International Journal of Membrane Science and Technology, 2024, Vol. 11, No 1, pp 106-111

Selective Recovery of Lithium Hydroxide from Spent NCA ($LiNiCoAlO_2$) Powder

Jei-Pil Wang[1]*, Taeyi Kang[2], Taejun Jeon[3], Gyudong Ryu[4]

[1,2,3,4]Department of Metallurgical Engineering, Pukyong National University, Busan 48513, Republic of Korea. E-mail: jpwang@pknu.ac.kr

Abstracts: This research was conducted on the method of recovering the lithium hydroxide and valuable metal from the NCA-based cathode active materials in the spent lithium-ion batteries. The recovery rate of lithium depends on the reaction temperature, retention time, reaction time during H_2 reduction and solid-liquid ratio. Lithium hydroxide and valuable metals were recovered under each experimental condition, and the following optimal process conditions were determined based on the results of experiment. Based on the charging of 10g of NCA powder, the optimal process conditions were determined as follows: the reaction temperature of 700℃; the retention time of 3hrs; and the H_2 gas flowrate of 300cc/min; the leaching time of 1hr for water leaching; the solid-liquid ratio of the sample and distilled water at 1:30; the stirring speed of 300rpm at room temperature, and the recovery rate of 92.30% was achieved.

Keywords: Lithium ion Battery, NCA($LiNiCoAlO_2$), Active Cathode Material, LiOH

1. INTRODUCTION

Due to their excellent output, energy density, and lifespan, lithium-ion batteries are widely used in various industries such as portable electronic products, electric vehicles, and grid-scale energy storage. Of the key materials in this battery, the cathode material has a great impact on cost and performance. The cathode material determines the capacity and average voltage of the battery, and it is composed of LCO($LiCoO_2$), NCM ($LiNiCoMnO_2$), NCA($LiNiCoAlO_2$), LMO($LiMnO_2$), and LFP($LiFePO_4$) depending on the material.

Researches on high-Ni-based cathode active materials with low cobalt content and high nickel content are increasing with the purpose of satisfying commercial requirements such as high energy density, light weight, and low cost in line with the expansion of the electric vehicle market. One of them, the layered NCA cathode material, which is a representative high-Ni cathode active material, contains more than 85% of Ni and has a high theoretical capacity (280mAhg^{-1}) and operating voltage (3.6V). Therefore, it is one of the cathode materials that are being intensively developed.

Currently, lithium carbonate and lithium hydroxide are used as raw materials for lithium used in lithium-based secondary batteries. However, in the case of the lithium used for the properties of high-performance batteries, the use of lithium hydroxide rather than lithium carbonate is increasing. Since High Ni-based batteries are required in the mid- to long-term and the synthesis temperature is lowered, the lithium hydroxide, which has a lower decomposition temperature, becomes more important than the lithium carbonate, which has a high decomposition temperature, to prevent deterioration in reactivity.

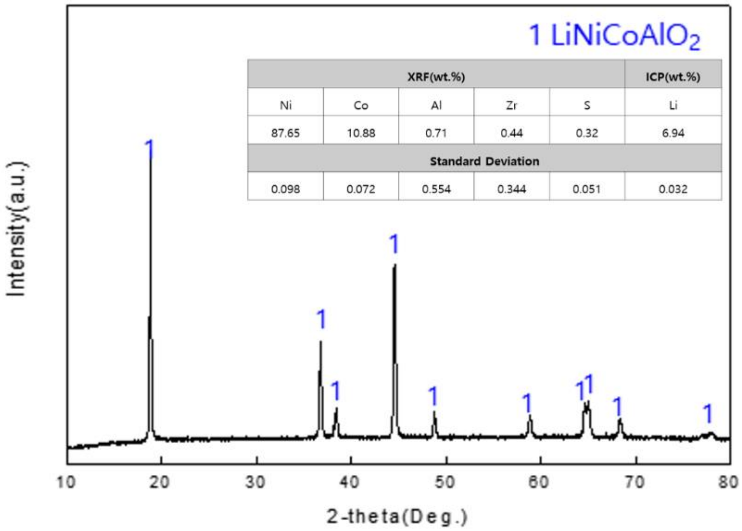
The industrial importance of secondary batteries is expanding due to the rapid penetration of electric vehicles, increasing the demand every year. The use of electric vehicles is increasing, and accordingly, research and development on the spent battery processing technologies is continuously expanding. Most of researches on the recovery of valuable metals and lithium from the cathode materials in the spent lithium ion batteries are conducted through acid solution leaching, which may lead to environmental problems. Therefore, it is necessary to develop an eco-friendly process to solve these problems.

