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Environmental Impact Analysis of Waste Lithium-Ion Battery Cathode Recycling

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ABSTRACT

This study introduces the current status of recycling technology for waste lithium-ion batteries, with a focus on the environmental impact during the recycling process of waste lithium-ion battery cathode materials. Composition of lithium-ion battery was analyzed in order to estimate which components are potentially dangerous to the environment. Heavy metals are main pollutants and change the pH of the environment; also, organic solvent actively reacts with oxidants and reducing agents in the environment. Other parts of waste battery mainly impact an air during the combustion or thermal decomposition generating toxic lithium, cobalt oxides, other gases. Sources of air, water, noise pollution, solid waste, and toxic chemicals generated in the recycling process were identified. Air pollutants generated at every stage of the process of positive electrode materials recycling include dust, acidic gases, and organic gases. The wastewater is generated mainly from the discharge pretreatment and cathode recovery processes (leaching and extraction). Although the wastewater volume is relatively small, its composition is complex, poorly biochemical and toxic (lithium compounds, organic solvents, etc.). In the dismantling process, plastic connectors, circuit boards, high-voltage wiring, powders, collectors and pool electrode material casings are generated as solid waste. Corresponding pollution prevention and control measures are suggested to prevent environmental pollution during the recycling process of waste lithium-ion battery cathode materials.

Keywords: lithium-ion battery, waste battery, cathode, environmental impact, pollution.

INTRODUCTION

Because of high energy density, high operating voltage, long cycle life, and high safety (Li et al., 2021), lithium-ion batteries (Li-ion batteries) are widely used in 3C products (Zhang et al., 2022), electric vehicles (Schmuch et al., 2018), stationary energy storage wells and other fields (Zhu et al., 2015). Due to the rapid development of electronical industry and new energy automobile industry, a large number of used batteries will be produced after the decommissioning of electrical vehicles (Zeng, 2022). Therefore, the disposal plan for decommissioning batteries has gradually become the focus of research in the Li-ion battery industry. After the power battery is retired, there are different ways to place it according to its capacity retention rate. Waste Li-ion batteries with a capacity retention rate of about 80% are generally converted to energy storage batteries for echelon utilization, and those with the capacity retention rate of 45–60% can be used for auxiliary frequency modulation of thermal power generation. Waste batteries with a capacity retention rate of 30–45% can be used as backup power supply for communication equipment in the power system. When the capacity retention rate of batteries is lower than 30%, they need to be dismantled and recycled (Han et al., 2014, Xiao et al., 2020, Wu, 2021).

Cathode materials of Li-ion battery usually contain cobalt, nickel and manganese with certain biological toxicity, polluting the soil and water if battery is discarded (Ishchenko et al., 2024). In many cases, the organic solvent in the electrolyte is directly put into the environment without treatment causing a pollution. For example, lithium hexafluorophosphate, when mixed with water, generates hydrofluoric acid that is of great harm to the environment (Wei et al., 2023, Wang and Huang, 2021). From the perspective of resource recovery, China's (main Li-ion batteries producer) cobalt reserves are 80,000 tons, accounting for about 1.1% of the world's total cobalt resources. Due to the large cobalt ore gap, China needs to import a large amount of cobalt every year (Jiang et al., 2021). China's lithium reserves are 8.1 million tons, accounting for 6.3% of the global total reserves, but due to poor mining conditions and high development costs, the external dependence of lithium resources is as high as 67% (Rong, 2018). Recycling cobalt, lithium and other resources from used Li-ion batteries can effectively alleviate the pressure of cobalt and lithium resources import (Hlavatska et al., 2021). With the large-scale decommissioning of power batteries in the future, the valuable metals obtained through recycling can meet more than half of the raw material demand for lithium-ion battery materials (Wang and He, 2020). Therefore, recycling Li-ion batteries can reduce the amount of minerals mined, and reduce the harm of mining to the environment while protecting raw mineral resources. The efficient recycling of waste Li-ion batteries transforms waste to resources, which is conducive to the formation of a dynamic and sustainable cycle in the manufacturing, use and recycling of Li-ion battery industry (Xing et al., 2023), and can reduce the harm to the environment, with multiple benefits such as resources, economy and environment. Therefore, it is of great significance to study the recycling technology of waste Li-ion batteries. In the same time, recycling processes can be harmful to the environment as well. Therefore, when trying to get resources from waste, it is important to choose appropriate method with minimal impact to the environment. The goal of this study is to analyse waste lithium-ion batteries recycling process, with a focus on cathode materials, and its environmental impact.

