

Recycling of Li(Ni,Co,Mn)O₂ via a chlorination technique

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Abstract—A new approach to recycle Li(Ni,Co,Mn)O₂ (NCM, Ni:Co:Mn=1:1:1) is introduced and experimentally demonstrated. Chlorine gas was employed as a reaction agent to selectively extract Li from NCM. Through a reaction at 550 °C for 4 h under a 180 mL/min Ar+20 mL/min Cl₂ flow, Li was converted into water-soluble LiCl, while the initial transition metals (Ni, Co, and Mn) were converted into a spinel-type oxide phase. Minor amount of transition metals, which reacted with Cl₂ to produce transition-metal chlorides, were recovered in the subsequent precipitation step. An amount of 94.9 wt% of transition-metal recovery ratio was achieved through the recovery processes. The amount of Li recovered as Li₂CO₃ was 35.8 wt% of the initial amount. A new NCM was successfully re-synthesized using the recovered materials as well as additional Li₂CO₃, resulting in a layered NCM structure. The re-synthesized NCM was electrochemically evaluated by fabricating a CR2032 coin cell which exhibited a capacity of 105 mAh/g.

Keywords: Li-ion Battery, Recycle, Cathode Material, Chlorination, Transition-metal Recovery

INTRODUCTION

Sales of lithium-ion batteries (LIBs) are rapidly growing owing to global efforts to replace traditional combustion engine vehicles with electric vehicles (EVs), which run on LIBs instead of fossil fuels. It has been reported that EV registrations increased by 41% in 2020, while global car sales decreased by 16% due to the pandemic situation [1]. The lifetime of a LIB installed in an EV is estimated to be ten years due to the gradual decrease in performance given the repeated charge/discharge cycling. Used LIBs can be utilized in other applications, such as energy storage systems, as they still maintain around 70-80% of their initial capacity. However, at some point, all LIBs should be disposed of. Considering the skyrocketing growth of the LIB market, considerable amounts of LIB waste will accumulate in the near future. As LIBs contain valuable metals such as Li, Co, Ni, and Mn, recycling these devices can contribute to reducing the burden of disposal and increasing the economic benefits related to the materials.

The recycling of LIBs has mainly focused on cathode materials owing to the economic importance of these materials in comparison with the anode material, which is normally carbon. Previous approaches for the recycling of cathode materials can be categorized into pyrometallurgical and wet methods [2-4]. The former

utilizes oxygen as a reacting agent at a high temperature (>1,000 °C) to separate transition metals in mixed ingot form at the bottom of a reactor while other metals react with oxygen to float on the top of the reactor. This method has the disadvantage of Li loss via evaporation and the consequent separation of transition-metal alloys. The latter, on the other hand, utilizes strong acid solutions to dissolve the cathode materials, with each metal recovered by controlling the pH or adding precipitation agents. The wet method is more widely accepted owing to its low energy consumption and the individual recovery of constituent metals.

In this work, we propose a novel approach to re-synthesize Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ (NCM), a widely employed high-energy LIB cathode material. This approach uses chlorine gas to extract Li selectively from NCM. It was previously demonstrated that chlorine gas selectively reacts with Li in Li₂ZrO₃, resulting in LiCl and ZrO₂ as reaction products in the temperature range of 450-600 °C [5]. Selective chlorination was also demonstrated in a mixture of various oxides, where selective chlorination of SrO in concrete waste was proposed as a route to decontaminate radioactive waste generated during decommissioning of nuclear power plants [6]. In addition, the chlorination technique was applied for selective recovery of Zr from cladding hulls of used nuclear fuels, which is a mixture of a Zr-based alloy and various nuclear fuel oxides mainly consisting of U₃O₈ or UO₂ [7-9]. Zirconium readily reacts with Cl₂ at 300-400 °C to produce volatile ZrCl₄ while nuclear fuel oxides remain as their oxide forms. The selectivity of chlorine gas was brought to this work in order to utilize the different chlorination characteristics between

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Li and transition metals. Therefore, this work is focused on a demonstration of the entire process to identify its feasibility as a recycling technique for NCM.

