A Comparative Study of LiNCA Cathode Recycled from Spent Lithium-Ion Batteries and Synthesized from Metal Precursor

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Abstract: *Spent lithium NCA (LiNCA) battery was recycled using organic and inorganic acids and the performances were compared against the cathode synthesized from precursor. The metals in the spent cathode were leached using sulfuric or citric acid and coprecipitated into ternary metal oxalate (TMO) after reduction and lithium separation. Subsequently, the coprecipitated solution was used for cathode synthesis. Leaching efficiencies for nickel, cobalt and aluminum using citric acid were 85.6, 94.1, and 99%, respectively, while the efficiencies using sulfuric acid were 96, 98, and 100%, respectively. TMO produced from coprecipitation had the same physical characteristics. It was important to acknowledge that all cathodes also had similar physical characteristics. The electrochemical tests showed that commercial cathodes had the highest capacity of 150 mAh/g. This was followed by those from precursors, sulfuric acid leaching, and citric acid leaching, which recorded 142, 135, and 130 mAh/g, respectively. Based on the cycle test at 1C, the sample from citric acid leaching was 86% after 20 cycles compared to others at 82–83%. The results suggested that spent LiNCA could be regenerated into new cathodes using acid with performance comparable to those synthesized from precursor. This presented a viable alternative for LiNCA cathode synthesis.*

Keywords: *spent LiNCA; cathode; precursor; leaching; ternary metal oxalate*

■ INTRODUCTION

Lithium-ion batteries (LIBs) are increasingly in demand, leading to a higher need for the raw materials required in the production process. Many heavy metals discovered in spent LIBs are not only commercially valuable and naturally scarce but pose a risk of environmental contamination. Recovering these metals can lower the cost of new LIBs, reduce the extraction of minerals, and lessen dependence on specific suppliers [1-7]. Among the various spent LIBs, LiNCA ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) is one of the most developed and commonly used cathode methods materials. This type of battery is often used in electronic equipment and electric vehicles due to its high capacity [8-9]. Each tone of LiNCA cathode material contains 72.2, 488.7, 92.0, and 14.1 kg of Li, Ni, Co, and Al, respectively, with a combined economic value estimated at USD 13,700 [4]. As a variant of lithium nickel oxide (LNO), the material is co-doped with the metal Al and cobalt Co, enhancing thermal and electrochemical characteristics as well as stability [10-11]. It is favored for high-power applications, such as hybrid electric vehicles, due to substantial power capability and large capacity [12-13]. During the battery charging, aluminum (Al^{3+}) remains electrochemically inactive while nickel (Ni^{4+}) and cobalt (Co^{4+}) oxidize sequentially. The thermal stability is evident, with an exothermic point and a significantly greater O_2 evolution compared to $LiNiO_2$ (LNO = 200 °C; LiNCA = 31 °C) [11].

LiNCA cathode can be manufactured using the solid-state method, which typically includes synthesizing ternary metal oxalate (TMO) from a precursor [14-16]. Ni-sulfate, Co-sulfate, and Al-sulfate were dissolved in hot water with a molar ratio of 80:15:5, followed by the addition of excess oxalic acid to precipitate NiCoAl-oxalate. TMO was then separated, dried, and reacted with lithium carbonate (Li_2CO_3) or lithium hydroxide (LiOH) to produce LiNCA cathode.

Hydrometallurgy, which consists of three stages, namely preparation (pre-treatment), metal extraction (reduction and leaching), and product manufacturing (precipitation and reaction), was used to recover Ni, Co, and Al [17-19]. During pre-treatment, the anode and cathode were separated from other components in LIBs, changing the compound's structure into metal, metal oxide, and Li_2CO_3. The reduction was conducted by adding a carbon-containing material (lignite, acetylene black, or another) as a reducing agent and heating the mixture in a furnace at 750 °C for 6 h [20-24]. The reduced cathode was then leached serially with carbonated water to selectively extract Li_2CO_3 [25-30], followed by acidic solution leaching of Ni, Co, and Al. Different kinds of acids, such as inorganic (HCl, H_2SO_4, and HNO_3) or organic acids (citric acid, oxalic acid, and lactic acid), could be adopted as solvent for the process [17,20,31-35]. The final recovery step was precipitation or co-precipitation with the addition of a chelating agent (ammonia, oxalic acid, and others). Precipitation was used when metal salts were the end product [36-37], while co-precipitation was adopted [38-41] when the process was intended for cathode production. Excess of oxalic acid as a chelating agent facilitated co-precipitation, leading to the formation of TMO. Oxalates were separated from the filtrate, dried, and calcined at 450 °C for 6 h to form TMO, which served as a precursor for producing NCA cathodes.

Previous studies on recycling LIBs did not include the recovery of Li metal, leading to the continued use of new sources, such as LiOH or Li_2CO_3, in the manufacture of subsequent batteries. However, this study incorporates the recovery of Li_2CO_3 spent cells. It also provided new information on the use of spent anodic material, a practice rarely documented in battery recycling processes. In this study, LiNCA-type LIBs were recycled through a leaching process comprising sulfuric and citric acid. This process followed the reduction of the spent cathode by the spent anode as a reducing agent, with Li recovery achieved using carbonated water. Furthermore, the leaching solution was coprecipitated into TMO using oxalic acid. Cathode synthesis was conducted by lithiation between TMO and Li_2CO_3, part of which was obtained from Li recovery. For comparative purposes, the cathode was also synthesized using precursor materials of Ni-sulfate, Co-sulfate, and Al-sulfate. The performance of the cathode was then compared with the commercial counterpart. The results of this study are expected to contribute to reducing the potential for environmental pollution due to the increasing number of spent LIBs and decrease the cost associated with the production of batteries.

This study was conducted on a laboratory scale using LiNCA type of LIBs. Technical citric and sulfuric acids were adopted, representing organic and inorganic acids. The spent anode from the LiNCA battery served as the reducing agent. The reference cathode was synthesized from Ni-sulfate, Co-sulfate, and Al-sulfate precursors, all of which were technical materials, in addition to commercial LiNCA cathodes. Electrochemical testing was limited to charging-discharging capacity at 0.1 C (20 mA/g) and cycle testing at a constant discharging rate of 1 C (200 mA/g). The recycling study was conducted using hydrometallurgy, which produces hazardous acid waste fluid. Previous reports have outlined issues such as freshwater contamination and terrestrial acidification associated with this method. To mitigate environmental impact, acid waste needs to be treated to prevent further pollution of water sources. Additionally, to prevent accidents during the study, it is crucial to handle the corrosive acid and use LIBs carefully due to the contents of hazardous substances such as poisonous electrolytes or residual electrical components.

