

RAPID COMMUNICATION

Recycling of LiMO₂ cathode materials by a chlorination-based Li extraction technique

Min Ku Jeon^{*,†}, Sung-Wook Kim^{*}, Hyungsub Kim^{**}, and Kyoung Sun Kim^{***}

^{*}Decommissioning Technology Research Division, Korea Atomic Energy Research Institute, 111, Daedeok-daero 989, Yuseong-gu, Daejeon 34057, Korea

^{**}Neutron Science Division, Korea Atomic Energy Research Institute, 111, Daedeok-daero 989, Yuseong-gu, Daejeon 34057, Korea

^{***}Department of Chemical and Biomolecular Eng., Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Korea

(Received 31 March 2022 • Revised 2 June 2022 • Accepted 13 July 2022)

Abstract—The recycling of Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ (NCM) and LiCoO₂ (LCO), which are cathode materials for Li-ion batteries, was demonstrated via a chlorination-based Li extraction technique. The recycling process follows a chlorination - washing/filtering - drying - mixing - re-synthesis process. Around 86% of Li was removed through the chlorination - washing/filtering steps. The resulting transition metal oxide powder was dried and then mixed with Li₂CO₃, a Li precursor. Re-synthesis experiments were conducted at 900 °C for 24 h and the weight of the final products was 88.5 and 88.0 wt% of their input amounts in NCM and LCO, respectively. Structural changes were analyzed by X-ray diffraction to confirm the absence of impurity phases in the re-synthesized specimens. Electrochemical evaluation revealed that the re-synthesized NCM and LCO exhibit corresponding initial specific capacities of 157 and 153 mAh/g.

Keywords: Cathode Material, Li-ion Battery, Recycle, Chlorination, Re-synthesis

INTRODUCTION

Electric vehicles are at the forefront of transportation innovation with the help of advancements in Li-ion battery (LIB) technology and governmental support for a carbon-neutral society. Naturally, the production of LIBs is increasing rapidly, and it is time to consider the fate of these devices, as the lifespan of LIB cathodes is estimated to be 8-10 years [1,2]. Besides toxicity and the fire risk associated with spent LIBs, cathode materials, especially layered lithium-transition metal oxides, are attractive for recycling due to their high cost, which accounts for approximately 40% of the overall cost of LIBs.

Hydrometallurgical and pyrometallurgical techniques are well-known approaches for the recycling of cathode materials [1-3]. The former utilizes acid solutions to dissolve cathode materials. Each metal is selectively recovered through precipitation (pH control or addition of reactive agents) or solvent extraction. This hydrometallurgical technique benefits from selective recovery of each constituent metal and low operation temperature (<100 °C), while long operation time (~1 week) and requirement for multiple purification steps are major drawbacks. The pyrometallurgical technique operates at a high temperature (>1,000 °C) to achieve a transition metal ingot on the bottom of a reactor. Though this technique offers a simple system, the transition metal ingot requires subsequent steps to separate each transition metal. In addition, it is difficult to recover Li because it is oxidized and vaporized during the high temperature process. A combination of these two techniques is also feasi-

ble as proposed by Umicore [1]; an alloy of valuable metals (Co, Ni, and Cu) is recovered via the pyrometallurgical technique, while oxides of Li, Mn, Fe, and Al are disposed as slag. Each metal of the Co-Ni-Cu alloy is selectively recovered via the hydrometallurgical technique.

Recently, a chlorination-based Li extraction technique for oxide cathode recycling (CHLORE) was introduced as a new way to recycle Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ (NCM) [4], a cathode material widely used in LIBs [5]. The key to this technique is the selective conversion of Li into LiCl, which is highly soluble in water. For NCM, 88.1 wt% of transition metals with a spinel-oxide structure can be recovered after the chlorination, water washing, and filtering/drying steps. Some of the transition metals that were chlorinated could be recovered in a subsequent Na₂CO₃ precipitation step, amounting to 6.8 wt% of the initial amount. Li was recovered in the form of Li₂CO₃ through subsequent drying - dissolution/filtering - drying steps with a recovery ratio of 35.8%. The overall recovery ratio for the transition metals was 94.9 wt%, with the important aspect being that most of the transition metals were recovered after the chlorination step.

