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A Fast Metals Recovery Method for the Synthesis of Lithium Nickel Cobalt Aluminum Oxide Material from Cathode Waste

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Abstract: An approach for a fast recycling process for Lithium Nickel Cobalt Aluminum Oxide (NCA) cathode scrap material without the presence of a reducing agent was proposed. The combination of metal leaching using strong acids (HCl, H₂SO₄, HNO₃) and mixed metal hydroxide co-precipitation followed by heat treatment was investigated to resynthesize NCA. The most efficient leaching with a high solid loading rate (100 g/L) was obtained using HCl, resulting in Ni, Co, and Al leaching efficiencies of 99.8%, 95.6%, and 99.5%, respectively. The recycled NCA (RNCA) was successfully synthesized and in good agreement with JCPDS Card #87-1562. The highly crystalline RNCA presents the highest specific discharge capacity of a full cell (RNCA vs. Graphite) of 124.2 mAh/g with capacity retention of 96% after 40 cycles. This result is comparable with commercial NCA. Overall, this approach is faster than that in the previous study, resulting in more efficient and facile treatment of the recycling process for NCA waste and providing 35 times faster processing.

Keywords: NCA; Li-ion battery; hydrometallurgical; recycle; resynthesis

1. Introduction

In these advanced times, Lithium ion (Li-ion) batteries have become the prime technology for energy storage in portable electronics such as laptops, smartphones, powerbanks, and electric vehicles. Previously, the most commonly used and successfully commercialized Li-ion battery used LiCoO₂ (LCO), but there are too many limitations of LCO, such as the high cost of cobalt and poor thermal stability. Recently, other types of Li-ion battery were found, such as $Li_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA), $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ (NMC), and $LiFePO_4$ (LFP) [1], and they became promising candidates as substitutes for LCO. The demand for Li-ion batteries increased significantly from 1990 to 2016 [2]. However, increasing Li-ion battery usage results in the accumulation of spent Li-ion batteries (Libs) which can cause serious environmental issues [2]. Recycling spent Li-ion batteries. Recycling would involve the recovery of valuable metals followed by regeneration to a new active material. Among the three recent types of Li-ion Battery, NCA has attracted the most attention for use in Li-ion batteries due to its high potential relative to Li (3.7 V) which promotes high energy density and high



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capacity characteristics. Because of its superior performance, TESLA use NCA batteries for their Electric Vehicles (EVs) [1,3]. It is predicted that the demand for NCA will increase to 39,000 tons in 2025 [2]. Recycling processes could also minimize the cost of raw materials while reducing the threat that the waste poses for the environment.

The recycling processes for Li-ion battery waste (spent libs or scrap) are divided into three steps, namely, pretreatment, metal extraction, and product preparation [4]. The aim of the pretreatment process is to separate the cathode material from other components like Al foil, plastics, Fe, etc., which involves a mechanical process [5], solvent dissolution [6–8] or NaOH dissolution [9–11], ultrasonic-assisted separation [12,13], etc. The metal extraction is a significant step in the recycling process which changes the solid metals into their solution state or alloy form to facilitate metal recovery. The three types of metal extraction techniques are hydrometallurgical [14,15], pyrometallurgical [16,17], and bio-hydrometallurgical [18–20]. The hydrometallurgical process is the most commonly used process due to its advantages such as ease of processing, lower energy demands, and a highly pure product with fewer gas emissions [12,21]. Leaching is a main step in the hydrometallurgical process whereby acids are used to dissolve the valuable metals into solution. Various inorganic acids such as HCl, H₂SO₄, and HNO₃ [21–24] and organic acids such as citric acids, malic acids, oxalic acids, etc. [25–28] are usually used as the leaching agent (leachant) to leach out the valuable metals contained in the material. The inorganic acids present a satisfactory performance during leaching and achieve higher efficiency of metal extraction than organic acids [29]. Techniques that are used to prepare the final products from the leaching filtrate include solvent extraction [10,30–33], electrochemical techniques [34–36], selective precipitation [21,37–40], and co-precipitation [41–43]. Among these, co-precipitation is the most efficient technique for the recovery of more than one metal (mixed metal) due to a higher level of homogeneity and spherical/sphere-like products [44]. Based on our literature study, the hydrometallurgical method has been successfully applied to the recycling and resynthesis of LCO, LFP, and NMC [7,9,41,45]. However, there remains a lack of research into the recycling and resynthesis of NCA material.

