A Reductive Pre-Treatment to Improve NCA Cathode Material Hydrometallurgical Recycle Process

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Abstract. NCA or LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (NCA) Battery is one lithium ion batteries (LIBs) that is often used in electric vehicles as an energy storage device due to its high capacity and energy density. Along with the popularity of electric vehicles, the production of NCA cathode materials has also increased so resulting in accumulation of LIBs waste in the future. The purpose of this study is to recycle NCA via hydrometallurgical route. The effect of reducing agent addition during the pretreatment process was investigated. Stearic acid, oxalic acid, citric acid and glucose were used as the reducing agent. Sulfuric acid and citric acid solution were used as the leaching agent. XRD analysis confirmed the occurrence divalent Ni due to reduction process. Based on the AAS analysis, it can be concluded that the reduction process affects the leaching behavior significantly. The highest leaching concentration of Ni and Co is obtained using glucose as the reducing agent during the pre-treatment.

1. Introduction
The use of Lithium ion batteries (LIBs) have highly increased since it was commercialized in 1990s. Almost all electronic devices such as handphones, cameras and laptops as well as power bank used LIB as its energy storage. LIBs have also been used to provide power to electric vehicles (EV), either hybrid electric vehicles (HEV) or plug-in hybrid electric vehicles (PHEV), for environmentally friendly purposes. Now, LIBs that have been commercialized use various types of oxide and phosphate as their active materials of cathode, such as LiCoO$_2$, LiMn$_2$O$_4$, LiFePO$_4$, LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (NCM), and LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (NCA) [1]. Since 2012 global EV registration and global EV stock have increased, particularly in China and the US [2]. So that the production of cathode material will increase as well. However, every LIBs such as NCA battery has end-of-life and discharging it to the environment directly is considered harmful since it contains heavy metals and toxic substances. Thus, an effort of reusing the heavy metals via recycling especially the metal recovery is necessary hence it will not negatively impact the environment [3].
In the recycling process, the hydrometallurgical processing is more widely used because it produces end products with high purity, it has high efficiency and energy saving. For the recycling process using the hydrometallurgy method, it was proposed to obtain the cathode material from the electrode by separation of Al foil using the NaOH dissolution method. The cathode material can be directly recycled or reprocessed to be a new cathode material via process of hydrometallurgy. Some organic acids or inorganic acids can be used as the agent of leaching. However, even though the leaching process is considered faster compared to pyro-metallurgy and bio-metallurgy techniques, the leaching time can be reduced by adding reducing agents such as ascorbic acid and hydrogen peroxide. The reducing agents facilitate the leaching process since it is easier to leach heavy metals in lower oxidation state \[3,4\].

In a previous study, Muzayanha et al., 2019\[5\], studied the effect of the heating time of the pretreatment solids (NCA cathode material that has been separated from Al foil) at 800°C by variation of 2 hours and 4 hours. Based on the results, the heating time of 4 hours is the optimal time due to the high reduction of transition metals. The study of the effect of heating on the reduction reaction has also been conducted \[6\]. Therein, in this study, it would be investigated the effect of various reducing agents added during the pre-treatment process towards the leaching behavior of NCA cathode materials. 4 M H\(_2\)SO\(_4\) and 1.5 M citric acid was used as the inorganic and organic leaching agents, respectively.

2. Method

2.1. Pretreatment Process

The pretreatment process was carried out by NaOH dissolution method for separation of cathode material from Al sheet. The cathode was obtained from spent NCA type LIBs provided by UNS Battery Manufacturing Plant. After disassembled from the case, the cathode was cut into small pieces and was added to 5M NaOH solution for 2 hours. A reaction that occurs follows equation 1 listed below:

\[
2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \rightarrow 2\text{NaAlO}_2 + 3\text{H}_2
\]

Cathode material that has been separated from Al foil was washed by using hot water for removing the rest of NaOH. It was then dried in the oven. The dry cathode material was calcined in the furnace at 800 °C for 4 hours to remove acetylene black (AB) and polyvinylidene difluoride (PVDF). As an effort of reducing the transitional metal oxidation state, 10%w/w of various reducing agents such as Citric Acid (RNCA-CA), Oxalic Acid (RNCA-OA), Stearic Acid (RNCA-SA) and Glucose (RNCA-G) were added to the cathode powder before the heating process. The C, O, and H content of each reducing agents are displayed in table 1.