In this work, the CHLORE process was employed to recycle NCM and LiCoO₂ (LCO) with some modifications as shown in Fig. 1. As noted above, the CHLORE process still offers an excellent transition metal recovery ratio of 88.1 wt% without the Na₂CO₃ precipitation step. Therefore, in the present study, the transition metals recovered after the chlorination step were directly employed for the re-synthesis, and the steps for recovery of transition-metal chlorides and Li₂CO₃ were eliminated. The chlorination time for NCM was reduced from 4 h in the previous work [4] to 2 h based on the chlorination behavior of NCM [6]. It was found that 86.8% of Li was removed after chlorination under this condition. The other con-

[†]To whom correspondence should be addressed.

E-mail: minku@kaeri.re.kr

Copyright by The Korean Institute of Chemical Engineers.

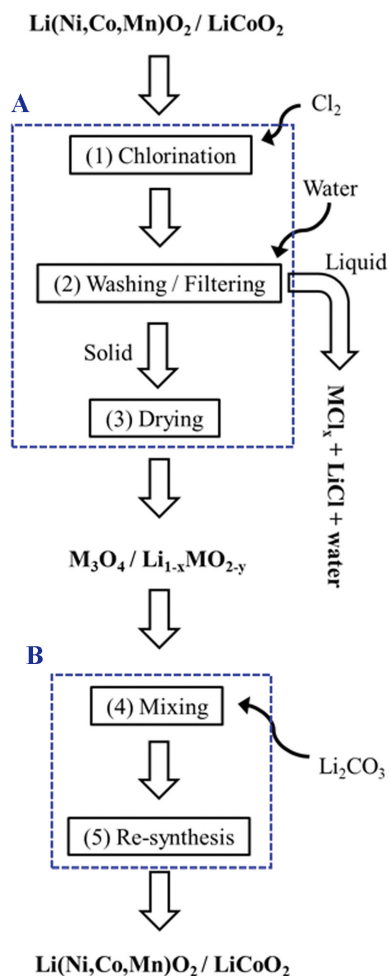


Fig. 1. Process flow diagram of the modified CHLORE process for recycling of NCM and LCO.

ditions of reaction temperature (550°C) and gas flow rate ($180\text{ mL/min Ar}+20\text{ mL/min Cl}_2$) were kept identical in the present work. The chlorination condition of LCO utilized a reaction temperature of 500°C , a gas flow rate of $190\text{ mL/min Ar}+10\text{ mL/min Cl}_2$, and a reaction time of 8 h based on earlier work [7]. A Li removal ratio of 86.3% was reported after chlorination under this condition. In addition, the re-synthesis condition was modified in the present work, because an initial specific capacity of 105 mAh/g previously observed in the re-synthesized NCM [4] was significantly lower than the typical values of 160 mAh/g in NCM [4]. Previously, the mixture of the recovered transition metal and Li_2CO_3 of 20% excess amount was heated at 900°C for 3 h under an air atmosphere [4]. This condition was changed to a stoichiometric amount of Li_2CO_3 and reaction time of 24 h in the present work.

EXPERIMENTAL

In the first set of steps (Process A in Fig. 1), Li was removed to recover transition metal oxides in their spinel-oxide form. The (1) chlorination experiments used a quartz reactor (40 mm diameter) equipped with an electrical furnace to control the chlorination temperature. The inlet of the reactor was connected to a gas supply