■ EXPERIMENTAL SECTION

Materials

The 18650 cylinder cells of spent NCA batteries were provided by the Center of Excellence for Electrical Energy Storage (CE-FEEST), Universitas Sebelas Maret, in cooperation with PT. Pertamina, and used as raw material. The spent batteries were characterized to determine the composition. In this study, the reagents used included 2 M NaOH (Merck, Darmstadt, Germany), N_2 and CO_2 gas (Aneka Gas Industri, Jakarta, Indonesia), citric acid and sulfuric acid (PT. Atlantik Sejahtera Raya, Banten-Indonesia), oxalic acid (YC Chemicals Ltd., China), Li_2CO_3 (Merck Darmstadt, Germany), EN grade nickel sulfate hexahydrate (Zenith, Brazil), cobalt sulfate heptahydrate (Rubamin, India), as well as aluminum sulfate octadecahydrate (Mahkota, Indonesia). Additional materials included polyvinylidene difluoride (PVDF; MTI, USA), acetylene black (AB; MTI, Richmond, CA, USA), *N*-methyl-2-pyrrolidone (NMP, MTI, USA), anode sheet (Graphite, MTI, America), cathode sheet (Al foil, MTI, America), Celgard separator (MTI, America), and commercial LiNCA cathode (Sichuan Brivo Lithium Materials, Sichuan, China). Demineralized water was used for battery discharging, cathode leaching, dissolving reagents, and preparing samples for characterization.

Instrumentation

This study adopted several instruments for comprehensive analysis. X-ray diffraction (XRD, Bruker D8 advance) was performed using Cu Kα radiation at a diffraction angle of 10–80°, wavelength of 1.4506 Å, and increments of 0.02°. Fourier transform infrared spectrum (FTIR; IR-Spirit Shimadzu FTIR spectroscope, Shimadzu, Kyoto, Japan) of the sample was measured using the Q-ATR method at a wavenumber range of 400–4000 cm^{-1}. To determine the metal concentration, atomic absorption spectroscopy (AAS, Thermo Scientific ICE 3500) was conducted, using the flame method with pure acetylene (C_2H_2) and O_2 as fuel and oxidant, respectively. Scanning electron microscopy (SEM, JCM-7000 JEOL, Tokyo, Japan) examination was conducted at an electron potential of 10 kV. NETWARE Battery analyzer (China) was used to evaluate the electrochemical performance of batteries using a galvanostatic charge-discharge test conducted at a constant temperature.

Procedure

Reduction of spent cathode and separation of Li content

Cathode and anode films were separated from the other components following the disassembly of the spent LIBs. To separate the cathode from its Al sheet, a solution of 4 M NaOH (Merck, Darmstadt, Germany) was used, while hot water was applied to extract the anode from the Cu sheet. The separated materials were then dried in an oven at 60 °C for 6 h. The dried cathode and anode were mixed in a ratio of 80:20, crushed, and heated in a furnace running N_2 at 700 °C for 6 h. Subsequently, XRD was performed to examine the changes in the composition and crystalline structure of each reduced spent cathode.

Li content in the reduced cathode was separated by a carbonated water leaching process in a 1 L three-neck flash glass equipped with a mechanical stirrer. The set included placing 500 mL of water and 50 g of reduced cathode inside the neck flash, before supplying 4 L of CO_2 gas per min by a high-pressure CO_2 gas cylinder equipped with a flowmeter. Carbonated water leaching was conducted at the surrounding temperature for 150 min. After leaching, the residual reduced cathode was filtered from the filtrate. The solid was analyzed using XRD to ensure the disappearance of the Li_2CO_3 peak. Meanwhile, FTIR was adopted to determine whether the transmittance of the compound had disappeared. The filtrate was then evaporated to obtain precipitated Li in the form of Li_2CO_3.

Leaching Ni, Co, and Al and dissolving precursors

Following the selective leaching of Li, the remaining reduced cathode was leached to recover the contents of Ni, Co, and Al. This process included placing a 1.5 M citric acid solution with 5% v/v of H_2O_2 in a 1000 mL three-neck flash glass. The solution was stirred mechanically, containing a 500 mL solution of 1.5 M citric acid and 20 g of solid Li-leaching residue. Before adding 75 mL of H_2O_2, the liquid was stirred and heated to 80 °C using an electric heater. Leaching occurred at 80 °C and standard atmospheric pressure for 150 min. Subsequently, the residual material was removed by filtration, and the filtrate was analyzed using AAS to determine the concentration of Ni, Co, and Al. The same experiment was conducted by replacing the 1.5 M citric acid solution with a 1.5 M sulfuric acid solution. The results helped in understanding the differences in leaching efficiency and the characteristics of the precursors and cathodes produced.

The metal precursors were aluminum sulfate octa decahydrate, cobalt sulfate heptahydrate, and nickel sulfate hexahydrate. A glass beaker containing 1.0 M of an 80:10:5 molecular ratio of Ni:Co:Al solution was heated to 60 °C for 30 min while continuously stirring.

Co-precipitation of TMO

An excess of oxalic acid was dissolved into the filtrate of leaching and/or precursor solution. The mixture was vigorously agitated at 80 °C for 2 h until a bright green precipitate of TMO appeared. It was then left for 4 h to allow a complete precipitation before separating the precipitate from the filtrate. Following drying, all TMO was examined using XRD to identify the compounds present in the diffraction pattern as well as their intensities. FTIR was adopted to detect the presence of specific compounds based on transmittance, while SEM was used to examine the structure of TMO particles.

