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Research Article

Mass Balance of Nickel Manganese Cobalt Cathode Battery Recycle Process

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Abstract. Batteries made from lithium, nickel, manganese, and cobalt are widely used, especially in the electrical industry, because they have high specific capacity, high safety, and low production costs. According to the International Energy Agency, the consumption of batteries used for electric vehicles will increase from 8 million in 2019 to 140 million in 2030. As a result, the waste produced is also increasing. This type of lithium-ion battery, which contains heavy metal elements such as nickel, manganese, and cobalt, can be recycled. This research aims to calculate the mass balance of the recycling process for nickel manganese cobalt (NMC) battery cathodes. The processing process begins with mixing, leaching, filtration, and drying, and the results of the filtration process are molarity adjustment, flame-assisted spray pyrolysis, and calcination. Based on the results of mass balance calculations for the NMC recycle battery cathode, the amount obtained was 43.427 kg/batch from 100 kg of raw material from cathode waste. Data was also obtained on the successfully recycled metals, namely NiO, MnO, CoO, Fe_2O_3, MgO, Al_2O_3, Cr_2O_3, and Li_2O. The research results show that NMC battery waste can be an opportunity for the NMC metal supply chain to reduce environmental pollution.

Keywords: NMC Battery, Mass Balance Calculation, Leaching, Recycle

1. Introduction

Lithium nickel manganese cobalt (NMC) batteries are widely used because they have high specific capacity, high safety, and low production costs and are commonly used for electric vehicles and portable electronics (Batteries et al., 2021; Zolkiffly et al., 2024). According to the International Energy Agency (IEA), the consumption of batteries used for Electric Vehicles (excluding two- or three-wheeled vehicles) will continue to increase, increasing from around 8 million in 2019 to 50 million in 2025 and approaching 140 million in 2030, this increase is in line with the average annual growth rate is close to 30% (Yu et al., 2022).

Used Lithium-ion Batteries (LIB) contain heavy metal elements, such as nickel (Ni) and cobalt (Co), which are classified as carcinogenic and mutagenic materials, as well as toxic organic electrolytes that negatively impact human health and the environment (Hernandez et al., 2023). As important raw materials for synthesizing LIB cathode materials, Li and Co are more in demand than other metals because of their relatively low abundance and high price (Kaya, M., 2022). If toxic metals and other harmful substances are not disposed of properly, it will not only lead to a waste of resources but also harm the environment (Fan et al., 2020).

Considering the need for effective use of this limited resource and environmental sustainability, used lithium-ion batteries must be properly handled and recycled (Fan et al., 2020; Du et al., 2022). Because lithium-ion batteries are complex products, many recycling schemes are possible, and there are three basic processing schemes, namely pyrometallurgy (smelting), hydrometallurgy (leaching), and direct recycling (physical processes) (Lu et al., 2021). These three basic processes can be carried out after removing and dismantling the battery and separating the electrode material from the used LIB (Wu et al., 2023). The processing components can be combined in different ways, depending on factors such as the quantity and characteristics of available materials and the quantity and value of materials that can be recovered (Gaines, 2018).

2. Method

NMC cathodes are made through a hydrometallurgical process. The hydrometallurgical process is an environmentally friendly method commonly used in LIB cathode recycling (Refly et al., 2020; Davies et al., 2024; Nasser et al., 2021). Several previous studies reviewed various hydrometallurgical methods developed in the last ten years to recycle lithium-ion battery cathode materials from multiple battery chemistries, including $LiNiMnCoO_2$ (NMC) to recover cobalt, nickel, manganese, and lithium (Jung et al., 2021). The process consists of pre-treatment (discharge, calcination, and grinding), followed by metal extraction, separation, or material retention to obtain the final product (Refly et al., 2020; Zhou et al., 2021).

The metal extraction from the cathode can be done by bioleaching and acid leaching to obtain a solution containing metal ions. However, acid leaching is preferred over bioleaching because the process is more straightforward and relatively fast. There are two types of acids that can be used as leaching agents: organic and inorganic. This research used HNO_3 as an inorganic acid (Refly et al., 2020; Zhou et al., 2021) and hydrogen peroxide (H_2O_2) as a reducing agent (Jung et al., 2021; Biswa et al., 2023). Equation 1 shows the leaching reaction mechanism of various lithium-ion battery cathodes using HNO_3 as a leaching agent:

$$2LiNiMnCoO_{2(s)} + 14HNO_{3(aq)} + 5H_2O_{2(aq)} \rightarrow 2LiNO_{3(aq)} + 2Ni(NO_3)_{2(aq)} + 2Mn(NO_3)_{2(aq)} + 2Co(NO_3)_{2(aq)} + 12H_2O_{(aq)} + O_{2(g)} \quad (1)$$

Several methods are used to synthesize NMC-type cathode materials, such as combustion, sol-gel, hydrothermal or solvothermal, emulsion drying, and co-precipitation. The most commonly used method is co-precipitation, followed by spray pyrolysis and solid-state reaction (Voronov et al., 2016). In this research, the Flame Assisted Spray Pyrolysis method was used. The Flame Assisted Spray Pyrolysis (FASP) method is a method for making nanoparticles by atomizing and then spraying a solution of raw materials (precursors) to form small granules and feeding them into a flame to produce a product in the form of powder particles (Purwanto et al., 2014).

