

The Comparison of Lithium Carbonate Recovered from Single Type and Unknown Mixed Type of Lithium-Ion Batteries through a Simple Way Carbonated Water Leaching

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Abstract: Lithium is a rare earth element, but it is important in LIB manufacturing. Spent LIBs is a potential source of lithium. The research aim was to recover lithium from spent LiNCA and mixed LIB through selective leaching using carbonated water. The spent cathode and anode were separated by dismantling and dissolving using NaOH and hot water. The spent cathode was reduced by mixing with 20% spent anode and heating at temperature of 650 °C for 6 hours. The reduced cathodes of 25 g were mixed with 250 ml of water and flowed by 2 L/minute of CO₂ gas for 150 minutes at ambient temperature. The residue was separated from filtrate. The reduced cathode and residue were examined by XRD and FTIR, while filtrate was heated for evaporating solvent to obtain precipitated Li₂CO₃. The precipitated Li₂CO₃ was 0,151 g/g of LiNCA and 0,034 g/g of mixed spent cathode. The characteristics of Li₂CO₃ recovered from spent LiNCA closed to pure Li₂CO₃ even above the commercial Li₂CO₃ and met the requirements as an active precursor material for manufacturing LIB cathodes. Meanwhile Li₂CO₃ recovered from spent mixed cathode had some impurities and was needed further purification process.

1 Introduction

Lithium is one of the rare earth minerals that currently has a sharp increase in demand. The demand for lithium in 2025 is predicted to reach 500,000 tons per year [1]. In addition, only a few countries own the natural lithium resources of the world, namely Chile 52%, China 22.27% Argentina 13.92, Australia 10.44% [2]. In addition, Li is found in nature in the form of a lithium salt with a very low concentration of around 17 ppm, so it is classified as a rare earth, and its extraction is a long and complicated [3].

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The potency of spent LIBs from cellular phones and laptops in Indonesia is large. By assuming that half of Indonesia's population, 125 million people, have cellular phones where each cellular phone has an average capacity of 3000 mAh with a specific capacity of 200 mAh/gram, and the battery life is 2 years (750 cycles capacity), then there are 937.5 tons of spent cathode per year. The same quantity obtained spent LIB from the laptop. Spent LIBs usually contain 5%–7% lithium [4]. So that every ton of spent LIBs cathodes has a lithium content of between 50-70 kg. So, there are 100-140 tons of Lithium source per year, only from spent LIB of cellular phone and laptop. The problems were the spent LIBs came from different types of LIBs and scattered in existence.

In general, the recovery of metals in spent LIB can be carried out in three ways: hydrometallurgy [5]–[12], biometallurgy [13], [14], and pyrometallurgy [15]–[17]. Hydrometallurgy is an extraction process that includes metal refining and recycling using a chemical or leaching agent. The chemical used was usually an acid solution and the type of acid used depends on the metal to be extracted [5], [7]–[9], [11], [12], [18]–[20]. Lithium metal could be extracted using carbonated water [21], while other metals such as nickel and cobalt can use a stronger acid solution.

Selective recovery of Li metal through the hydrometallurgical process can be carried out either by selective leaching followed by precipitation or by leaching of metals followed by selective precipitation. A selective leaching has been conducted by reducing the spent cathode using lignite as a reducing agent followed by leaching with carbonated water [21]) or Na₂CO₃ solution [22]. The other research was with H₂O₂ reducing agents and sulfuric acid leaching agents [23], hydrochloric acid and citric acid [8] continued with selective precipitation to separate each metal [23].

The recovery of lithium in the cathode of spent LIB through hydrometallurgy consisted of three stages: preparation (pretreatment), metal extraction (reduction and leaching), and product manufacture (precipitation and reaction) [5], [7]–[9], [11], [12], [18]–[20]. Pretreatment was to separate the cathode and anode from other components in LIBs, including emptying the remaining energy in spent LIBs by soaking in salt water (NaCl) for 2 days, separation of cathode layer and the anode layer from other components and separation cathode from the aluminum sheet with NaOH solution [24],[25] and anode from the copper sheet with hot water.