EXPERIMENTAL

The experiments here were conducted following the process diagram described in Fig. 1. In each experiment, 2.00 g of NCM powder (Ni:Co:Mn=1:1:1, purchased from MSE Supplies (USA)) was employed. The entire process was categorized into four sections: A. Recovery of transition-metal oxides, B. Recovery of transition-metal chlorides, C. Recovery of Li₂CO₃, and D. Re-synthesis of NCM.

Section A (Recovery of transition-metal oxides) is composed of three processes: (1) chlorination reaction, (2) washing/filtering, and (3) drying. During the (1) chlorination reaction process, a quartz tube with a diameter of 4 cm was employed as a chlorination reactor, which was equipped with an electrical furnace in the middle for proper control of the reaction temperature. The reaction atmosphere was controlled by controlling the flow rate of each reaction gas (Ar and Cl₂) using mass flow controllers (MFCs, Model 3660 for Ar and Model 5400 for Cl₂, Kofloc Co., Ltd, Japan). After weigh-

ing out 2.00 g of NCM, it was placed in an alumina boat, which was then placed in the middle of the quartz reactor. The electrical furnace began to heat the reactor to 550 °C after the reactor was purged with Ar gas for at least 2 h. When the reactor reached to 550 °C, the flow rates of Ar and Cl₂ were set to 180 mL/min and 20 mL/min, respectively, for 4 h. The flow of Cl₂ was stopped after the reaction was complete and the reactor was then cooled to room temperature within 1 h. After the (1) chlorination reaction, the NCM samples were immersed in 120 mL of deionized (DI) water overnight and then filtered to separate the solid and solution phases through the (2) washing/filtering process. An additional 100 mL of DI water was used for complete washing. The filtered powder was sent to the (3) drying process, where the sample was dried in an oven at 120 °C for 2 h to achieve transition-metal oxides.

Section B (Recovery of transition-metal chlorides) consists of (4) precipitation/filtering and (5) drying processes. In the (4) precipitation/filtering step, Na₂CO₃ was employed as a precipitation agent with an excess of 10% based on a stoichiometric amount equivalent to LiCl. The filtered powder, which is a transition-metal precipitate, was sent to the (5) drying process, where it was put in an oven at 120 °C for 2 h.

Section C (Recovery of Li₂CO₃) is composed of (6) drying, (7) dissolution/filtering, and (8) drying processes. The liquid-phase product of process (4) was transported to the (6) drying process, where the sample was dried at 120 °C for 16 h. During the (7) dissolution/filtering process, a stoichiometric amount of water to dissolve NaCl was added to the powder product of (6), followed by filtering. The solid product recovered in (7) was sent to the (8) drying process, where the sample was dried in an oven at 120 °C for 2 h. Process (7) was repeated twice to remove NaCl completely.

Section D (Re-synthesis of NCM) consists of (9) mixing and (10) re-synthesis processes. In the (9) mixing process, the metal components recovered in Sections A and B were mixed with the Li₂CO₃ recovered in Section C along with additional Li₂CO₃ incorporated to compensate for losses from the recovery processes and from evaporation during the high-temperature synthesis. The final amount of excess Li was set to 20%. The (10) re-synthesis process was conducted by heating the mixture at 900 °C for 3 h under an air atmosphere.

Intermediate and final products were analyzed using X-ray diffraction (XRD, Bruker D2 Phaser) and inductively coupled plasma-atomic emission spectrometry (ICP-AES, Thermo Scientific iCAP 7400 duo) techniques to analyze of structural changes and compositions, respectively.

An electrochemical evaluation of the re-synthesized NCM sample was conducted by fabricating CR2032 coin cells. The re-synthesized NCM powder was put into NMP (n-methyl-2-pyrrolidone) as a solvent along with PVDF (Polyvinylidene fluoride) as a binder with conductive carbon (super P) at a weight ratio of 8:1:1 (NCM:PVDF:carbon) to obtain a homogeneous slurry. This slurry was cast on an aluminum foil and then dried in a vacuum oven to fabricate a cathode electrode. A CR2032 coin cell was assembled using the fabricated cathode, a Li anode, 1 M LiPF₆ in EC/DMC (ethylene carbonate/dimethyl carbonate) as an electrolyte, with a fiber membrane as a separator. The coin cell was evaluated in CCCV (constant current-constant voltage) mode with a constant current