MATERIAL AND METHODS

In this study, composition of lithium-ion battery was analyzed in order to estimate which components are potentially dangerous to environment. Based on chemicals properties, known natural regularities, and literature review, potential environmental impact pathways were identified. The environmental assessment of waste lithium-ion battery recycling process has been done for the case study of positive electrode material. Each stage of positive electrode material recycling process was analyzed in details. Then, sources of air, water, noise pollution, and solid waste were analyzed. Besides, toxic chemicals and other potential pollutants that might be generated in recycling process were identified.

Composition of lithium-ion batteries

Li-ion batteries are known to be composed of positive electrode, negative electrode, separator layer, binder, electrolyte, and organic solvents. The positive electrode is the component with the highest volume and cost in Li-ion batteries, and it is also the main research object for the development in the battery industry. Li-ion batteries are classified according to the types of positive electrode materials mainly including lithium cobalt oxide (LCO battery), lithium manganese oxide (LMO battery), lithium iron phosphate (LFP battery), lithium nickel cobalt manganese oxide (NCM battery), and lithium nickel cobalt aluminium oxide (NCA battery). Among them, ternary materials (NCM and NCA batteries) have become the main choices for new energy passenger vehicle power batteries due to their high energy density advantages (Zou et al., 2013). The composition, environmental impact characteristics, and potential environmental impact pathways of Li-ion batteries are summarized in the Table 1. As can be seen from the Table 1, serious environmental pollution can be caused by the cathode material (mainly metals): air, water and soil are pollutants recipients. Heavy metals like nickel, cobalt and manganese pollute and change the pH of the environment. Another source of water/soil pollution is organic solvent as it actively reacts with oxidants and reducing agents in the environment. Other parts of waste battery mainly impact an air during the combustion or thermal decomposition generating toxic lithium, cobalt oxides, other gases. In the waste Li-ion battery, positive electrode material (containing metals) is the most valuable for recycling. That is why this paper mainly discusses the pretreatment and recycling technology of positive electrode material recovery.

Positive electrode material recycling process

Today, the recycling methods for waste Li-ion batteries mainly include cascading recycling and dismantling recycling. Cascading recycling refers

Table 1. Composition of Li-ion batteries, their environmental impact characteristics and potential environmental impact pathways

Major component	Chemicals	Environmental impact characteristics	Potential environmental impact pathways
Positive electrode	Lithium cobalt oxide (LCO battery), lithium manganese oxide (LMO battery), lithium iron phosphate (LFP battery), lithium nickel cobalt manganese oxide (NCM battery), lithium nickel cobalt aluminium oxide (NCA battery)	Due to pH changes, heavy metal ions are released to the external environment	Surface water, groundwater, soil
Negative electrode	Graphite	Combustion generates CO and CO_2 emission; carbon powder dust can explode when exposed to open flames	Air
Separator layer	Polyethylene, polypropylene	Combustion generates CO and CO_2	Air
Binder	Polyvinylidene fluoride, polytetrafluoroethylene	Decompose at high temperature generating HF gas	Air
Electrolyte	Lithium hexafluorophosphate	Highly corrosive, decomposes into HF when exposed to water, reacts with strong oxidants, and generates P_2O_5 during combustion (Xu et al., 2008)	Air
Organic solvents	Ethyl carbonate propylene carbonate, dimethyl carbonate, diethyl carbonate	React with acids, bases, strong oxidants, and reducing agents, hydrolysis generates acids and alcohols, and combustion can generate CO and CO_2	Air, surface water, groundwater, soil