Reduction of spent cathodes can be done separately or together with the leaching process. The reduction process is separately carried out by adding a material containing carbon (lignite, acetylene black, or other) to the spent cathode and heating it at a temperature of 650-750 °C [10], [12], [21]. The spent cathode and spent anode as a reducing agent were mixed with a certain ratio, pulverized, and heated in a furnace at 750 °C for 6 hours. During reduction, there was a change in the structure of the compound in the cathode to become metal, metal oxide, and lithium carbonate (Li₂CO₃). The flowing nitrogen gas (N₂) was purposed to increase the possibility of lithium carbonate (Li₂CO₃) formation.

Leaching is a selective dissolution process in which only certain metals can dissolve. Impurity minerals will remain in solid form and are referred to as residues. The purpose of this leaching process was to extract the lithium from reduced cathodes using a leaching agent. The leaching agent used must meet the criteria as an effective leaching agent, which can selectively dissolve metals in large quantities. The leaching agent used in lithium recovery was carbonated water because of the high solubility of lithium carbonate in carbonated water. In addition, other metals such as nickel and cobalt have low solubility in carbonated water, so only lithium carbonate would be extracted.

Precipitation can occur when the concentration of dissolved ions has reached its solubility limit. The precipitation was carried out by controlling the solubility of substances in the solution through changes in pH, temperature, or solvent. To obtain Li in the form of Li₂CO₃, precipitation was performed by controlling the solubility through a change in temperature.

Previous research stated that the recovery of lithium from the spent cathode of LiNCA using the hydrometallurgical method showed a very good results, where the recovery of lithium reached 94% at a solid-liquid (L/S) ratio of 6% and 74% at 10% L/S. Lithium carbonate obtained from precipitation has very good purity and is close to pure Li_2CO_3 and better than commercial Li_2CO_3 [26]. In addition, when the Li_2CO_3 obtained was used as a precursor to manufacture the LiNCA cathode, the cathode obtained had better performance than the commercial LiNCA cathode (Jumari 2022). The purpose of this study was to recover lithium metal from spent unknown-type lithium-ion batteries from cellphones or laptops and the results were compared with Li_2CO_3 recovered from spent LiNCA (single spent LIB).

2 Materials and Methods

2.1 Reduction of spent cathode

An unknown type of cellular phone Spent LIBs were obtained from a cellular phone repair counter in Singosaren Plaza Solo, and a spent LIB type NCA 18650-cylinder cell (as a comparison) was obtained from CE-FEEST UNS. Both sources of spent LIBs were dismantled separately followed by separation of cathode film and anode film from the other LIB components. The cathode and anode were then separated from its Al sheet and Cu-sheet using 4 M NaOH (Merck, Darmstadt, Germany) and water, respectively and dried in the oven. The dried cathode and anode as reducing agents were mixed with a certain ratio, milled and heated in a furnace for 6 hours at 700 °C under flowing N_2 (Aneka Gas Industri, Jakarta, Indonesia). All reduced spent cathode were then analyzed the change of the crystalline structure and composition using X-ray Diffraction (XRD, D8 Advance) and Fourier transform infrared spectroscopy (FTIR; IR-Spirit Shimadzu FTIR spectroscopy, Shimadzu, Kyoto, Japan).

2.2 Selective Leaching

Carbonated water leaching of reduced cathode was carried out in a 500 ml three-neck flash glass with a mechanical stirrer. A certain mass of reduced cathode and 250 ml of water were added into neck flash with a solid- liquid ratio of 10%. Carbonated water leaching was conducted by flowing 2 L/minute of CO_2 from high pressure CO_2 gas cylinder equipped with flowmeter for 150 minutes under ambient atmosphere. After leaching, the rest of solid of reduced cathode was then separated by filtration for the examination of composition using X-ray Diffraction (XRD, D8 Advance) and Fourier transform infrared spectroscopy (FTIR; IR-Spirit Shimadzu FTIR spectroscopy, Shimadzu, Kyoto, Japan).

