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Carbothermic Reduction Roasting of Cathode Active Materials Using Activated Carbon and Graphite to Enhance the Sulfuric-Acid-Leaching Efficiency of Nickel and Cobalt

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Abstract: Carbothermic reduction-roasting tests of NCM (nickel, cobalt, and manganese) cathode active materials with carbon sources such as activated carbon and graphite followed by sulfuric acid leaching were performed to investigate the effects of roasting temperature, molar mixing ratio of cathode active materials and carbon sources, and type of cathode active materials. When the virgin NCM622 materials were roasted with activated carbon, the peaks of Ni and Co metals were observed in the XRD data. The leaching efficiencies of Li, Ni, Co, and Mn increased to over 99.9% within 120 min in all samples roasted at 600 °C–900 °C, but, at the beginning of leaching, the leaching efficiencies increased more slowly with increasing roasting temperature. The leaching efficiencies of Ni and Co decreased with decreasing the molar mixing ratio of active cathode materials and carbon sources, but the leaching efficiencies were more than 99.9% in all ratios. These results indicate that roasting can enhance the leaching of cathode active materials and improve the conventional leaching process using hydrogen peroxide.

Keywords: lithium ion battery; recycling; carbothermic reduction; activated carbon; graphite



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1. Introduction

The Korean government announced in October 2020 that it would achieve carbon neutrality by 2050, and that recycling is a key factor for the goal [1]. Since electric vehicles are also an important way toward carbon neutrality, there has been increasing demand for lithium ion batteries (LIB) [2–4]. In 2021, the EU announced a new EU regulatory framework, which includes a recycled-content declaration requirement [5]. This regulation would apply to industrial batteries, EV batteries, and automotive batteries containing cobalt, lead, lithium, or nickel in active materials. Mandatory minimum levels of recycled content would be set to 12% cobalt, 85% lead, 4% lithium, and 4% nickel in 2030, increasing to 20% cobalt, 10% lithium, and 12% nickel in 2035 [5].

Various cathode active materials have been used in lithium ion batteries such as LCO (lithium cobalt oxide), NCM (lithium nickel cobalt manganese oxide), NCA (lithium nickel cobalt aluminum oxide), and LFP (lithium iron phosphate) [6]. Nickel and cobalt are recognized as target metals in LIB recycling because Ni-rich cathode materials have been used for high-end electric vehicles [7]. SungEel HiTech, a representative LIB recycler in Korea, runs an LIB-recycling process consisting of pretreatment, leaching, solvent extraction, and evaporation/electrowinning, where H₂SO₄ with H₂O₂ is used as a leaching medium for the leaching process [8,9]. The H₂O₂ in this recycling process is used as a reductant because the oxidation state of metals is higher than +3 in cathode active materials [10,11]. Although the company recovers valuable metals successfully from spent LIB using the

process, it is difficult to operate the leaching process continuously because the amount of H_2O_2 added varies depending on waste LIB.

Flotation processes as pretreatments have been examined to separate graphite and cathode materials [12] or to recover Cu and Al from ground-LIB particles [13]. Although graphite was recovered, it is difficult to reuse graphite as anode materials. Because carbon such as graphite can act as a reductant, it is better to use graphite components as reductants than to recover graphite in LIB-recycling processes, in which graphite could enhance the dissolution of metal in cathode materials by reducing the oxidation state of metals from +3 to +2 or less in leaching processes. Therefore, a pretreatment process using roasting with a carbon source as a reductant was proposed [14–21]. In these conventional studies, it was reported that the metals in the cathode materials were reduced to monoxide or metal [14,15] with graphite or with graphite [14,15,17–21] and CO_2 [16]. Ammonia or electrochemical leaching was tested with NCM powder [20,21], but the use of sulfuric acid is economical and advantageous for the recovery of Ni and Co as sulfate [22–24]. In other conventional studies [18,20], water leaching for the selective leaching of Li was performed before sulfuric acid or ammonia leaching, but the leaching efficiency of Li was not more than 95%.

Conventional LIB recyclers have proceeded with various types of LIB or cathode materials, which can contain anode materials such as graphite. Therefore, when spent LIB without graphite is recycled, other carbon sources should be added. In the present study, carbothermic reduction roasting processes with carbon sources such as activated carbon and graphite were investigated as a pretreatment process, in which activated carbon was selected because it can be obtained easily and economically. The effects of roasting temperature, molar mixing ratio of cathode active materials and carbon sources, and type of cathode active materials were examined to investigate the leaching behaviors of Li, Ni, Co, and Mn from the cathode active materials after roasting.