Synthesis of NCA cathode material

NCA cathode material was prepared through a solid-state reaction between Li_2CO_3 and each TMO produced by coprecipitation with a molar ratio of 1.05:2 in a tubular quartz furnace containing pure oxygen. High-temperature calcination was performed at 450 °C for 6 h, before sintering at 700 °C for 12 h came next. The resulting LiNCA was ground, sieved through a 100-mesh screen, and stored in an oven until further usage. Physical examination was conducted using XRD to determine the compounds present and their intensities, while FTIR was adopted to identify specific chemicals based on transmittance. The morphology of the material was examined using SEM, and the results were compared with those of commercial NCA. For electrochemical testing, both the synthesized LiNCA and commercial NCA were evaluated in type 18650 cylindrical cells. The LiNCA was mixed with AB and PVDF in a mass ratio of 92:3:5. This mixture was dissolved in NMP to form a homogeneous slurry, which was applied onto 200 μm-thick aluminum foil using the doctor blade method. Subsequently, the coated foil was dried overnight in a vacuum oven at 80 °C. The same procedure was followed to fabricate both the LiNCA cathode and the anode sheet. To assemble a battery jelly roll, the anode and cathode were compressed separately and rolled together with a Celgard separator. An approximate 1:1.15 ratio was ensured between the anode and cathode capacity. The positive cap was soldered after the jelly roll was placed inside the cylindrical cell. After filling the electrolyte ($LiPF_6$), the cell was aged in an Ar-filled glove box for a day. The entire cell performance was examined using the NEWARE battery analyzer. The current density was set to 20 mA/g (0.1 C), with a voltage range of 2.7–4.3 V.

■ RESULTS AND DISCUSSION

Reduction of the Spent Cathode of NCA and Li Leaching

By combining the cathode and anode in an 80:20 ratio and heating to 700 °C for 4 h, the structure of the cathode was changed. During reduction, the chemical structure of the cathode was modified, as shown in Eq. (1-5) [27].

$$C + 12LiMO_2 \rightarrow 6Li_2O + 4M_3O_4 + CO_2 \quad (1)$$

$$C + 4LiMO_2 \rightarrow 2Li_2O + 4MO + CO_2 \quad (2)$$

$$C + 2M_3O_4 \rightarrow 6MO + CO_2 \quad (3)$$

$$CO_2 + Li_2O \rightarrow Li_2CO_3 \quad (4)$$

$$C + 2MO \rightarrow 2M + CO_2 \quad (5)$$

XRD testing was performed on the spent cathode to observe structural changes both before and after reduction, as shown in Fig. 1. According to the XRD pattern, the peaks of the spent cathode resembled those of the Joint Committee on Powder Diffraction Standards (JCPDS) reference of NCA, while the reduced cathode

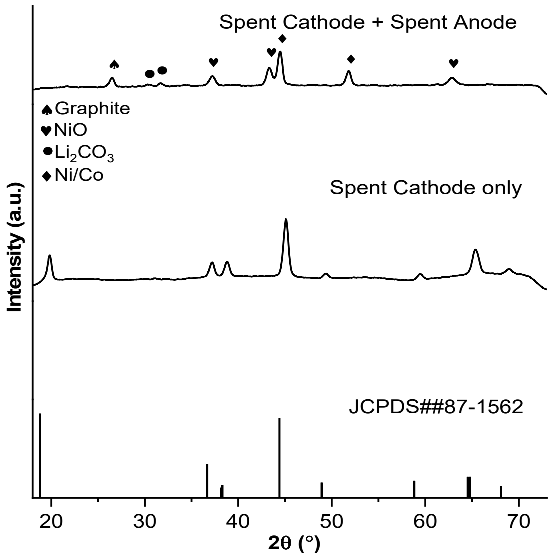


Fig 1. XRD pattern of reduced spent cathode of LiNCA with an anode-reducing agent

appeared to have some distinct peaks. This suggested the disappearance and appearance of certain and new peaks when the spent cathode was reduced by heating and the addition of an anode as a reducing agent. The observations signified a structural change in spent LiNCA during the reduction process. After reduction, new peaks were formed at 2θ of 43 and 51°, featuring the existence of metals Ni and Co, as well as Al at 2θ of 43°. A small peak in the region 2θ of 20–35° suggested the formation of $LiAlO_2$ and Li_2CO_3. The other comparable study that used lignite as a reducing agent supported the results, showing the conversion of Ni, Co, and Al to a metallic state. The reduction process also led to the formation of Li_2CO_3 and $LiAlO_2$. Li present in these compounds facilitated selective leaching with carbonated water [41].

Li_2CO_3 was selectively leached at a high liquid-solid ratio due to its poor solubility. The solubility of the compound was 13.3 g/L at 20 °C and dropped as the temperature increased [37]. According to Yi et al. [42] carbonated water leaching was carried out using Eq. (6-11) as follows;

$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} \quad (6)$$

$$H_2CO_{3(aq)} \rightleftharpoons HCO_3{}^-{}_{(i)} + H^+{}_{(i)} \quad (7)$$

$$Li_2CO_{3(s)} + H^+{}_{(i)} \rightleftharpoons 2Li^+{}_{(i)} + HCO_3{}^-{}_{(i)} \quad (8)$$

$$Li^+{}_{(i)} + HCO_3{}^-{}_{(i)} \rightleftharpoons LiHCO_{3(aq)} \quad (9)$$

$$Li_2CO_{3(s)} + H_2CO_{3(aq)} \rightleftharpoons 2LiHCO_{3(aq)} \quad (10)$$

A three-phase solid-liquid-gas reaction occurred during carbonated water leaching;

$$Li_2CO_{3(s)} + H_2O_{(aq)} + CO_{2(g)} \rightleftharpoons 2LiHCO_{3(aq)} \quad (11)$$

After the leaching procedure, filtering was utilized to remove the residue from the solution. The residue was then dried in an oven while the filtrate was subjected to precipitation. Compared to the cathode before leaching, the resultant residue was analyzed using XRD and FTIR spectroscopy, as shown in Fig. 2. Before leaching, peaks corresponding to Li_2CO_3 appeared in the reduced cathode. Fig. 2(a) showed that the peaks disappeared from the XRD pattern of reduced LiNCA after water leaching, leaving those of other components unchanged.