Previously, Joulie et al. [21] investigated the leaching efficiency using strong acids and the recovery of metals (nickel and cobalt) via selective precipitation processing for which the optimum leaching result was given by 4M HCl, 90 °C, 18 h, and a solid loading rate of 50 g/L. However, the leaching process needed a long processing time with a low solid loading rate, which is inefficient in terms of time and energy. Then, Sandhya et al. [8] proposed a synthesis process for material for anodes that involved mixed oxides of nickel and cobalt from spent NCA batteries using concentrated HCl leaching and co-precipitation with NaOH followed by microwave heat treatment. However, complex equipment and a large amount of energy were also required in the recycling process. No report has been found regarding the resynthesis of NCA material from a leaching stream of NCA waste, which is one of the most promising cathode materials with features such as specific high capacity, high energy density, and a long life cycle [21,46].

Hence, in this work, we propose a fast process for the resynthesis of NCA material via mixed metal hydroxide precipitation of nickel, cobalt, and aluminum from a leaching stream of NCA scrap. NCA scrap is unused and/or residual cathode film that is produced in the cutting process during the battery production process. The resynthesis of NCA material from waste has not been found in the literature. The leaching process used various strong acids (HCl, H₂SO₄, HNO₃) without the presence of a reducing agent. The effect of heat treatment before the leaching process on powder separated from Al foil was studied. Unlike the previous study by Joulie et al., this work proposed the recycling and also resynthesis of NCA material with a high solid loading rate of 100 g/L of leaching, which is necessary to enhance the productivity of the leachate and the final product. Based on our best knowledge, this approach has never been reported by other researchers. Fast, efficient, and easy processing will be served using this approach. The electrochemical performance was tested using full cell batteries using graphite as an anode. In this work, the performance of the recycled NCA material is comparable with that of commercial NCA; hence, a proof of concept is provided.

2. Materials and Methods

2.1. Experimental Process

2.1.1. Pretreatment

NCA scrap was obtained from a Battery Manufacturing Facility which is operated by Sebelas Maret University. During battery production of the NCA type, the cutting process of the cathode film leaves some residual and/or reject film (namely, NCA scrap) which is collected for recycling. The pretreatment process for scrap is usually simpler than that for spent libs. NCA scrap contains Al foil which must be separated by immersion with agitation in an alkaline solution (5M NaOH) for 2 h. The dissolved Al in NaOH is converted to sodium aluminate in the reaction shown in Equation (1):

$$2Al_{(s)} + 2NaOH_{(aq)} + 2H_2O_{(liq)} \rightarrow 2NaAlO_{2(aq)} + 3H_{2(g)}.$$
 (1)

The active material that was peeled from the Al foil was filtered and washed using demineralized water to remove the remaining NaOH, and the residue was heated at 80 °C in an oven. In order to eliminate the acetylene black and polyvinylidene difluoride (PVDF), which can slow the process of metal dissolution, the residue was calcined at 800 °C for 2 and 4 h. The effect of heating time was studied. The obtained powder was then ground to minimize the particle size to improve surface area contact and accelerate the reaction rate during leaching.

2.1.2. Acid Leaching of NCA Scrap

First, the powder was leached completely in concentrated HCl (Merck, Darmstadt, Germany) to determine the total concentrations of all metal ions (Ni²⁺, Co²⁺, and Al³⁺). The leaching process was performed in a 500 mL, three-necked, and round-bottomed flask. A water bath was used to maintain the desired temperature. The leaching process was conducted at a solid-to-liquid ratio of 100 g/L, an acid concentration of 4M, temperature of 80 °C, and leaching time of 60 min. An overhead stirrer was used for agitation during the leaching process. The leachate residue was filtered using filter bag paper. The concentrations of metal ions (Ni²⁺, Co²⁺, and Al³⁺) in the leachate were measured using Atomic Absorption Spectroscopy (AAS) in order to determine the leaching efficiency. The effects of various acids (HCl, HNO₃, H₂SO₄/Merck, Darmstadt, Germany) and leaching behaviors were studied.