system composed of two mass flow controllers (MFCs) to control the Ar (Model 3660, Kofloc co. Ltd., Japan) and Cl_2 (Model 5400) flow rates independently. The outlet of the reactor was connected to a dry scrubber system which utilizes pellet-type gas adsorbents to eliminate unreacted Cl_2 gas in the exhaust gas stream. In each experiment, 2.00 g of NCM or LCO was employed. The pristine NCM and LCO cathode materials were purchased from MSE supplies (USA). For NCM, an initial specific capacity range of $160\text{--}165\text{ mAh/g}$ was guaranteed by the manufacturer in the $4.35\text{--}2.7\text{ V}$ range at a rate of 0.2 C. For LCO, an initial specific capacity of 157 mAh/g was guaranteed by the manufacturer in the $4.0\text{--}3.0\text{ V}$ range at a rate of 0.1 C. Weighed samples were loaded onto an alumina boat and then positioned in the center of the quartz reactor. Before heating the reactor, it was purged using Ar gas at a flow rate of 200 mL/min for at least 2 h to remove the air inside the reactor. When the reactor reached the target temperature, the flow rates of Ar and Cl_2 were set to their target values and then maintained during the reaction. The condition for the chlorination of NCM involved a gas flow of $180\text{ mL/min Ar}+20\text{ mL/min Cl}_2$, a reaction temperature of 550°C , and a reaction time of 2 h. On the other hand, the condition for LCO was a gas flow of $190\text{ mL/min Ar}+10\text{ mL/min Cl}_2$, a reaction temperature of 500°C , and a reaction time of 8 h. After chlorination step (1), the specimens were immersed in 100 mL of deionized (DI) water for at least 12 h to dissolve the LiCl and transition-metal chlorides. The resulting solid-liquid mixture was separated through washing/filtering step (2). During the washing step, 100 mL of additional DI water was used for complete washing. The filtered powder went through a drying step (3), during which the specimens were dried at 120°C for 2 h in an oven.

In process B, the resulting chlorination product, which is a mixture of M_3O_4 and $\text{Li}_{1-x}\text{MO}_{2-y}$, was (4) mixed with a stoichiometric amount of Li precursor, Li_2CO_3 ($\geq 99.0\%$, Sigma-Aldrich), using a rotating mixer for 24 h. Re-synthesis step (5) was done by heat-treating the chlorination product- Li_2CO_3 mixture at 900°C for 24 h in an air atmosphere using a box furnace.

Crystal structural analyses of the re-synthesized specimens were conducted by an X-ray diffraction (XRD) technique using a Bruker D2 Phaser system. The surface morphology of the re-synthesized specimens was analyzed using a scanning electron microscope (SEM, Hitachi SU-8020).

Electrochemical evaluation of the re-synthesized NCM and LCO specimens was conducted by fabricating CR2032 coin cells. To achieve a homogeneous slurry, the re-synthesized specimens were immersed in N-methyl-2-pyrrolidone (NMP, $\geq 99.5\%$, Aldrich) as a solvent along with polyvinylidene fluoride (PVDF, Wellcos) as a binder and conductive carbon (super P) at a weight ratio of 8:1:1 (re-synthesized powder : PVDF : carbon). A cathode electrode was fabricated by casting this slurry onto aluminum foil, followed by drying in a vacuum oven. This cathode was employed to fabricate a CR2032 coin cell along with a Li anode and 1 M lithium hexafluorophosphate (LiPF_6) in ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1 v/v PanaXEttec) as the electrolyte and a fiber membrane separator (grade GF/E, Whatman). Evaluations of the coin cells were conducted in CCCV (constant current-constant voltage) mode at a constant current of 20 mA/g in a voltage range of $2.5\text{--}4.3\text{ V}$. Once the voltage reached 4.3 V during charging, it was main-