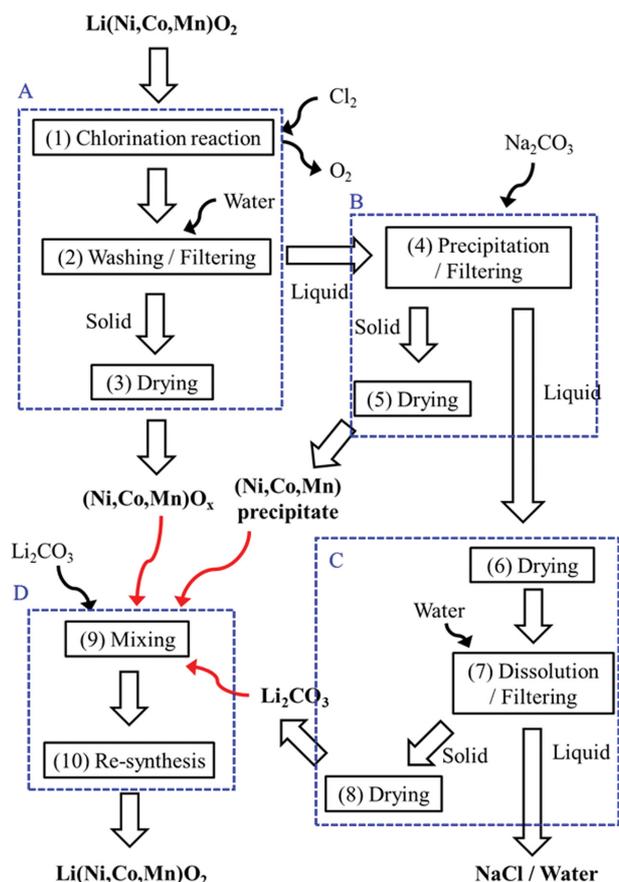


Fig. 1. Flow diagram of the chlorination process for the recycling of NCM, a process composed of four sections. Section A: recovery of transition-metal oxides, Section B: recovery of transition-metal chlorides, Section C: recovery of Li₂CO₃, and Section D: re-synthesis of NCM.

of 20 mA/g in a voltage range of 2.5–4.3 V. Once the voltage reached 4.3 V during charging, it was maintained at this level for 20 min.

RESULTS AND DISCUSSION

1. Section A. Recovery of Transition-metal Oxides

The key technique in this process is the selective extraction of Li via a (1) chlorination reaction process. Here, Li is converted