2.1.3. Resynthesis of NCA

The leachate from HCl, H₂SO₄, and HNO₃ contained metal ions (Ni²⁺, Co²⁺, and Al³⁺) and was next processed by mixed metal hydroxide co-precipitation using NaOH (Asahi, Cilegon, Indonesia) and ammonia (Merck, Darmstadt, Germany) as the precipitant and monodentate ligand, respectively. First, the ammonia solution and 5M NaOH were added to the 500 mL batch reactor. The process was controlled at pH 11–12 and heated to a constant temperature of 60 °C for 6 h. At constant pH, the aging process was conducted for 20 h. This co-precipitation experiment used an overhead stirrer at high speed (more than 900 rpm). Then, the greenish precursors were filtered and washed using deionized water to eliminate the remaining NaOH and other impurities. The precursors were dried in an oven at 80 °C overnight. The –OH precursors which resulted in the leaching processes using hydrochloric acid, nitric acid, and sulfuric acid were denoted P-HA, P-NA, and P-SA. The –OH precursor was then tested using X-ray fluorescence (D2 Phaser Bruker, Karlsruhe, Germany) to determine the metal content and Fourier Transformed Infrared Spectroscopy (Shimadzu, Japan) to identify the functional groups of the –OH precursor.

Next, the precursor was mixed with LiOH (Merck, Darmstadt, Germany) using a mortar and pestle until homogeneity was achieved. The molar ratio of Li to metal ions was adjusted to 1.03:1 using the hydroxide salts of metals. Then, the mixture was calcined at 550 °C for 6 h and was further sintered at 800 °C for 12 h under an oxygen stream in a muffle furnace. Finally, the NCA material was obtained.

The NCA material was ground and screened into fine NCA particles (referred to here as Recycled NCA or RNCA). A flow chart of the RNCA synthesis appears in Figure 1, in which the leaching processes of RNCA using hydrochloric acid, nitric acid, and sulfuric acid are denoted RNCA-HA, RNCA-NA, and RNCA-SA.



Figure 1. Flow chart of the recycled Lithium Nickel Cobalt Aluminum Oxide (RNCA) recycling process.

2.2. Characterization and Electrochemical Testing

The structure of the NCA crystals was investigated by X-ray diffraction (D2 Phaser Bruker, Germany) with a 2θ value that ranged from 10° to 70° at a 2θ increment of 0.02°. Scanning Electron Microscopy (Jeol JSM-6510LA, Tokyo, Japan) was used to observe the morphology of the NCA particles. The metal ion concentrations (Ni²⁺, Co²⁺, Al³⁺) were analyzed using Atomic Absorption Spectroscopy (PinAAcle 900T Perkin Elmer, Waltham, MA, USA).

The electrochemical performance was tested using a cylindrical cell (type 18650). The anode, separator, and electrolyte were composed of graphite, celgard, and LiPF₆, respectively. To fabricate the cathode sheet, the RNCA material (active material) was mixed with a conductive agent (acetylene black/AB, MTI, Richmond, CA, USA) and a binder (polyvinylidene difluoride/PVDF, MTI, USA) in solvent (N-methyl-2-pyrrolidone/NMP, MTI, USA) to an RNCA/AB/PVDF mass ratio of 92:3:5. The homogeneous slurry was then coated via a doctor's blade technique onto Al foil to a thickness of 200 μ m. The cathode sheet was dried in a vacuum oven at 80 °C overnight until it was ready for assembly in a glovebox. For comparison, fresh NCA powder purchased from BTR (China) was assembled and tested in a cylindrical cell (labelled Commercial NCA/Com-NCA). The electrode fabrication process for the anode sheet (graphite, MTI, America) was the same as that for the cathode. The ratio of the capacity of the cathode and the anode was 1:1.15. The full cell performance was analyzed using NEWARE Battery analyzer and BTS software.

3. Results and Discussion

3.1. Pretreatment

A pretreatment process which used NaOH dissolution to dissolve Al foil was employed to separate the powder from the Al foil. In order to eliminate PVDF (binder) and acetylene black (conductive agent), the obtained powder was heated to 800 °C. In this experiment, the powder was processed at 800 °C at various heating times of 2 and 4 h (the samples were denoted P-01 and P-02). After heating at 800 °C, the PVDF and AB were assumed to be burned according to the findings of previous studies [7,47,48], which is beneficial for the leaching process [28].