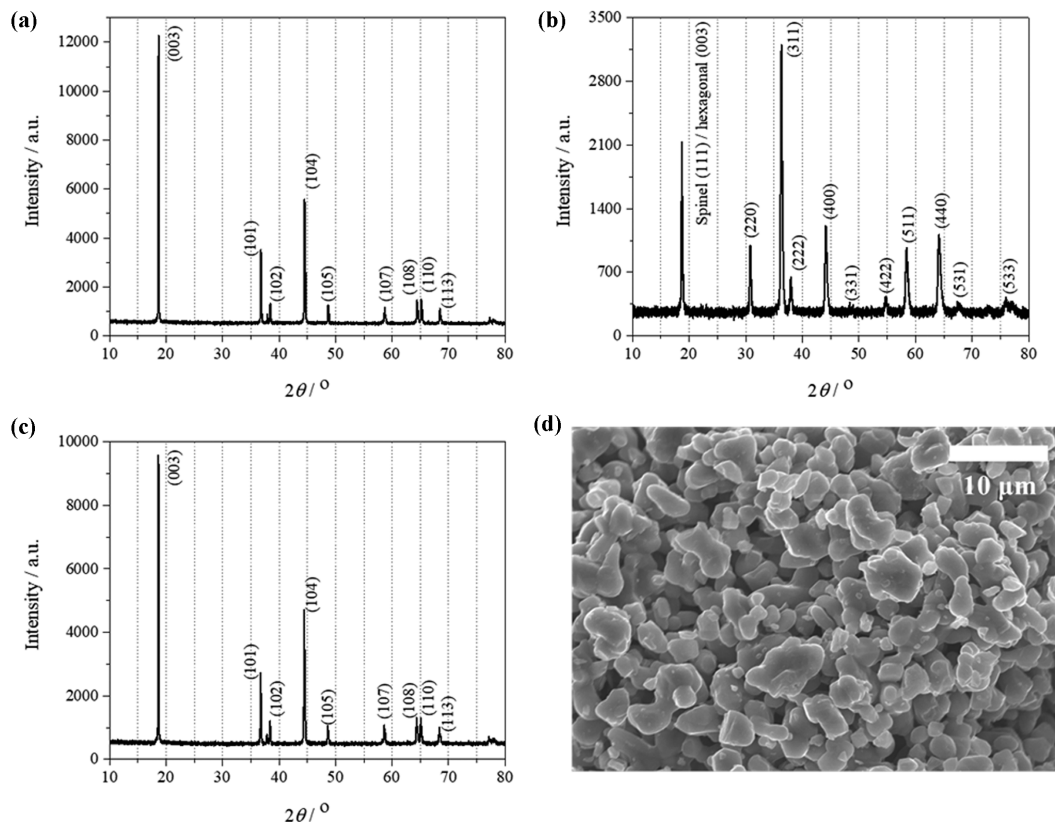


Fig. 2. XRD patterns of (a) pristine NCM (hexagonal structure), (b) NCM after chlorination-washing/filtering-drying (mainly spinel and minor hexagonal structures), and (c) re-synthesized NCM (hexagonal structure). (d) A SEM image of the re-synthesized NCM.

tained at this level for 20 min.

RESULTS AND DISCUSSION

1. Re-synthesis and Electrochemical Evaluation of NCM

Fig. 2 shows XRD patterns of the pristine NCM, NCM after process A, and NCM after process B, which is the final re-synthesis product. Comparing the patterns in Figs. 2(a) and (b), it is clear that the layered hexagonal structure was changed to the spinel-type M_3O_4 phase after chlorination. However, the relatively high intensity of the peak at 18.7° indicates that the layered hexagonal phase remained, as noted in the figure. This finding is in agreement with previous work [6] in which the crystal structural changes of NCM after chlorination under various conditions were investigated. At 550°C , an increase in the chlorination time resulted in an increase in the proportion of the M_3O_4 phase. Though the Li removal ratio increased with an increase in the reaction time, Li was not completely removed after 8 h of chlorination; a Li removal ratio of 95.5% was observed [6]. After 2 h of chlorination, identical to the experimental condition of the present work, a Li removal ratio of 86.8% was reported [6]. The re-synthesized NCM, shown in Fig. 2(c), exhibited an XRD pattern identical to that of the pristine NCM, meaning that the re-synthesis was conducted successfully. The lattice parameters were $a=2.865$ and $c=14.258$ Å in the re-synthesized NCM, which are close to the corresponding values of $a=2.861$ and $c=14.243$ Å in the pristine NCM. The weight of the final re-synthesis product

was 1.77 g, which is 88.5 wt% of the input amount. Chlorination of the transition metals accounts for the loss observed in the re-synthesized NCM. The SEM image of the re-synthesized NCM shown in Fig. 2(d) indicates that plate shaped particles with diameters of 4-6 μm were mixed with smaller spherical particles with a diameter of 1-2 μm .