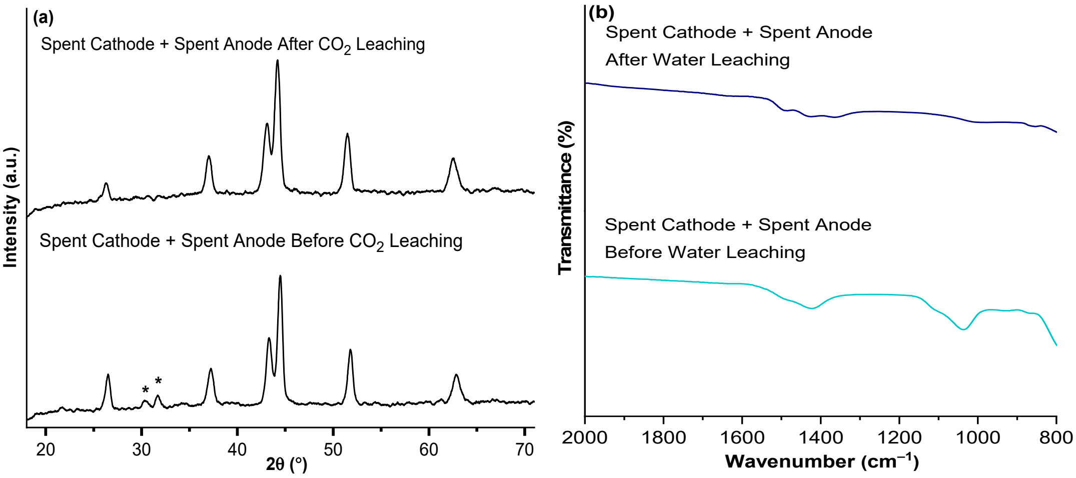


Fig 2. Test on the reduced cathode of spent NCA before and after carbonated water leaching: (a) XRD pattern (b) FTIR spectra

As shown in Fig. 2(b), FTIR analysis also played a role in the disappearance of Li_2CO_3 from the residue. This graphic showed how the transmittance of the $-CO_3$ functional groups vanished on the decreased cathode due to water leaching.

Leaching of Ni, Co, and Al Using Citric Acid and Sulfuric Acid

Metals of Ni, Co, and Al were leached simultaneously using both citric and sulfuric acid, and the results are presented in Table 1. The leaching results showed that using sulfuric acid increased the effectiveness of metal leaching in spent LIBs. The leaching efficiency was 96, 98, and 100% for Ni, Co, and Al metals, respectively, while citric acid provided an efficiency of 86.94 and 99%, as confirmed by earlier studies. When sulfuric acid was adopted as a leaching solvent, the recovery of metals was above 95% for Ni [17] and ranged from 86–99%, for Ni, Co, and Al [43], respectively. Adopting a reducing agent for the spent anode and sulfuric acid for leaching the spent MNC-type cathode led to recoveries of 99, 97, and 99%, for Ni, Mn, and Co, respectively [44]. In contrast, citric acid provided efficiencies of Ni 98%, Co 91%, and Mn 99% [17].

When H_2O_2 was present, metallic metals such as Ni and Co were oxidized and became metal oxide through the reactions of Eq. (12) and (13) [45];

$$Ni_{(s)} + H_2O_{2(aq)} \rightarrow NiO_{(s)} + H_2O \tag{12}$$

$$Co_{(s)} + H_2O_{2(aq)} \rightarrow CoO_{(s)} + H_2O \tag{13}$$

The following mechanism caused metal oxide to dissolve in either sulfuric or citric acid solution, as shown in Eq. (14-16) [46];

$$2H_2O_{2(aq)} + 4H^+_{(aq)} + 4e^-_{(aq)} \rightarrow 4H_2O_{(aq)} \tag{14}$$

$$4C_6H_8O_{7(aq)} \rightarrow 4H^+_{(aq)} + 4\left(C_6H_7O_7\right)^-_{(aq)} \tag{15}$$

$$\begin{aligned} 4\left(C_6H_7O_7\right)^-_{(aq)} + NiO_{(s)} \rightarrow 4\left(C_6H_7O_7\right)_2 Ni_{(aq)} \\ + \frac{1}{2}O_{2(g)} + 4e^- \end{aligned} \tag{16}$$

The overall reaction was shown in Eq. (17);

$$\begin{aligned} 2NiO_{(s)} + 4C_6H_8O_{7(aq)} + 2H_2O_{2(aq)} \\ \rightarrow 2\left(C_6H_7O_7\right)_2 Ni_{(aq)} + 4H_2O + O_2 \end{aligned} \tag{17}$$

The following were the reactions of other metal oxides in Eq. (18) and (19);

$$\begin{aligned} 2CoO_{(s)} + 4C_6H_8O_{7(aq)} + 2H_2O_{2(aq)} \\ \rightarrow 2\left(C_6H_7O_7\right)_2 Co_{(aq)} + 4H_2O + O_2 \end{aligned} \tag{18}$$

$$\begin{aligned} Al_2O_{3(s)} + 6C_6H_8O_{7(aq)} + 2H_2O_{2(aq)} \\ \rightarrow 2\left(C_6H_7O_7\right)_3 Al_{(aq)} + 5H_2O + O_2 \end{aligned} \tag{19}$$

Co-precipitation of TMO and Its Characterization

After Ni, Co, and Al were leached, the filtrate was treated with TMO (NCA oxalate) coprecipitation. This process includes an additional oxalic acid chelating agent to create NCA oxalate, which was precipitated and filtered [47]. Fig. 3 presents the results of XRD and FTIR testing on TMO, while Fig. 4 shows the results of SEM testing.

XRD peaks shown in Fig. 3(a) for all TMOs correspond to nickel oxalate dihydrate and are in line with results from earlier studies. JCPDS nickel oxalate and TMO generated by precursor coprecipitation, citric acid, and sulfuric acid leaching had identical peaks at all 2θ. This suggested that the three TMOs had similar characteristics. Fig. 3(b) showed the infrared absorption pattern in FTIR, which verified the presence of oxalate. The O–C–O group, with visible vibrations at wavelengths of 1,300 and 1,635 cm^{-1}, was identified as the source of this pattern. Furthermore, the wavelength of NCA oxalate was approximately 3,400 cm^{-1}, signifying the presence of hydrate crystals with OH/H_2O groups. Each of the three TMOs had the same absorption pattern and

Table 1. AAS test results on the cathode leaching solution for spent NCA (Ni, Co, and Al content in spent LIBs 3552, 346.5, and 250 ppm)

No.	Leaching agent	Volume (mL)		Solid (g)	Concentration (ppm)			Leaching efficiency (%)		
		Acid solution	H_2O_2		Ni	Co	Al	Ni	Co	Al
1.	Citric acid 1.5 M	500	10	20	3440	425	245.1	85.6	94.1	99.0
2	Sulfuric acid 1.5 M	500	10	20	3938	442	249.5	96.0	98.0	100