This research was conducted on the method of recovering the lithium hydroxide and valuable metals from the cathode material in the spent lithium ion battery through H_2 thermal reaction and water leaching of the cathode active material NCA.

2. MATERIEL AND METHODS

2.1. Experimental Materials

In this experiment, the cathode active materials in the spent NCA($LiNiCoAlO_2$)-based lithium ion batteries were used. XRD(X-Ray Diffraction), XRF(X-Ray Fluorescence), and ICP (Inductively Coupled Plasma) analysis were conducted to confirm the composition and phase. The results of XRD, XRF, and ICP-OES analysis of the NCA powder were expressed in Figure 1 and the results of XRD analysis confirmed that the sample existed as a $LiNiCoAlO_2$ compound. The results of XRF and ICP-OES analysis confirmed that the sample was composed of Ni 87.65 wt.%, Co 10.88 wt.%, Al 0.71 wt.%, Li 6.94 wt.% and trace amounts of impurities.



XRF(wt.%)					ICP(wt.%)
Ni	Co	Al	Zr	S	Li
87.65	10.88	0.71	0.44	0.32	6.94
Standard Deviation					
0.098	0.072	0.554	0.344	0.051	0.032

Figure 1. XRD pattern and XRF, ICP-OES analysis results of $LiNiCoAlO_2$

2.2. Experimental Methods

The research was intended to recover LiOH, Ni, and Co from NCA($LiNiCoAlO_2$) cathode material through an eco-friendly drying process. The phase separated by hydrogen reduction of NCA powder was separated into a solution and residue through water leaching and filtration. After that, it was dried at 95°C for 8 hours to separate LiOH powder and Ni, Co mixed powder. The H_2 thermal reaction and reaction time according to the temperature condition and retention time, and the effect of water leaching according to the solid-liquid ratio were tested. At this time, the phase change, Li recovery rate, and chemical composition were confirmed through XRD, XRF, and ICP analysis.

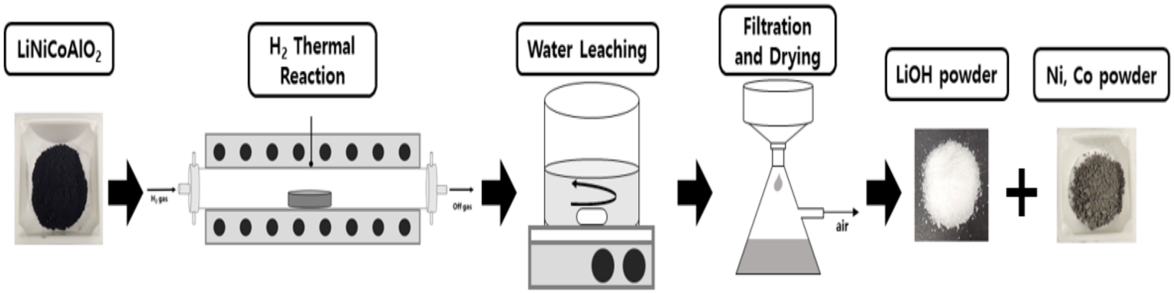


Figure 2. Overall experimental process diagram.