Electrochemical evaluation results are shown in Fig. 3 for the pristine and re-synthesized NCM specimens. The pristine NCM exhibits a specific capacity of 171 mAh/g in the first charge-discharge cycle, which was reduced to 168 mAh/g after repeating the charge-discharge cycles 20 times. A specific capacity of 157 mAh/g is observed in the first charge-discharge cycle of the re-synthesized NCM. It decreased to 142 mAh/g after repeating the charge-discharge cycles 20 times. Though the specific capacity values of the re-synthesized NCM are slightly lower than that of the pristine NCM, it still exhibits reasonable electrochemical performance [5]. Recalling the Li removal ratio of 86.8%, there are two possible explanations of the electrochemical performance of the re-synthesized NCM. First, the hexagonal structure that remained after chlorination does not function, while the re-synthesized NCM originating from the spinel structure functions properly. Second, the hexagonal structure functions properly, while the capacity of the re-synthesized NCM originating from the spinel structure is relatively low. Though the actual reason remains unclear, it is obvious that the modified CHLORE process is a promising approach for NCM recycling. In addition, the relatively low capacity of 105 mAh/g observed in our previous

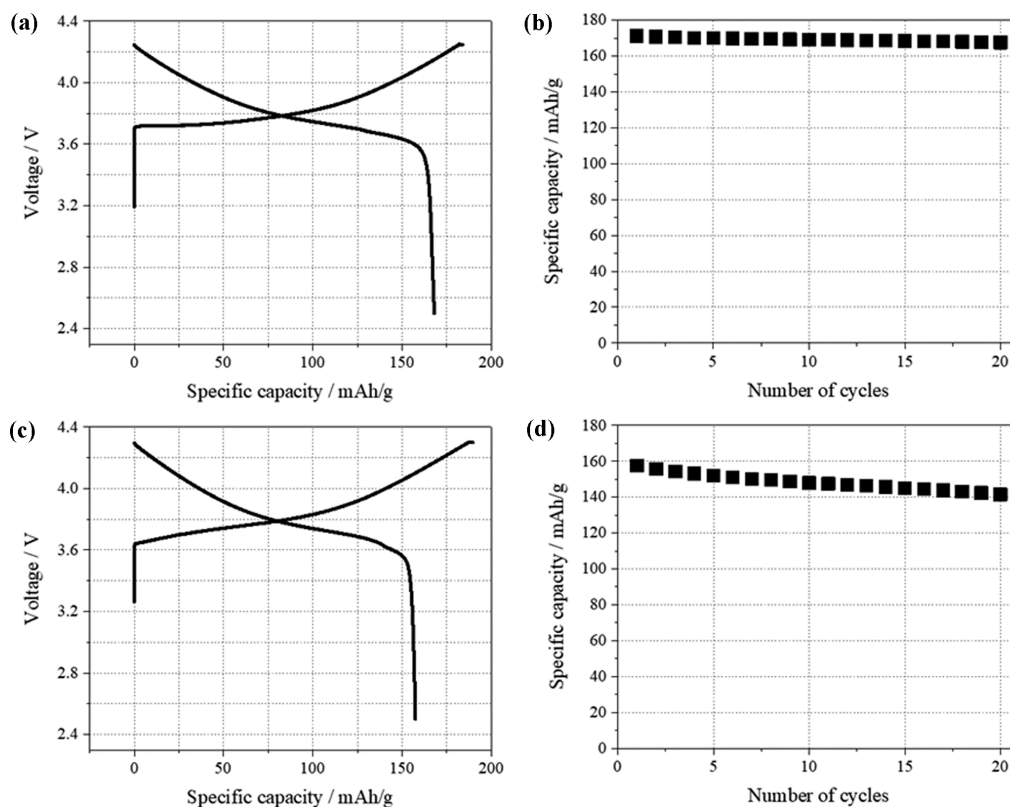


Fig. 3. Charge-discharge test results of CR2032 coin cells fabricated using (a) pristine and (c) re-synthesized NCM in the cathode. Cycling performance of the (b) pristine and (d) re-synthesized NCM measured for 20 cycles at a current rate of 20 mA/g.