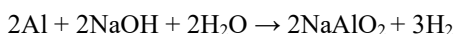
2.3 Precipitation of Li

Recovery of Li as Li_2CO_3 was conducted by precipitating of leaching filtrate solution and evaporating the solvent. Leaching filtrate solution was heated at 100 °C till all water evaporated and wet solid obtained was then dried in the oven flowed by Nitrogen at 60 °C for 6 hours. The dried solid was then examined by XRD and Fourier transform infrared spectroscopy (FTIR; IR-Spirit Shimadzu FTIR spectroscopy, Shimadzu, Kyoto, Japan). The obtained results were compared with those of Li_2CO_3 recovered from LIB of LiNCA, commercial Li_2CO_3 (Sichuan Brivo Lithium Materials, Sichuan, China) and pure Li_2CO_3 (Merck, Darmstadt, Germany).

3 Results

3.1 Pretreatment and Reduction of spent cathode of NCA

During pretreatment, especially separation of spent cathode from Al sheet, Al sheet reacted with NaOH in solid-liquid phase by the following reaction. Aluminum sheet reacted with sodium hydroxide to produce sodium aluminate in the form of a slurry, while hydrogen gas would evaporate. The cathode was still in solid form and separated from the slurry by filtration, then dried by heating in an oven. While separation of anode from Cu sheet was only physical separation, where anode would be separated from Cu sheet when hot water was added.



Reduction of spent cathode was a process for changing the structure of cathode by adding a reducing agent and heating at a certain temperature. Here, the reducing agent used was spent anode with a ratio of 20% of spent cathode and the mixture heated at 700 °C for 4 hours. During reduction, the compound structure of the cathode changed following the reaction [27]. Figure 1 depicts the XRD examination of the reduced cathode of LiNCA.

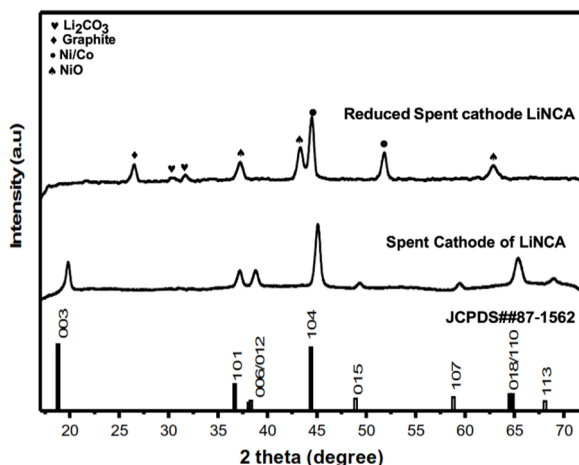
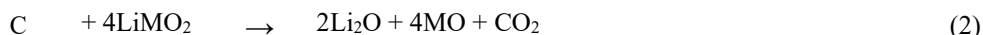
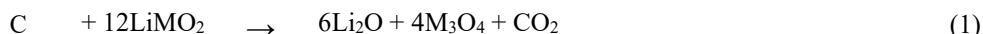


Fig. 1. XRD pattern of spent cathode and reduced spent cathode of LiNCA

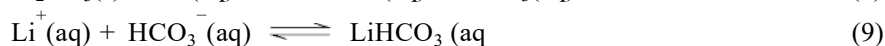
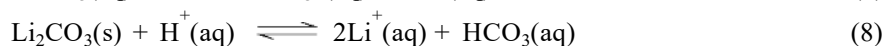
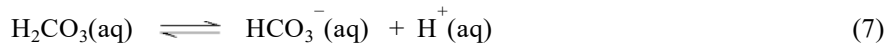
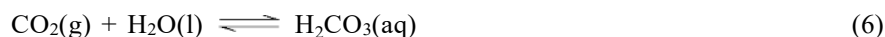
Based on the XRD pattern, the spent cathode had similar peaks to the JCPDS reference of NCA. When the spent cathode was reduced by heating and addition with spent anode as a reducing agent, some peaks disappeared and some new peaks appeared in the XRD pattern. They showed that the addition of a spent anode during the reduction process significantly changed the structure of the spent LiNCA. Reduction of Spent LiNCA with a reducing agent of spent anode gave new peaks appearing at 2θ of 43° and 51° indicating the presence of metal Ni and Co.

and 2θ of 43° of metal Al. A small peak in the range 2θ 20-35° indicated the presence of LiAlO_2 and Li_2CO_3 . These results were well confirmed by the other similar research which spent lignite as a reducing agent [21]. This explained that a part of metal Ni, Co, and Al in the form of compound NCA were reduced to be metal of Ni, Co, and Al. The reduction process was also followed by the formation of Li_2CO_3 . Because of metal Li had been in form of Li_2CO_3 , it could be selectively leached using carbonated water. For this research spent anode was chosen as reducing agent due to the availability and low price.