3. RESULTS AND DISCUSSIONS

3.1. H_2 Reduction

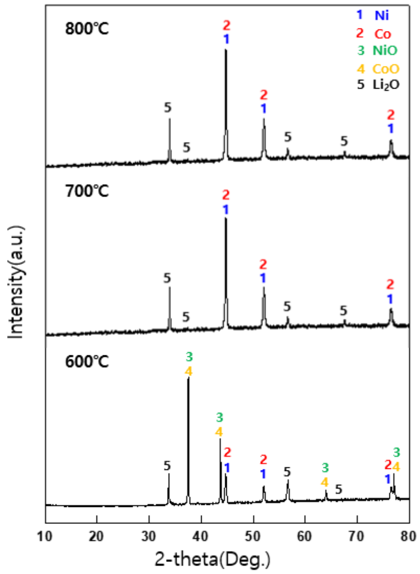
3.1.1. Effect on Temperature

H_2 reduction is a process of changing the compound phase of NCA powder into the phase of Li_2O and a valuable metal. The expected reaction formula is shown below. The results of TGA analysis confirmed a rapid weight loss around 600℃ in H_2 gas atmosphere. The H_2 reduction was conducted at the temperature condition of 600°C, 700°C and 800°C as variable, and the H_2 gas flow rate of 300cc/min and the retention time of 3 hours were maintained constant. The results of experiment were expressed in Figure 3 through XRD analysis. As a result of the analysis, only Li_2O, Ni, and Co phases were observed under the temperature conditions after 700°C, which confirmed that phase separation and reduction occurred simultaneously. Therefore, the optimal reaction temperature for phase separation and reduction from $LiNiCoAlO_2$ through H_2 thermal reaction is 700°C.

$$LiNiCoAlO_{2(s)} + H_{2(g)} \rightarrow Li_2O_{(s)} + Ni_{(s)} + Co_{(s)} + Al_2O_{3(s)} + H_2O_{(g)}$$

3.1.2. Effect on Retention Time

Based on the optimal reaction temperature determined above, an experiment was conducted to determine the optimal retention time for H_2 reduction. Excluding the previous experiment and the retention time, the temperature was fixed at 700℃ under the same conditions, and the retention time was changed to 1hr, 2hrs, and 3hrs. The results of XRD analysis were expressed in Figure 4. As shown in the figure, the phase separation and reduction occurred at the time of reaction for 1hr, but the Li phase was observed as Li_5AlO_4 rather than Li_2O. This was considered that due to insufficient reaction time, Li and Al contained in NCA were not separated. From the reaction time of 2hrs, phase separation and reduction into Li_2O, Ni, and Co occurred, but at a reaction time of 2hrs, a significantly lower intensity value of Li_2O was observed in comparison to 3hrs. Therefore, the optimal conditions for the phase separation and reduction process through H_2 reduction from NCA were determined as follows: reaction temperature of 700°C; H_2 gas flow rate of 300cc/min; and retention time of 3hrs when charging 10g of NCA cathode active material.



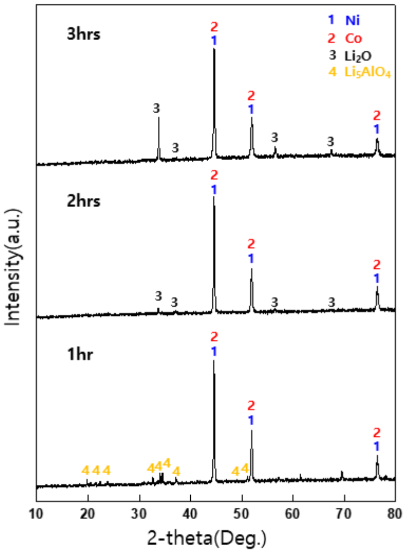


Figure 3. XRD pattern of heat reacted $LiNiCoAlO_2$ at 600℃~800℃ (left)

Figure 4. XRD pattern of heat reacted $LiNiCoAlO_2$ at 1hr~3hrs (right)