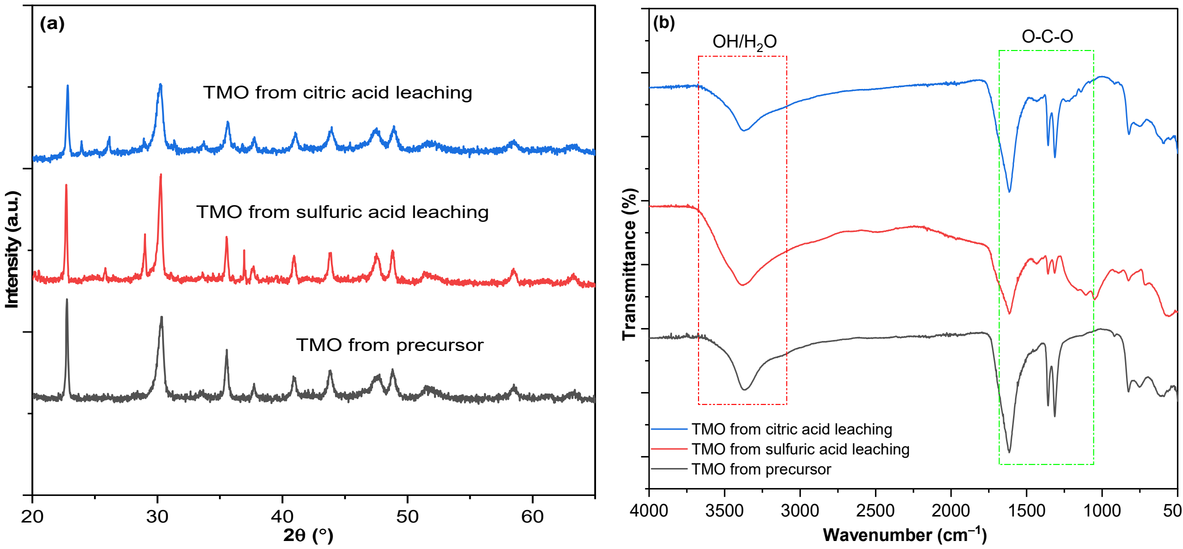


Fig 3. Comparison of (a) XRD patterns and (b) FTIR spectra of TMO from leaching using citric acid, sulfuric acid, and precursor

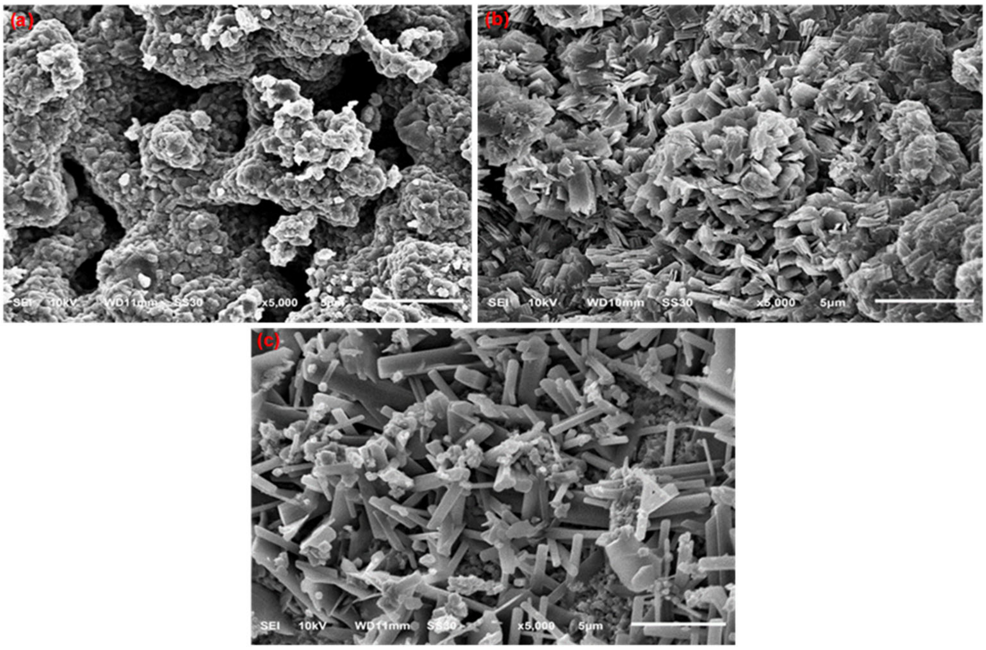


Fig 4. SEM test results on TMO (NCA oxalate) coprecipitation results (a) citric acid leaching, (b) sulfuric acid leaching, and (c) precursor

were crystals of NCA oxalate hydrate. TMO SEM test results are presented in Fig. 4, and particles with pseudo-spherical appearance and an estimated size of 5 µm were observed in all TMO, either obtained from leaching solution using citric and sulfuric acid or from precursor solution. However, rapid crystallization during precipitation caused the particles to agglomerate.

Synthesis of LiNCA and Its Characterization

Physical characteristic of LiNCA

LiNCA cathodes were produced using all TMOs, whether derived from leaching or precursors. To complete the synthesis, TMO and Li_2CO_3 formed a solid reaction with a mole ratio of 1.05:1. The mixture was ground into a fine powder in a ball mill, then exposed to oxygen gas and heated (sintering) at 800 °C for 15 h and calcined at 450 °C for 6 h. The final result is LiNCA cathode, which was ground, sieved, and dried at 60 °C using a mesh size of 100. Subsequently, the cathode was subjected to physical characterization using XRD, FTIR, and SEM as well as electrochemical testing with a battery analyzer to determine its capacity and life cycle. XRD, FTIR, and SEM tests were performed to compare NCA generated by leaching with citric and sulfuric acids to that synthesized from precursors. Fig. 5 and 6 show the physical test results of the obtained cathode.