2. Materials and Methods

Three kinds of cathode active materials (NCM), such as virgin NCM622, waste cathode powder, and black powder were used in this study, in which the waste cathode powder was generated from battery-material manufacturing processes and the black powder was generated from an LIB recycling process using spent LIB. All samples were obtained from an LIB manufacturer or recycler in Korea. The metal contents of Li, Ni, Co, and Mn are given in Table 1, which were measured using an optima 8300 ICP-OES (inductively coupled plasma optical emission spectrometer, PerkinElmer Inc., Waltham, MA, USA) after acid-digestion with aqua regia, and, in the case of black powder, graphite components were removed by roasting at $950\text{ }^\circ\text{C}$. The content of graphite was 25.6%, calculated from the roasting test.

Table 1. Metal composition of samples used in this study (mass%).

	Li	Ni	Co	Mn	Others
Virgin material	9.4	54.5	19.4	16.6	-
Waste material	9.2	54.3	19.1	17.4	-
Black powder ¹	9.6	44.7	23.2	21.4	1.1 ²

¹ The metal contents of black powder were calculated excluding the graphite component. ² Other metals indicate Cu and Al.

The Gibbs free energies of metal oxides such as Li_2O , MnO , Mn_2O_3 , NiO , CoO , and Co_3O_4 , where Li, Mn, Ni, and Co are main components of NCM, were investigated for temperature using Outokumpu HSC Chemistry 5.11 to understand the behaviors of metal oxides by carbothermic reduction. The NCM samples were mixed with activated carbon (98%, Junsei Chemical, Co. Ltd., Tokyo, Japan) or graphite powder (reagent-grade, Kanto Chemical, Co. Inc., Tokyo, Japan) for roasting tests, and the molar ratio was adjusted from 1:1 to 1:10. The mole of active cathode material was calculated based on the chemical formula, $Li(Ni_{0.6}Co_{0.2}Mn_{0.2})O_2$, where its molecular weight was calculated to be 96.93 g/mol. The reduction of Li, Ni, Co, and Mn in the cathode material needs

4 electrons, which could be provided from the oxidation of C to CO_2 (C^{4+}). The mixtures were isothermally reduced in a horizontal tube furnace (ID 60 x L 1000). An alumina boat loaded with 10 g of the mixture was placed in the middle of the tube, and the total gas-flow rate was fixed at 0.7 L/min Ar. The temperature range was from 600 to 900 °C, and the residence time was fixed at 60 min.

Before the leaching tests, a 1 mol/L H_2SO_4 solution was prepared with sulfuric acid (95%, Junsei Chemical Co., Ltd., Tokyo, Japan). The leaching tests of the cathode samples before and after roasting were performed in a 500 mL, four-necked Pyrex glass reactor using a heating mantle to maintain the temperature. The reactor was fitted with a reflux condenser and an agitator. The reflux condenser was inserted into one port to avoid solution loss at high temperatures. In a typical run, 200 mL of 1 mol/L sulfuric acid solution was poured into the reactor with an agitation speed of 400 rpm. After the temperature of solution reached the thermal equilibrium at 90 °C, 5 g of the roasted sample was added to the reactor in all the experiments. During the leaching tests, 3 mL of the solution was withdrawn periodically at a desired time interval (5–120 min) by a syringe. The sample was filtered using a 0.45 μm membrane filter, and the obtained filtrate was diluted with 5% HNO_3 solution. The leach residue was digested with aqua regia, and the solution was diluted with distilled water. All experimental procedures are summarized in Figure 1.