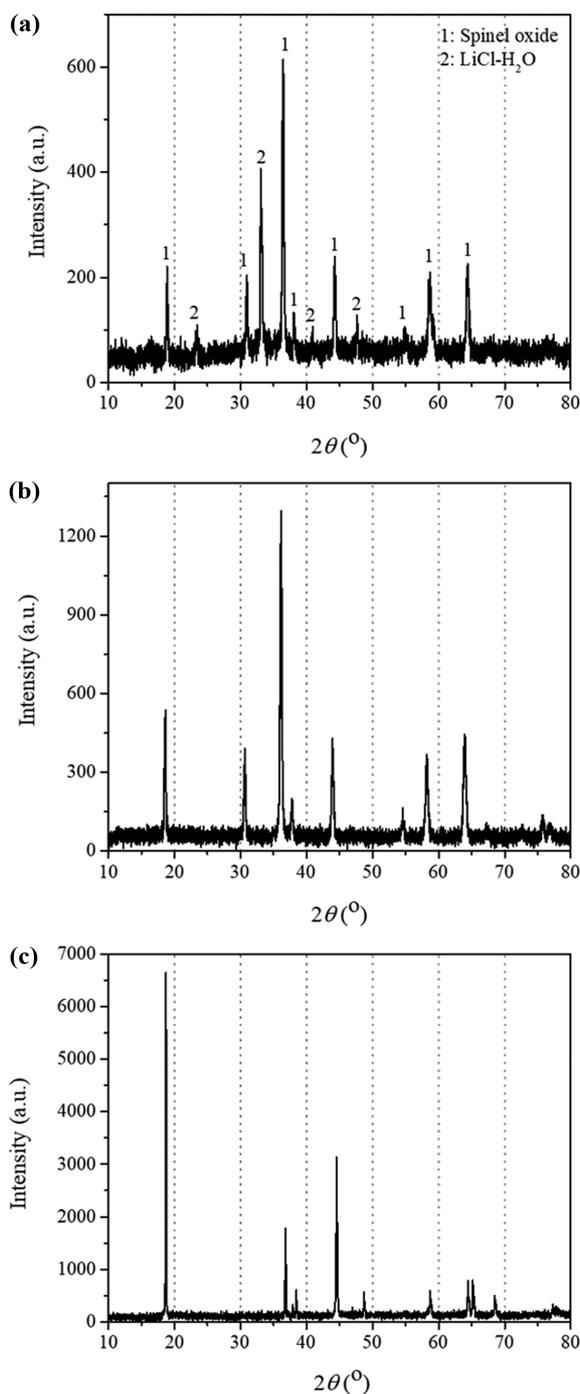


Fig. 2. XRD measurement results of NCM after (a) the (1) chlorination reaction process and (b) the (3) drying process. (c) XRD measurement result of pristine NCM.

into water-soluble LiCl while transition metals remain in their oxide forms, insoluble in water. The feasibility of the (1) chlorination reaction was investigated by reacting NCM at 550 °C for 4 h under a 180 mL/min Ar+20 mL/min Cl₂ flow. Fig. 2(a) shows the XRD measurement results, where a spinel-type oxide phase was identified along with the LiCl-H₂O phase. This LiCl-H₂O phase, which was produced as a result of handling the sample in air owing to the hygroscopic nature of LiCl, disappeared after the (2) washing/filtering and (3) drying processes, as shown in Fig. 2(b). The washing process was an easy step owing to the high solubility of LiCl, 84.5 g/100 g H₂O [10]. Compared to the XRD measurement results of pristine NCM samples before the chlorination reaction (Fig. 2(c)), it is obvious that the layered NCM phase was completely converted to the spinel-type oxide phase after the chlorination reaction. The ICP-AES measurement result revealed that 88.9% of Li was removed through the chlorination reaction and washing processes. This result suggests that chlorine gas can be an effective reagent for the selective extraction of Li from NCM. However, based on the ICP-AES analysis, 88.1 wt% of the transition metals initially present in the starting material was recovered as a spinel-type oxide. This result suggests that the transition metals partially reacted with chlorine gas to be converted into their chloride forms, which are volatile and soluble in water [11–14].

2. Section B. Recovery of Transition-metal Chlorides

The transition-metal chlorides in the liquid phase could be recovered via the (4) precipitation/filtering step by adding Na₂CO₃ as a precipitation agent, as shown in Fig. 3(a). Here, Na₂CO₃ converts LiCl dissolved in the solution into Li₂CO₃ as well, while it does not precipitate owing to its relatively high solubility of 1.30 g/100 g H₂O at 25 °C [10]. Therefore, to react with both the transition-metal chlorides and LiCl, the amount of Na₂CO₃ employed in (4) was

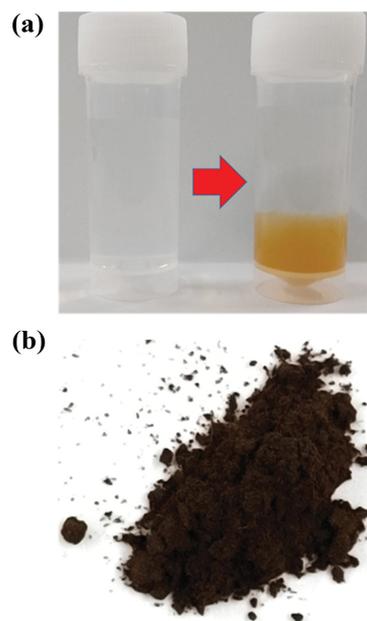


Fig. 3. (a) Photographs of the liquid phase after the (2) washing/filtering process (left) and after the addition of Na₂CO₃ into the liquid phase (right). (b) Photograph of the recovered transition-metal precipitate after the (5) drying process.

set to 110% of the stoichiometric amount required to convert all LiCl into Li₂CO₃. The precipitated powder was recovered by filtering and then sent to the (5) drying process to achieve dried transition-metal precipitates, as shown in Fig. 3(b). The ICP-AES result confirmed that 6.8 wt% of the initial amount of the transition metals was recovered through Section B. This result emphasizes that the chlorination technique can be economical owing to high transition-metal recovery ratio of 94.9 wt% through the entire process.