| Reducing Agent | Chemical Formula | Molecular Weight | % C   | % H   | % O   | C/O   | H/O   |
|----------------|------------------|------------------|-------|-------|-------|-------|-------|
| Citric Acid    | C\(_6\)H\(_8\)O\(_7\) | 192              | 37.5% | 4.2%  | 58.3% | 0.64  | 0.75  |
| Oxalic Acid    | C\(_2\)H\(_2\)O\(_4\) | 284.5            | 76.0% | 12.7% | 11.3% | 6.73  | 9.0   |
| Glucose        | C\(_6\)H\(_12\)O\(_6\) | 180              | 40%   | 6.7%  | 53.3% | 0.75  | 1.0   |

2.2. Leaching Process

A batch leaching process was conducted using a three-neck flask equipped with a water bath. In this process H\(_2\)SO\(_4\) 4M was used as a leaching agent and the ratio of solid-liquid was 200 gL\(^{-1}\). The leaching process was carried out at a temperature of 80°C for 1 hour. The leaching solution was filtered. The Ni,
Co and Al content were examined using AAS. The reaction that occurs can be seen in the equation as follows:

$$2\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05} + 3\text{H}_2\text{SO}_4 \leftrightarrow \text{Li}_2\text{SO}_4 + 0.3\text{CoSO}_4 + 1.6\text{NiSO}_4 + 0.05\text{Al}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O} + 0.5\text{O}_2$$  

(2)

3. Result and Discussion

3.1. Pretreatment

The change of the structural characteristics of the material caused by the addition of reducing agents during the pretreatment were observed. The structural characteristics were examined by X-Ray Diffraction (XRD) and the result was depicted in Figure 1. Commercial NCA (BTR, China) and JCPDS were used as the reference. Pure NCA has a layered hexagonal structure. A good hexagonal layered structure can be detected from the double splitting of 006/012 and 018/110 peaks\[7,8\].

Figure 1. The X-ray diffraction patterns of pre-treated NCA waste using various reduction agents

Based on Figure 1, samples with the addition of reducing agents such as RNCA-SA (stearic acid), RNCA-OA (oxalic acid), RNCA-G (Glucose), RNCA-CA (citric acid) were compared to samples without the addition of reducing agents (RNCA) and Commercial NCA (NCA-Com). Sample with no reducing agent addition (RNCA) has similar pattern with the commercial NCA and JCPDS reference. However, the peaks of diffraction patterns in each sample with reducing agent has different patterns with commercial NCA and JCPDS reference. From these phenomena we can conclude that the addition of reducing agents during the pre-treatment process is altering the structure of NCA cathode significantly. The RNCA-OA sample has a slightly similar pattern with commercial NCA, however the 104 peak was widened and the double splitting in 006/102 and 018/110 disappeared forming a single peak confirming that the ordering of layered structure was reduced. On the other hand, NCA-G, NCA-CA, and NCA-SA has low 003 peak intensity and new peaks emerged at 20 of 37°, 43° and 64° which indicate that in the samples has inactive divalent compounds NiO (Nickel II oxide). Small peaks at 20 range of 20-35° indicate the presence of Li$_2$CO$_3$. This explains that the reducing process of Ni from Ni$^{3+}$ to Ni$^{2+}$ occurred and followed by the formation of Li$_2$CO$_3$. High reduction effects can be caused by high C/O and H/O values that can be seen in table 1. It is predicated that the leaching process will be accelerated. It also can be predicted that RNCA-G, RNCA-CA and RNCA-SA have high leaching efficiency compared to other samples \[9,10\].
3.2. Leaching Process using H$_2$SO$_4$

The leaching process aimed to verify the XRD results. H$_2$SO$_4$ with 4M concentration has been used as a leaching agent, at 80°C for 1 hour. The solid to liquid ratio was 200 gL$^{-1}$. Leaching behavior of Ni, Co and Al of each samples which was pre-treated using various reducing agent were displayed in figure 2.

![Figure 2](image)

**Figure 2.** Leaching behavior of NCA powder treated with various reducing agents in 4M H$_2$SO$_4$ at 80°C for 1 h

The higher concentration the higher the efficiency of leaching. Spent cathode of NCA with no reducing agent (RNCA) was used as the reference. Based on the figure, it could be concluded that the addition of reducing agents during the pretreatment significantly affected the leaching behavior of NCA samples, with exception of Al. Both Ni and Co dissolution increased significantly compared to RNCA.