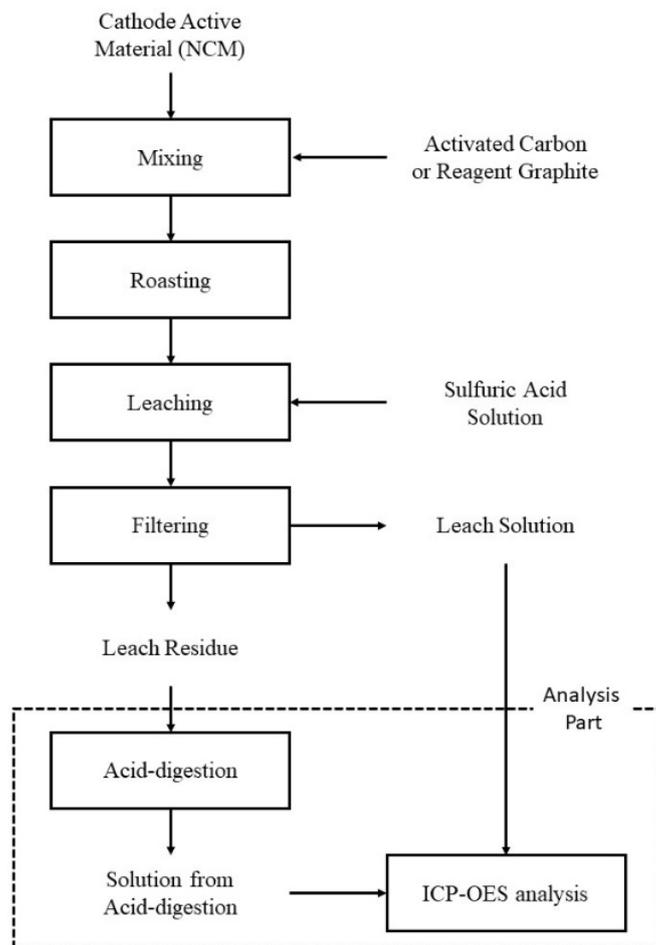


Figure 1. Flowchart of the experimental procedures in this study.

The phase change was characterized by X-ray diffraction (XRD, D/Max 2500, Rigaku, Tokyo, Japan) and by scanning-electron microscopy (SEM, MIRA-3, Tescan Co., Brno, Czech Republic). The concentration of Li, Ni, Co, and Mn was measured using an optima 8300 ICP-

OES (inductively coupled plasma optical emission spectrometer, PerkinElmer Inc., Waltham, MA, USA). The leaching efficiencies of metals were calculated using the following equation:

$$\text{The leaching efficiency (\%)} = M_{\text{solution}} / (M_{\text{solution}} + M_{\text{residue}}), \quad (1)$$

where M_{solution} and M_{residue} represent the mass of metals in the leach solution and leach residue, respectively.

3. Results and Discussion

The NCM cathode active materials are found to be oxides, although the oxidation state of metals is higher than +3 [10,11], and the crystal structure of cathode is transformed from a hexagonal crystal system to a monoclinic crystal system during repeated charging and discharging. However, there has been little information about the Gibbs free energy of active materials. Therefore, the carbothermic reduction processes of metal oxides such as Li_2O , MnO , Mn_2O_3 , NiO , CoO , and Co_3O_4 were expressed to predict the reduction process, as a route represented in Figure 2, which was created using the software of Outokumpu HSC Chemistry 5.11. As shown in Figure 2, the Gibbs free energies decreased with increasing temperature; 1350 °C or higher is required to reduce Li_2O or MnO to Li or Mn metal, whereas CoO or NiO can be reduced to Co or Ni metal at 600 °C or lower.

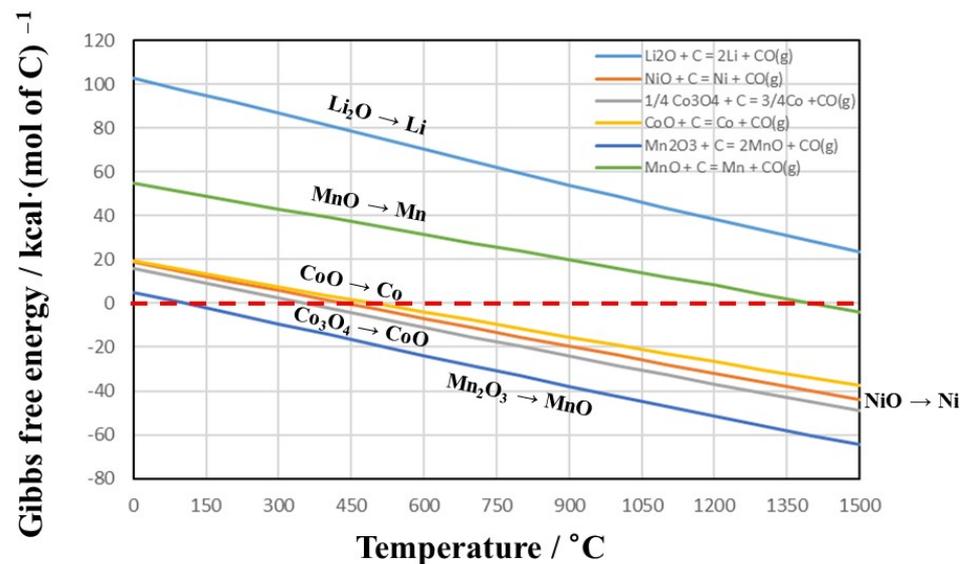


Figure 2. Gibbs free energies of metal oxides with temperature.