3. Section C. Recovery of Li₂CO₃

The liquid product of (4), which contains Li₂CO₃ and NaCl as well as excess Na₂CO₃, is transported to the (6) drying process to remove water. The XRD measurement result and a photograph of the dried powder are shown in Fig. 4(a), where Li₂CO₃ and NaCl

were identified. Based on the weight of the sample, calculations demonstrated that 63.8 wt% of the initial Li was recovered from the liquid phase. Recalling that 88.9 wt% of Li was removed after the (1) chlorination reaction process, it is estimated that 25.1 wt% (=88.9-63.8 wt%) of Li was lost during the chlorination process owing to the evaporation of LiCl. In the (7) dissolution/filtering process, the stoichiometric amount of water required to dissolve NaCl was added to the Li₂CO₃-NaCl mixture with the goal of the selective dissolution of NaCl. This approach is based on solubility gap between Li₂CO₃ and NaCl, which are 1.30 and 36.0 g/100 g H₂O at 25 °C, respectively [10]. Here, the solubility of Na₂CO₃ is 30.7 g/100 g H₂O at 25 °C, which is close to that of NaCl. To obtain high-purity Li₂CO₃, process (7) was repeated twice and the sample

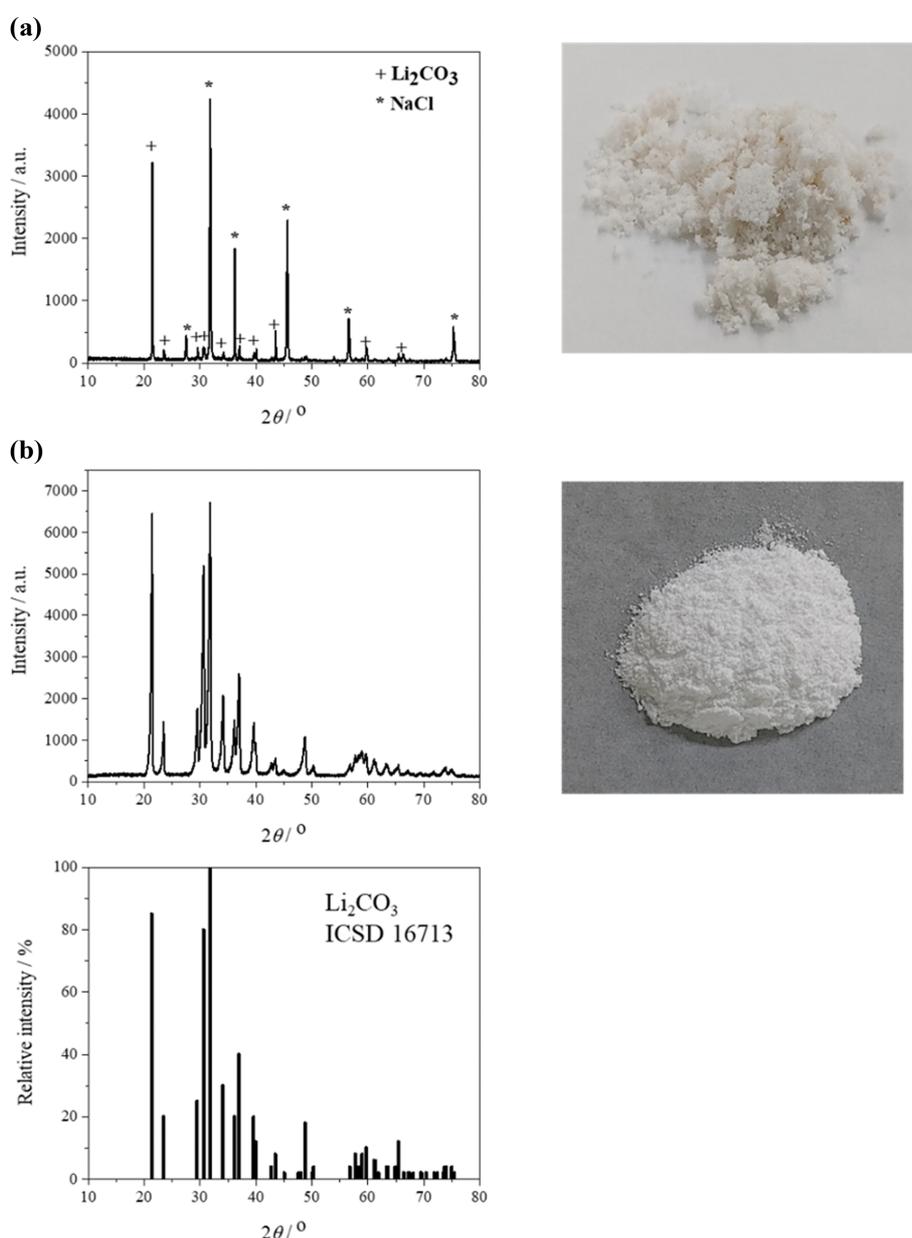


Fig. 4. XRD measurement result and photograph of Li₂CO₃ obtained after (a) the (6) drying process and (b) the (8) drying process. The XRD peak pattern of the Li₂CO₃ reference (ICSD ID 16713) is also shown below.

was then sent to the (8) drying process. The XRD measurement result and a photograph of the Li_2CO_3 are shown in Fig. 4(b), where no signs of NaCl could be found. A reference XRD pattern of Li_2CO_3 from ICSD 16713 is also shown below in Fig. 4(b) for comparison. The ICP-AES result confirmed that the ratio of Na in the final product was lower than 1 wt% (metal ratio). The final amount of Li recovered as Li_2CO_3 was 35.8% of the initial amount. These results suggest that the Li recovery process needs improvement to minimize the loss of Li during the (1) chlorination reaction and (7) dissolution/filtering processes. For example, Li loss levels can be reduced during the (1) chlorination reaction by lowering the reaction temperature, optimizing the gas flow rate, or installing a condenser at the outlet of the reactor to solidify and recover the evaporated LiCl. Optimization of the (7) dissolution process, including the amount of water per turn and the number of turns, as well as the application of other solvents such as methanol can be solutions to improve the recovery ratio of Li_2CO_3 .