![Figure 3](image)

**Figure 3.** Leaching Efficiency of NCA powder treated with various reducing agents in 4M H$_2$SO$_4$ at 80 °C for 1 h
Leaching efficiency of each samples which is pre-treated using various reducing agents are displayed in Figure 2. Based on the figure, we know that RNCA-G has the highest Ni and Co leaching efficiencies compared to the other samples, followed by RNCA-SA, RNCA-OA and RNCA-CA in particular order. High leaching efficiency in RNCA-G, RNCA-SA and RNCA-CA can be attributed to the presence of a divalent atom which is confirmed by XRD analysis in Figure 1. The presence of a divalent atom promotes the leaching process. The reducing effect is predicted to be caused by the C and H (table 1) content in the reducing agent. High C/O and H/O content reduce the atom significantly. However high value of C/O can cause carbon deposit in the NCA particle during the heat treatment. This carbon deposit hinders the mass transfer during the leaching process. This explains the reason behind the lower leaching efficiency of RNCA-SA compared to RNCA-G even though it has the highest C/O and H/O value. The leaching behavior of Al has inconsistent results with the other atom because Al has low initial concentration which affects the sample reading during the AAS measurements [3–6].

3.3. Leaching Process using Citric Acid
In this study, 1.5 molar of Citric Acid was also used as a leaching agent with a ratio of solid-liquid of 80 gL-1 and the same conditions at 80°C for 1 hour, to find out whether the reducing agent affects the leaching process using organic acid. Figure 4 displayed the comparison of leaching behavior between every pre-treated sample. Meanwhile, leaching efficiency was displayed in figure 5. RNCA-SA leaching behavior in H₂SO₄ was used as the reference.

![Figure 4. Leaching behavior of NCA powder treated with various reducing agents in 1.5 molar citric acid at 80°C for 1 h](image)

Based on figure 4 and figure 5, the conclusion was that all the samples leached using citric acid as the leaching agent have low leaching efficiency compared with RNCA-SA leached in H₂SO₄. H₂SO₄ is a much stronger acids compared to citric acid. In addition, citric acid solution has lower concentration (1.5M) compared to H₂SO₄ solution (4M). Increasing citric acid concentration also increases the viscosity of the leaching agent which hinders the mass transfer during the leaching process, resulting in a much inferior result. Previous study had claimed that the drawback of using organic acid as a leaching agent is its tendency to form a complex metal-organic solution which makes the leaching agent become unable to react with the metal oxides. Equation 3-5 shows the leaching reaction between mixed oxide with citric acid.

\[
\begin{align*}
\text{NiO} + 2\text{C}_6\text{H}_8\text{O}_7 & \rightarrow \text{Ni}^{2+} + \text{H}_2\text{O} + 2\text{C}_6\text{H}_7\text{O}_7^- \\
\text{Co}_2\text{O}_3 + 4\text{C}_6\text{H}_8\text{O}_7 & \rightarrow 2\text{Co}^{2+} + 2\text{H}_2\text{O} + 4\text{C}_6\text{H}_7\text{O}_7^- + 1/2\text{O}_2 \\
\text{Al}_2\text{O}_3 + 6\text{C}_6\text{H}_8\text{O}_7 & \rightarrow 2\text{Al}^{3+} + 3\text{H}_2\text{O} + 6\text{C}_6\text{H}_7\text{O}_7^-
\end{align*}
\]
Figure 5. Leaching Efficiency of NCA powder treated with various reducing agents in 1.5 molar citric acid at 80°C for 1 h

For this reason, it was necessary to study the effect of leaching time on the process of leaching using citric acid as a leaching agent. Figure 6 showed the concentration of metal leached from spent cathode with variation of leaching time. From figure 6, it could be seen that the longer the leaching time the higher the concentration of metals dissolved in the leaching agent.
Figure 6. The concentration of metal leached from spent cathode with variation of leaching time

4. Conclusion
A novel pre-treatment process by adding various reducing agents during the heat treatment was proposed. In this study, stearic acid, oxalic acid, citric acid and glucose were used as the reducing agent. The effect of the reducing agent on the structural characteristics of NCA powder were successfully examined. The reducing agent can reduce the Ni\(^{3+}\) to Ni\(^{2+}\) forming a stable NiO compound. The higher the C/O and H/O content, the clearer the NiO peaks. The leaching behaviour of the pre-treated NCA powder has improved significantly. The highest leaching efficiency occurred on the reducing agent of glucose. In conclusion, this approach was considered as a promising treatment to be adapted for large-scale recycle processes of spent LIBs, especially spent NCA cathode material.

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