The virgin NCM622 samples were mixed with activated carbon in a molar ratio of 1:10 and then roasted at 600 °C–900 °C under Ar atmosphere. Figure 3 shows the XRD results of the virgin NCM622 and roasted products. As shown in Figure 3, the peaks of the NCM cathode active material were observed before roasting, and the peaks of the metal or oxide forms of Ni, Co, and Mn were shown when increasing the roasting temperature to 800 °C. When increasing the temperature further to 900 °C, only metal forms were observed. These results indicate that the lattice of anode material was collapsed by roasting and that parts of nickel and cobalt oxides were reduced to metal. Figure 4 shows SEM images of samples roasted at 700 °C, where Ni, Co, and Mn existed together, and each metal component did not grow as an independent granular.

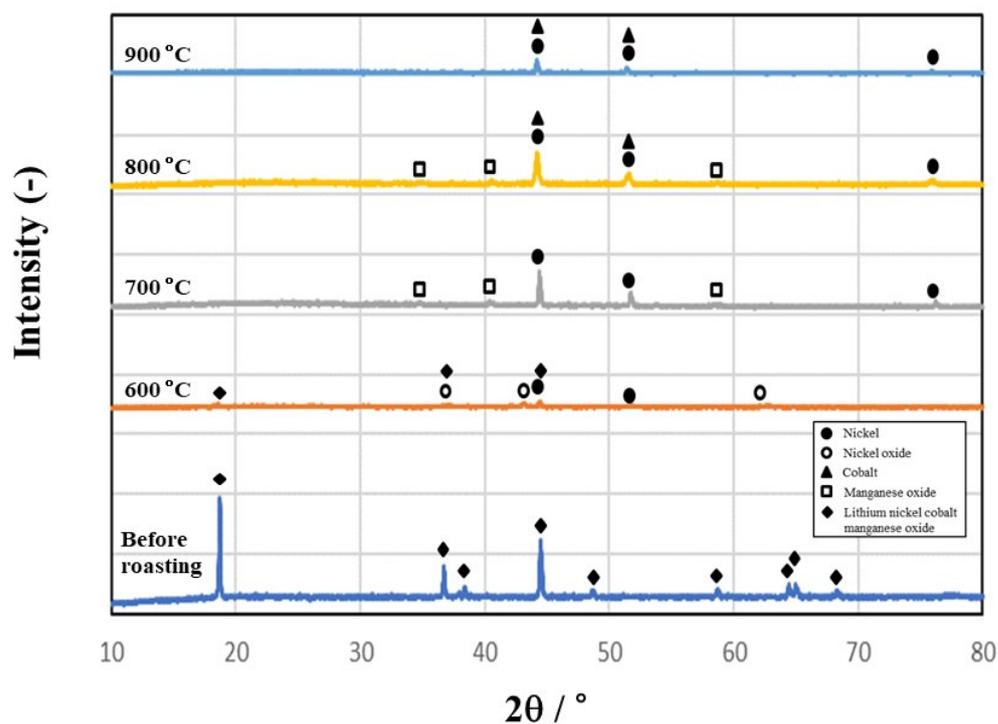


Figure 3. XRD data of virgin NCM622 active cathode material and samples roasted at 600 °C–900 °C.

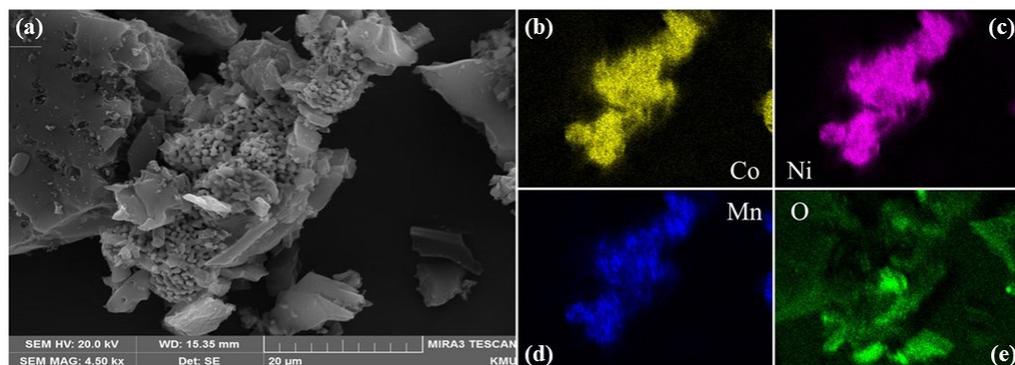


Figure 4. SEM images of (a) sample roasted at 700 °C and EDS results of (b) Co, (c) Ni, (d) Mn, and (e) O.