A previous study reported that CO_2 gas was formed during the heat treatment process. This occurrence was caused by the redox reaction between acetylene black (AB) and the cathode material

during which the transition metals were reduced from a high charge to a low charge [49]. For NCA material, the oxidation states of the transition metals are trivalent (Li⁺, M³⁺, O⁴⁻). When the reduction reaction occurs, the state of the transition metals changes from trivalent to a divalent state. To verify the redox reaction and the effect of heat treatment on the NCA structure, the collected powders (P-01 and P-02) were analyzed using XRD.

The XRD patterns of the P-01 and P-02 samples compared to the sample before heating (denoted B-HT) can be seen in Figure 2. Based on a structural analysis, the XRD pattern indicates a hexagonal layered material which is similar to commercial NCA. However, the split peaks of I_{006}/I_{012} and I_{018}/I_{110} on P-01 and P-02 were merged into a single peak. This occurance can be caused by hydrofluoric acid (HF)released from decomposition of PVDF (binder) which attack the NCA material at a high temperature and lead to form lithium fluoride (LiF) [50]. According to previous studies, the merged peaks show the destruction of the layered structure of the material [51].



Figure 2. XRD pattern of NCA powder before heat treatment (B-HT) and after heat treatment at 800 °C for 2 or 4 h (P-01 and P-02 samples).

In addition, there is a change in the peak intensity of I_{003} and I_{004} after heat treatment in all samples. In this experiment, the intensity ratios of I_{003}/I_{004} for P-01 and P-02 were 1.0112 and 0.644. Yang et al. reported that the reduction of metals can be evaluated by the value of the intensity ratio of I_{003}/I_{104} [49]. The acetylene black contained in the powder acts as a reducing agent [52] which promotes the reduction reaction of the transition metals in NCA during heat treatment [49]. From XRD analysis, it is predicted that higher reduction of metals occurred in the P-02 sample than in the P-01 sample; this in turn predicted more inactive divalent nickel compounds (NiO) of metals in the P-02 sample which can better facilitate the leaching process [49]. Therefore, this work used pretreatment conditions at 800 °C and a 4 h heating time for the next process.

Before any further treatments, we tested the performance of the B-HT and P-02 samples as the cathode and graphite as the anode in a cylindrical battery (full cell). The charge–discharge curve is presented in Figure 3 with voltage range of 2.7–4.2 V. The first cycle was used for formation, and the coulombic efficiencies of B-HT and P-02 were 34.3% and 31.5%. The specific discharge capacities of B-HT and P-02 were too low compared to the theoretical capacity of NCA (200 mAh/g)—46.7 and 41.1 mAh/g at 4 mA/g, respectively. The P-02 capacity result corresponds to the XRD analysis which showed deterioration of the NCA structure after heat treatment. Although the XRD pattern of B-HT is quite good, it has poor specific capacity in battery performance. This may be caused by the washing effect of NCA after NaOH dissolution which leads to a reaction between NCA and water that forms nickel hydroxide and nickel oxide hydroxide on the NCA surface. The presence of nickel hydroxide and nickel oxide hydroxide on the NCA surface. The presence of nickel hydroxide and nickel oxide hydroxide on B-HT powder can affect the electrochemical properties and can block Li⁺ diffusion during de-lithiation/lithiation [53]. Also, the PVDF and AB on the B-HT samples act as inactive materials which can reduce the specific capacity (mAh/g). Therefore, such further treatment is necessary to enhance the electrochemical performance of NCA. In this work, acid leaching and mixed

metal hydroxide co-precipitation were applied as further processing to the P-02 sample in order to recover valuable metals and resynthesize NCA material.



Figure 3. Specific Discharge Capacity (mAh/g) of the B-HT and P-02 Samples.

3.2. Leaching Process

In order to determine the most efficient leaching process for metal ions, various strong acids (HCl, H_2SO_4 , HNO₃) were tested as leaching agents operating at an acid concentration of 4M, temperature of 80 °C, and leaching time of 60 min. Also, metal ion extraction over time (2.5–60 min) was observed.