to the use of batteries that have been phased out from electric vehicles with high energy demands in energy storage systems or electric tools with low energy demands. When the battery performance cannot be met even in cases of low energy demands, dismantling recycling is adopted (Lu et al., 2022). Since the cathode material is the most cost-effective component of Li-ion battery, the recycling mainly involves the recovery of metals such as nickel, cobalt, manganese, and lithium from the cathode material. Waste Li-ion batteries are usually recycled in two ways: pyrometallurgical process and wet process. The pyrometallurgical process occurs in an ultra-high temperature environment, where the negative electrode, electrolyte, plastic, and separator in the battery are burned and decomposed. The metal elements of positive electrode are recycled in the form of alloys or oxides (Wang et al., 2020). Although pyrometallurgical process has high compatibility with battery types and does not require classification and treatment of waste batteries, many materials cannot be recovered due to the high energy consumption, and the recovery of lithium elements still needs to be further combined with wet processes. The wet recovery process of waste Li-ion batteries mainly includes discharge pretreatment, disassembly and crushing, separation of positive electrode materials, and metal element recovery.

Discharge pretreatment

There may still be residual electricity in waste Li-ion batteries. To avoid potential hazards such as explosions or spontaneous combustion during the dismantling process, it is necessary to discharge the batteries before dismantling (Castillo et al., 2002). Generally, waste batteries are placed in an electrolyte solution (usually carbonate electrolytes (K_2CO_3 and Na_2CO_3) or sulphate electrolytes ($FeSO_4$, $MnSO_4$) (Rouhi et al., 2022)) and the remaining electricity is discharged.

Dismantling and crushing

After deep discharge pretreatment, waste Li-ion batteries are disassembled, crushed, and screened to achieve preliminary separation of electrode materials from separator, metal case, aluminium foil, and other materials. At the same time, combined with magnetic separation, ultrasound, flotation and other technologies, further separation is achieved.

Separation of positive electrode materials

In the manufacturing process of Li-ion batteries, the active material of the positive electrode is combined with the solvent through an organic solvent binder. After disassembly, fragmentation, and separation, the positive electrode material is mixed with binder polyvinylidene fluoride (PVDF) and conductive agent. The presence of PVDF and conductive agent can affect the leaching efficiency of metal elements from the positive electrode material (Tian et al., 2021). In industry, calcination and pyrolysis are commonly used to remove binders and conductive agents from positive electrode materials. The principle of calcination and pyrolysis is based on the fact that the positive electrode material, PVDF and conductive agents undergo different thermal decomposition or transformation temperatures, and the temperature is controlled to decompose PVDF, thereby achieving further separation of positive electrode materials.

Recovery of metals

In the wet recovery process of waste Li-ion batteries, the efficient separation and recovery of various elements such as nickel, cobalt, manganese, lithium, copper, and aluminium from the positive electrode is a key task. First, inorganic acids are used to dissolve the powder of the positive electrode material, and the metal elements in the positive electrode material are leached into the solution in the form of ions. Due to the mixing of multiple metal elements in the leaching solution, low-cost methods must be used to effectively separate each metal. Today, extraction separation is widely used in industry to separate metals. The commonly used extractants include P204 (di (2-ethyl, hexyl) phosphate, also known as diisooctyl phosphate) and P507 (2-ethylhexyl phosphate mono-2-ethylhexyl ester). These extractants can be used to separate metals like nickel, cobalt, manganese, and lithium. Nickel, cobalt, and manganese ultimately exist in the form of sulphates, which then crystallize into nickel sulphate, cobalt sulphate, and manganese sulphate products with required purity. During the wet recovery process, sodium carbonate is added to the lithium rich solution for lithium precipitation, and the lithium element is ultimately recovered in the form of lithium carbonate. The wet recycling process can provide high-purity metal element products and recover most of the metals from waste Li-ion batteries. The entire recycling process is under mild conditions, so the wet recycling process has become the preferred process for recycling waste Li-ion batteries in industry (Zeng et al., 2012).