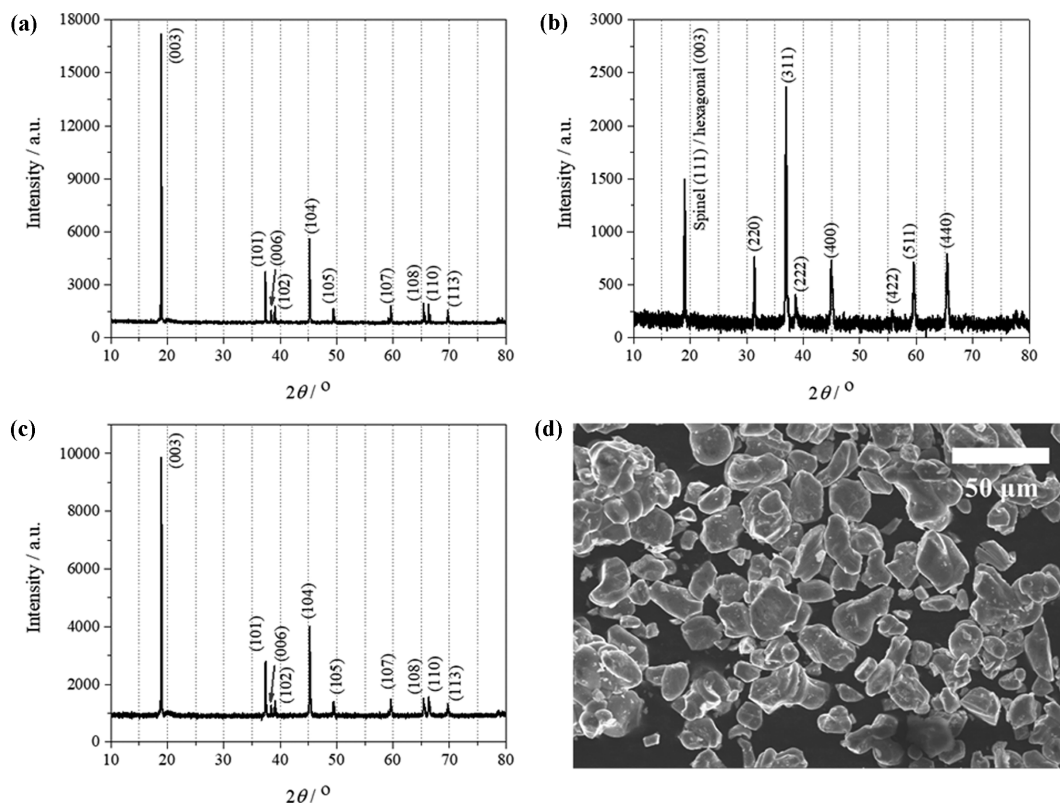


Fig. 4. XRD patterns of (a) pristine LCO (hexagonal structure), (b) LCO after chlorination-washing/filtering-drying (mainly spinel and minor hexagonal structures), and (c) re-synthesized LCO (hexagonal structure). (d) A SEM image of re-synthesized LCO.