3.2 Selective Leaching of Li

As mentioned above, metal transformation from cathode to metal, and metal oxide, as well as Li_2CO_3 , occurred during reduction. As such, lithium was able to be separated by performing simple water leaching. The solubility of lithium carbonate was 13.3 g L^{-1} at 20°C , and it decreased with increasing the temperature. To obtain a high efficiency, the water leaching must be performed in a high liquid-solid ratio with the result of leaching of low concentration of Li_2CO_3 and low temperature.

Carbonated water has been used for the recovery of high-purity Li_2CO_3 from salt lake brine [28] which was adopted for this research. When a mixture of water and reduced spent cathode was injected with CO_2 gas, Li_2CO_3 would transform to be more soluble LiHCO_3 with the following mechanism [29].



The total reaction was three phases of solid-liquid-gas reaction.

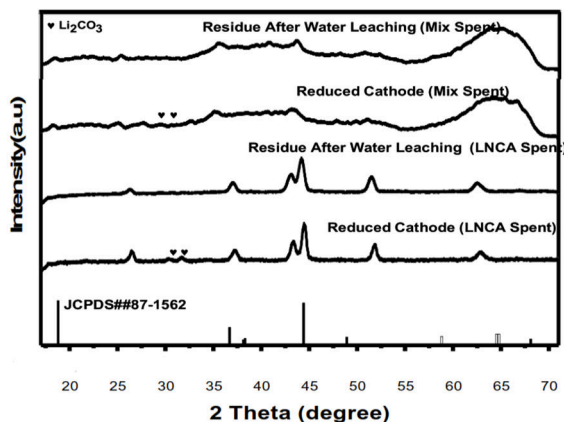
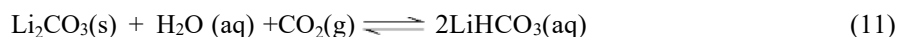


Fig. 2. XRD examination of reduced cathode before and after (residue) water - CO_2 leaching.

After the water leaching was complete, the residue and leaching solution were separated by filtering. Furthermore, the residue was dried by heating in an oven while the leaching filtrate entered the precipitation process. The resulting residue was tested for X-Ray Diffraction (XRD) and Fourier Transform Infra-Red (FTIR) compared to those of reduced cathode before leaching. The results of the XRD tests from the residue and reduced cathode was depicted in Figure 2.

It could also be seen that the peaks of Li_2CO_3 disappeared in the XRD pattern of residue after water leaching, either in spent LiNCA or in spent mixed cathode, and the peaks of other substances were still not change, while peaks of Li_2CO_3 appeared in reduced cathode. It proved that water leaching only leached Li_2CO_3 . The disappearance of Li_2CO_3 from residue after water leaching was also enhanced by FTIR examination, as shown in figure 3. In this figure, transmittance of functional groups of $-\text{CO}_3$ decreased or disappeared on residue after water leaching.