Figure 5 shows the leaching behaviors of Li, Ni, Co, and Mn from the samples roasted at 600 °C–900 °C in a 1 mol/L sulfuric acid solution at 90 °C and at 400 rpm with 2.5% pulp density (5g/200 mL). The leaching efficiencies increased rapidly within 15 min, and all leaching efficiencies reached over 99% at 60 min. In the cases of Li and Mn, the leaching efficiency increased from 73.6% and 76.7% at 600 °C to 99.2% and 97.2% at 800 °C, respectively, at 10 min of leaching time. Figure 6 shows the leaching efficiencies of Ni and Co at 10 min of leaching time with the roasted temperatures. The leaching efficiencies of Ni and Co decreased from 94.8% and 96.4% in the sample roasted at 600 °C, to 88.1% and 86.8% at 900 °C, respectively. At the beginning of leaching at approximately 10 min, the leaching efficiencies of Ni and Co decreased with increasing roasting temperature, but all leaching efficiencies increased over 99% within 60 min.

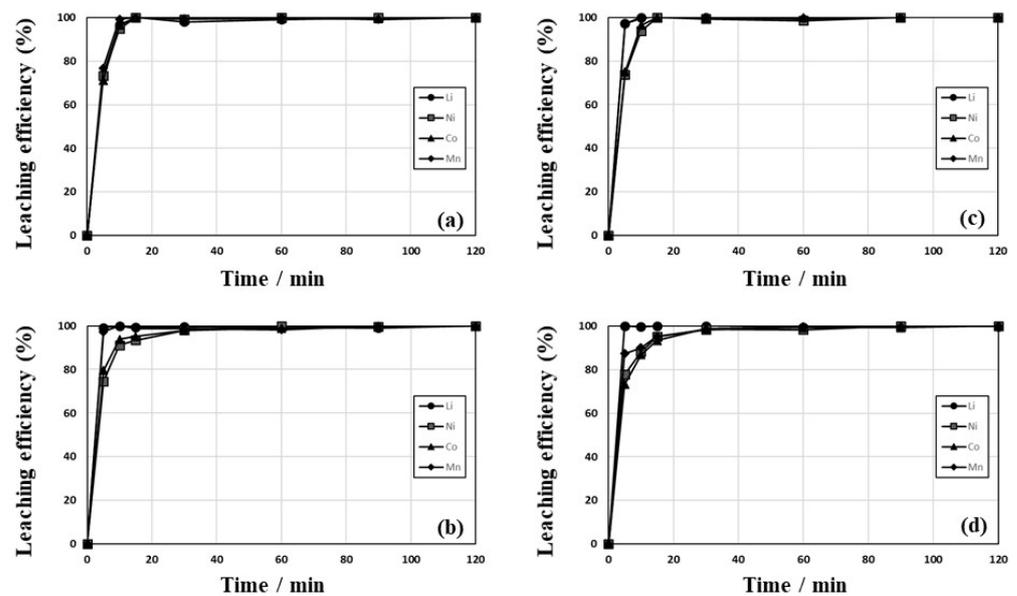


Figure 5. The leaching behaviors of Li, Ni, Co, and Mn from samples roasted at 600 °C (a), 700 °C (b), 800 °C (c), and 900 °C (d).

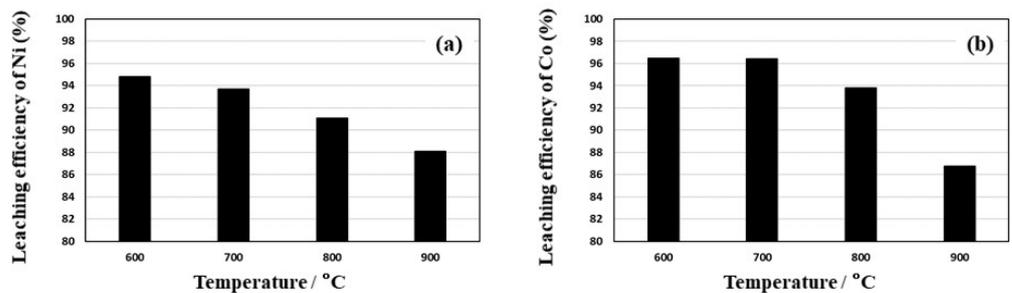


Figure 6. Leaching efficiencies of Ni (a) and Co (b) from samples roasted at 600 °C–900 °C.