Figure 4. shows the effect of various acids on the leaching efficiency for the P-02 sample at concentrations of 4 M by heating at 80 °C for 1 h. In the present study, HCl shows the highest rates of leaching efficiency for Ni and Co in this experiment, which agrees with the results of a previous study [21]. Clearly, HCl is more suitable for the leaching of metal ions from NCA material as it achieved a rate of leaching efficiency that surpassed 95% for all metal ions. The great performance of HCl in the leaching process was due to the Cl⁻ ions in HCl; these showed high reactivity towards metals, resulting in a rapid attack on the metals [21,22].



Figure 4. The effect of various acids on the leaching efficiency of NCA scrap (4M, 80 °C, 1 h).

Table 1 shows a summary of the leaching conditions used in metal recovery from NCA using HCl in previous works compared to this work. Based on the listed data, the leaching process in this work obtained high-efficiency metal recovery with a short leaching processing time and the absence of a reducing agent in spite of a high solid loading rate. Such phenomena may be caused by the reduction of ion metals during the pretreatment process which simplifies the leaching process.

Material Sources	Leaching Agent	Solid to Liquid (S/L) Ratio (g/L)	Temperature (°C)	Time (h)	Reducing Agent	Efficiency	Reference
Commercial NCA	4M HCl	50	90	18	-	Ni, Co, Al: 100%, 100%, 100%	[21]
Spent NCA Battery	Concentrated HCl	-	-	-	-	-	[8]
NCA Scrap	4M HCl	100	80	1	-	Ni, Co, Al: 99.8%, 95.6%, 99.5%	This work

Table 1. Summary of leaching conditions used in metal recovery from NCA using HCl from previous works and the present work.

In order to ensure that the pretreatment process with heating produces high-efficiency metal extractions, Figure 5 shows a comparison of HCl leaching at an acid concentration of 4M, temperature of 80 °C, and leaching time of 60 min using the P-02 sample (after pretreatment with heating), B-HT (after pretreatment without heating), and commercial NCA. The results show that the leaching efficiencies of Ni, Co, and Al in B-HT were the lowest compared to P-02 and commercial NCA. The presence of PVDF and AB contained in B-HT may also be the reason for the poor leaching efficiency by inhibiting the diffusion of metals into solution. Therefore, the pretreatment process with heating provides a significant improvement in the leaching behavior of valuable metals under such conditions, e.g., high solid loading rate, short processing time, and absence of a reducing agent.



Figure 5. Comparison of leaching between P-02, B-HT, and commercial NCA (4M HCl, 80 °C, 1 h).

The leaching behavior using various leaching agents is shown in Figure 6 and is similar for all metals. The metals showed their highest leaching rates in the first 15 min of the leaching process, after which the leaching rate began to decelerate. The acid consumption during the beginning of leaching and the increasing metal ion concentrations increasing the viscosity of the medium are the main reasons for such occurrences.



Figure 6. Leaching behavior using various acids during 60 min of processing (4M, 80 °C): (**a**) Nickel; (**b**) Cobalt; (**c**) Aluminum.

Based on the results of the leaching efficiency, Co showed a lower efficiency of extraction during leaching than either Ni or Al. Ni and Co were confirmed as residing in a trivalent state within the NCA material. Ni^{2+} is the stable state of Ni metals, so metal extraction from Ni^{3+} into Ni^{2+} is easy. The reactions between Al and strong acids are slow at room temperature, but the leaching reaction became both faster and easier when heat was applied. Because Co is in a stable state at Co^{3+} , extraction from Co^{3+} to Co^{2+} was difficult, causing the leaching reaction to be slow [28,54]. The reaction during the leaching process is explained in Equations (2)–(4). When the metal oxides react with acids, the state of transition metals will change into a lower state [30,54]. Therefore, in this study, the reduction process of NCA leaching occurred in order to dissolve the metals into solution.

 $3HCl_{(aq)} + LiNi_{0.80}Co_{0.15}Al_{0.05}O_{2(s)} \rightleftharpoons LiCl_{(aq)} + 0.8NiCl_{2(aq)} + 0.15CoCl_{2(aq)} + 0.05AlCl_{3(aq)} + 1.5H_2O_{(liq)} + 0.5O_{2(g)}$ (2)

 $3H_2SO_{4(aq)} + 2LiNi_{0.80}Co_{0.15}Al_{0.05}O_{2(s)} \rightleftharpoons Li_2SO_{4(aq)} + 1.6NiSO_{4(aq)} + 0.3CoSO_{4(aq)} + 0.05Al_2(SO_4)_{3(aq)} + 3H_2O_{(liq)} + 0.5O_{2(g)}$ (3)

