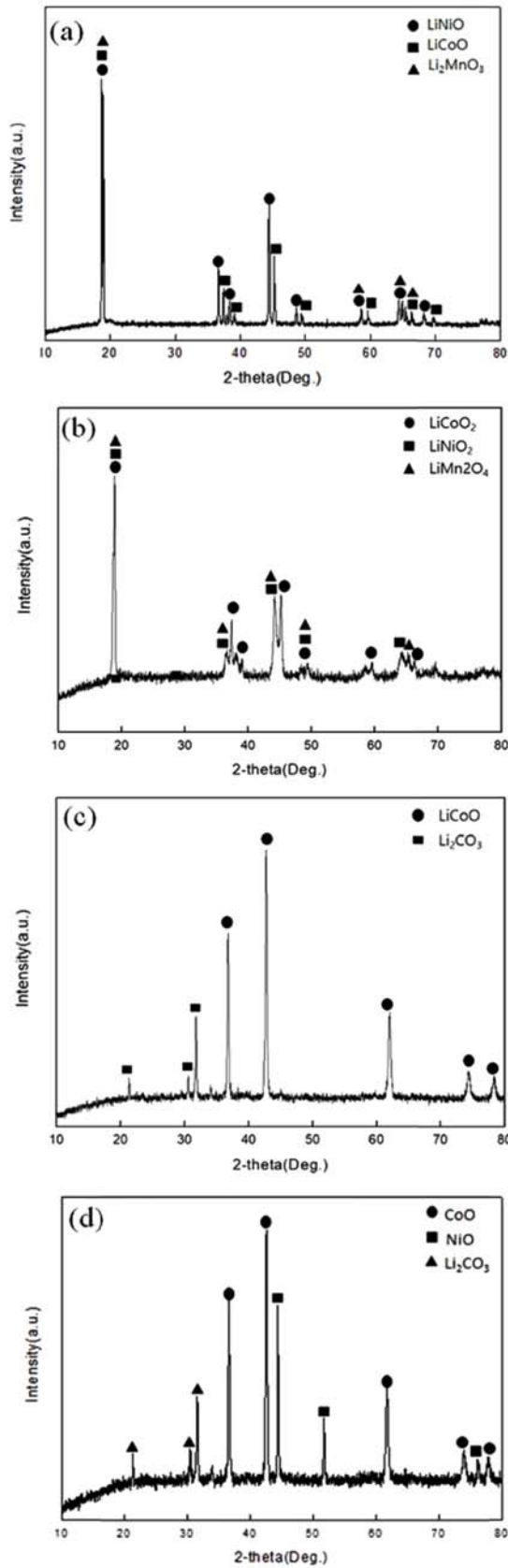


Fig. 4. XRD patterns of (a) Raw sample (b) After carbonation at 600°C (c) After carbonation at 700°C (d) After carbonation at 800°C.

Table 2. Chemical composition of NMC after carbonation

Element	EDS(Weight%)	ICP(Weight%)
Li	-	6.021
C	22.61	-
O	41.87	-
Al	0.48	-
Mn	6.38	-
Co	18.31	-
Ni	10.34	-

Table 3. Solubility of Li_2CO_3 , NiO, CoO and MnO in water

Molecular formula	Solubility in water
Li_2CO_3	1.54 g/100mL(0°C)
	1.32 g/100mL(20°C)
	1.00 g/100mL(60°C)
	0.72 g/100mL(100°C)
NiO, CoO, MnO	Insoluble

6.52wt.% and the analyzed solution is 10 ml, when the ratio of the weight of distilled water to powder after carbonation is 30:1, we can predict that Li_2CO_3 in the sample after carbonation was completely dissolved in water.