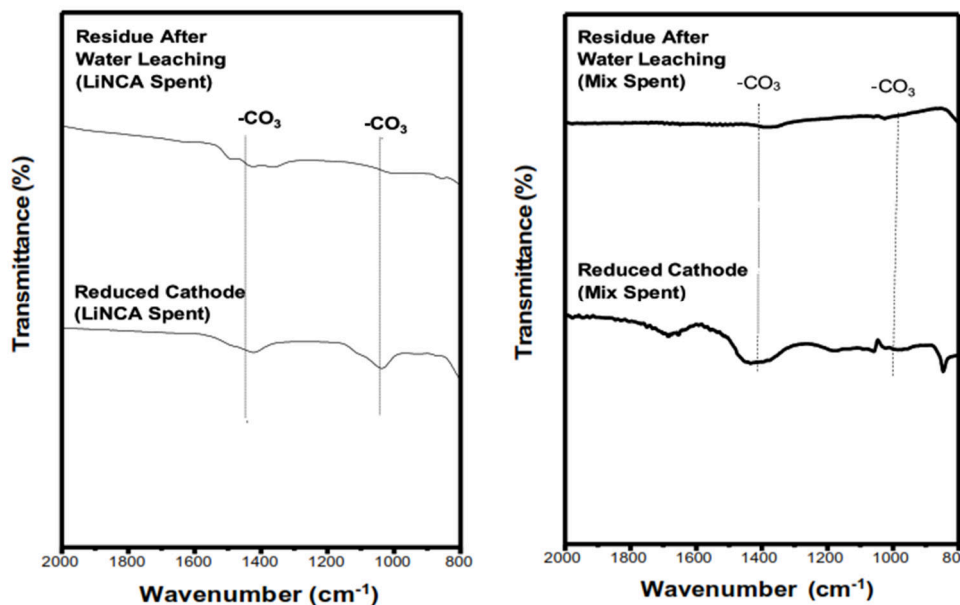
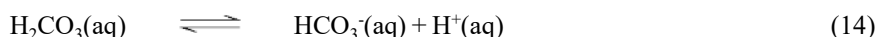


Fig. 3. FTIR examination on reduced cathode before and after (residue) water $-\text{CO}_2$ leaching: (left) spent LiNCA and (right) Mixed spent Cathode.

3.3 Precipitation of Li as Li_2CO_3

Recovery of Li metal from the filtrate of water leaching in the form of Li_2CO_3 was carried out by evaporation with heating at a temperature of $100\text{ }^\circ\text{C}$ until all the water evaporated and the solid formed was then dried in an oven at $50\text{ }^\circ\text{C}$ for 2 hours. When the filtrate was heated, CO_2 was liberated and Li_2CO_3 was formed by the following reaction [28].



The concentration of Li_2CO_3 in solution increased with the decrease in water caused by evaporation. Li_2CO_3 precipitated due to the increasing concentration and decrease the solubility caused by the increasing temperature. As known solubility of Li_2CO_3 in water decreased with increasing temperature. Solubility of Li_2CO_3 in water at temperatures of 303 K and 373 K were 1.33 and 0.72 g/100 ml H_2O , respectively. The longer the heating, the more water evaporated and the more Li_2CO_3 precipitated. All Li_2CO_3 was recovered by evaporating all water and dried in oven. The dried Li_2CO_3 was then examined by XRD and FTIR which were presented in Figure 4 and Figure 5. Precipitation of filtrate yielded products of Li_2CO_3 as much as 0,151 g/g reduced cathode of LiNCA (theoretically of 0,202 g/g reduced cathode) and 0,034 g/g reduced mixed spent cathode (theoretically of 0,066 g/g reduced cathode).

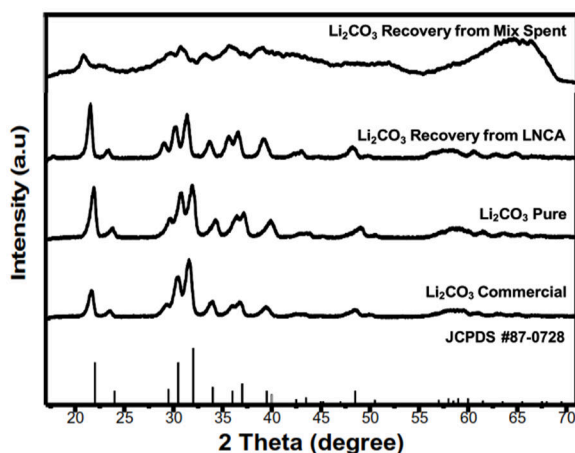


Fig. 4. The comparison of XRD patterns Li_2CO_3 commercial, pure, recovery from spent LiNCA, and recovery from spent Mixed cathode.