 $3HNO_{3(aq)} + LiNi_{0.80}Co_{0.15}Al_{0.05}O_{2(s)} \rightleftharpoons LiNO_{3(aq)} + 0.8Ni(NO_{3})_{2(aq)} + 0.15Co(NO_{3})_{2(aq)} + 0.05Al(NO_{3})_{3(aq)} + 1.5H_2O_{(liq)} + 0.5O_{2(g)}$ (4)

3.3. Characterization and Electrochemical Testing of Recycled NCA material

3.3.1. Functional Group Analysis of the -OH Precursor

After the leaching process, the filtrate was precipitated using ammonia and NaOH as the monodentate ligand and precipitant agent, respectively. The greenish –OH precursors from the leachates of HCl, HNO₃, and H₂SO₄ were obtained and denoted P-HA, P-NA, and P-SA. The functional groups of the –OH precursor were identified using Fourier Transformed Infrared Spectroscopy (FT-IR), shown in Figure 7. These results are in agreement with those of previous research on Ni(OH)₂ nanoplates [55,56].



Figure 7. FT-IR analysis of the –OH precursor from the leachates of H₂SO₄, HNO₃, and HCl; denoted as P-SA, P-NA, P-HA (M: metal).

The sharp peak at approximately 3630 cm^{-1} indicates the stretched bond of O–H (disturbed hydroxyl) from the free Ni–OH groups. The band at approximately 3450 cm^{-1} is characteristic of Ni(OH)₂ and the vibrational mode of OH (free hydroxyl), while the peak at 1630 cm^{-1} is the vibrational mode of water molecules (H–O–H). The presence of CO_3^{2-} was detected at approximately 1380 and 1100 cm^{-1} . This may be caused by an interaction between Ni(OH)₂ and CO₂ under an air atmosphere during the storing of –OH precursors, which implies that the –OH precursor still contained slight amounts of CO_3^{2-} and H₂O. Based on FTIR, P-HA has the weakest band at around 1380 and 1100 cm⁻¹, indicate a slight amount of CO_3^{2-} ions. These conditions may be caused by a small amount of residual product (NaCl) remaining in the –OH precursor (P-HA) from the co-precipitation process which could inhibit the interaction between Ni(OH)₂ and CO₂ [57]. The reactions during the leaching process using HCl and mixed metal hydroxide co-precipitation are explained in Equations (5)–(7), where MO₂ is a metal oxide. Hence, from FTIR analysis, it was found that P-HA is more resistant towards CO₂ than P-SA and P-NA.

$$4HCl_{(aq)} + MO_{2(s)} \rightleftharpoons MCl_{2(aq)} + 2H_2O_{(liq)} + Cl_{2(g)}$$

$$\tag{5}$$

$$MCl_{2(aq)} + 2H_2O_{(liq)} + NH_{3(aq)} \rightleftharpoons M(NH_3)^{2+}{}_{(aq)} + 2Cl^{-}{}_{(aq)} + 2H_2O_{(liq)}$$
(6)

$$M(NH_3)^{2+}_{(aq)} + 2Cl^{-}_{(aq)} + 2H_2O_{(liq)} + 2NaOH_{(aq)} \rightleftharpoons M(OH)_2(s) + 2NaCl_{(aq)} + NH_{3(aq)} + 2H_2O_{(liq)}$$
(7)

3.3.2. Structure Analysis of Recycled NCA

Next, the –OH precursors (P-HA, P-NA, P-SA) were processed to resynthesize NCA material which was mixed with LiOH (mol ratio = 1:1.03) and then calcined and sintered in a muffle furnace in order to obtain Recycled NCA material (denoted RNCA). The obtained RNCA types from various forms of –OH precursors (P-HA, P-NA, P-SA) were denoted RNCA-HA, RNCA-NA, and RNCA-SA.

The structures of RNCA were characterized using XRD. Figure 8 shows the XRD patterns of RNCA-HA, RNCA-NA, and RNCA-NA, which revealed that all samples are similar and a good fit to JCPDS #87-1562. These results show that the RNCA crystal phase is α -NaFeO₂ with a R3m space group. The explicit splits at I₀₀₆/I₀₁₂ and I₀₁₈/I₁₁₀ indicate the favorable hexagonal layered structure of RNCA.