Environmental impact analysis of the recycling process of positive electrode materials

The recycling of waste Li-ion battery cathode materials has significant environmental benefits, but the emissions of pollutants during the recycling process also have adverse effects on the environment (Ai, 2023). Therefore, it is necessary to analyse the pollution sources and provide practical and feasible pollution prevention and control measures to reduce their impact on the environment. According to the analysis of the wet recycling process mentioned above, the pollution generation process and the impact on various environmental factors during the recycling of waste Li-ion battery cathode materials are analysed as follows.

Sources of exhaust gas pollution

The sources of air pollution generated during the recycling process of positive electrode materials include all the stages: dismantling, crushing and screening, calcination and pyrolysis, acid leaching, extraction, and product drying. The main pollutants in exhaust gas are shown in the Table 2. Gaseous pollutants generated in the process of positive electrode materials recycling can be divided into dust containing gases, acidic gases, and organic gases. Dust containing waste gas is mainly treated using cyclone dust collectors, bag filters, or water spray towers and their combination processes (Wang et al., 2022). Acidic waste gas is mainly treated using alkaline spray towers. According to the concentration of pollutants in acidic waste gas and emission control requirements, single-stage, two-stage, or even three-stage alkaline spray towers can be used. Organic waste gas can be treated using adsorption or catalytic combustion processes, and the selection of organic waste gas treatment measures should be determined comprehensively based on the amount of waste gas, pollutant concentration, and other factors.

Water pollution sources

The wastewater is generated mainly from the discharge pretreatment and positive electrode material recovery processes. The pollutant composition in the wastewater generated is relatively simple, mainly composed of salts such as sodium

Table 2. Main pollutants in exhaust gas

Process	Main pollutants
Dismantling	Fluorides Nonmethane hydrocarbons
Crushing and screening	Solid particles containing nickel, cobalt, manganese, lithium, etc.
Separation (calcination and pyrolysis)	Solid particles containing nickel, cobalt, manganese, lithium Fluorides Nonmethane hydrocarbons
Acid leaching	Inorganic acids such as sulfuric acid
Extraction	Nonmethane hydrocarbons
Product drying	Solid particles containing nickel, cobalt, manganese, lithium, etc.

sulphate, and the organic content is relatively low. Also, wastewater from acid leaching stage and extraction stage contains a large number of lithium cobaltate, lithium iron phosphate, methyl pyridinium alkanone, ultrafine carbon powder and low-molecular-weight esters. Although the wastewater volume is relatively small, its composition is complex, poorly biochemical and toxic. To provide wastewater treatment, three-effect evaporation or mechanical vapor recompression (MVR) evaporator is generally used for desalination (Yu et al., 2022). After desalination treatment, the water can be reused as pulping water, and the wastewater is not discharged.

Solid waste

In the dismantling process of Li-ion batteries, plastic connectors, circuit boards, high-voltage wiring are separated and become a waste. A lot of other waste are also generated, such as powders, collectors and pool electrode material casings (Fan et al., 2016). Storage of industrial solid waste should meet environmental protection requirements such as leakage prevention, rain prevention, and dust prevention.

To prevent a pollution, the recycling process should be continuously optimized to reduce pollutants generation and decrease their impact on the soil and groundwater environment. Secondly, anti-leachate measures should be strengthened to effectively prevent pollutants from entering the soil and groundwater environment. Finally, soil and groundwater tracking and monitoring should be carried out as required, and timely detection and measures should be taken to eliminate pollution sources. Figure 1.