During water leaching, the ratio of distilled water to

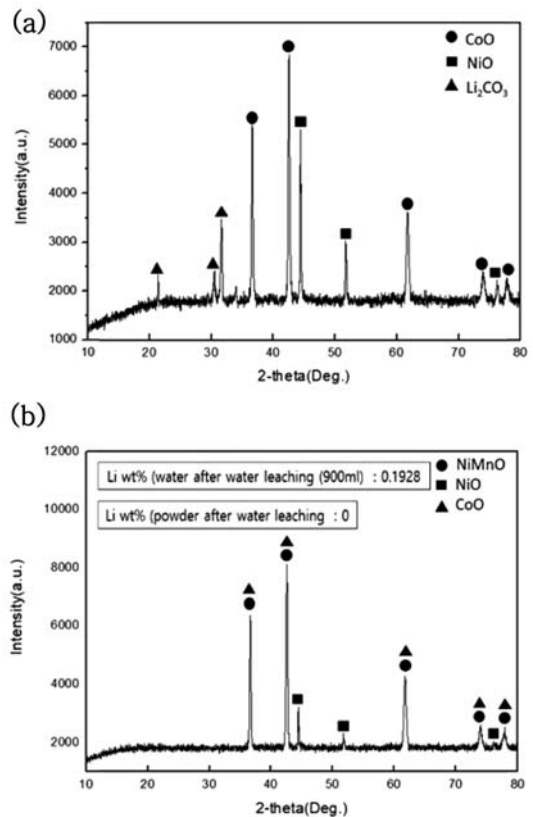


Fig. 5. XRD patterns of NMC system waste Li-ion battery powders after water leaching. (a) After carbonation at 800°C (b) Powder After water leaching

NMC sample after carbonation was set as 30:1 and was done for 5 hours, and powder and solution were separated through a decompressed filter after water leaching. The phase change during water leaching of dried powder after filtering was observed through XRD analysis, and the results are shown in Fig. 5. Also, to confirm the Li_2CO_3 amount dissolved in the solution, ICP of powder and ICP analysis of the solution were performed, and the results are shown in Table 4.

When the water leaching of NMC powder after carbonation was processed, Li_2CO_3 phase was all dissolved in the solvent and concentrated and we confirmed that only NiO, CoO, and NiMnO phases remained in the powder after the decompressed filter

3.4. Li Behavior during the Overall Process

Along with the results of the weight change of the sample during the overall process and ICP analysis results, Li content by step is shown in Table 4.

Powder after water leaching and lithium content in the solution after water leaching were calculated and are shown in Table 4. The ratio of distilled water to powder after carbonation was set to be 30:1, and after water leaching for 5 hours, 1.735 g of Li was dissolved in NMC powder after carbonation and we confirmed that it was completely dissolved in water without Li_2CO_3 and concentrated in the solution. Based on the results, when leaching three times at a 10:1 ratio or water leaching of distilled water to sample at a ratio of 30:1 was processed, we confirmed that Li_2CO_3 was completely dis-

solved and concentrated in the solution.

4. Conclusions

Though phase separation and water leaching followed by carbonation of the cathode active material NMC(LiNi-CoMn) powder of waste lithium ion batteries, the following results for Li_2CO_3 recovery after separating Li_2CO_3 and metallic oxides (NiO, MnO, CoO) were obtained.

1) The phase separation for waste lithium battery powder in the NCM system in CO_2 gas atmosphere through carbonation occurred at 650°C – 800°C and the phase separation of Li_2CO_3 and metallic oxides (NiO, MnO, CoO) occurred.

2) Only some had phase separations at 600°C , 700°C and 800°C , and there was phase separation of three phases such as LiNiO, LiCoO, and Li_2MnO_3 into NiO, CoO, and Li_2CO_3 phases after CO_2 carbonation.

3) By using the solubility difference of Li_2CO_3 and NiO, CoO, and MnO phases, water leaching was processed and the ratio of distilled water to NMC powder after carbonation was set to be 30:1 and was done for 5 hours. When a decompressed filter was used, Li_2CO_3 was completely dissolved and concentrated in the solution. NiO, MnO, and CoO phases remained inside the powder after filtration and Li_2CO_3 and metallic oxides (NiO, MnO, CoO) were completely separated.

Acknowledgement

This study was supported by the R&D Center for Valuable Recycling(Global-Top R&BD Program) of the Ministry of Environment.(Project No.:2016002220001) and was also supported by the BB21+ Project in 2018.

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Table 4. Weight change of sample and change of Li content in the overall process and content of Li in the process

Process	Raw sample	After carbonation
Weight (gram)	30	32.07
Chemical Composition of Li	6.52	6.05
Li Weight (gram)	1.95	1.93
Process	Solution after water leaching	Powder after water leaching
Volume (milliliter) or Weight (gram)	900 ml	26.24 g
Chemical Composition of Li	0.1928	Non detect
Li Weight (gram)	1.735	Non detect

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