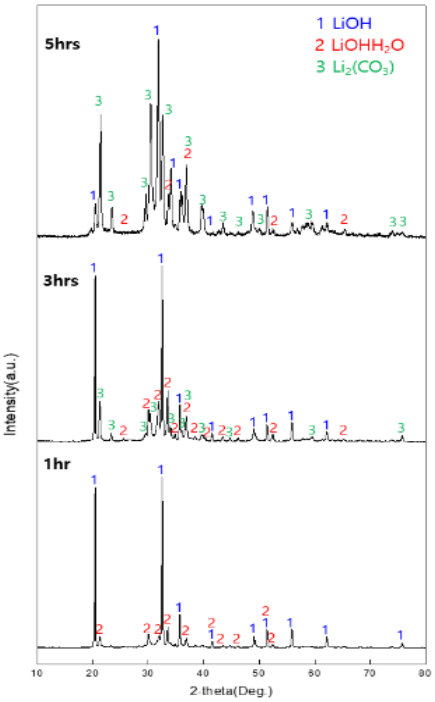
3.2. Water Leaching and Filtration

3.2.1. Effect on Leaching Time

Leaching is a process of separating Li by using distilled water to separate Li_2O, whose phase was separated from NCA powder and valuable metals. Since Li_2O forms LiOH due to the difference in solubility in water, and Ni, Co, and Al_2O_3 are insoluble in water during water leaching, they can be separated into solutions and residues after filtration. To examine the effect of the leaching time, the solid-liquid ratio of H_2 reduced product and distilled water was maintained at 1:50; the stirring speed was maintained at 300 rpm at room temperature; and the water leaching time was changed to 1hr, 3hrs, and 5hrs as variables. After water leaching, the solution was separated through vacuum filtration and dried at 95°C. for 8 hours to recover the powder. The recovered powder was analyzed through XRD. As shown in Figure 5 below, only LiOH phase was observed at leaching time of 1hr, but Li_2CO_3 phase was also observed after 3hrs of leaching time, which is because LiOH in the solution absorbs carbon in the air, changing the phase to Li_2CO_3. Therefore, 1hr was determined as the optimal leaching time to recover LiOH

3.2.2. Effect on Solid-Liquid Ratio

To examine the effect of the solid-liquid ratio, the stirring speed of 300 rpm and the water leaching time of 1hr at room temperature were set as fixed conditions. After H_2 thermal reaction, the solid-liquid ratio of the sample and distilled water was changed to 1:10, 1:30, and 1:50 during the experiment. After water leaching, the solution was separated through vacuum filtration, and then dried at 95°C percentage of the weight of Li in the recovered LiOH powder in comparison to the weight of Li in the raw material after ICP analysis. The results of recovery rate calculation were expressed in Table 1 below. The recovery rate was calculated to be 84.33% at the solid-liquid ratio of 1:10, 92.30% at 1:30, and 92.57% at 1:50. Since the recovery rate was insufficient in comparison to the amount of distilled water used after the solid-liquid ratio of 1:30, 1:30 was determined as the optimal solid-liquid ratio condition.



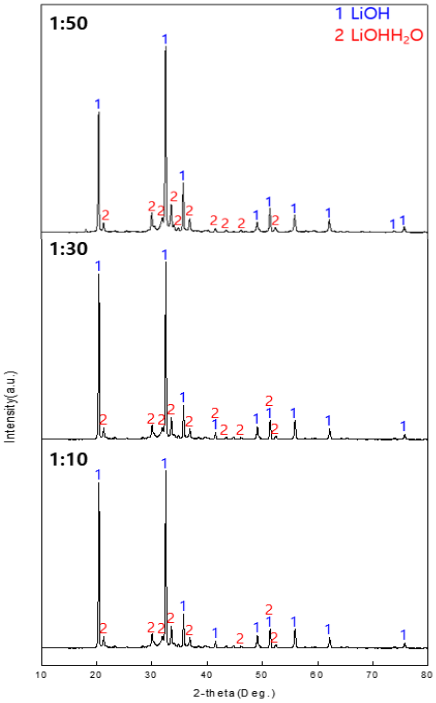
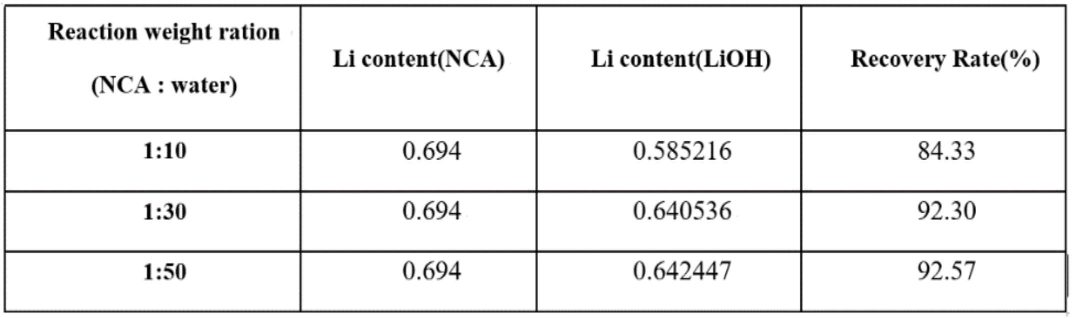


Figure 5. XRD pattern of powder of drying the solution in the water leaching process(leaching time) (left)

Figure 6. XRD pattern of powder of drying the solution in the water leaching process(solid-liquid ratio) (right)