The effects of carbothermic reduction roasting with activated carbon on the leaching of Ni and Co are shown in Figure 7. The NCM622 sample was roasted at 700 °C with a 1:10 molar ratio for 1 h, and then, the roasted product was leached in a 1 mol/L H_2SO_4 solution at 90 °C and at 400 rpm with 2.5% pulp density for 2 h. In the case of NCM622 leaching without roasting, the leaching efficiencies of Ni and Co were 60.5% and 56.8%, respectively, while the leaching efficiencies increased over 99% by roasting NCM622 with activated carbon. These results suggest that roasting with carbon sources enhances the leaching of cathode active materials. In the same leaching tests, the leaching efficiencies of Li and Mn increased over 99% within 2 h regardless of roasting. Figure 8 shows the effects of various mixing ratios of NCM622 and activated carbon on the leaching efficiencies of Ni, Co, Mn, and Li. Under most ratios, although the leaching efficiencies indicate rates above 99% regardless of the ratio, the leaching efficiencies of Ni and Co were slightly lower at the ratios of 1 and 2.

The effects of reductants such as activated carbon and graphite on the leaching were investigated after roasting at 700 °C with a 1:10 molar ratio for 1 h followed by leaching in a 1 mol/L sulfuric acid solution at 90 °C and at 400 rpm with 2.5% pulp density. Generally, because graphite was used as an anode material, the effects of roasting with activated carbon and graphite on the leaching were compared. In this study, the difference in leaching efficiencies was not observed when using activated carbon and graphite as reductants, as shown in Figure 9, but the carbothermic reduction with carbon sources enhanced the leaching efficiencies.

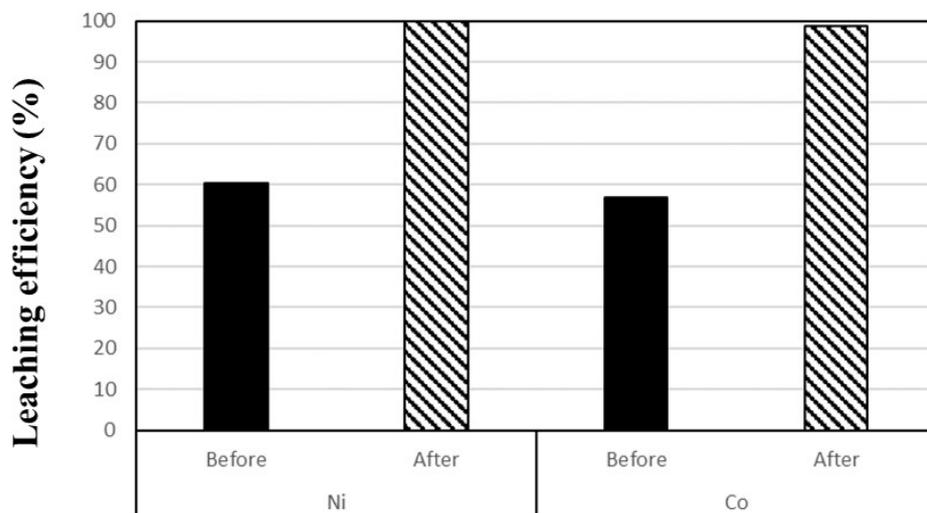


Figure 7. The leaching efficiencies of Ni and Co from samples before and after roasting.