Figure 8. XRD patterns of RNCA using different leaching agents.

The calculation of the lattice parameters from the XRD patterns is presented in Table 2. The lattice parameters show similar results for all samples. The values of c, a, and c/a from the RNCA samples are in accordance with those of NCA material from previous research on NCA synthesis [44,55,58,59]. The intensity ratio of the I_{003}/I_{104} peak identifies the degree of cation mixing in the NCA structures. Cation mixing is a phenomenon caused by the presence of Ni²⁺ ions in Li⁺ and Ni³⁺ lattices due to the similarity of their ionic size [51]. A higher intensity ratio of the I_{003}/I_{104} peak results in lower levels of undesired cation disorder. Based on Table 2, all samples have I_{003}/I_{004} greater than 1.2, indicating a low degree of cation mixing [44,55,59,60]. The ratio of c/a represents the degree of crystallinity and stability of the RNCA material [59,61]. RNCA-HA had the highest c/a ratio in the present study, implied high crystallinity of the material. This was probably due to the small amounts of residual product (NaCl) remaining in the P-HA sample after the co-precipitation process (see Equations (2)–(4)), influencing crystal formation during the sintering process. The previous research showed that the presence of salt (NaCl) could increase the crystallinity of the material [46], resulting in a better predicted charge–discharge performance [62].

Table 2. Lattice parameters of RN	CA
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Samples	Lattice Parameters		c/a	I002/I104	V (Å ³)
	a (Å)	c (Å)	_ •/•	-003/-104	V (2X)
RNCA-HA	2.8692	14.2857	4.9789	1.6102	101.8506
RNCA-NA	2.8630	14.2134	4.9645	1.7003	100.8947
RNCA-SA	2.8629	14.2278	4.9697	1.4458	100.9885

In order to calculate the values of the crystallite sizes of RNCA samples, the Debye–Scherrer Equation was used (Equation (5)), where D_p is the average crystallite size, λ is the X-ray wavelength (1.54178 Å), k is the Scherrer constant (0.9~1), *B* is the FWHM (Full Width at Half-Maximum) of the XRD peak, and θ is the XRD peak position.

$$D\mathbf{p} = \frac{\mathbf{k}\,\lambda}{B\cos\theta}\tag{8}$$

Figure 9 presents the crystallite size of all RNCA samples. From the figure, it can be seen that the crystallite sizes of RNCA-HA, RNCA-NA, and RNCA-SA were 23.27, 29.04, and 28.87 nm, respectively. It can be concluded that all of the RNCA samples had a small crystallite size.



Figure 9. Crystallite sizes of RNCA Samples.

The morphology of the RNCA samples was studied using SEM. The SEM images in Figure 10 show the morphology of all RNCA material at $1000 \times$ and $5000 \times$ magnifications. All RNCA material shows a sphere-like morphology and micro-sized secondary particles consisting of submicron primary particles. The average diameter of the primary particles is approximately 311~353 nm. However, the morphologies of the particles are heterogeneous and large amounts of aggregates are formed. This may be caused by the difficult precipitation of Al(OH)₃, which is confirmed by the K_{sp} data. This situation could inhibit the particle growth and spherical particle formation [58,63] which is responsible for the formation of aggregates.

3.3.3. Electrochemical Performance of Recycled NCA

After the RNCA materials were completely synthesized, for commercial applications, the final products of RNCA were tested using a full cell (18650-type of cylindrical battery) using graphite, celgard, and LiPF₆ as the anode, separator, and electrolyte, respectively; this cell was then analyzed using a NEWARE Battery analyzer and BTS software. Figure 11 shows the charge–discharge capacity of the RNCA material for voltages ranging from 2.7 to 4.2 V at 4 mA/g. The first cycles of the RNCA batteries were used for formation, and the coulombic efficiencies of the first cycle were 71.2% (Commercial NCA), 69.7% (RNCA-HA), 68.6% (RNCA-NA), and 68.2% (RNCA-SA). According to a previous study, the loss of discharge capacity in the first cycle may be caused by a local defect in the interlayer space during the de-lithiation process involving the oxidation of Ni²⁺ to Ni³⁺ in the 3a Li site and resulting in a capacity loss during the lithiation process [64]. However, the values of the coulombic efficiencies of RNCA samples in the first cycle are insignificantly different when compared to that of commercial NCA.