4. Section D. Re-synthesis of NCM

During the (8) mixing process, $(\text{Ni,Co,Mn})\text{O}_x$ from process (3), $(\text{Ni,Co,Mn})\text{CO}_3$ from process (5), and Li_2CO_3 from process (7) were mixed with additional Li_2CO_3 to compensate for the loss of Li during processes (7) and (9). In the final step, NCM was re-synthesized by heating the mixture. The XRD measurement result of the re-synthesized product is shown in Fig. 5(a), where layered NCM peaks are clearly identified without any other by-products. Compared to the XRD measurement result of the pristine NCM shown in Fig. 2(c), no signs of any noticeable difference could be found. According to the XRD measurement results, the hexagonal lattice parameters were changed from $a=2.863 \text{ \AA}$ and $c=14.217 \text{ \AA}$ in the pristine NCM to $a=2.847 \text{ \AA}$ and $c=14.164 \text{ \AA}$ in the re-synthesized NCM. The metal ratio of re-synthesized NCM calculated using the ICP-AES results was $(\text{Li}:\text{Ni}:\text{Co}:\text{Mn})=(1.11:0.32:0.34:0.34)$, which was similar to $(1.12:0.33:0.33:0.34)$ in the pristine NCM. The charge-discharge test result of the coin cell is shown in Fig. 5(b), where stable operation was observed at 105 mAh/g. In cycling performance test, shown in Fig. 5(c), 86.4% of the initial capacity was maintained after repeating 100 cycles. The capacity value of the re-synthesized NCM is somewhat lower than the typical values of around 160 mAh/g [4]. There can be several reasons for this low capacity in the re-synthesized NCM such as incomplete removal of Li, inhomogeneity of transition metals in atomic scale, and unoptimized synthesis condition. As a preliminary report, this work does not contain optimized conditions for the chlorination, separation, and synthesis processes. Optimization of the process conditions is under way in order to achieve high capacity in the re-synthesized and will be reported in the near future. Nonetheless, the findings of this work are sufficient to prove that the re-synthesis of NCM via the chlorination technique is a feasible option. This technique offers a relatively simple process with a high transition-metal recovery ratio of 94.9 wt%, important as transition metals are the most valuable assets in used LIBs.