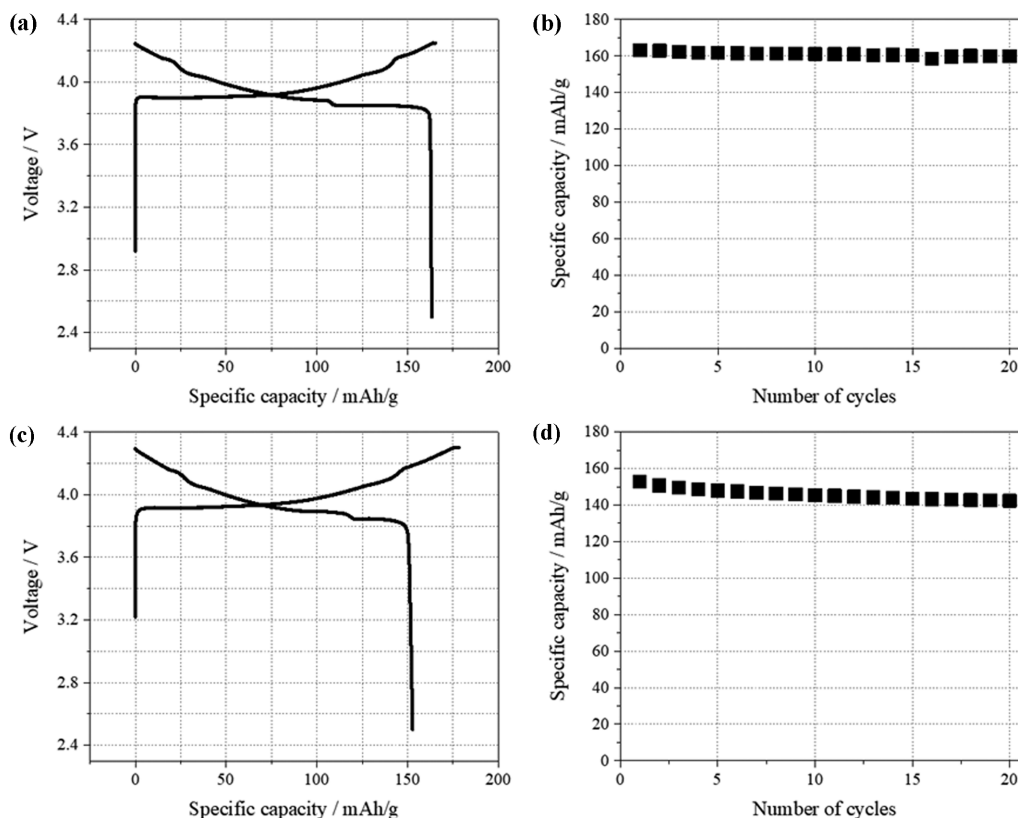


Fig. 5. Charge-discharge test results of CR2032 coin cells fabricated using (a) pristine and (c) re-synthesized LCO in the cathode. Cycling performance of the (b) pristine and (d) re-synthesized LCO measured for 20 cycles at a current rate of 20 mA/g.

work [4] was obviously due to an un-optimized re-synthesis condition, such as an excess amount of Li precursor and a short heating time.

2. Re-synthesis and Electrochemical Evaluation of LCO

XRD patterns of the LCO specimens are shown in Fig. 4. The structural transition from the hexagonal structure in the pristine LCO to the spinel-type Co_3O_4 structure after chlorination is clearly shown in the figure. However, the relatively high intensity at 19.04° indicates the presence of a layered hexagonal phase after chlorination, as in the NCM case. A Li removal ratio of 86.3% was reported after chlorination under a condition identical to that in this work [7]. In the XRD pattern of the re-synthesized LCO, no signs of the spinel structure were found, resulting in a pattern identical to that of the pristine LCO. The lattice parameters calculated using the XRD patterns were $a=2.817$ and $c=14.046$ Å in the re-synthesized LCO, which are close to those of $a=2.817$ and $c=14.061$ Å in the pristine LCO. This result confirms that the re-synthesis was conducted successfully without noticeable impurity phases. The amount of the final re-synthesis product was 1.76 g, which is 88.0 wt% of the initial weight. This loss of Co is explained by the chlorination of Co_3O_4 , which was observed at a temperature above 300°C [8]. A SEM image of the re-synthesized LCO is shown in Fig. 4(d), where plate shaped particles with diameters of 10-30 μm can be observed. Recalling that the particle size of the re-synthesized NCM is in the range of 4-6 μm , the particle size of the re-synthesized LCO is remarkably larger than that of NCM.