Based on Fig. 5(a), XRD analysis of NCA cathode, utilized as a reference (JCPDS 87-1562), showed identical peak strength and 2θ. This proved that all three cathodes had similar LiNCA compositions with comparable crystallinity and structural characteristics. Fig. 5(b) showed that FTIR analysis confirmed the presence of carbonate species in all cathodes, attributed

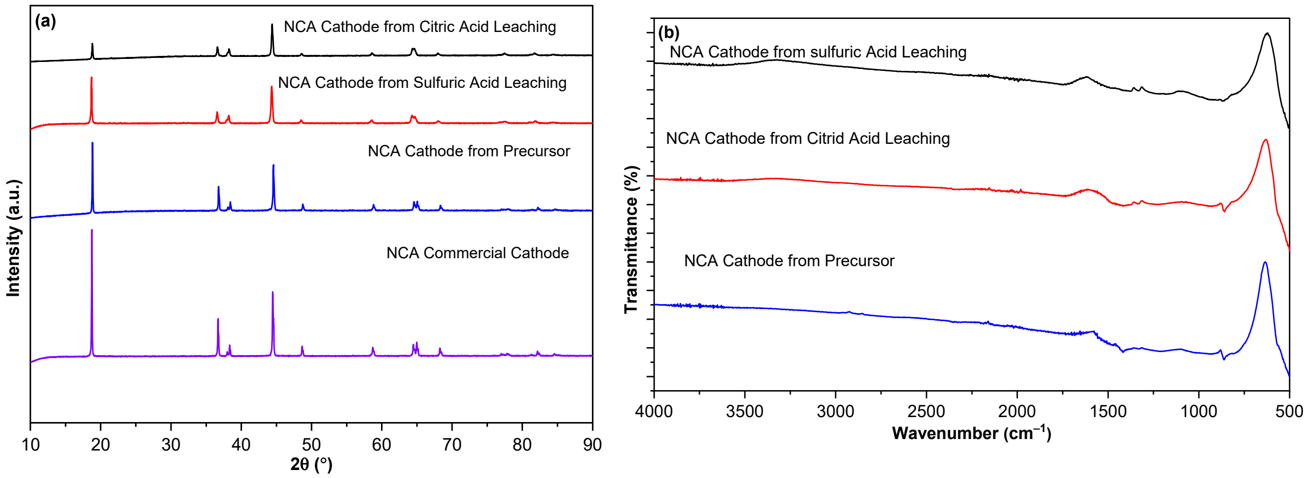


Fig 5. Comparison of (a) XRD patterns and (b) FTIR spectra of NCA cathode from leaching using citric acid, sulfuric acid, and from precursor

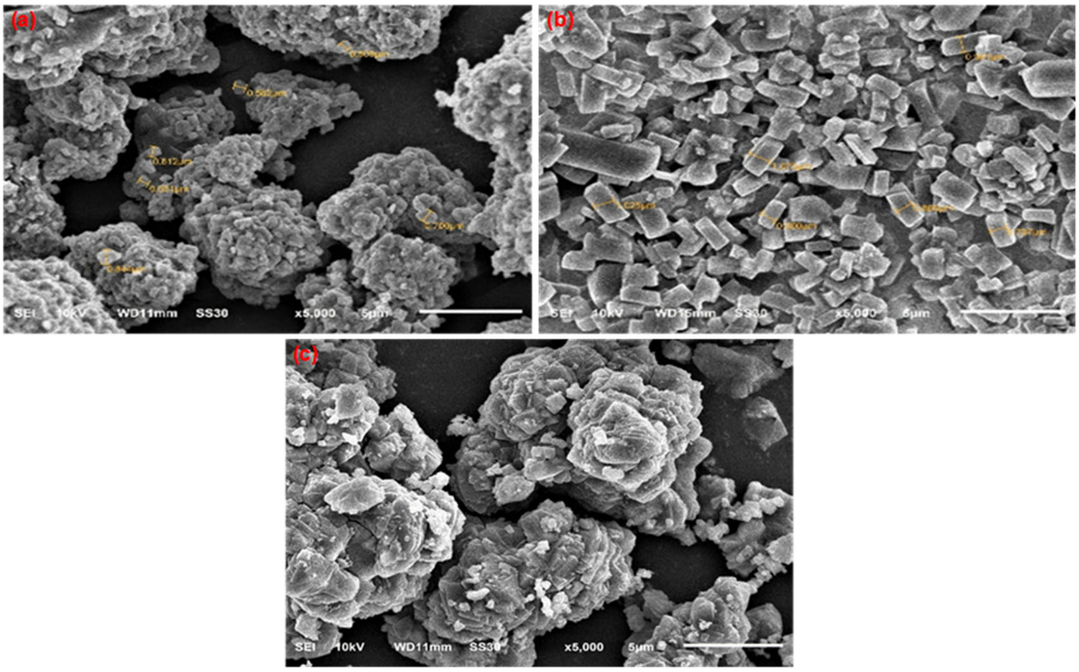


Fig 6. SEM test results on NCA cathode obtained from (a) citric acid leaching, (b) sulfuric acid leaching, and (c) precursor

to surface-resident Li_2CO_3 residues. The presence of these carbonated groups on the surface of the material may lead to unfavorable interactions with the electrolyte.

The morphological properties of the three NCAs are presented in Fig. 6, according to the results of the SEM test. Larger secondary particles, averaging 6–10 µm in size, were typically present in all investigated cathodes. These particles aggregate from source particles that were sub-micron-sized. The disintegration of TMO at high temperatures led to the quasi-porous form of secondary particles, potentially causing losses of approximately half of the mass.

Electrochemical performances of LiNCA cathode

LiNCA electrochemical testing was conducted in a cylindrical cell of type 18650. Its material was dissolved in water alongside PVDF binder and AB as a conductive agent, at a mass ratio of NCA:AB: PVDF 92:3:5. The mixture formed a homogeneous slurry which was applied 200 µm thick onto aluminum foil and allowed to dry in a vacuum oven at 80 °C over the night. The same electrode production process was used to create both the LiNCA cathode and the anode sheet. Anode and cathode electrodes are rolled together, separated by a Celgard, to form a battery coil. Furthermore, the capacity ratio between the anode and cathode was maintained at 1:1.15. After being coiled, the electrodes were inserted into cylindrical cells, and the coils were soldered to positive caps. The electrolyte ($LiPF_6$) was added to a glove box under an argon gas environment to prevent contamination. Complete cell performance was investigated using China's NEWARE battery analyzer, with a current density of 20 mA/g (0.1 C) in a voltage range of 2.7–4.3 V. The results of battery capacity testing on NCA cathode synthesized from leaching spent LIBs, precursors, and commercial NCA are shown in Fig. 7 and 8.