Figure 10. SEM images of RNCA material: (a,b) RNCA-HA; (c,d) RNCA-NA; (e,f) RNCA-SA.



Figure 11. Specific Discharge Capacity of all RNCA samples at 0.02 C.

From the charge–discharge curve at 4 mA/g, the discharge capacities of Commercial NCA, RNCA-HA, RNCA-NA, and RNCA-SA are 133.40, 124.156, 119.570, and 116.567 mAh/g, respectively; the values for recycled NCA are slightly different to that of commercial NCA. The highest specific discharge capacity measured in the present study was obtained by RNCA-HA. This result corresponds

to the XRD pattern of RNCA-HA which has the highest crystallinity, and this confirms that high crystallinity has a strong impact on the discharge capacity [59,62]. Compared with the P-02 and B-HT samples, resynthesis of RNCA via the hydrometallurgical route delivered better discharge capacities that were improved by more than 150% over that of heat treatment.

The results of ratability and cyclability tests on the RNCA-HA and commercial NCA are displayed in Figure 12. Ratability or rate performance was assessed by charging and discharging the battery cells at various rates. In this study, the battery cells were charged and discharged at 4, 20, 40, 100, and 200 mA/g. From the data in Figure 11, the results show that the specific capacities of RNCA-HA and Commercial NCA have similar ratability behaviors. The specific capacities of both samples slightly decrease from 4 to 200 mA/g; the capacity retentions at various rates are presented in Table 3. The capacity drops of RNCA-HA and commercial NCA from 4 to 200 mA/g are 27.4% and 25.2%, which are only slightly different. From the data in Table 3, the RNCA-HA has a larger capacity drop than commercial NCA, which may be caused by the large amount of aggregation of primary particles that formed in RNCA-HA. Based on the SEM images, some primary particles did not agglomerate into larger secondary particles. Loose submicron primary particles have a larger surface area and are reactive with electrolytes during the charge-discharge process, which could lead to side reactions forming a passivation surface [46,65,66] and cause a defect in the electrochemical performance. After being cycled at 200 mA/g, the cells were charged and discharged at 4 mA/g five times to prove the reversibility of Li-ion insertion and de-insertion. A slight capacity drop was observed in each sample. Overall, each battery was stable or exhibited a small capacity decrease from the 4 to 200 mA/g. Also, RNCA-HA showed a higher retention of capacity (96%) after 40 cycles at 100 mA/g than commercial NCA (93.4%) in a cycling test. It was confirmed that the high crystallinity of RNCA-HA influences the stability in electrochemical performance [59,62]. Both samples have high coulombic efficiencies of over 99%. Clearly, the electrochemical performance of RNCA-HA is comparable with that of commercial NCA in full cell testing.



Figure 12. Performance test of RNCA-HA: (a) Ratability; (b) Cyclability at 100 mA/g.

Samples	Capacity Retention (%)						
Samples	4 mA/g	20 mA/g	40 mA/g	100 mA/g	200 mA/g	4 mA/g	
RNCA-HA	100	94.2	85.9	82.7	72.6	99.2	
Commercial NCA	100	95.2	86.2	82.4	74.8	99.2	

Table 3. Capacity retention of RNCA-HA and commercial NCA at various rate.

4. Conclusions

The regeneration of a sphere-like-shaped NCA material was successful using a fast process that involved leaching and mixed metal hydroxide co-precipitation. HCl, H₂SO₄, and HNO₃ were used as the leaching agents. The highest leaching efficiency occurred when using HCl with a high solid loading rate, short processing time, and absence of reducing agent; the metal efficiencies were 99.8% for Ni, 95.6% for Co, and 99.5% for Al. The XRD patterns of all samples were similar and well indexed to JCPDS. SEM images showed loose submicron primary particles which influenced the electrochemical performance. RNCA-HA has the highest specific discharge capacity of 124.156 mAh/g with capacity retention of 95.988% after 40 cycles at 100 mA/g. Large amounts of aggregates on the morphology caused side reactions during the charge–discharge process, resulting in a slight defect on the ratability test. However, this approach is promising for adaptation to large-scale production considering the simple and efficient process for resynthesizing NCA material and that the performance is comparable with that of commercial NCA.

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