The electrochemical characteristics of the LCO specimens were

evaluated through repeated charge-discharge cycling, as shown in Fig. 5. An initial specific capacity of 163 mAh/g was observed in the first charge-discharge cycle of the pristine LCO. The capacity was slightly reduced to 160 mAh/g by the 20th charge-discharge cycle. The re-synthesized LCO exhibited an initial specific capacity of 153 mAh/g in the first charge-discharge cycle, which decreased to 142 mAh/g by the 20th cycle. Though the specific capacity values of the re-synthesized LCO are relatively low compared to those of the pristine LCO, they are acceptable [5]. This outcome proves that the modified CHLORE process is feasible for LCO recycling. In consideration of simple process and high recovery ratio of transition metals, the economic feasibility of this process means it can compete with other recycling techniques [1-3].

Though it was clarified that the modified CHLORE process is a promising route for the recycling of cathode materials, there are many possible future exploration paths. The XRD and electrochemical measurement results suggest that the incomplete removal of Li during chlorination does not negatively affect the re-synthesized NCM and LCO, presumably because the Li remaining after chlorination is present in the layered hexagonal structure, which functions properly after the re-synthesis step. An approach to recycle NCM or LCO after removing less Li may clarify the effect of the incomplete removal of Li. In addition, optimizing the re-synthesis process, such as the reaction route, type and amount of Li precursor, the reaction temperature, and the reaction time, may improve the electrochemical performance of re-synthesized cathode materials. The chlorination behavior of degraded cathode materials is also

an issue to be addressed prior to commercialization of the CHLORE process, as there are various Li-O bonds in degraded cathode materials [9] resulting in various chlorination mechanisms.

CONCLUSIONS

The recycling of NCM and LCO via the modified CHLORE process was demonstrated successfully. An amount equivalent to 88.5 wt% of the NCM input was recovered as the final re-synthesis product. The re-synthesized NCM exhibited an initial specific capacity of 157 mAh/g, which is close to that of 171 mAh/g in the pristine NCM. The weight of the final re-synthesis product was 88.0 wt% of the LCO input. The re-synthesized LCO showed an initial specific capacity of 153 mAh/g, slightly lower than that of 163 mAh/g in the pristine LCO. The outcome of this work proves that the proposed CHLORE process is a promising route to recycle lithium metal oxide cathode materials due to its high recovery ratio and simple process.

ACKNOWLEDGEMENTS

This work was supported by the National Research Foundation

of Korea (NRF) grant funded by the Korea Government (MSIT) (NRF-2021R1F1A1056492).

REFERENCES

1. T. Or, S. W. D. Gourley, K. Kaliyappan, A. Yu and Z. Chen, *Carbon Energy*, **2**, 6 (2020).
2. G. Harper, R. Sommerville, E. Kendrick, L. Driscoll, P. Slater, R. Stolkin, A. Walton, P. Christensen, O. Heidrich, S. Lambert, A. Abbott, K. Ryder, L. Gaines and P. Anderson, *Nature*, **575**, 75 (2019).
3. H. Bae and Y. Kim, *Mater. Adv.*, **2**, 3234 (2021).
4. M. K. Jeon, S.-W. Kim, H.-C. Eun, K.-Y. Lee, H. Kim and M. Oh, *Korean J. Chem. Eng.*, **39**, 1472 (2022).
5. N. Nitta, F. Wu, J. T. Lee and G. Yushin, *Mater. Today*, **18**, 252 (2015).
6. M. K. Jeon, S.-W. Kim, M. Oh, H.-C. Eun and K. Lee, *Korean J. Chem. Eng.*, In press (2022), <https://doi.org/10.1007/s11814-022-1166-4>.
7. M. K. Jeon and S.-W. Kim, *Korean J. Chem. Eng.*, **39**, 2109 (2022).
8. T. A. Anufrieva and L. E. Derlyukova, *Russ. J. Inorg. Chem.*, **52**, 1840 (2007).
9. H. Wang, Y.-I. Jang, B. Huang, D. R. Sadoway and Y.-M. Chiang, *J. Electrochem. Soc.*, **146**, 473 (1999).