Flow diagram of the NMC battery recycling process: mixing, leaching, filtration, filtration drying, molarity adjustment, flame-assisted spray pyrolysis (FASP), and calcination (Syaifulloh, 2022). 15.5 M of HNO_3 was diluted to 0.75 M by adding water at 30 °C and mixed in a mixing tool. The metal was dissolved from the solid phase into a liquid phase using a leaching process at a temperature of 60 °C. Subsequently, the results of the leaching process were filtered to obtain cathode residue, residue, and water content. Filtration drying is sent to the IPAL. At this stage, the molarity adjustment process increases the amount of metal from leaching to obtain a cathode with the desired composition, wherein the cathode compounds (Li, Ni, Co) are dissolved with HNO_3 and H_2O_2. Next, the flame-assisted spray pyrolysis (FASP) process stage functions to produce oxide with nano-sized particles where thermal decomposition occurs, which requires high temperatures. The final stage of the calcination process is the formation of metal oxide as the raw material for the battery cathode and removing CO_2 and O_2.

The mass balance is an application of the law of conservation of mass, where mass cannot be created or destroyed. The total mass entering a system will be the same as the total mass leaving the system (Himmelblau, 1974)

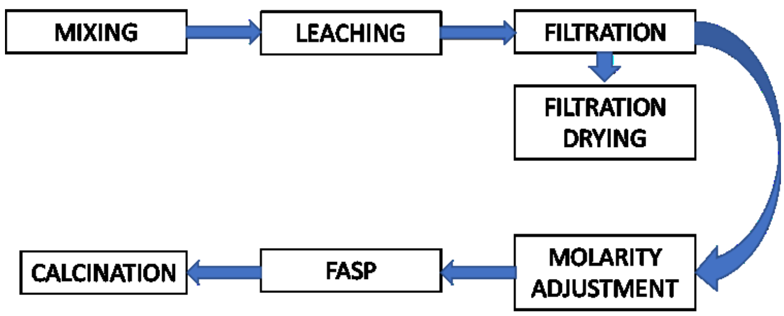

Figure 1. NMC cathode battery recycling flow diagram

3. Result and Discussion

3.1 Mass Balance

Figure 2 shows the mass balance of each process stage in the battery recycling process. In the mixing process, 15.5 M of HNO_3 was diluted to 0.75 M by adding H_2O at 30°C, pressure 1 atm, and then mixed until homogenous. Next, in the leaching process, the metal was dissolved from the solid phase into the liquid phase, where 0.75 M HNO_3 is added with 1.7% volume H_2O_2 as an oxidizer and cathode material is added, assuming 100 kg containing several compounds (Ni, Mn, Co, Fe, Mg, Al, Cr, and Li) as the main ingredients and under process conditions of temperature 60°C, pressure 1 atm, and cathode leaching effectiveness (Li 83%, Ni 71.15%, Mn 85.82%, and Co 99.76%). The results of the leaching process will be dissolved compounds, residue, and O_2. In the filtration process, cathode residue deposits were extracted from the leaching results, where dissolved compounds and other components will be separated from the existing residue under process conditions of 60°C temperature, 1 atm pressure, 100% filtration effectiveness, and 30% water content. Furthermore, in the drying process, residues or sediments were separated from their water content at the temperature of 100°C, the pressure of 1 atm, and 100% drying effectiveness. Then, the resulting residue and water content obtained can be sent to wastewater treatment plants.