The results of this work propose another route for the separate recovery of the constituent metals of NCM. As discussed above, it was estimated that 25 wt% of Li and 5.1 wt% of transition metals are lost via evaporation during the chlorination reaction process. Thus, it would be possible to convert and vaporize the constituent

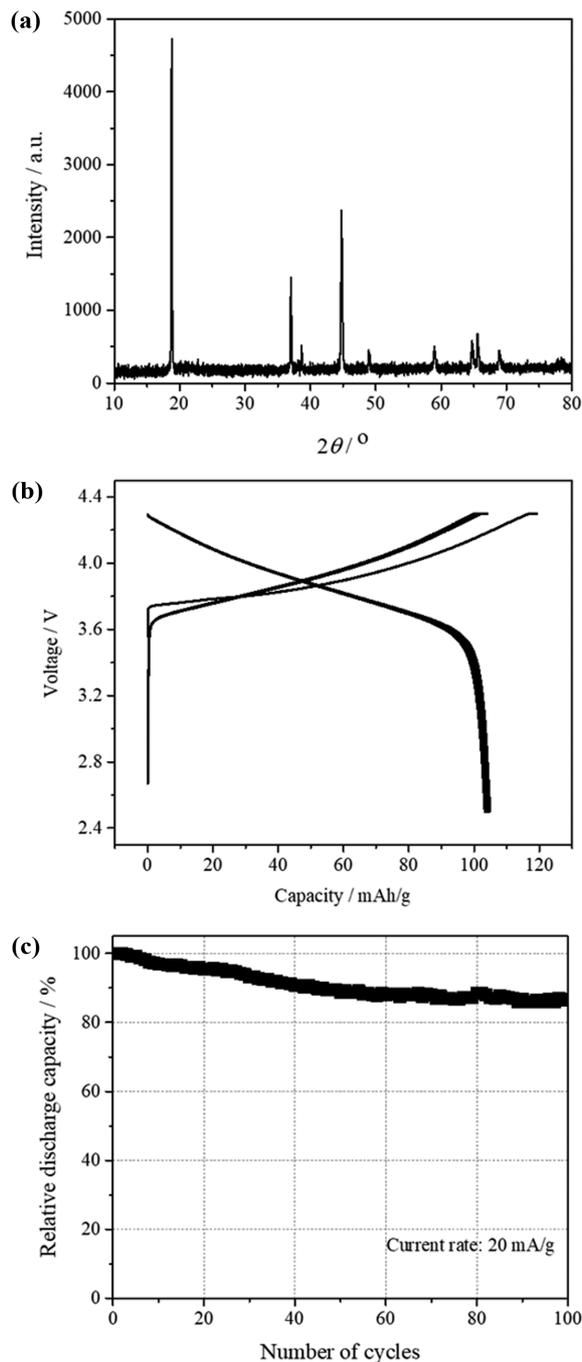


Fig. 5. (a) XRD measurement results of re-synthesized NCM. (b) Charge-discharge test result of a CR2032 coin cell fabricated using re-synthesized NCM in the cathode. (c) Cycling performance of the re-synthesized NCM measured for 100 cycles at a current rate of 20 mA/g.

atoms selectively by controlling the chlorination reaction conditions to recover each element in its chloride form by installing a condensing system in conjunction with the chlorination reactor.

CONCLUSIONS

The entire process of the chlorination technique was success-

fully demonstrated to recycle NCM. Despite the relatively simple process, 94.9 wt% of transition metals was recovered and utilized for the re-synthesis of NCM, operating stably at 105 mAh/g in a coin cell test. However, the low recovery ratio of Li, 35.8 wt%, remains an issue to be resolved before feasible commercial application of this process. Optimizing the chlorination reaction conditions and the Li₂CO₃/NaCl separation process may bring about a higher Li recovery ratio and strengthen the economic aspects of the chlorination technique for the recycling of NCM.

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