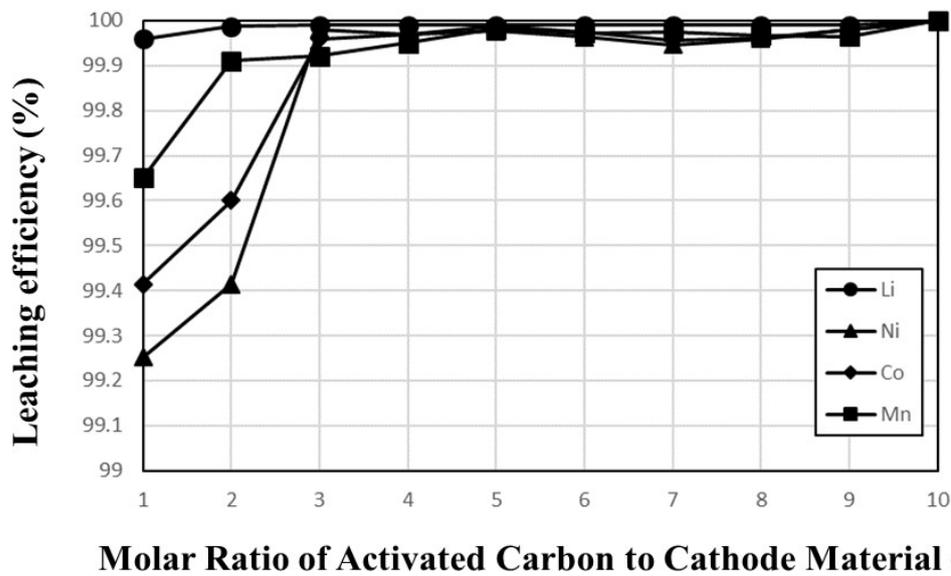


Figure 8. The leaching behaviors of Li, Ni, Co, and Mn with molar mixing ratio of NCM622 and activated carbon.

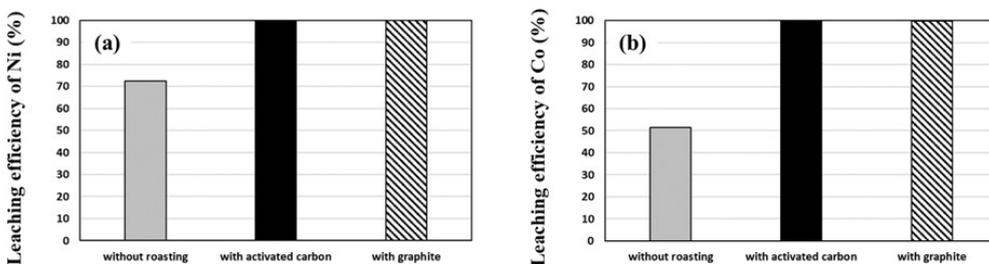


Figure 9. The leaching behaviors of Ni (a) and Co (b) from the waste cathode powder before and after roasting at 700 °C with activated carbon or graphite.

Currently, in Korea, there are very few end-of-life electric vehicles, and recycling companies in Korea have treated lithium-ion batteries generated from manufacturing processes. Therefore, leaching tests were performed with scrapped active cathode material obtained from manufacturing processes, and the samples were roasted at 700 °C with a 1:10 molar ratio for 1 h followed by leaching in a 1 mol/L sulfuric acid solution at 90 °C

and at 400 rpm with 2.5% pulp density. The leaching behaviors of Ni and Co are shown in Figure 10, where the leaching results of Li and Mn are not shown because the leaching efficiencies increased rapidly over 99.9% within 10 min. Although the leaching efficiency of Ni increased more slowly than that of Co, the leaching efficiencies increased over 99.9% within 30 min, as shown in Figure 10a. The effects of the molar ratio of the graphite-to-cathode material were also investigated using the scrapped active cathode material, and, as shown in Figure 10b, the leaching efficiency of Ni increased by increasing the molar ratio even though the efficiency was over 99.6% when the ratio was 1:1, whereas the leaching efficiency of Co remained over 99.9%.

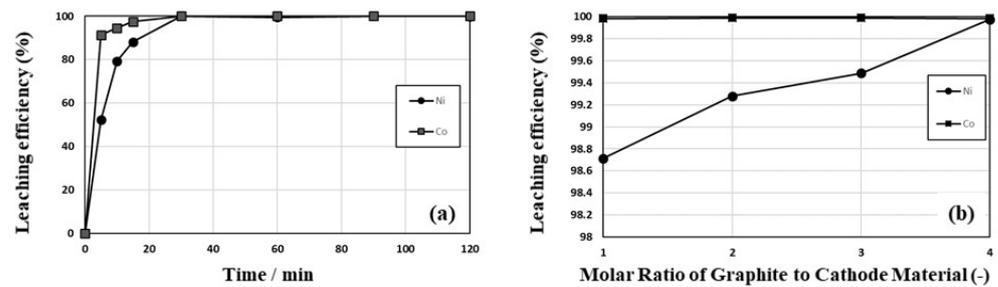


Figure 10. The leaching of Ni (a) and Co (b) from the waste cathode powder after roasting at 700 °C with graphite followed by 1 mol/L H₂SO₄ leaching.