Table 1. Li recovery rate calculation



Reaction weight ration (NCA : water)	Li content(NCA)	Li content(LiOH)	Recovery Rate(%)
1:10	0.694	0.585216	84.33
1:30	0.694	0.640536	92.30
1:50	0.694	0.642447	92.57

CONCLUSION

This research was conducted on the method of recovering LiOH powder and Ni, Co powder through H_2 reduction and water leaching of NCA powder, which is a cathode active material in the spent lithium secondary battery. To increase the recovery rate of LiOH, the optimal conditions of reaction temperature, retention time, leaching time, and solid-liquid ratio for H_2 reduction were determined. After the experiment, the filtered solution was dried; the Li content was measured and the recovery rate was calculated through ICP-OES analysis; and the phase of residue was analyzed through XRD analysis. As suggested by the results of experiment, the optimal process conditions derived for selectively recovering LiOH, Ni, and Co from NCA powder were determined as follows: reaction temperature of 700℃; retention time of 3hrs; H_2 gas flowrate of 300cc/min, and leaching time of 1hr during water leaching; solid-liquid ratio of sample and distilled water at 1:30; and stirring speed of 300 rpm at room temperature for H_2 reduction based on 10g of NCA powder charged. LiOH powder was recovered through filtration and drying, and the lithium recovery rate was calculated to be 92.30%.

Acknowledgment

This research was supported by the BB21plus funded by Busan Metropolitan City and Busan Techno Park and "Regional Innovation Strategy (RIS)" through the National Research Foundation of Korea(NRF) funded by the Ministry of Education(MOE)(2023RIS-007).

REFERENCE

[1] Zhu Huang, et al. “Hydrogen reduction of spent lithium-ion battery cathode material for metal recovery: Mechanism and kinetics.” Frontiers in Chemistry 10:1019493(2022)

[2] Park, H. K., The Research and Development Trend of Cathode Materials in Lithium-Ion Batteries, Journal of the Korean Electrochemical Society, 11(3) (2008) 197-210.

[3] S.Y. Kim, S.H. Choi, E.J. Lee and J.S. Kim, “Synthesis and electrochemical performance of Ni-rich NCM cathode materials for lithium-ion batteries”, J. Electrochem. Soc. 20 (2017) 67.

[4] Li, Li, et al. "Preparation of LiCoO2 films from spent lithium-ion batteries by a combined recycling process." Hydrometallurgy 108.3 (2011): 220-225.

[5] Kang, Jingu, et al. "Recovery of cobalt sulfate from spent lithium ion batteries by reductive leaching and solvent extraction with Cyanex 272." Hydrometallurgy 100.3 (2010): 168-171.

[6] Yang-kook Sun, et al. “A novel cathode material with a concentration-gradient for high-energy and safe lithium-ion batteries.” Advanced Functional Materials, vol. 20(3), pp. 485-491, Feb. 2010

[7] Zeng, X., Li, J., Singh, N., Recycling of Spent Lithium-Ion Battery: A Critical Review, Critical Reviews in Environmental Science and Technology, 44(10) (2014) 1129−1165.

[8] Zhang, Pingwei, et al. "Hydrometallurgical process for recovery of metal values from spent lithium-ion secondary batteries." Hydrometallurgy 47.2 (1998): 259-271.

[9] Moon J. H., Cobalt recovery from spent lithium-ion battery and recycling of active cathode material. Master, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul, Korea, 03722. (2013).

[10] Song, X., Hu, T., Liang, C., et al.), Direct regeneration of cathode materials from spent lithium iron phosphate batteries using a solid phase sintering method, RSC Advances, 7(8) (2017) 4783−4790.

[11] Whittingham, M. S., 2004 : Lithium batteries and cathode materials. Chemical reviews, 104, pp.4271-4302.

[12] Kim, K. J., 2008 : Recovery of lithium hydroxide from spent lithium carbonate using crystallizations. Separation Science and Technology, 43(2), pp.420-430.

[13] Joo, S. Y., Shim, H. W., Choi, J. J., et al., 2020 : A Method of Synthesizing Lithium Hydroxide Nanoparticles Using Lithium Sulfate from

Spent Batteries by 2-Step Precipitation Method, Korean Journal of Metals and Materials, 58, pp.286-291.

DOI: https://doi.org/10.15379/ijmst.v11i1.3549