Noise pollution sources

The noise sources in the process of positive electrode materials recycling mainly include

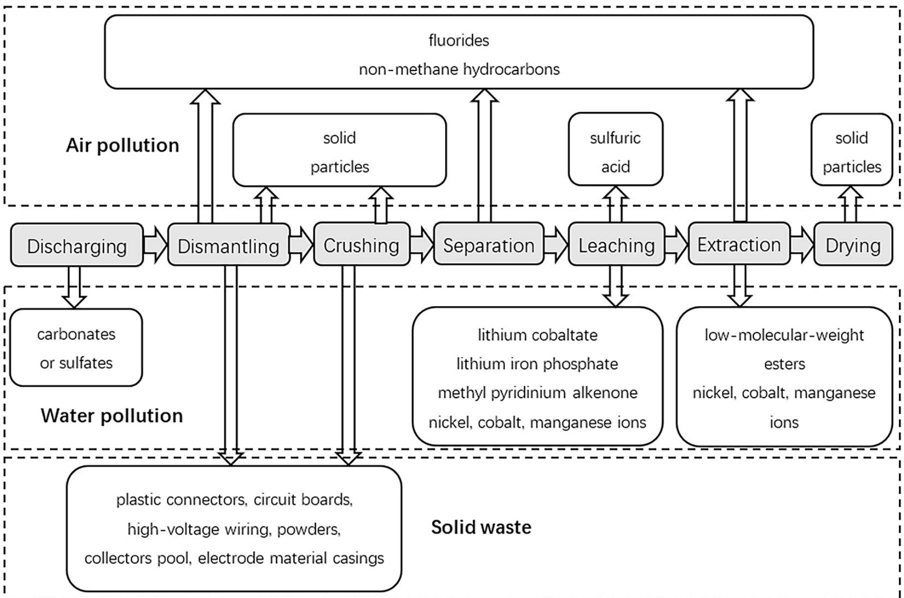

Figure 1. Environmental pollution during waste lithium-ion battery cathode recycling

crushers, fans, and pumps (Zhong et al., 2022). Low noise equipment is preferred, as well as the equipment with anti-vibration foundation. Silencers must be installed at the inlet and outlet of the fans. The above-mentioned comprehensive noise reduction measures can effectively reduce the impact of noise emissions on the external environment during the recycling process.

CONCLUSIONS

In summary, taking into account the impact of environment, safety, resources, economy and other aspects, efficient and environmentally friendly waste Li-ion battery recycling is very relevant nowadays. With the development of the new energy vehicle industry, the application of Li-ion batteries in electric vehicles has increased sharply, and the recycling of waste Li-ion batteries has become an important environmental protection and resource sustainability issue. Due to the complexity and diversity of the structure and composition of waste Li-ion batteries, the recycling process is more complex, but the recycling of waste batteries can not only alleviate the shortage of important strategic metals (Ni, Co, Li, etc.), but also reduce the waste of resources and environmental pollution. Li-ion battery recycling has been industrialized, but there are still many problems to be solved. For example, exhaust gases generated during pyrolysis process will have a negative impact on the environment. Therefore, the emission of fluorine-containing gas and organic matter needs to be effectively controlled during pyrolysis. Chemical separation requires the use of harmful chemical reagents, which can lead to environmental pollution. Therefore, in the pre-treatment separation process of waste Li-ion batteries, more environmentally friendly separation methods should be developed to reduce the negative impact on the environment. In the leaching process, acid recovery is low and the disposal of waste liquid is difficult. To achieve the recycling target, we propose the following initiatives:

1. When designing batteries, materials harmless to the environment and human health should be selected. Especially in the use of adhesives, separators, electrolytes, electrode materials and enclosures, non-toxic and easily degradable materials should be selected.
2. Redesign the battery structure to make it easy to disassemble.
3. All the information about the battery (most importantly its basic components) is described in detail outside the battery, and an information sharing model is established between the government and the user to track the production, use, recycling, reuse of each battery, and finally completely scrapped and re-entered the recycling process.

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