The charge-discharge curve for each NCA cathode in an NCA/graphite cell at 0.1 C (20 mA/g) of current is shown in Fig. 7. Specific discharge capacity (SDC) can be obtained with a coulombic efficiency of approximately 80–82% and specific charge capacity (SCC) ranging from 140 mAh/g (NCA resulting from leaching citric acid) to 160 mAh/g (commercial NCA). Commercial NCA cathodes were the most capable in terms of capacity of 150 mAh/g. This was followed by NCA from precursors (142 mAh/g), sulfuric acid (135 mAh/g), and citric acid leaching (130 mAh/g). The low columbic efficiency could be attributed to the formation of SEI in

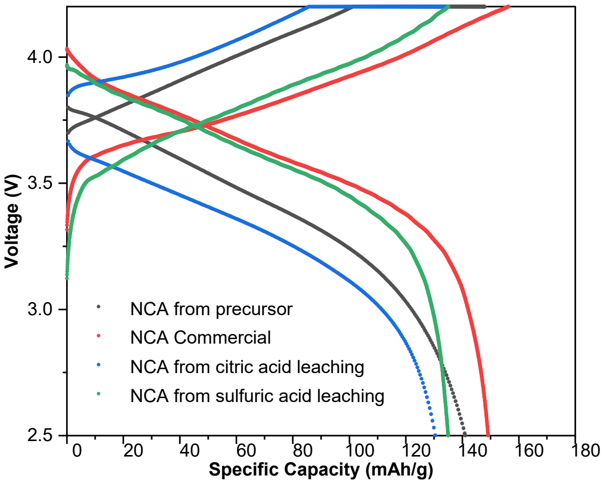
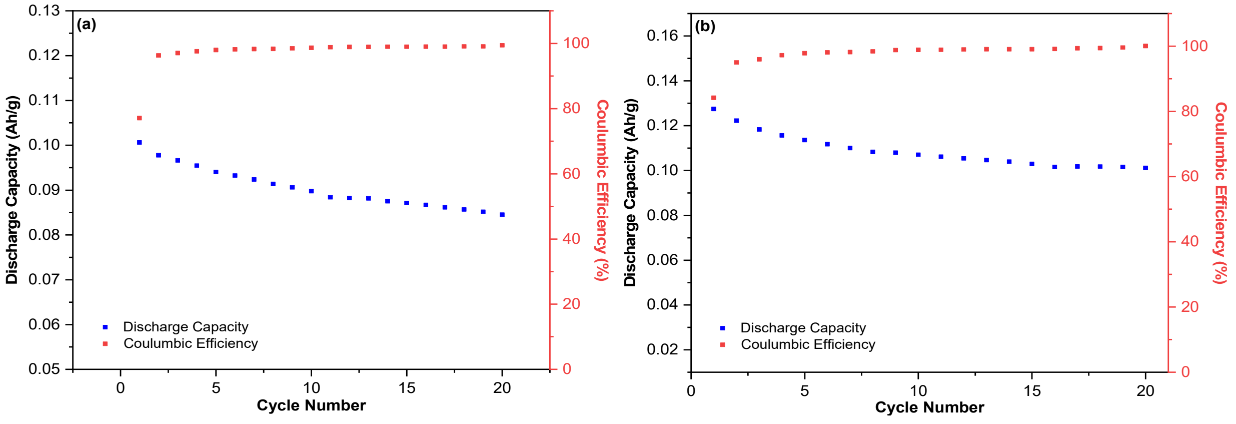


Fig 7. Performance of electrochemistry features of the charging-discharging capacity on NCA (at a voltage of 2.7–4.3 V and a current of 20 mA/g (0.1 C)



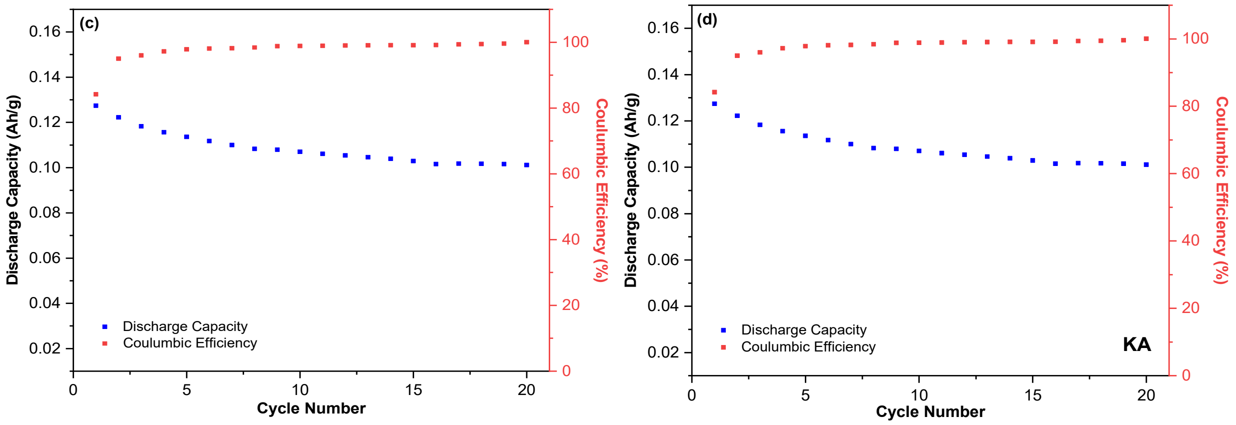


Fig 8. The charging-discharging cycle's performance characteristics on NCA are derived from (a) citric acid leaching, (b) sulfuric acid leaching, (c) precursor, and (d) commercial. The current used in the cycle is 200 mA/g (1 C)

the anode material, CEI in the cathode material, as well as the side reaction between Li_2CO_3 and electrolyte which is in line with the FTIR result [42-43]. The highest capacity was discovered in commercial NCA cathodes, followed in order of highest capacity by NCA from precursors, as well as sulfuric and citric acid leaching, respectively. All of the acquired NCA had good capacity and remained in the allowable range. Many factors, such as variations in the leaching efficiency of Ni, Co, and Al, can lead to variances in the composition of TMO and NCA obtained. These factors could also create discrepancies in NCA capacity from different sources. NCA capacity from the precursor was slightly higher than that resulting from leaching, ensuring an ideal composition for LiNCA cathode. This was possible because the solution composition of precursors can be changed to fully satisfy the Ni:Co:Al mole ratio of 80:15:5. Commercial NCA is made from precursors and has a flawless composition. It also has consistent manufacturing circumstances and a slightly higher capacity than other cathodes. LIBs obtained from citric acid leaching had a slightly lower capacity compared to those from sulfuric acid leaching. This difference is due to the lower Ni composition achieved through citric acid leaching, which had an efficiency of 86%. As previously observed, Ni metal is a capacity contributor, the greater the content in the cathode the greater the LIB capacity. Meanwhile, Co and Al function as cycle and thermal stabilizers, respectively [48-49].