Figure 4 showed that Li_2CO_3 recovered from LiNCA had the same peaks as JCPDS Li_2CO_3 and did not show any other peaks. This showed that Li_2CO_3 recovery had high purity. Peaks of Li_2CO_3 recovery had the same height as pure Li_2CO_3 , even higher than commercial Li_2CO_3 , which is commonly spent as a precursor for the manufacture of LIB cathode active materials. This showed that Li_2CO_3 recovery had a higher crystallinity than commercial Li_2CO_3 and was the same as pure Li_2CO_3 . Thus, Li_2CO_3 recovery was suitable to be used as a precursor for the synthesis of LIB cathode active material.

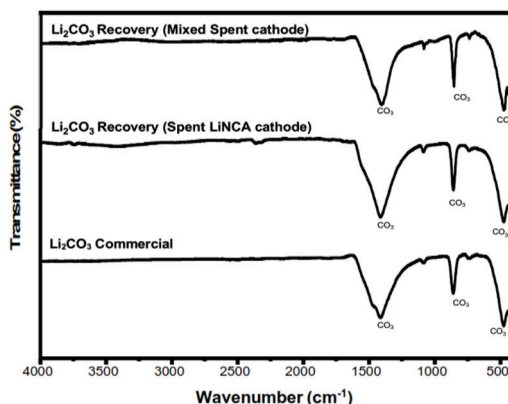


Fig. 5. The comparison of FTIR spectra of Li_2CO_3 commercial, recovery from spent LiNCA, and recovery from spent Mixed cathode.

The different results were shown by Li_2CO_3 obtained from spent mixed cathode. Besides the peaks from Li_2CO_3 , there were several peaks from other compounds. This showed that there were impurities contained in Li_2CO_3 . In addition, the height of peaks of Li_2CO_3 recovered from spent mixed cathode was lower than those of commercial Li_2CO_3 , which means its crystallinity was lower than that of commercial Li_2CO_3 . In order to be used as a precursor for synthesis LIB cathode active material, Li_2CO_3 recovered from spent mixed cathode had to be processed for purification.

Both Li_2CO_3 obtained from either spent LiNCA or spent mixed cathode had the same level of transmittance at the wave number associated with the Li_2CO_3 compound in the FTIR test (Figure 5). Similarly, the transmittance of commercial Li_2CO_3 , which was used as a comparison.

4 Conclusions

Lithium is an important element in LIB manufacturing, and its need is highly increase. It is a rare element on earth and has a limited source. There is enormous potential as a source of lithium, namely from spent LIBs. In this paper, selective recycling to recover lithium from either single type of LiNCA or unknown type of spent mixed LIB. The process consisted of reduction with a spent anode, selective leaching with carbonated water as a solvent, and precipitation of Li_2CO_3 . The spent LIB cathode and anode were separated by dismantling and dissolving using NaOH and hot water. The spent cathode was mixed with the 20% spent anode and heated at temperature of 650 °C for 6 for the reduction process. The reduced cathode was tested by XRD. 25 g of reduced cathodes were mixed with 250 ml of water and flowed by 2 L/minute of CO_2 gas for 150 minutes at ambient temperature. The metal solid was separated from the solution. The solids (residue) were examined by XRD and FTIR, and the solution (filtrate) was further processed through the precipitation of Li_2CO_3 . The precipitation of filtrate was carried out by heating for the evaporation of solvent until all the water evaporated. The yield of solid was collected as the final product as much as 0,151 g/g reduced cathode of LiNCA (theoretically of 0,202 g/g reduced cathode) and 0,034 g/g reduced mixed spent cathode (theoretically of 0,066 g/g reduced cathode). XRD and FTIR test results showed that the characteristics of Li_2CO_3 recovered from spent LiNCA close to pure Li_2CO_3 , even above the commercial Li_2CO_3 . Thus, Li_2CO_3 recovered spent LiNCA met the requirements as an active precursor material for manufacturing LIB cathodes. XRD and FTIR test results showed that Li_2CO_3 recovered from spent mixed cathode had some impurities and was needed further process to meet the requirements as an active precursor material for manufacturing LIB cathodes.

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