The molarity adjustment process serves as a process of calculating the number of moles of metal resulting from leaching to obtain a cathode with the desired composition, wherein the cathode of the compounds (Li, Ni, Co) dissolved in HNO_3 and H_2O_2 will be carried out by calculating and adding moles of metal with the compound. $LiNO_3.6H_2O$, $Ni(NO_3)_2$. $6H_2O$, and $Co(NO_3)_2$. $6H_2O$ with process conditions of 60°C temperature, 1 atm pressure, and 100% effectiveness. The next stage of the flame-assisted spray pyrolysis (FASP) process functions to produce oxide from nano-sized particles. Thermal decomposition occurs during this process, which requires high temperatures. The dissolved compounds, HNO_3 and H_2O_2, will be subjected to a flame spray pyrolysis process with a precursor solution that is sprayed at high temperature with the help of Liquefied Petroleum Gas (LPG) gas which contains 30% C_3H_8, 70% C_4H_8 and O_2 gas compounds at operating temperature conditions of 600 °C, 1 atm pressure, and 100% effectiveness. Therefore, this process aims to produce metal oxides and waste gases, namely CO_2, H_2O, NO_2, and O_2 gases. The calcination process releases gases in the form of oxides, producing powder in the form of oxides with high purity. In this process, metal oxide results are obtained from the FASP process, which will be carried out at a high-temperature calcination process with Li_2CO_3 added to compensate for the loss of Li during calcination and under operating conditions of temperature 800°C, pressure 1 atm, and effectiveness of 99%. This process produces metal oxides, unreacted soluble compounds, and waste gases (CO_2 and O_2) (Syaifulloh, 2022).

Based on the diagram of NMC cathode recycling from batteries, the amount obtained was 43.527 kg/batch from the amount of raw material metal added, around 226.32 kg/batch. The yield obtained was 19%, and the successfully recycled metals were NiO, MnO, CoO, Fe_2O_3, MgO, Al_2O_3, Cr_2O_3, and Li_2O.

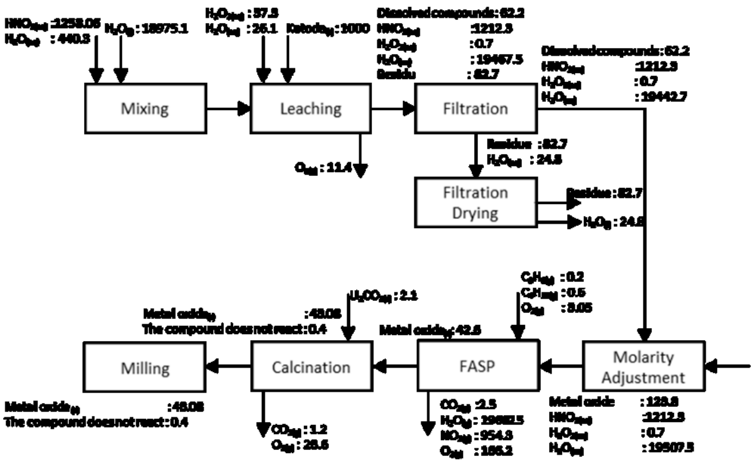

Figure 2. Results of the NMC cathode recycle battery mass balance flow diagram

4. Conclusion

Recycle lithium-ion battery cathode materials using a hydrometallurgical process. The recycled battery is the Nickel Manganese Cobalt (NMC) type, which consists of lithium nickel manganese cobalt oxide ($LiNiMnCoO_2$) metal. The recycling process consists of battery grouping, pre-treatment (discharge, dismantling, separation, drying, grinding, and sieving), and treatment (which consists of mixing acid reactor, heater, leaching, filtration, drying filtration, molarity adjustment, flame-assisted spray pyrolysis, calcination, and milling) to obtain the final product. Metal extraction (leaching) from the cathode can be done using acid leaching to obtain a solution for metal ions. The use of inorganic acids (nitric acid, HNO_3) and reducing agents (hydrogen peroxide, H_2O_2) in metal extraction shows an excellent result. In the NMC battery recycling process, the process that plays a role in recovering the metal needed from the used NMC cathode battery is the leaching process. The use of HNO_3 and H_2O_2 as solvents can extract around 62.2% of the required metals, which are marked as dissolved compounds. The second important process is the formation of metal oxide through the flame-assisted spray pyrolysis (FASP) process, which produces nano-sized NMC-mixed metal oxide. Finally, the calcination process provides a pure NMC cathode by removing the gases incorporated in the NMC metal resulting from the FASP process. Preparation of mass balance calculations for the inorganic leaching process (HNO_3) using 0.75 M HNO_3 + 1.7% H_2O_2, a solid-to-liquid ratio of 20 gr/L, and a temperature of 60 °C, with leaching efficiency reaching 83%, 71.15%, 85.82%, and 99.76% for Li, Ni, Mn, and Co metals, respectively. Experiments on recycling used lithium battery cathodes produced nano-sized NMC cathode powder using mass balance calculations with a value of 43,527 kg/hour or 86 tons/year. Based on the results of mass balance flow diagram calculations for producing NMC (Nickel Manganese Cobalt) cathode recycle batteries, the yield of NMC cathode recycle batteries was 19%. The research results provide information that waste NMC batteries can be an opportunity for the NMC metal supply chain to meet the need for lithium-ion batteries in line with the increasing need for electric vehicles and can also reduce environmental pollution.

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