Fig. 8 shows the results of the cycle test, conducted 20 times with charging and discharging at a current of 1 C (200 mAh/g). According to the data, DC gradually lowers as the number of cycles increases. For commercial NCA cathodes, as well as those synthesized from precursor and sulfuric acid leaching, the cycle performance at 1 C had a capacity retention of 84% and an initial capacity of 102–130 mAh/g after 20 cycles. Meanwhile, NCA from citric acid leaching yields a retention of 86% of 102 mAh/g. Despite having the lowest capacity, citric acid leaching had a greater cycle capability. This is due to the possibility that a higher ratio of Co, results from its more efficient leaching than Ni. Co-metal is recognized as a stabilizing element in the NCA cathode. Compared to other cathodes, commercial NCA had a slightly higher capacity due to consistent manufacturing circumstances. The performances (capacity and cycles) obtained were well confirmed and in line with previous studies [44-46].

This study provides good results for recycling used LIBs and can be considered promising for the sustainability of LIB technology. Despite being limited to LiNCA type, the same method can be applied to oxide-structured LIBs such as lithium nickel manganese cobalt oxide (NMC), lithium cobalt oxide (LCO), and lithium manganese oxide (LMO) [39,50-53]. For lithium iron phosphate (LFP)-type LIBs with different structures, adjustments to the recycling method are necessary [54].

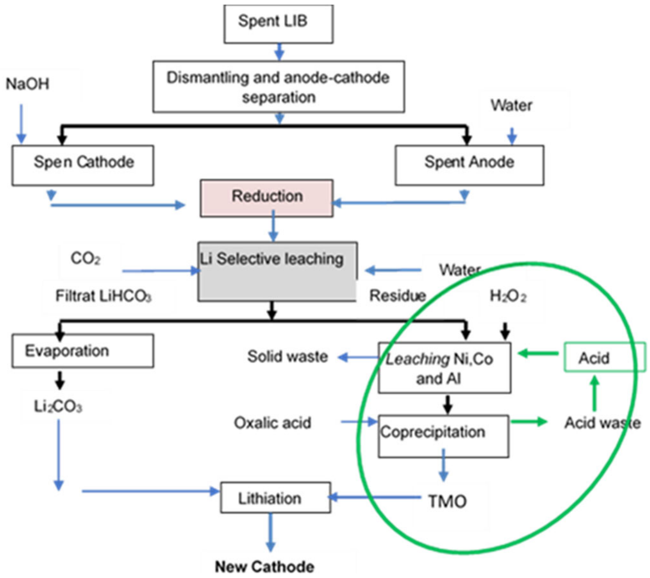


Fig 9. The schematic of the study using acid in a cyclic manner for recycling LIBs

Additionally, the hydrometallurgy method can be extended to metal recovery from non-LIB materials such as spent catalysts and electronic waste [55-56].

The results showed that spent LiNCA was regenerated into new cathodes using citric acid or sulfuric acid. The performance achieved was comparable to cathodes synthesized from precursors. This suggested a viable alternative for LiNCA synthesis. In this study, the use of technical materials also facilitated scaling up to a larger production level. The recycling method must be adjusted to produce satisfactory results because different lithium-ion battery types have distinct chemicals and molecular structures.

The high consumption of acid during the recycling of LIBs significantly increased costs and led to the generation of hazardous acid waste. However, this liquid acid waste had the potential to be repurposed as a leaching agent. Further study was directed to adopt it in subsequent leaching processes or use the acid leaching agent cyclically, as shown in Fig. 9. This was expected to reduce acid usage and acid waste production.

■ CONCLUSION

In conclusion, this study showed that the leaching efficiencies with citric acid were 85.6, 94.1, and 99% for Ni, Co, and Al, while sulfuric acid achieved efficiencies of 96, 98, and 100%, respectively. All TMO obtained from oxalic acid coprecipitation had the same physical characteristics as confirmed by XRD, FTIR, and SEM tests. Physical testing on the cathodes synthesized from the three TMOs also confirmed similar physical characteristics. However, the electrochemical test results showed slightly different results. In terms of capacity, commercial cathodes had the highest capacity of 150 mAh/g. This was followed by those synthesized from precursors, sulfuric acid leaching (135 mAh/g), and citric acid leaching (142, 135, and 130 mAh/g). From the cycling capability at a discharge rate of 1 C, the cathode from leached citric acid was the best at 86% after 20 cycles compared to others at 82–83%. The results of the new LiNCA regenerated from spent LIB through hydrometallurgy using citric acid or sulfuric acid showed good performance. The performance achieved was comparable to cathodes synthesized from precursors. This suggested a viable alternative for LiNCA synthesis.

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■ CONFLICT OF INTEREST

There is no conflict to declare.

■ AUTHOR CONTRIBUTIONS

Conceptualization: Arif Jumari, Agus Purwanto; Data curation: Cornelius Satria Yudha, Arif Jumari; Formal analysis: Agus Purwanto, Cornelius Satria Yudha; Investigation: Arif Jumari, Cornelius Satria Yudha, Enni Apriliani; Methodology: Arif Jumari, Agus Purwanto, Cornelius Satria Yudha; Project administration: Arif Jumari; Supervision: Agus Purwanto, Wara Dyah Pita Rengga, Anne Zulfia Syahrial; Validation: Arif Jumari, Agus Purwanto; Visualization: Cornelius Satria Yudha, Enni Apriliani;

Writing - original draft, Arif Jumari; Writing - review and editing, Agus Purwanto, Anne Zulfia Syahrial, Wara Dyah Pita Rengga.

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