Generally, in recycling processes of LIB, pretreatments such as dismantling, crushing, and screening have been performed before leaching processes, and the product obtained from the pretreatment processes contains active cathode and anode materials, which is called black powder. Figure 11 indicates the leaching behaviors of Ni and Co from the black powder with and without roasting, which was performed at 700 °C with a 1:4 molar ratio for 1 h. The reagent-grade graphite was added to the black powder to reach the molar ratio. The leaching test was conducted in a 1 mol/L sulfuric acid solution at 90 °C and at 400 rpm with 2.5% pulp density. The leaching efficiencies increased rapidly within 30 min, and then gradually. When the black powder was roasted, the leaching efficiencies increased to over 99.9% while the leaching efficiencies of Ni and Co increased to 77.6% and 86.5%, respectively, using the black powder without roasting.

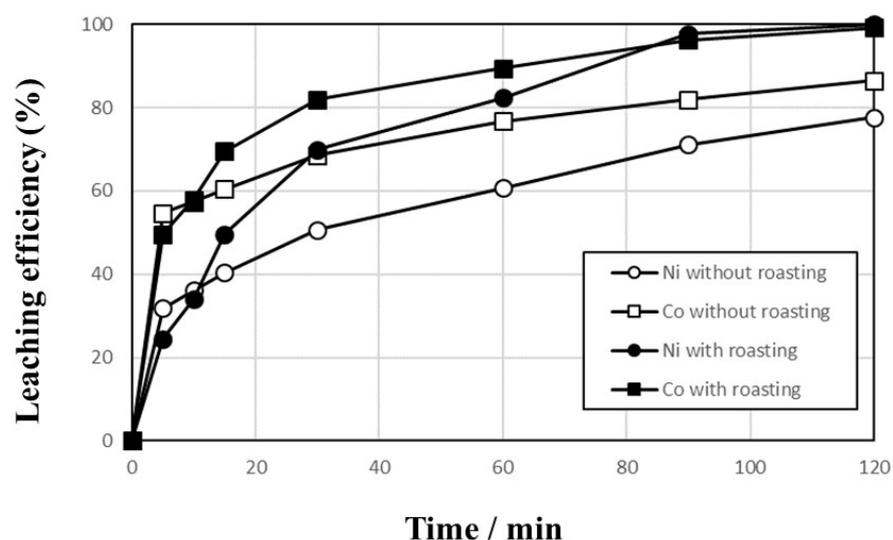


Figure 11. Leaching behaviors of Ni and Co using the black powder before and after roasting with graphite at 700 °C followed by H₂SO₄ leaching.

As discussed above, in the conventional leaching process for active cathode material or black powder, H₂O₂ has been used as a reductant. It was difficult to convert the

conventional leaching process to a continuous process by using H₂O₂. Furthermore, hydrogen peroxide has been found to be unstable and expensive [25–29]. Therefore, pretreatment using roasting with carbon sources could be substituted for the conventional process using H₂O₂ and to enhance the efficiency of the leaching process for LIB recycling.

4. Conclusions

Three kinds of NCM cathode active materials were roasted with two carbon sources, activated carbon and graphite, and then, the leaching behaviors of Li, Ni, Co, and Mn were investigated in sulfuric-acid-leaching tests.

When the virgin NCM622 materials were roasted with activated carbon, the peaks of Ni and Co metals were observed in the XRD data. The leaching efficiencies of Li, Ni, Co, and Mn increased to over 99.9% within 120 min in all samples roasted at 600 °C–900 °C, but, at the beginning of leaching, the leaching efficiencies increased more slowly by increasing the roasting temperature. The lower the molar mixing ratio of cathode active materials and carbon sources, the lower the leaching efficiencies of Ni and Co, but the leaching efficiencies of Ni and Co were more than 99.9% in all ratios. These results indicate that carbothermic reduction roasting with carbon sources can enhance the leaching efficiencies of Ni and Co, regardless of the NCM cathode active materials such as virgin, scrapped, and black powder. Furthermore, activated carbon could be used instead of graphite in NCM cathode active materials without anode materials such as graphite.

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Conflicts of Interest: The authors declare no conflict of interest.

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